

**"ALTERNATE CYCLOCOPOLYMERIZATION:
SYNTHESIS OF A NOVEL CLASS OF IONIC
POLYMERS AND THEIR APPLICATIONS"**

BY

IBRAHIM YAHIA YAAGOOB MOHAMED

**A Dissertation Presented to the
DEANSHIP OF GRADUATE STUDIES**

**KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN, SAUDI ARABIA**

**In Partial Fulfillment of the
Requirements for the Degree of**

DOCTOR OF PHILOSOPHY

In

CHEMISTRY

DECEMBER, 2018

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

This thesis, written by **IBRAHIM YAHIA YAAGOOB MOHAMED** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **DOCTOR OF PHILOSOPHY IN CHEMISTRY**.



Dr. Khalid Alhooshani

Department Chairman



Dr. Salam A. Zummo
Dean of Graduate Studies



22/4/19
Date



Dr. Hasan Ali Saleh Al-Muallem
(Advisor)



Dr. Mohammad Abu Jafar Mazumder
(Co-Advisor)



Prof. Dr. Shaikh Asrof Ali
(Member)



Dr. Musa M. Musa
(Member)



Dr. Faizur Rahman
(Member)

© IBRAHIM YAHIA YAAGOOB MOHAMED

2018

Dedicated to

My

*Parents, Brothers,
Wife and Sisters*

*Mentors whose love and supports know no
bounds*

ACKNOWLEDGMENTS

All praises and glory be to Allah for his limitless help and guidance for making it possible for me to accomplish my Ph.D. study successfully. Peace and blessings of Allah be upon his prophet Muhammed (S.A.W).

I would like to express my gratitude and unreserved appreciation to my dissertation advisor Dr. Hasan Ali Saleh Al-Muallem and co-advisor Dr. M. A. Jafar Mazumder. The success of this work is credited to their tireless support, guidance and a priceless idea. I am indebted to my dissertation committee member the distinguished Prof. Sk. Asrof Ali for invaluable support and guidance especially on the polymer synthesis and characterization.

Great thanks to my other dissertation committee members Dr. Musa M. Musa, Dr. Faizur Rahman (Research Institute (RI), KFUPM) for their sincere help and constructive suggestion and contribution towards the success of this work.

Special thank goes to the current chairman of chemistry department Dr. K. AL Hooshani, past Chairman Dr. A. A. Al-Saadi, faculty members and staff of the chemistry department for their support and help.

I am grateful to Mr. Al-Zaki, Mansour in charge of NMR, Mr. Naim Mohammad in charge of TGA, Mr. Irshad Baig, Mr. Darwin, Mapanao, in charge of UV-Vis. My appreciation also goes to Dr. Aamer Al-Ahmed (Research Institute (RI), KFUPM) for allowing me to use his UV-Vis.

My appreciation goes to my fellow graduate students, my lab mates, and all members of the Sudanese community at KFUPM.

My profound gratitude and appreciation to my family both immediate and extended for their affection, encouragement, moral support, and prayers. Special thanks to my great brother Mr. Abdullah Yahia for his unlimited help forever, to my wife Dr. Dania Yousif for her patience and prayers, and my awesome and beloved Son Mohammed my gift from the god he was born during that tough time, then life changed with more blessings.

Finally, I would also like to appreciate King Fahd University of Petroleum and Minerals through the Chemistry Department for giving me the scholarship opportunity and providing excellent research facilities and support of this research work.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	V
TABLE OF CONTENTS	VI
LIST OF TABLES	XII
LIST OF FIGURES	XIV
LIST OF SCHEME.....	XVII
LIST OF ABBREVIATIONS	XIX
ABSTRACT.....	XX
ملخص الرسالة.....	XXIII
CHAPTER 1 INTRODUCTION	1
1.1 Ionic Polymers by Cyclopolymerization	3
1.2 Literature Review	7
1.2.1 Synthesis and Polymerization of Quaternary Ammonium Compounds	7
1.2.2 Chemicals to Control Scale Formation in Desalination Plants	10
1.2.3 Sorbents for the removal of toxic metal ions.....	12
1.2.4 Sorbents for the removal of organic dyes from aqueous medium	13
1.3 Present State of the Problem.....	17
1.4 Objectives.....	18

CHAPTER 2 SYNTHESIS AND APPLICATION OF POLYZWITTER IONIC AND POLYAMPHOLYTIC MALEIC ACID-ALT (DIALLYLAMINO) PROPYL PHOSPHONATES	26
2.1 Abstract.....	27
2.2 Introduction.....	28
2.3 Experimental	32
2.3.1 Materials.....	32
2.3.2 Physical Methods	32
2.3.3 Polymer synthesis.....	33
2.3.4 Potentiometric Titrations	39
2.3.5 Antiscalant behavior of the synthesized polymers.....	39
2.4 Results and Discussion.....	40
2.4.1 Synthesis of alternate copolymers.....	40
2.4.2 Solubility behavior	42
2.4.3 TGA Curves, FT-IR and NMR Spectra.....	43
2.4.4 Viscosity measurement	45
2.4.5 Basicity constant	49
2.4.6 Scale inhibition study.....	57
2.5 Conclusion	61
CHAPTER 3 SCOPE OF SULFUR DIOXIDE INCORPORATION IN ALKYLDIALLYLAMINE-MALEIC ACID-SO₂ TERCYCLOPOLYMERIZATION.....	62
3.1 Abstract.....	63
3.2 Introduction.....	64
3.3 Experimental	66

3.3.1	Materials.....	66
3.3.2	Physical methods.....	66
3.3.3	Synthesis of methyldiallylamine (7) and its hydrochloride salt 8	67
3.4	Polymer Synthesis	68
3.4.1	Procedure for 1 or 5/2/SO ₂ terpolymerization.....	68
3.4.2	Free radical polymerization of monomer 8	71
3.4.3	Photo-chemical initiated polymerization of monomer 8	73
3.4.4	Copolymerization of 8 with SO ₂	73
3.4.5	Methyldiallylamine (7) and maleic acid (2) ion pair 12.....	73
3.4.6	Copolymerization of 7 and MA 2.....	74
3.4.7	Procedure for 7 or 8/2/SO ₂ terpolymerization.....	74
3.4.8	Procedure for 15/2/SO ₂ co- and terpolymerization	76
3.5	Determination of Basicity Constant by Titration	77
3.6	Use of Synthesized PA 13 as an Antiscalant	79
3.7	Results and Discussion.....	80
3.7.1	Polymer synthesis.....	80
3.7.2	Solubility behavior	83
3.7.3	TGA curves and spectroscopic characterization	83
3.7.4	Viscosity behaviors	88
3.7.5	Basicity Constant.....	89
3.7.6	Scale inhibition study.....	91
3.8	Conclusion	94
 CHAPTER 4 FAST REMOVAL OF METHYLENE BLUE AND Hg(II)		
FROM AQUEOUS SOLUTION USING A NOVEL		
SUPER-ADSORBENT CONTAINING RESIDUES OF		
GLYCINE AND MALEIC ACID..... 96		
4.1	Abstract.....	97

4.2	Introduction.....	98
4.3	Experimental	101
4.3.1	Materials.....	101
4.3.2	Physical methods.....	101
4.3.3	Synthesis of monomer 1	102
4.3.4	Resin Synthesis	102
4.3.5	Ion exchange capacity (IEC)	103
4.3.6	Swelling coefficient.....	104
4.3.7	Adsorption of MB	104
4.3.8	Adsorption/Desorption experiment	105
4.4	Results and Discussion.....	106
4.4.1	Resin synthesis	106
4.4.2	TGA analysis of CPZA 4 and CAPE 5	107
4.4.3	pH Dependency of q_t	108
4.4.4	Adsorption kinetics at various temperatures	109
4.4.5	Infrared spectra.....	113
4.4.6	Activation energy (E_a).....	116
4.4.7	Adsorption isotherm	116
4.4.8	Adsorption thermodynamics	120
4.4.9	SEM images and EDX	122
4.4.10	Effect of added salt NaCl on the MB uptake.....	123
4.4.11	Regeneration and reuse of resin	124
4.4.12	Immobilization mechanism	124
4.4.13	Removal of Hg(II).....	126
4.4.14	Removal of Anionic Dye Methyl Orange (MO) and Simultaneous Removal of MB and Hg(II) from Aqueous Solution.....	127
4.4.15	Treatment of Industrial Wastewater	128
4.5	Conclusion	129

**CHAPTER 5 A RESIN CONTAINING MOTIFS OF MALEIC ACID
AND GLYCINE: A SUPERABSORBENT FOR
ADSORPTIVE REMOVAL OF BASIC DYE PARAROS
ANILINE HYDROCHLORIDE AND Cd(II) FROM WATER.... 130**

5.1 Abstract.....	130
--------------------------	------------

5.2 Introduction.....	131
------------------------------	------------

5.3 Experimental	135
-------------------------------	------------

5.3.1 Materials.....	135
5.3.2 Physical Methods	135
5.3.3 Synthesis of the Resins.....	136
5.3.4 PRH Adsorption	136
5.3.5 Adsorption/Desorption of PRH	138

5.4 Results and Discussion.....	139
--	------------

5.4.1 Resin Synthesis	139
5.4.2 TGA analyses	140
5.4.3 Effect of pH on Adsorption	141
5.4.4 Adsorption Kinetics.....	142
5.4.5 Infrared spectra.....	146
5.4.6 Energy of Activation	147
5.4.7 Thermodynamics of adsorption	148
5.4.8 SEM Images and EDX	152
5.4.9 Mechanism of adsorption	153
5.4.10 Recycling.....	154
5.4.11 Removal of Cd(II) and Simultaneous Removal of PRH and Cd(II) from Aqueous Solution...	154
5.4.12 Industrial wastewater remediation.....	155

5.5 Conclusion	157
-----------------------------	------------

CHAPTER 6 CONCLUSION AND FUTURE WORK.....	159
6.1 Conclusion	159
6.2 Future Work.....	161
CHAPTER 7 REFERENCES	163
VITAE.....	190
LIST OF PUBLICATIONS	191

LIST OF TABLES

Table 2.1	Cyclocopolymerization ^a of monomers 1, 12 and 13 with maleic acid 2	34
Table 2.2	Protonation of polymer 15 (ZH_2^+) at 23 °C	55
Table 2.3	Protonation of polymer 4 (ZH^+) at 23 °C	56
Table 2.4	Percent scale inhibition in the presence of PZ 4 and PA 15 in 3 CB ^b supersaturated CaSO ₄ solution at 40 °C.	60
Table 3.1	Attempted cycloterpolymerization ^a of monomers 1a, 1b and 5 with maleic acid 2 and SO ₂ .	70
Table 3.2	Attempted cycloterpolymerization of monomer 7 or 8 with SO ₂ and maleic acid 2.	75
Table 3.3	Attempted cycloterpolymerization of monomers 15 with SO ₂ and maleic acid 2.	77
Table 3.4	Protonation of polymer 13 (ZH_2^+) at 23 °C.	79
Table 3.5	Percent scale inhibition in the presence of PA 13 in 3 CB ^a supersaturated CaSO ₄ solution at 40 °C.	93
Table 4.1	BET surface area analysis of CAPE 5.	107
Table 4.2	Kinetic parameters for MB adsorption on CAPE 5.	113
Table 4.3	Various isotherm constants for MB adsorption on CAPE 5 at 298 K.	118
Table 4.4	The R_L values and % MB removal of MB on CAPE 5 at 298 K.	119

Table 4.5	Thermodynamic (ΔG° , ΔH° , ΔS°) data for MB adsorption on CAPE 5.	121
Table 4.6	The R_L values and % MB removal of MB on CAPE 5 at 298 K.	125
Table 4.7	Hg(II), MB and methyl orange removal from aqueous solution (20 mL) at pH 5.3 by CPZA 4 (50 mg) at 298 K.	127
Table 4.8	Metal ions and MB concentrations in wastewater before and after treatment with CAPE 5 at 298 K.	128
Table 5.1	Lagergren Kinetic Model and Intraparticle Diffusion Model Parameters for Pararosaniline Adsorption on Resin 5 at Different Temperatures.	145
Table 5.2	Langmuir, Freundlich, and Temkin, Isotherm Model Constants for Rosaniline Adsorption on CAPE 5 at 298 K.	150
Table 5.3	Thermodynamic (ΔG° , ΔH° , ΔS°) data for PRH adsorption on CAPE 5.	151
Table 5.4	Comparison of Cd^{2+} and Rosaniline (RA) Dye Concentrations in Wastewater and Deionized Water Samples Before and After the Treatment with Resin 4 or 5 at 298 K.	156
Table 5.5	A comparative Adsorption Capacities (q_m) of Resin 5 for PRH (or Basic Fuchsin) with other Types of Adsorbents.	157

LIST OF FIGURES

Figure 1.1 Interconversion of the pH-responsive polymers.....	2
Figure 1.2 Antipolyelectrolyte behavior of polyzwitterions. Dashed lines () indicate intrachain attraction.....	5
Figure 2.1 ^1H NMR spectrum of (a) 12, (b) 18, (c) 15, and (d) 8 in D_2O	36
Figure 2.2 ^{13}C - NMR spectrum of (a) 12, (b) 19, (c) 8, (d) 14, and (e) 15 in D_2O	37
Figure 2.3 TGA curves of 4 and 15	45
Figure 2.4 The viscosity behavior at 30 °C of polyampholyte 15.....	48
Figure 2.5 The viscosity behavior at 30 °C of polyzwitterion 4 (prepared by acid hydrolysis of 15 from entry 6, Table 2.1)	49
Figure 2.6 Plot for the apparent log K_i versus degree of protonation (α) in salt-free water	54
Figure 2.7 Conductivity of a supersaturated solution of CaSO_4 in the presence (5,10,15,20 ppm) of 4 and 15 (20 ppm) and in the absence (blank) of antiscalant.....	60
Figure 3.1 TGA curves of 13.	84
Figure 3.2 ^1H NMR spectrum of (a) 12, (b) 9, (c) 10, and (d) 13 in D_2O	86
Figure 3.3 ^{13}C NMR spectrum of (a) 12, (b) 9, (c) 10 , (d) 13, and (e) 4a in D_2O	87
Figure 3.4 The viscosity behavior at 30 °C of polyampholyte 13	89

Figure 3.5 Plot for the apparent $\log K_i$ versus degree of protonation (α) in salt-free water	91
Figure 3.6 Conductivity of a supersaturated solution of CaSO_4 in the presence (5, 10, 15, 20 ppm) of 13 and in the absence (blank) of antiscalant.	93
Figure 4.1 TGA analysis (a) of CPZA 4 and CAPE 5, and pH dependency (b) of adsorption capacity (q) of resin 5 for MB at various pHs.....	108
Figure 4.2 Adsorption kinetics of MB % removal at various temperatures.	110
Figure 4.3 Kinetic study of MB adsorption on CAPE 5.....	111
Figure 4.4 The infrared spectra of MB, acidic resin 4, basic resin 5, and MB-loaded basic resin CAPE 5.	115
Figure 4.5 The activation energy for the adsorption process.....	116
Figure 4.6 The isotherm plots of Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich.	120
Figure 4.7 The thermodynamically Adsorption $\rightleftharpoons$ desorption process.....	121
Figure 4.8 The SEM and EDX images of MB loaded - CAPE 5.....	122
Figure 4.9 The % removal efficiency of MB in the presence of NaCl and % recovery efficiency.	123
Figure 4.10 The irreversibility process of MB towards a chemical adsorption and the pH-dependent surface charge of the resin via zeta potential measurement.	126
Figure 4.11 The Langmuir model for removal of Hg(II)	127
Figure 5.1 TGA (a) resin 4, 5 and the PRH-loaded resin. Plots (b) of q_{PRH} versus pH	

at 298 K.....	140
Figure 5.2 Percent PRH removal by resin 5 versus time at various temperatures.....	143
Figure 5.3 Adsorption from 2000 ppm PRH Solutions (100 mL) at pH 6.37 onto CAPE 5 (250 mg) at ●25, ●40, and ●55 °C:	144
Figure 5.4 IR Spectra of (a) PRH-loaded Resin 5, (b) Resin 5, (c) Resin 4, and (d) PRH.	147
Figure 5.5 Arrhenius plot (a) and Initial Concentration (b) Versus Equilibrium Adsorption Capacity of Resin 5 for PRH at pH 6.37 at 298 K.....	148
Figure 5.6 Nonlinearized Langmuir isotherm plots.....	151
Figure 5.7 (a) Equilibrium adsorption capacity of CAPE 5 versus temperature, (b) Vant Hoff plot.	152
Figure 5.8 SEM and EDX Analysis for CAPE 5 (a) Unloaded and (b) Loaded with PRH.	153
Figure 5.9 (a) Linear fits of Elovich kinetic model to the PRH adsorption at concentrations of 2000 ppm (100 mL) pH 6.37 in the presence of resin 5 (250 mg) at 25, 40 and 55 °C, (b) Adsorption/desorption repeated cycles of PRH onto resin 5.	154
Figure 5.10 (a) Langmuir isotherm of the adsorption of Cd ²⁺ ions on resin 4 at 298 K, 155	

LIST OF SCHEME

Scheme 1.1	Butler's cyclopolymerization protocol.....	3
Scheme 1.2	Cyclopolymerization of diallylammonium monomers 4, and sulfur dioxide. 4	
Scheme 1.3	Alternate copolymerization of hydrophobically substituted diallylamines 14 with maleic acid 8 produced 15.....	8
Scheme 1.4	Alternate copolymerization of cationic 16 and anionic 12 monomers produced polyampholytes 17.	9
Scheme 1.5	Copolymerization of diallyldimethylammonium chloride 10 and a functionalized maleamic acid 18 leading to a water-soluble polymer 19....	10
Scheme 1.6	Cyclopolymerization of a diallyl amine (DA) 20 monomer with maleic acid 8 produced 22.	19
Scheme 1.7	Copolymerization of hydrolyzed monomer 26 and MA 8 to give pH-responsive polymer 27.....	20
Scheme 1.8	Copolymerization of a DA monomer 29 with MA 8.	21
Scheme 1.9	Copolymerization of a DA monomer 34 with MA 8.	22
Scheme 1.10	Terpolymers of a DA monomer 39 with MA 8 and SO ₂	23
Scheme 1.11	Synthesize of cross-linked resin 42 via a DA monomer 26, MA, and cross-linker 41.....	24
Scheme 2.1	Synthesis of alternate copolymers from monomer 1/maleic acid 2 using cyclopolymerization protocol.....	30
Scheme 2.2	Synthesis of alternate copolymers from monomer 12/maleic acid 2	

and monomer complex 13 using cyclopolymerization protocol.....	31
Scheme 2.3 pH Induced changes in the charge types and densities in the backbone of 14 -17.	52
Scheme 2.4 pH Induced changes in the charge types and densities in the backbone of 3-8.....	53
Scheme 2.5 Percent scale inhibition (PSI) of some antiscalants synthesized via cyclopolymerization protocol.	59
Scheme 3.1 Synthesis of homocyclopolymer and alternate copolymers from monomeric pairs: A/maleic acid and A/SO ₂	65
Scheme 3.2 Terpolymerization of 1 or 5/MA/SO ₂	69
Scheme 3.3 Synthesis of homopolymer from 8, alternate copolymers from 7/MA, 8/SO ₂ and terpolymers from 7 or 8/MA/SO ₂	72
Scheme 3.4 Synthesis of alternate copolymers from 15/MA and 15/SO ₂ and terpolymers from 15/MA/SO ₂	76
Scheme 3.5 pH induced changes in the charge types in the backbone of 13, 19-21.	78
Scheme 4.1 Synthesis of cross-linked polyzwitterionic/anionic resins.	100
Scheme 4.2 Electrostatic interaction between the resin, cationic dye and Hg(II).	109
Scheme 5.1 Synthesis of Cross-linked Polyzwitterionic/Anionic Resin.	134
Scheme 5.2 pK _a and pK _h values of several acidic centers.....	141

LIST OF ABBREVIATIONS

AIBN	: Azosobutyronitrile
AMPH	: 2,2'-azobis(2-methylpropionamidine) dihydrochloride
APS	: Ammonium Persulfate
CAPE	: Cross-linked Anionic Polyelectrolyte
CB	: Concentrated Brine
CPZA	: Cross-linked Polyzwitterionic Acid
CSC	: Critical Salt Concentration
DTS	: Dispersion Technology Software
EDX	: Energy-Dispersive X-ray
FTIR	: Fourier Transformation Infrared Spectroscopy
IEC	: Ion Exchange Capacity
LCST	: Lower Critical Solution Temperature
MA	: Maleic Acid
MB	: Methylene Blue
PA	: Polyampholyte
PRH	: Pararosaniline Hydrochloride
PSI	: Percent Scaling Inhibition
PTA	: Polytetraanion
PZ	: Polyzwitterion
PZDA	: Polyzwitterion/Dianion
PZTA	: Polyzwitterion/Trianion
RO	: Reverse Osmosis
RU	: Repeating Unit
SEM	: Scanning Electron Microscopy
TGA	: Thermogravimetric Analysis
WCDA	: Waste Catalyst-Derived Adsorbent

ABSTRACT

Full Name : [Ibrahim Yahia Yaagoob Mohamed]
Thesis Title : ["Alternate Cyclocopolymerization: Synthesis of a Novel Class of Ionic Polymers and their Applications"]
Major Field : [Chemistry]
Date of Degree : [December, 2018]

A class of specialty diallylamine salt monomers (**I**) consisting of methyl- and propylphosphonate, methylcarboxylate, and propylsulfonate pendants have been copolymerized with maleic acid (**II**) using Butler's cyclocopolymerization protocol. Ammonium persulfate-initiated alternate copolymerization of MA (**II**) with Monomer [(diallylamino)propyl]phosphonic acid hydrochloride (**Ia**) and *N,N*-diallyl-3-(diethylphosphonato)propylamine (**I-b**) afforded polyzwitterion (PZ): poly[(**Ia**-HCl)-*alt*-maleic acid] (**III**) and polyampholyte (PA): poly[(**I b**)-*alt*-maleic acid] (**IV**), respectively. PA (**IV**) by ester hydrolysis generated PZ (**III**). The pH-induced changes of backbone charges in tetraprotic (**III**) and diprotic (**IV**) were tested by viscosity measurements. Several protonation constants (or pK_a) of the CO_2^- (or CO_2H) and trivalent nitrogen (or protonated NH^+) in (**III**) and (**IV**) have been determined. The performance evaluation as an antiscalant in reverse osmosis (RO) fields were examined; PZ (**III**) at a concentration of 15 ppm revealed fabulous efficiency of $\approx 100\%$ in CaSO_4 scale inhibition from its supersaturated solution for many days at 40°C , whereas precipitation occurred within 10 min in the presence of 20 ppm of PA (**IV**).

Alternate copolymerization of diallylamine derivatives $[(\text{CH}_2=\text{CH}-\text{CH}_2)_2\text{NR}]$; $\text{R} = \text{Me}$ (**Ic**), $(\text{CH}_2)_3\text{PO}(\text{OEt})_2$ (**Ib**), and $\text{CH}_2\text{PO}(\text{OEt})_2$ (**Id**)]-MA (**II**) and [**I(c,b,d)**].HCl]-SO₂ pairs have been carried out thermally using ammonium persulfate initiator as well as UV radiation at λ of 365 nm. The reactivity ratios of ≈ 0 for the monomers in each pair [**I(c,b,d)**]-MA (**II**) and [**I(c,b,d)**].HCl]-SO₂ ensured their alternation in each copolymer. However, numerous attempted terpolymerization of [**I(c,b,d)**]-MA-SO₂ failed to entice MA (**II**) to participate to any meaningful extent. In contrast to reported literature, only 1-2 mol% of MA (**II**) was incorporated into the polymer chain mainly consisting of poly([**I(c,b,d)**]-*alt*-SO₂). Quaternary diallyldialkylammonium chloride $[(\text{CH}_2=\text{CH}-\text{CH}_2)_2\text{N}^+\text{R}_2 \text{Cl}^-]$; $\text{R} = \text{Me, Et}$ (**V**) also, did not participate in **V**-MA-SO₂ terpolymerizations. Poly(**Ic**)-*alt*-SO₂ (**VI**) is a stimuli-responsive polyampholyte; its transformation under pH-induced changes to cationic, polyampholyte-anionic, and dianionic polyelectrolytes has been examined by viscosity measurements. The pK_a of the two carboxylic acid groups and NH^+ in **VI** has been determined to be 2.62, 5.59, and 10.1. PA (**VI**), estimated as a potential antiscalant in reverse osmosis domains, at the concentrations of 5 and 20 ppm, imparted $\approx 100\%$ efficiency for CaSO₄ scale inhibition from its supersaturated solution for over 50 and 500 min, respectively, at 40 °C.

The novel pH-responsive resin which contains a high density of CO₂⁻ motifs as well as the chelating motifs of glycine residues have been synthesized as the first example of an alternate cyclopolymerization of diallylammonioethanoate $[(\text{CH}_2=\text{CHCH}_2)_2\text{NCH}_2\text{CO}_2^-]$ (**Ie**) and MA (**II**) in the presence of a cross-linker afforded a cross-linked polyzwitterionic acid (CPZA) (**VII**), which upon base treatment gave the corresponding cross-linked anionic polyelectrolyte (CAPE) (**VIII**). The resin CAPE (**VIII**) found to be a super-

adsorbent removed simultaneously methylene blue (MB) and Hg(II) from aqueous solution and spiked industrial wastewater; with remarkable efficacy having a maximum uptake (q_{MB}) of 2101 mg g⁻¹ for MB and 263 mg g⁻¹ for Hg(II) ions. The process showed an extraordinarily fast adsorption rate; the resin (250 mg) was able to trap 69, 78 and 99.4% MB from its 3000 mg L⁻¹ solution (100 mL) within 2, 3 and 30 min, respectively.

The resin CAPE (**VIII**) turned out to be a super-adsorbent for pararosaniline hydrochloride (PRH) removal from aqueous solution; having a maximum adsorption capacity q_{max} of 1560 mg g⁻¹ as determined by Langmuir adsorption isotherm.

The adsorption isotherms, kinetics, and thermodynamic parameters of the adsorption have been determined. The excellent recycling efficiencies ensured the reuse of the resin. The very impressive performance accorded the resin a prestigious place among many sorbents.

ملخص الرسالة

الاسم الكامل: ابراهيم يحيى يعقوب محمد

عنوان الرسالة: "البلمرة الحلقية المشتركة المتناوبة: إصطناع فئة جديدة من البوليمرات الأيونية وتطبيقاتها"

التخصص: الكيمياء

تاريخ الدرجة العلمية: ديسمبر 2018

تم إجراء بلمرة مشتركة لفئة خاصة من مونومرات ملح ثنائي أليل أمين **I** (محتوية على فوسفونات الميثيل، أو فوسفونات البروبيل، أو كربوكسيلات الميثيل، أو سلفونات البروبيل) لبلمرة مشتركة مع حمض المالبيك **II** باستخدام بروتوكول بتلر للبلمرة الحلقية (Butler's Cyclopolymerization). باستخدام البادئ فوق كبريتات الأمونيوم لبلمرة متناوبة مشتركة بين حمض المالبيك **II** مع مونومرات [ثنائي الأليل أمينو] هيدروكلوريد حمض الفوسفونيك (**I a**) و **N**، ثنائي أليل-3-(ثنائي إيثيل فسفوناتو) بروبييل أمين (**I-b**) تم تصنيع بولي زويتر أيون (PZ): بولي [**I a**-(حمض الهيدروكلوريك)-تناوب-حامض المالبيك] (**III**) و بولي أمفولايت (PA): بولي [**I b**-(تناوب-حمض المالبيك)] (**IV**)، على التوالي. وبتحلل الاستر في (IV) PA تم إنتاج (III) PZ. وقد تم إختبار التغييرات الناجمة عن الرقم الهيدروجيني لشحنات العمود الفقري في رباعي البروتون (**III**) وثنائي البروتون (**IV**) عن طريق قياسات اللزوجة. و تم تحديد عدة ثوابت البروتون (أو pKa) للـ CO_2^- (أو CO_2H) والنيتروجين ثلاثي التكافؤ (أو NH^+) البروتونية) في (**III**) و (**IV**). كما تم فحص تقييم الأداء كموانع ترسيب في مجالات التناضح العكسي (RO)؛ وقد أظهر استخدام (III) PZ بتركيز 15 جزء في المليون كفاءة رائعة تبلغ $\approx 100\%$ في تثبيط تشكل كبريتات الكالسيوم CaSO_4 من محلوله فوق المشبع لعدة أيام عند 40 درجة مئوية، في حين حدث الترسيب في غضون 10 دقائق في وجود 20 جزء في المليون من (IV) PA.

تمت إجراء البلمرة المشتركة المتناوبة لمشتقات ثنائي أليل أمين [$(\text{CH}_2=\text{CH}-\text{CH}_2)_2\text{NR}$; R= Me (**Ic**)]، و (**Ib**) $(\text{CH}_2)_3\text{PO}(\text{OEt})_2$ ، و (**II**) $\text{CH}_2\text{PO}(\text{OEt})_2$ و أزواج $[\text{I}(\text{c,b,d}).\text{HCl}]-\text{SO}_2$ حرارياً

باستخدام بادئ فوق كبريتات الأمونيوم وكذلك الأشعة فوق البنفسجية عند طول موجي (λ) 365 نانومتر. كانت نسب التفاعل تقريبا صفر ≈ 0 للمونومرات في كل زوج من (II) $[I(c,b,d)]-MA$ و $[I(c,b,d)]-SO_2.HCl$ مما يضمن تناوبهم في كل بوليمر مشترك. ومع ذلك، فقد فشلت العديد من محاولات البلمرة الثلاثية لـ $[I(c,b,d)]-MA-SO_2$ في نجاح مشاركة (II) MA إلى أي مدى يعتد به. على النقيض من الأبحاث المنشورة التي ذكرت، فقد تم دمج 1-2 مول٪ فقط من (II) MA في سلسلة البوليمر التي تتكون أساساً من $poly([I(c,b,d)]-alt-SO_2)$. وكذلك فإن ثنائي أليل ثنائي الكيل كلوريد الأمونيوم الرباعي (V) $[(CH_2=CH-CH_2)_2N^+R_2 Cl^-; R= Me, Et]$ لم يشارك أيضاً في البلمرة الثلاثية لـ $V-MA-SO_2$. البوليمر المشترك (VI) $Poly(Ic)-alt-SO_2$ هو بولي أمفولايت يستجيب للمؤثر؛ وقد تم فحص تحوله في ظل التغيرات التي يسببها الرقم الهيدروجيني إلى بولي الكتروليتات كاتيونية، أو بولي أمفولايت- أنيونية، أو ثنائي أنيونية بواسطة قياسات اللزوجة. وقد تم تحديد قوة الحمض pKa لمجموعتين من مجموعات حمض الكربوكسيلية و NH^+ في VI ووجد أنها تساوي 2.62، 5.59، و 10.1. وقد أعطي بولي أمفولايت (VI) PA ، والذي يُقدّر أنه مانع ترسيب محتمل في مجالات التناضح العكسي، عند استخدامه بتركيز 5 و 20 جزء في المليون، يوفر كفاءة $\approx 100\%$ لتثبيت تشكل كبريتات الكالسيوم $CaSO_4$ من محلولها فوق المشبع لأكثر من 50 و 500 دقيقة، على التوالي، عند 40 درجة مئوية.

تم تصنيع راتنجات جديدة مستجيبة لدرجة الحموضة والتي تحتوي على كثافة عالية من فئات الكربوكسيل CO_2^- وكذلك عناصر مخلية تحوي الجلايسين كأول مثال للبلمرة الحلقية المتبادلة للثنائي أمونيو إيثانوات $[(CH_2=CHCH_2)_2NCH_2CO_2^-]$ (Ie) وحمض المالليك (II) MA في وجود متشابك حيث أنتجت حمض بولي زويتر أيونك متشابك (VII) $(CPZA)$ ، والتي عند معالجتها بالقاعدة أعطت بولي الكتروليت أنيوني متشابك المقابل (VIII) $(CAPE)$. وقد وُجد أن الراتنج (VIII) $CAPE$ فائق الإمتصاص وأزال في وقت واحد الميثيلين الأزرق (MB) والزنابق (II) من محلول مائي ومياه الصرف الصناعي؛ مع فعالية ملحوظة وجد إمتصاص أقصى (qMB) 2101 mg g^{-1} للميثيلين الأزرق MB و 263 mg g^{-1} لأيونات الزنابق (II). كما أظهرت العملية معدل إمتصاص سريع للغاية؛ حيث أن الراتنج (250 مجم) كان قادراً على إزالة 69، 78 و 99.4٪ الميثيلين الأزرق MB من محلوله 3000 mg L^{-1} (100 مل) خلال 2، 3 و 30 دقيقة على التوالي.

تبين أن الراتنج CAPE (VIII) عبارة عن مادة فائقة الإمتصاص لإزالة باراروزانيلين هيدروكلوريد (PRH) من المحلول المائي؛ مع إمتلاك حد أقصى لسعة الإمتصاص يبلغ 1560 mg g^{-1} كما أظهرتها قياسات ايزوثرم لانجميور Langmuir للإمتزاز.

لقد تم تحديد أيسوثرم الإمتزاز، والحركية، ومعلومات الديناميكية الحرارية للإمتزاز. إن كفاءة إعادة التدوير الممتازة تضمن إعادة إستخدام الراتنج. كما أن الأداء المتميز للغاية يمنح هذا الراتنج مكانة مرموقة بين العديد من المواد الماصة.

CHAPTER 1

INTRODUCTION

Ionic polymers are those polymers having ionic groups in the polymer backbone. Such as carboxylate ($-\text{CO}_2^-$), phosphonate ($-\text{PO}_3^{2-}$), or sulfonate ($-\text{SO}_3^-$). There has been a remarkable academic and industrial significances in the preparation as well as properties of water-soluble ionic polymers. These polymers are of tremendous interest for their distinct appropriateness to various research applications. There are two main categories of water-soluble polymers; non-polyelectrolytes and polyelectrolytes. All water-soluble polymers share the common feature of having hydrophilic polar functional sets that may be non-ionic, anionic or cationic. The anionic and cationic polymers together are referred to as polyelectrolytes, whereas the non-ionic counter parts are called non-polyelectrolyte. In recent years, an overwhelming number of studies have concentrated on the water-soluble polymers. There are some reports, which attributed to the synthesis of assembling ionic copolymers introduced by Butler's cyclopolymerization method.

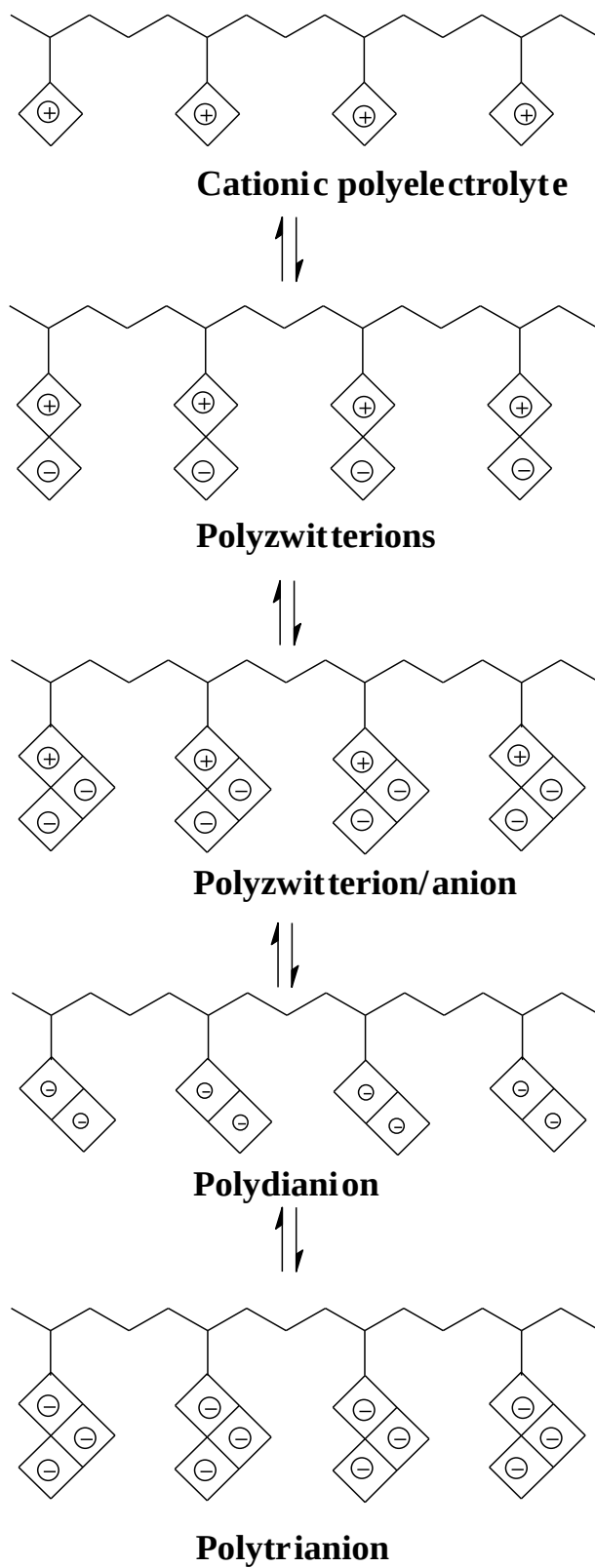
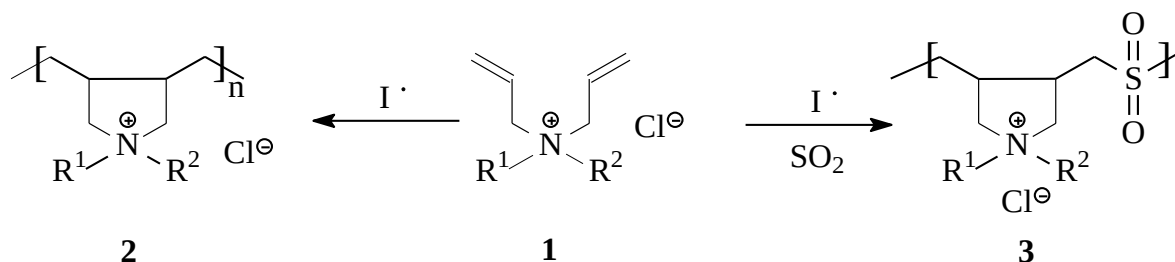


Figure 1.1 Interconversion of the pH-responsive polymers

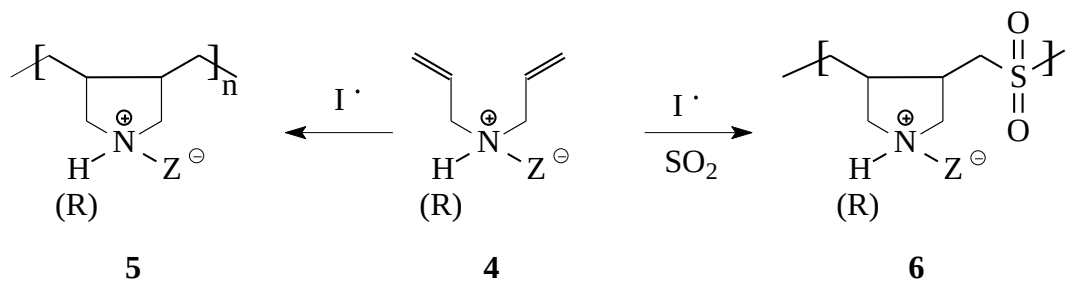
1.1 Ionic Polymers by Cyclopolymerization

Application of Butler's cyclopolymerization protocol [1-7] is instrumental in converting diallylammonium salts **1** into a plethora of industrially significant cyclopolymers **2** whose pyrrolidine ring-embedded architecture is considered to be the eighth most important structural type [8,9] (Scheme 1.1). Butler's cyclopolymer poly(diallyldimethylammonium chloride) has numerous publications and patents (> 1000): water purification and personal care formulation remain the important areas of its application [1]. The industrially important water-soluble cationic polyelectrolytes **3** can also be synthesized by the cyclopolymerization of diallyldimethylammonium chloride and sulfur dioxide [10-12].



Scheme 1.1 Butler’s cyclopolymerization protocol.

Using Butler's cyclopolymerization protocol, the polyzwitterions **5** can be synthesized from diallylammonium monomers **4**, which has both positive and negative charges in the same molecule ($M^{\pm}$). Likewise, the zwitterionic copolymers **6** have been synthesized by the cyclopolymerization of diallylammonium monomers **4**, and sulfur dioxide (Scheme 1.2) [2-4, 12-20]. However, the presence of both M^+ and M^- in the same polymer chain constitutes a polyampholyte with or without charge symmetry [14].



Scheme 1.2 Cyclopolymerization of diallylammonium monomers **4**, and sulfur dioxide.

The polyampholytes and polyelectrolytes exhibit ‘anti-polyelectrolyte behavior’ [17-23], which can be explained by the presence of added polyelectrolytes (*e.g.*, NaCl). Increasing the concentrations of NaCl increases the solubility and viscosity values due to the effective neutralization of the opposite charges of the polymers, and the polymers appear as collapsed or globular coil conformations. The opposite behavior is observed in a typical polyelectrolytes (i.e., the viscosity decreases with increasing the concentrations of NaCl), [Figure 1.2](#).

The commercial polyampholytes and polyelectrolytes derived from acrylate and acrylamides, considered to be biopolymers such as proteins and DNA, have been widely used in many industrial applications such as charge dispersing agents, textiles and colloids [15].

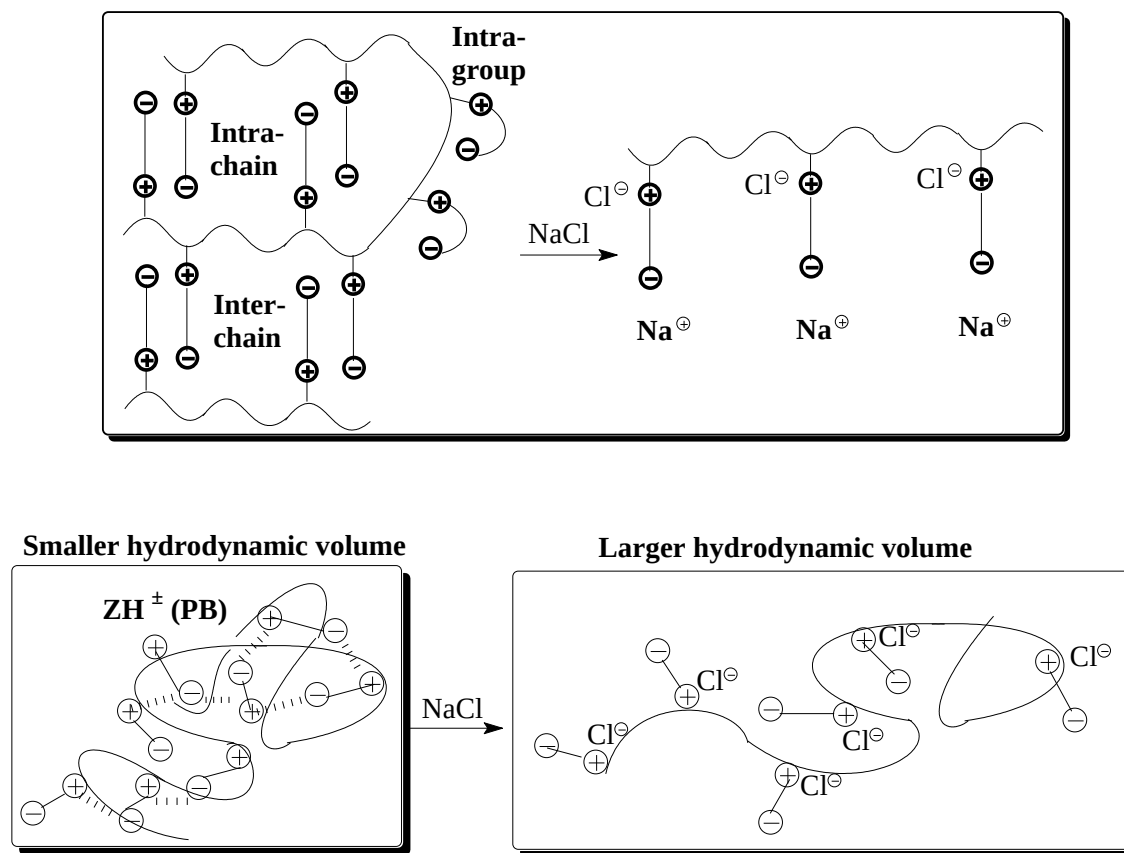


Figure 1.2 Antipolyelectrolyte behavior of polyelectrolytes. Dashed lines (||||) indicate intrachain attraction.

Sometimes, the zwitterionic interactions are so strong that it requires a large critical salt concentration (CSC) of NaCl to disrupt the intra- and interchain attractive interactions and permit its water solubility [10,24]. Due to the strong intragroup, intra- and inter-chain electrostatic interactions, the polyelectrolytes (PZs) maintain globular coil confirmations through ionically cross-linked network, and are usually insoluble in salt-free water [2,3,20,22,25,26]. The PZs exhibit ‘anti-polyelectrolyte behavior’. The viscosity value increases in the presence of added NaCl due to the effective neutralization of the opposite

charges of the polymers in a collapsed coil conformation [20,27,28]. The Na^+ and Cl^- ions shield (neutralize) the negative and positive charges in a dipolar motif, respectively, to different extents thereby leaving a net charge, which leads to the globule-to-coil transitions as a result of chain expansion of the polyelectrolyte (Figure 1.2).

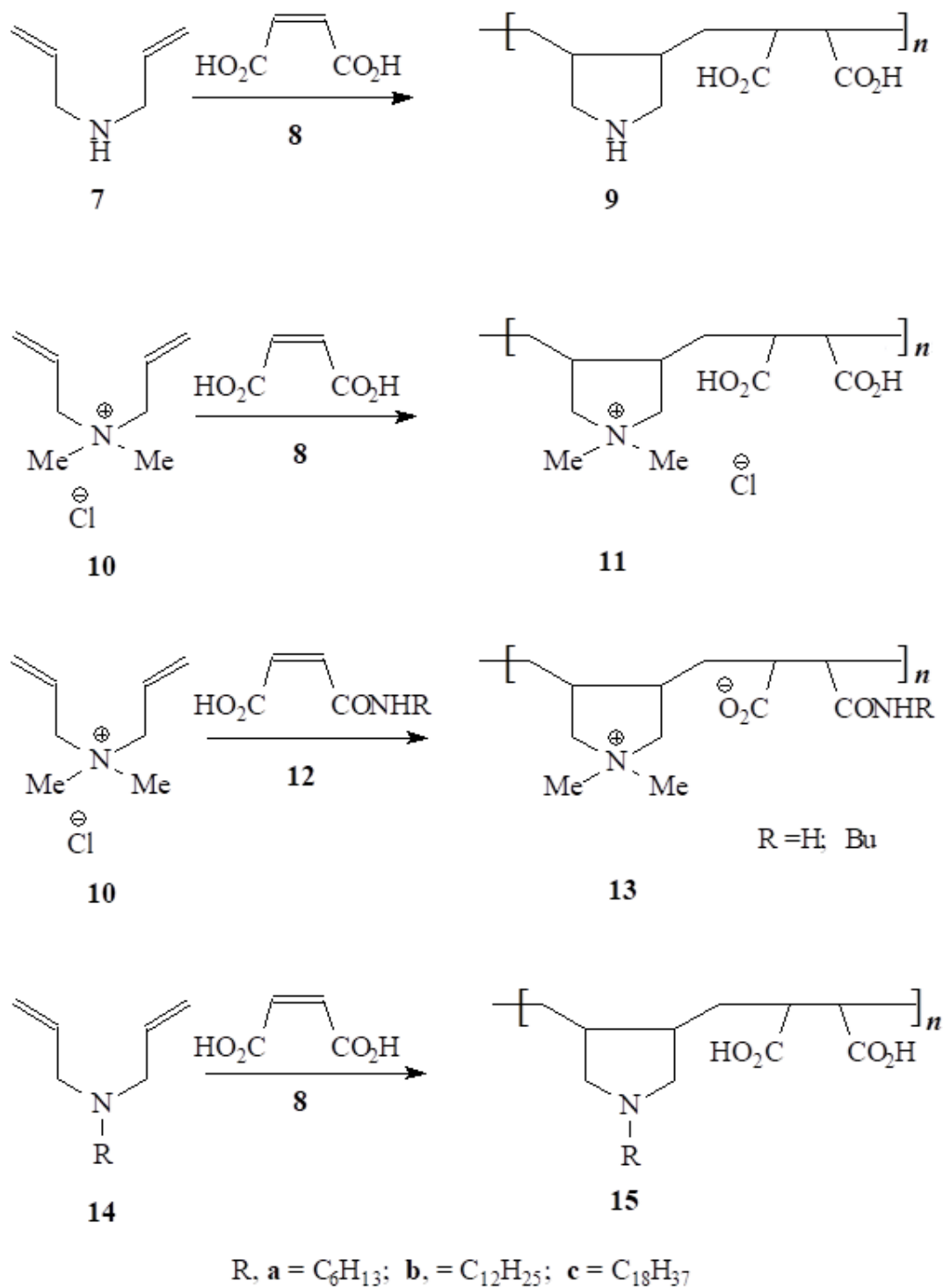
Radical copolymerization of maleic acid (MA) **8** with diallyl amine **7** results in polyampholytes **9**, which are completely or to high extent soluble in water (Scheme 1.3) [29]. Because of the strong interactions between the different charged moieties of the macromolecules, polyampholytes are either completely insoluble in water, or at the very least over a broad range of pH, too. Contrarily to this well-known behavior, the polyampholytes from MA and the allyl and diallyl amines were found soluble in water either over the whole range or over a major part of the pH. Dimethyldiallylammonium chloride **10** gave the copolymer **11** as shown in Scheme 1.3 [30]. The obtained copolymer **11** belonged to class IV low-toxicity substances, which exhibit pronounced antimicrobial activity with respect to some bacterial and fungal species.

1.2 Literature Review

1.2.1 Synthesis and Polymerization of Quaternary Ammonium Compounds

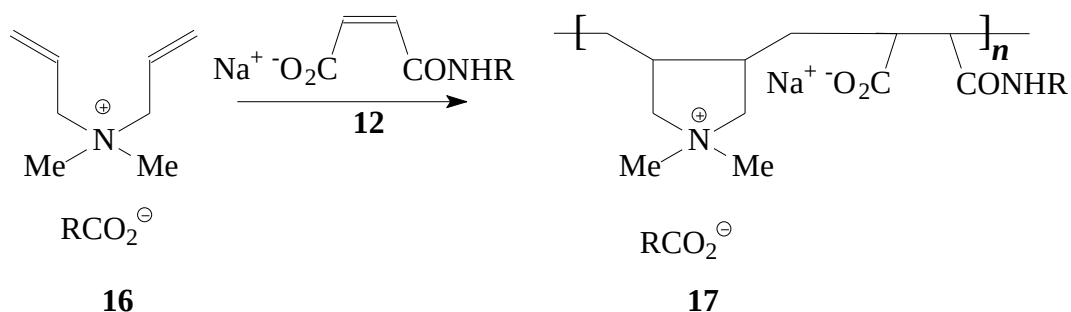
Koetz and coworkers [31,32] have reported synthesis of a series of hydrophobically modified polyampholytes **13** by copolymerizing the cationic monomer **10** and the anionic monomers maleamic acid or butylmaleamic acid **12** to examine the influence of hydrophobic side chains of the synthesized polyampholytes on the phase behavior as well as the properties of the polyampholyte-modified microemulsions (Scheme 1.3). Potentiometric behavior of polyampholytes **13** based on **10** and maleamic acid derivatives **12** have been studied (Scheme 1.3) [33,34].

The hydrophobically substituted diallylamines **14** bearing a hexyl, dodecyl, or octadecyl chain has been copolymerized with maleic acid to produce alternating copolymers **15** (Scheme 1.3). The copolymers were found to act as amphiphilic polyampholytes and dissolve best in the acidic or in the basic forms [35]. The amphiphilic poly(ampholyte): poly(*N,N*-diallyl-*N*-hexylamine-*alt*-maleic acid) **15a**, carrying simultaneously carboxylic acids, amines and hydrocarbon side chains (Scheme 1.3), was used as a matrix to stabilize inorganic ion species (anionic as well as cationic) created in aqueous solution from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{MoO}_4$ [36].



Scheme 1.3 Alternate copolymerization of hydrophobically substituted diallylamines **14** with maleic acid **8** produced **15**.

In a study conducted by Thünemann and co-workers, polyampholytes **17** with alternating cationic **16** and anionic **12** monomers were synthesized and complexed with fatty acids (dodecanoic acid and perfluorododecanoic acid) (Scheme 1.4). The formation of the polyelectrolyte-fatty acid complexes is self-assembled and produces nanoparticles with sizes in the range of 3-5 nm that were named dressed micelles [37].

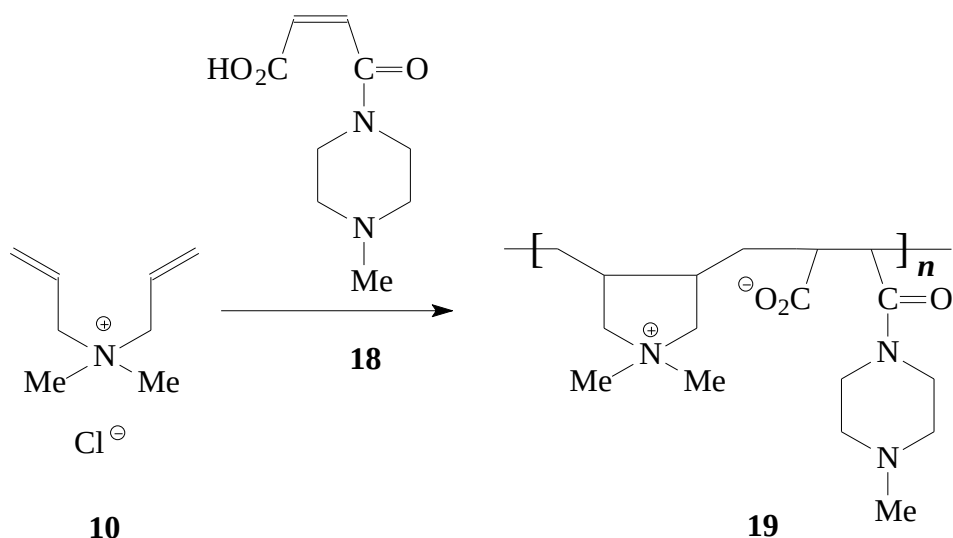


Scheme 1.4 Alternate copolymerization of cationic **16** and anionic **12** monomers produced polyampholytes **17**.

The water-soluble polymers are of tremendous interest for their distinct importance to multiple applied research. Water-soluble polymers are generated in large amounts, and are widely used in manufacturing consumer products. There are couple major types of water-soluble polymers: non-polyelectrolytes and polyelectrolytes. All water-soluble polymers participate the mutual element of bearing hydrophilic polar functional groups that may be non-ionic, anionic or cationic. The anionic and cationic polymers together are referred to as polyelectrolytes.

A water-soluble polyzwitterionic matrix possessing simultaneously charged species and complexing groups was synthesized by copolymerizing diallyldimethylammonium

chloride **10** and a functionalized maleamic acid **18** bearing an amine group suited for ionic complexation (Scheme 1.5). The matrix was used to stabilize inorganic species generated in solution from $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and/or $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ along with $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$. The presence of a complexing amine group in addition to the charged betaine moieties in the polymer permits to stabilize efficiently more than stoichiometric amounts of the cationic as well as the anionic species in the polymer-salt blends [38].



Scheme 1.5 Copolymerization of diallyldimethylammonium chloride **10** and a functionalized maleamic acid **18** leading to a water-soluble polymer **19**.

1.2.2 Chemicals to Control Scale Formation in Desalination Plants

The antiscalants are extensively used to control scale formation in desalination plants based on various processes such as Reverse Osmosis, Multi-Stage-Flash and other water treatment processes like cooling towers, boiler water, oil wells, *etc.*, [39]. The deposits

commonly encountered in desalination process include mineral scales (i.e., CaCO_3 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$, CaSO_4 , $\text{Mg}(\text{OH})_2$, corrosion products, polymeric silica and suspended matter [40]. The possible mechanism for the prevention of scale formation has been reported [41]. Various kinds of additives have been explored for controlling the deposition of alkaline scale (*e.g.*, calcium carbonate, magnesium hydroxide) and sulfate scale in desalination plants [42].

Typical additives used as antiscalants include polyphosphates, organophosphonates, poly(acrylic acid), poly(maleic acid), and copolymers containing a variety of functional groups such as carboxyl, acrylamide, sulfonic acid, ester, *etc.* Polymer-based materials are also used as antiscalants; the effectiveness of additives poly(maleic acid) (PMA) based Belgard EV 2000 and polyphosphonate (PPN) based DSB(M) in scale control has been reported [43]. The anionic form of the antiscalants helps prevent scale formation by sequestering the cations.

The use of poly(acrylic acid) and poly(acrylamide), often used as water-soluble polymers with anti-scale properties, do not show biodegradability [44]. Thus, there is a desire for biodegradable water-soluble polymers [45-47]. Sodium polyaspartate has been examined for its calcium ion-chelating ability [48,49].

Dispersants for polymeric silica, a cause for problems in desalination plants, based on phosphonate, carboxylate and sulfonates has been reported [50]. Exceptional chelating properties of compounds consisting of aminomethylphosphonic acid groups in a molecule have attracted great interest to synthesize low molecular-weight chelating agents containing these functional groups that should be able to form polymer-heavy metal ion complexes from wastewater [51-53]. The formation of soluble Ca^{2+} by the polymers will

restrain them from precipitating and thus blocking membranes in the reverse osmosis treatment in desalination plants.

1.2.3 Sorbents for the Removal of Toxic Metal Ions

Cross-linked polymeric materials containing chelating functional groups of amine, carboxylate, phosphonate, *etc.*, motifs have enabled a significant interest in the separation and removal of toxic metals. Functional groups having aminomethyl phosphonate motifs have shown exceptional chelating properties in the elimination of toxic metals from aqueous solutions [54,55]. Pollution caused by toxic metal ions has been found to have a large negative influence on the environment. Metal ions like Pb^{2+} , Zn^{2+} , Cu^{2+} and Cd^{2+} cause several diseases and disorders; for example, copper poisoning can cause liver and kidney damage, irritation of the respiratory system, whereas cadmium can cause nervous system damage, bone damage as well as other serious illness [56-61].

According to World Health Organization (WHO) standards, the maximum permissible concentration of copper in drinking water is 0.2 mg/L [62], while it is 0.2 and less than 2 mg/L for agriculture irrigation and ponds fish farming, respectively [63]. For protection of humans and the environment, it is very important to clear copper ions from environments. For Cd, the drinking water guideline value recommended by WHO is 0.003 mg/L [64]. It is hard for chemical precipitation technologies to treat economically low concentration (less than 5 mg/L) of cadmium. Ion exchange and reverse osmosis have been efficient in acquiring the metal concentration limits but at the expense of high operation and maintenance costs [65].

The polysulfobetaines (polyzwitterions) bearing charges of both positive and negative signs on the same repeating unit are a good candidates for the water technologies because of its dual role in removing the cationic or anionic effluent and they can impart anti-microbial properties [66]. Nowadays, researchers have concentrated on the syntheses of zwitterionic cross-linked inorganic/organic hybrid materials for the elimination of toxic heavy metal ions as well as organic dyes *via* electrostatic effects [67-69]. The literature given above explains many sorbent materials to remove larger concentrations of strontium ions; however, it remains challenging to develop new materials for removing strontium ions at ppb-levels.

1.2.4 Sorbents for the Removal of Organic Dyes from Aqueous Medium

Textile industries generates relatively large volumes of wastewater, and thus, [70] creates quantity good portion of effluents highly charged with pollutants which form a critical threat to the environment. For instance, at the order of one cubic meter of dye-contaminated water per ton of clothes manufacturing. Liquid and solid wastes resulted from these industries are difficult to treat. It is estimated that 10 – 15% of the dyes are lost in dye effluents during dyeing operations [71]. It is considered that the textile industries are responsible for 15% to 20% of the global water pollution [72]. Dye pollution in water leads to blocking the penetration of light desired for photosynthetic activities, inhibits the growth of biota, mutagenic, carcinogenic [72,73] and may produce chelates with metal ions exist in water that may be more toxic to aquatic creatures than the parent metal ions alone [74]. The annual production of dyes all over the world is approximated at 800,000 tones and around 50% of these are azo dyes [75]. Moreover, from an environmental perspective, the removal of synthetic dyes is an important issue. They include different

species of synthetic dyes, which are known to be a main source of environmental contamination in terms of both the volume of dye discharged and the effluent composition [76]. Dye effluents discharged from the dyestuff processing, dyeing, printing and textile industries act a sharp worldwide problem. Accordingly, these effluents need an initial treatment in order to reduce their contaminating load before being rejected into the natural environment.

Removing dyes from textile waste waters is somehow hard due to their high impedance to degradation and oxidation by classical techniques. [77]. for the time being, there is no single process able to provide sufficient treatment, mainly because of the complex nature of the effluents. [78]. Wastewaters can be treated by biological, chemical and physical approaches. By biological methods, many organic molecules existing in the wastewaters are degraded using microbial degradation, fungal decolorization or adsorption by microbial biomass and bioremediation systems [79]. Coagulation, chlorination, flocculation, classical oxidation and electrochemical processes are introduced as chemical methods. These techniques show efficiency for the treatment of wastewaters. The main disadvantages of the chemical processes are their high cost and accumulation of the concentrated sludge after the removal of dye.

Adsorption and membrane-filtration operations are mostly used as physical methods. Adsorption is a well-known equilibrium separation process and an effective technique for water decontamination operations [80]. Adsorptive removal of dyeing waste color is useful, due to its low cost, simplicity of process design, ease of operation, and insensitivity to toxic compounds [74]. Among potential sorbent substances, activated carbon is the most

important one for its high surface area and porous morphology, but its re-use is limited by the material loss during recovery. [81-84].

A study reported by Ozdemir and co-workers [85] investigated the possibility of melamineformaldehyde-urea (MFU) resin as an adsorbent for the removal of dye from leather industry wastewaters. Methylene blue, which is also known as tetramethylthionine, was used as a model dye to obtain the optimal conditions for the adsorptive treatment process. Parameters such as granule size, pH, contact time, column flow rate were optimized and studied by batch and column processes. They concluded that the adsorption capacity of the resin for methylene blue is greater than those of most unconventional sorbents.

Akazdam et al. [86] studied the removal of Acid Orange 7 dye from wastewater using the macroporous strongly basic anion exchange resin Amberlite FPA-98. They characterized the adsorbent by Fourier Transform-Infrared Spectroscopy (FTIR) and X Ray Diffraction (XRD). FTIR was used to study the principle mechanism for AO7 adsorption, and the results showed complexation and ion exchange appeared. In addition, they studied a batch adsorption by carrying out the removal of AO7 under various parameters such as contact time, pH, initial dye concentration, adsorbent dosage, agitation speed, and solution temperature. Experimental isotherm data were analyzed using Langmuir, Freundlich and Temkin isotherm equations and the isotherm constants were calculated using linear regression analysis for the determination of the isotherm parameters, which describe the adsorption process. They then concluded that the best fit was obtained by Langmuir model with a Langmuir maximum monolayer adsorption capacity of 200 mg/g at 303°K. A comparison of kinetic models applied to the adsorption of AO7 onto Amberlite FPA-98

was evaluated for the pseudo-first-order, the pseudo-second-order, Elovich, intraparticle diffusion and Bangham's kinetics models. The adsorption kinetic data were properly fitted very well with the pseudo-second-order kinetic model. Based on the results obtained, a summary that the concentrated solution gives better removal efficiencies was concluded. The thermodynamic parameters were also evaluated in the same study. The negative values of $\Delta H^\circ = -118.34 \text{ kJ/mol}$ and $\Delta S^\circ = -396.8272 \text{ J/K.mol}$ indicated respectively that the adsorption of AO7 onto Amberlite FPA-98 was exothermic; and spontaneous process. The Gibbs energy (ΔG°) increased when the temperature was increased from 298 to 323°K indicating a decrease in feasibility of adsorption at higher temperatures. The results have established good potentiality for the Amberlite FPA-98 to be used as a sorbent for the removal of AO7 from wastewater.

Song Cheng and coworkers [87] studied the removal of organic dyes from aqueous solutions using waste catalyst-derived adsorbent: Isotherm modeling and kinetic. By preparing a waste catalyst-derived adsorbent (WCDA) from mercury-containing waste catalyst (MCWC) obtained from polyvinyl chloride (PVC) production process by thermal treatment method via microwave-assisted CO₂ activation, to remove methylene blue (MB) and methyl orange (MO) from the aqueous solution, achieving the utilization of waste hazardous resources. After they investigated the physicochemical properties of WCDA and MCWC by N₂ adsorption, SEM, FTIR, Raman spectroscopy measurements and X-ray Photoelectron Spectra. MB and MO dyes were used as models, to evaluate the adsorptive performance of the WCDA. The equilibrium data were described by a Langmuir model with MB and MO adsorption capacity of the 260 mg g⁻¹ and 420 mg g⁻¹, respectively. The results indicated that the WCDA can adsorb MO easier than MB. The kinetic data were

accurately represented by a pseudo-second-order kinetic model. They also observed that the adsorption rate of the MO is larger than that of the MB. The same research group concluded that the preparation of WCDA is feasible and the WCDA can be a promising adsorbent for MB and MO removal from aqueous solution.

Xu et al. [88] reported a synthetic strategy of a novel triptycene and crown ether-based porous copolymer POP-TCE-15 bearing many attractive features, such as high surface area, good microporosity, hydrophobicity, and high densities of O heteroatom groups, by Friedel–Crafts reaction. They also reported its application as adsorbent for the removal of dyes such as MB, RhB (rhodamine B), and MO. They observed that POP-TCE-15 displayed the best performance, with a maximum adsorption capacity of MB, RhB, and MO of 787.4 mg g⁻¹, 421.9 mg g⁻¹, and 64.8 mg g⁻¹, respectively. The high adsorption capacity was explained by the electrostatic interaction between the positively charged cationic MB and the lone pair of electrons on the O atoms of crown-ether-15. The adsorption kinetics, isotherms, and regeneration of the adsorbent for the removal of MB, RhB, and MO were studied in detail. The mechanism of adsorption of the dyes on POP-TCE-15 was tentatively illustrated by theoretical quantum calculation. In conclusion, the fast adsorption kinetics, large adsorption capacity, excellent chemical stability, and good reusability make POP-TCE-15 an adsorbent with great potential for the removal of dyes from water.

1.3 Present State of the Problem

Polyphospho-, sulfo- and carbo-betaines (containing repeating unit of a phosphonate, sulfonate and carboxylate motifs), which seem to mimic for instance, phospholipid biomembranes, have offered many new applications [2,89]. Extraordinary chelating

properties of compounds containing aminomethylphosphonic acid groups have attracted considerable attention to synthesize low molecular-weight chelating agents containing these functional groups that should be able to form polymer-heavy metal ion complexes from wastewater [90-92]. The synthesis of a series of new pH-responsive polymers would pave the way to study cationic polyelectrolyte-to-polyzwitterionic-to-anionic polyelectrolyte transitions involving polymers having identical degree of polymerization. Poly(acrylic acid) and poly(acrylamide) are often used as water-soluble polymers with anti-scale properties, but they do not exhibit biodegradability [93]. Therefore, there is a demand for biodegradable water-soluble polymer.

In this work, novel cross-linked resins containing high charge density of -phosphonate and carboxylate motifs will be synthesized and tested for their efficiency as adsorbents for the removal of toxic metal ions such as Pb(II) and Cu(II) heavy metal ions as well as organic dyes (for instance: methylene blue, pararosaniline, and crystal violet) from aqueous solutions.

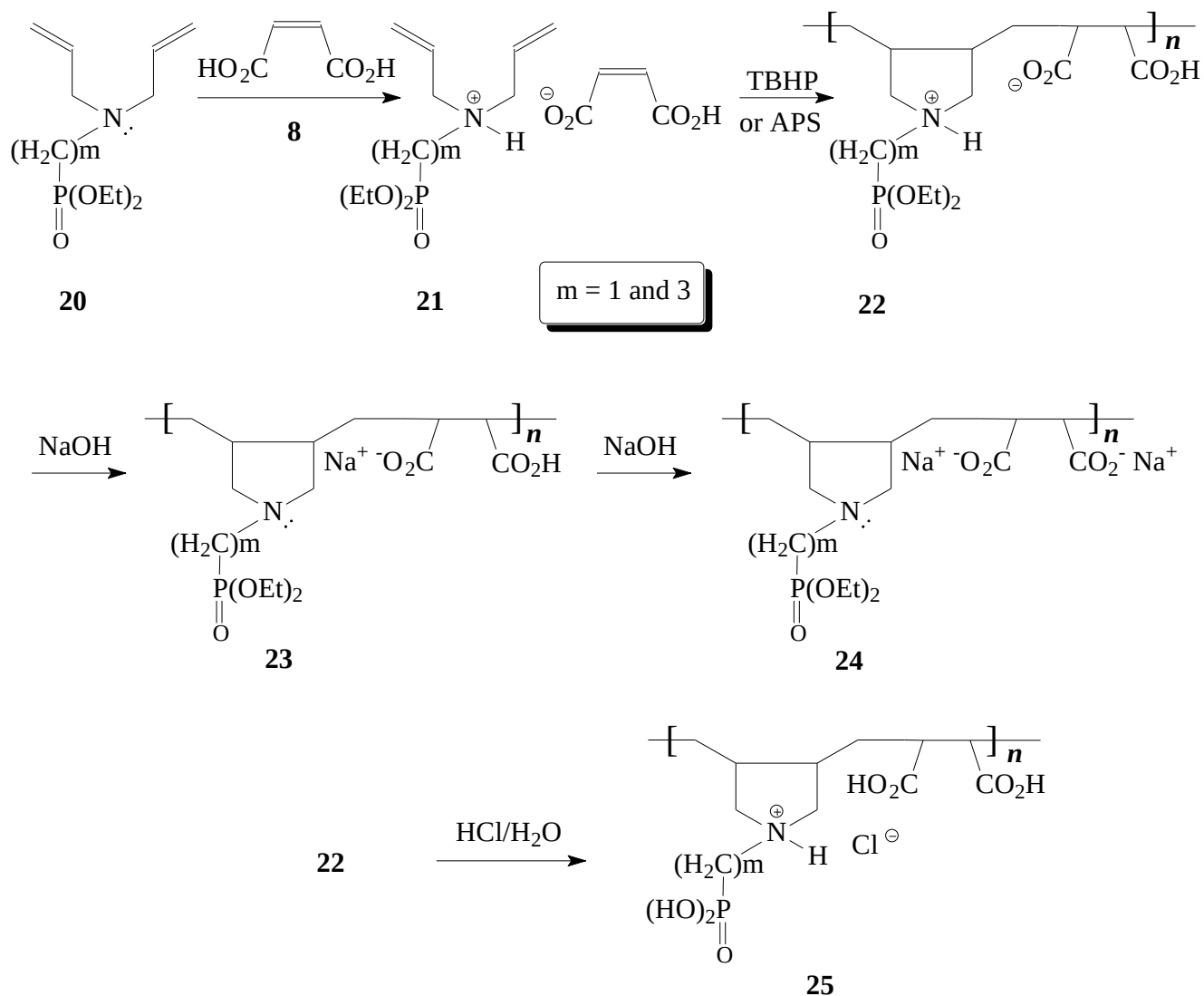
1.4 Objectives

The aim of this proposed research is to synthesize a novel series of pH-responsive polymers via cyclocopolymerization and cycloterpolymerization of specialty diallyl ammonium monomers and maleic acid. The aim of this research is two-fold: (i) synthesis of an interesting new class of ionic polymers, and (ii) their applications in various fields. The proposed work is thus of both academic and industrial interests. The presence of multiple cationic and anionic sites in a linear polymer and cross-linked resin is anticipated to sequester metal ions to prevent scale formation, and chelate harmful metal ions, respectively, in addition removal of organic dyes from their aqueous solutions.

More specifically, the proposed study have the following objectives:

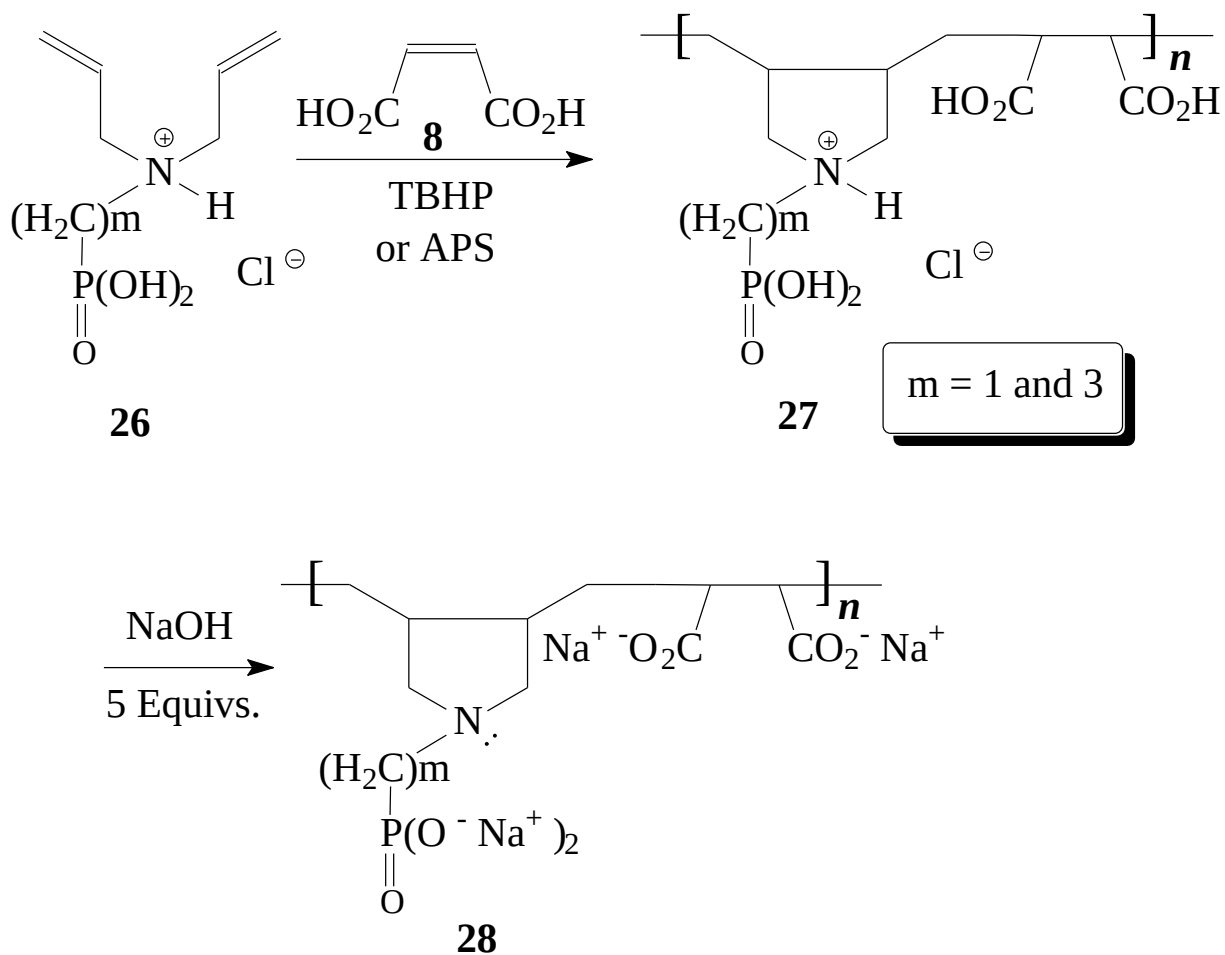
To have academic significance:

1. To synthesize a diallyl amine/ammonium (DA) monomer containing phosphonate motifs and their cyclopolymerization with maleic acid (Schemes 1.6).



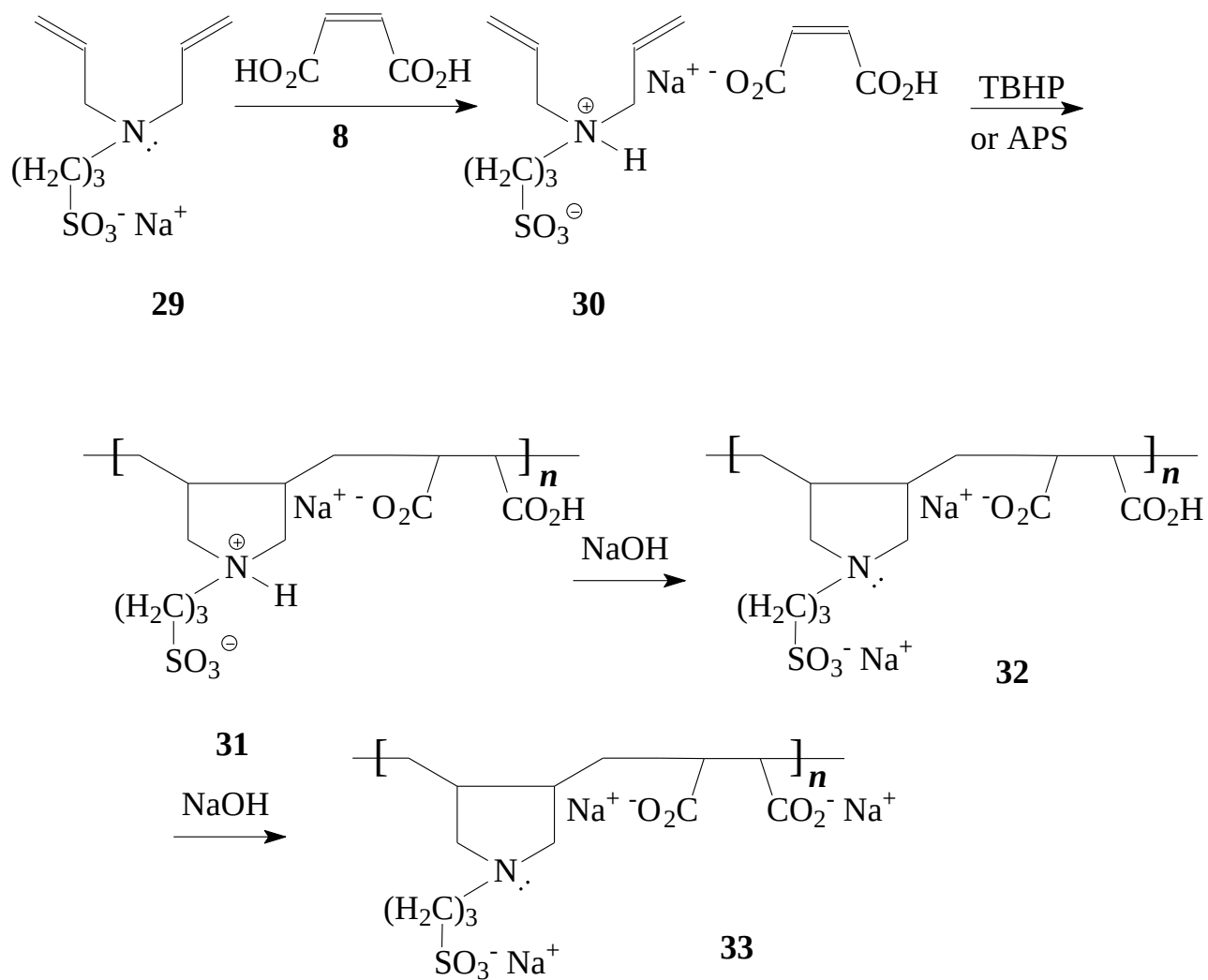
Scheme 1.6 Cyclopolymerization of a diallyl amine (DA) **20** monomer with maleic acid **8** produced **22**.

The hydrolyzed monomer **26** [94,95] and **8** will be copolymerized to give pH-responsive polymer **27** (Scheme 1.7).



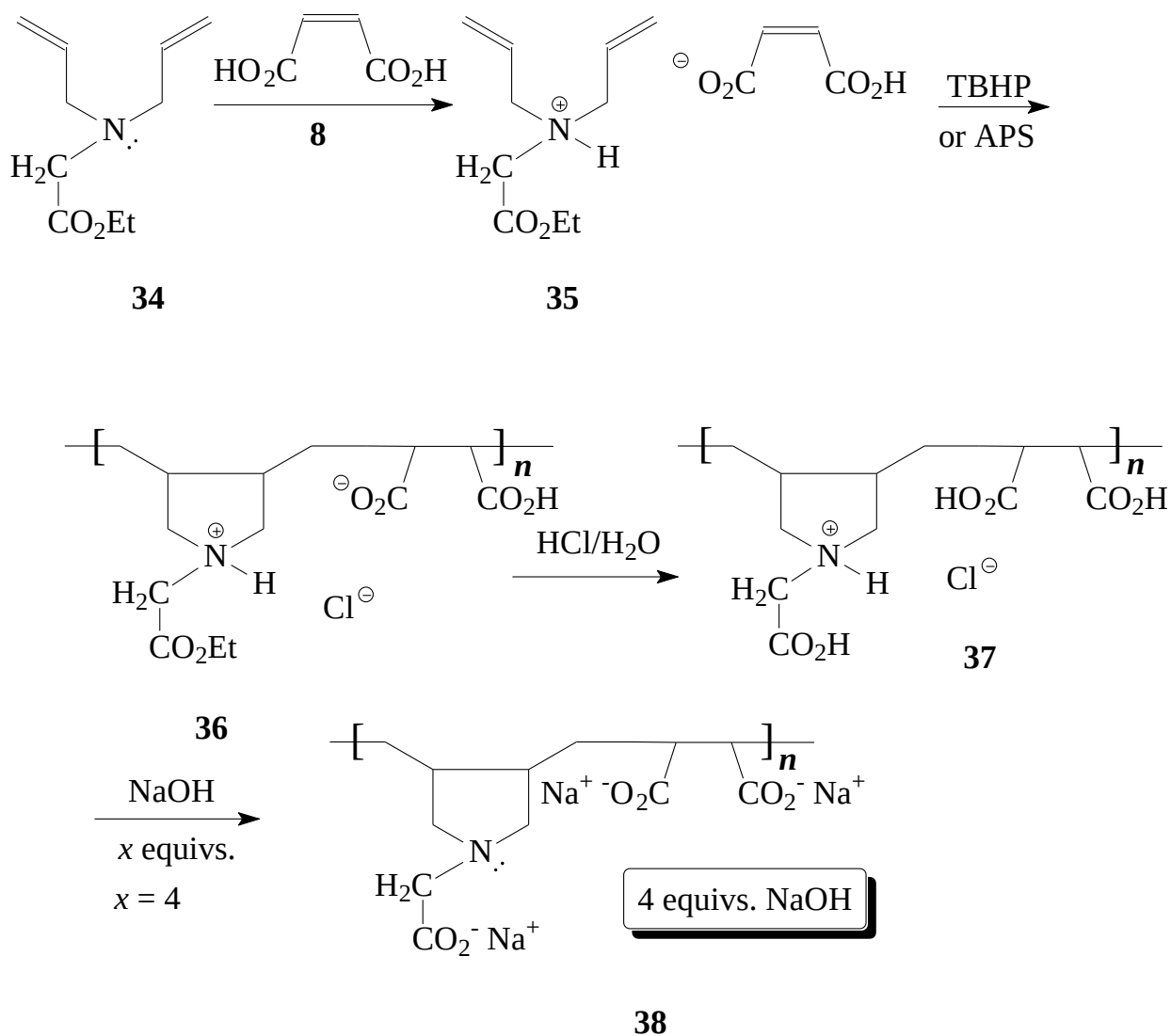
Scheme 1.7 Copolymerization of hydrolyzed monomer **26** and MA **8** to give pH-responsive polymer **27**.

2. To synthesize a DA monomer containing sulfonate pendant and its polymerization with maleic acid (Scheme 1.8).



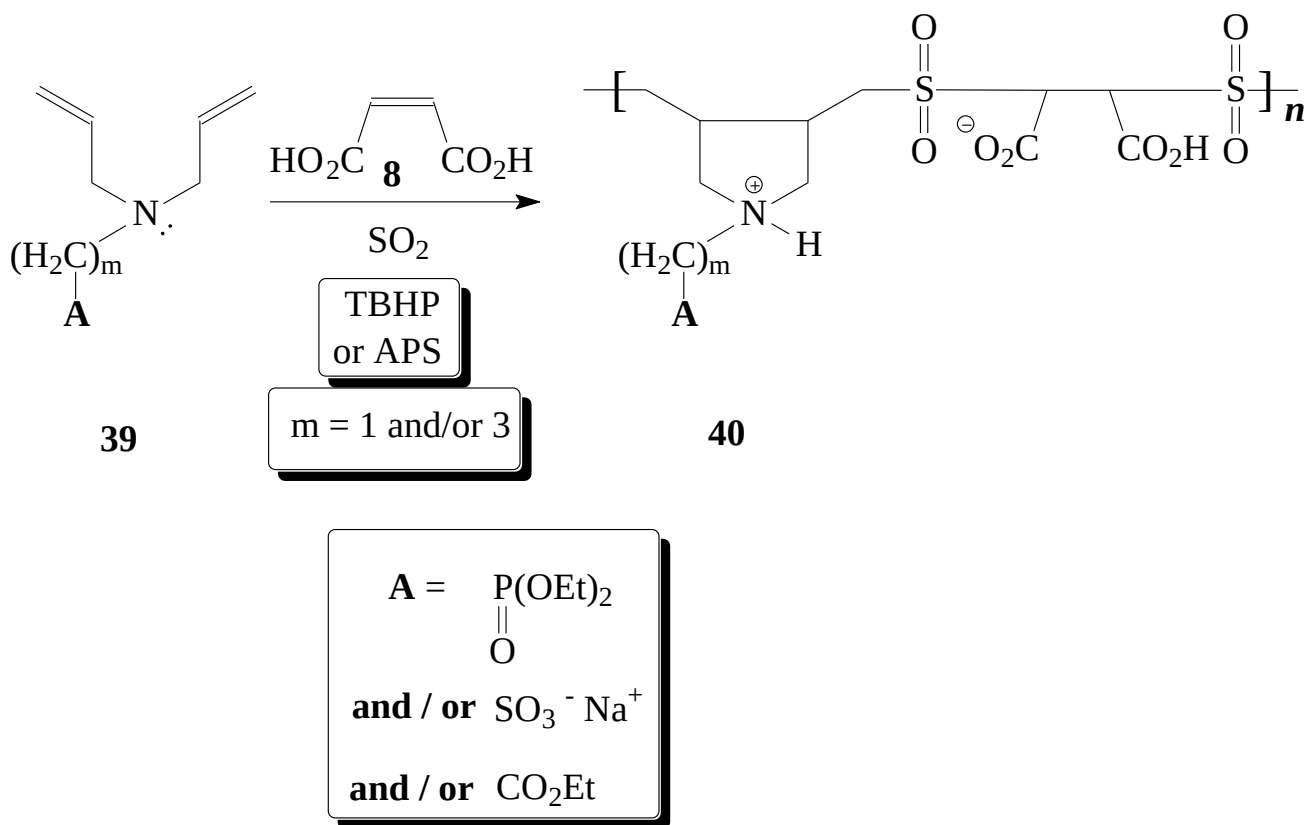
Scheme 1.8 Copolymerization of a DA monomer 29 with MA 8.

3. To synthesize a DA monomer containing carboxylate pendant and its polymerization with maleic acid ([Scheme 1.9](#)).



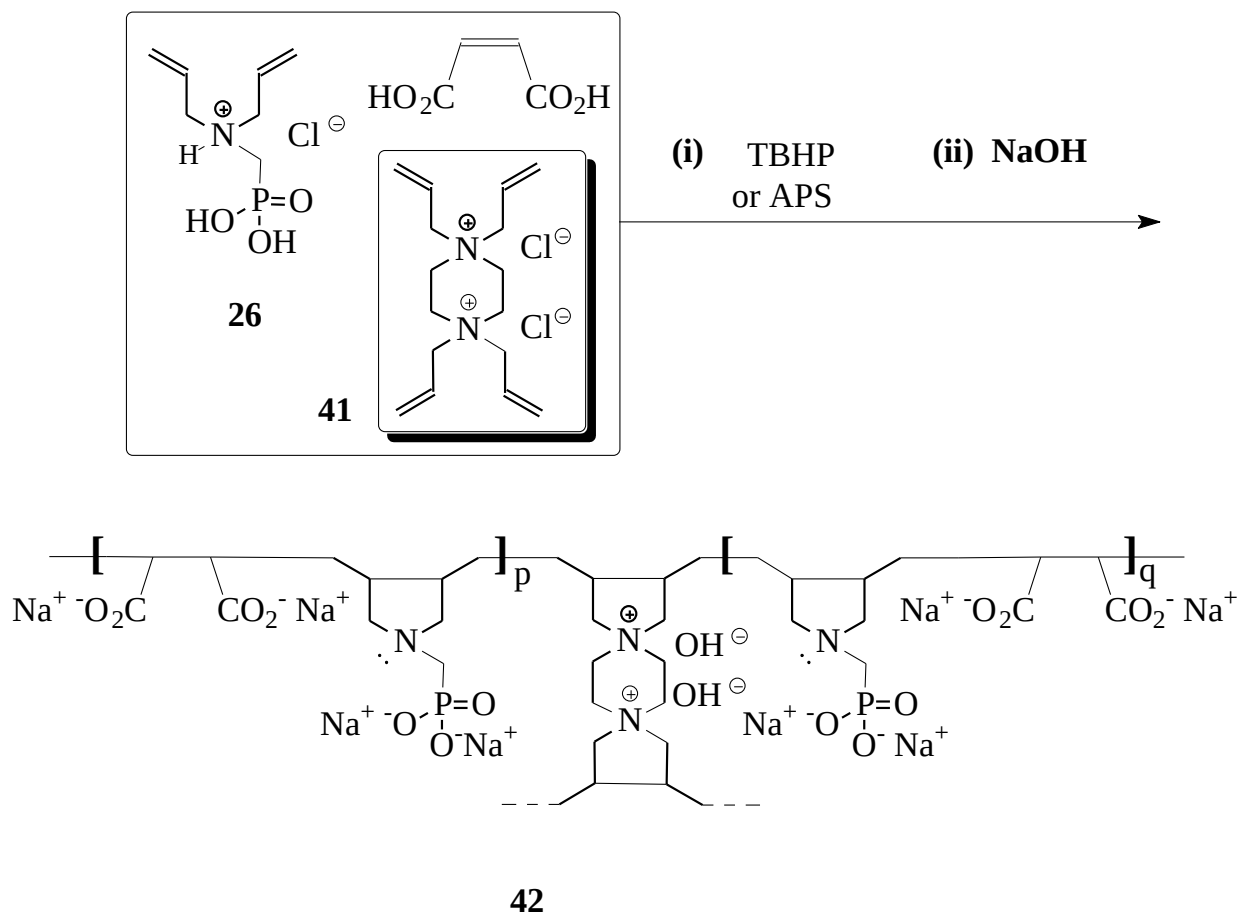
Scheme 1.9 Copolymerization of a **DA** monomer **34** with **MA 8**.

4. To synthesize cycloterpolymers of a DA monomer with maleic acid and SO₂
(Scheme 1.10).



Scheme 1.10 Terpolymers of a DA monomer **39** with MA **8** and SO₂.

5. To synthesize novel cross-linked resins containing phosphonate and carboxylate pendants (Scheme 1.11).



Scheme 1.11 Synthesize of cross-linked resin **42** via a **DA** monomer **26**, **MA**, and cross-linker **41**.

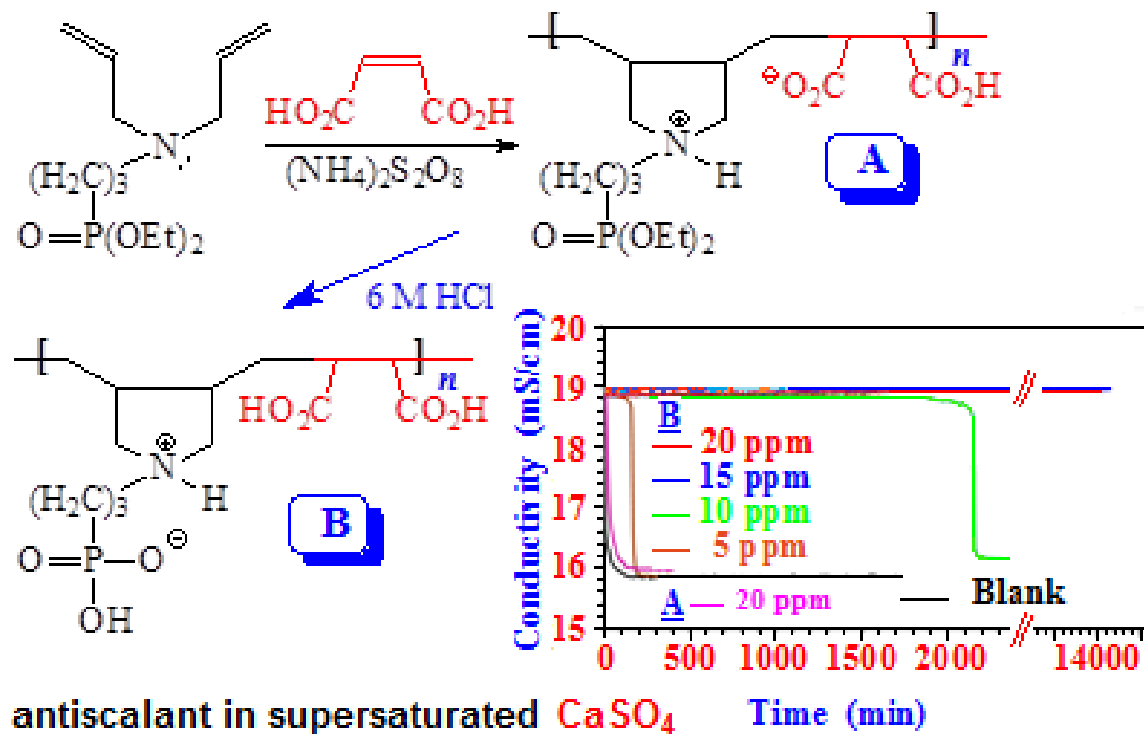
6. To study the solution behavior of the resulting polymers (Scheme 1.6 - 1.10) by interconverting to polyelectrolytes, polyelectrolytes, polyelectrolyte/anion.

To have industrial significance:

7. Evaluation (screening) of the synthesized polymers (Scheme 1.9) as antiscalant to prevent for instance of CaSO_4 and/or CaCO_3 scaling.
8. Evaluation of the cross-linked resins (Scheme 1.11) as adsorbents for the removal of toxic metal ions and some organic dyes from aqueous solutions.

CHAPTER 2

SYNTHESIS AND APPLICATION OF POLYZWITTERIONIC AND POLYAMPHOLYTIC MALEIC ACID-*ALT* (DIALLYLAMINO) PROPYL PHOSPHONATES



Graphical Abstract

2.1 Abstract

Ammonium persulfate-initiated alternate copolymerization of maleic acid with phosphonic acid monomer $[(\text{CH}_2=\text{CH}-\text{CH}_2)_2\text{NH}^+(\text{CH}_2)_3\text{PO}_3\text{H}_2 \text{ Cl}^-]$ (**I**) and phosphonate ester monomer $[(\text{CH}_2=\text{CH}-\text{CH}_2)_2\text{NH}^+(\text{CH}_2)_3\text{PO}_3\text{Et}_2 \text{ Cl}^-]$ (**II**) gave polyzwitterion (PZ): poly[(**I**-HCl)-*alt*-maleic acid] **III** and polyampholyte (PA): poly[(**II**)-*alt*-maleic acid] **IV**, respectively. PA **IV**, upon ester hydrolysis, gave PZ **III**. The pH-induced changes of backbone charges in tetraprotic **III** (with respect to each repeating unit) and diprotic **IV** were examined by viscosity measurements. PA **IV** exhibited antipolyelectrolyte character in the presence of neutral salt NaCl. Several protonation constants K of the CO_2^- and trivalent nitrogen in **III** and **IV** have been determined. The performance evaluation as a potential antiscalant in reverse osmosis (RO) plants were examined. **III** containing acid motifs of $-\text{PO}_3\text{H}_2$ at a concentration of 15 ppm demonstrated remarkable efficiency of $\approx 100\%$ in inhibition of CaSO_4 scale from its supersaturated solution for several days at 40°C , while precipitation occurred within 10 min in the presence of 20 ppm of **IV** containing ester motifs of $-\text{PO}_3\text{Et}_2$.

Keywords: pH-Responsive polymers; Cyclopolymerization; Polyzwitterion; Polyampholyte; Protonation constant; Polyphosphonate.

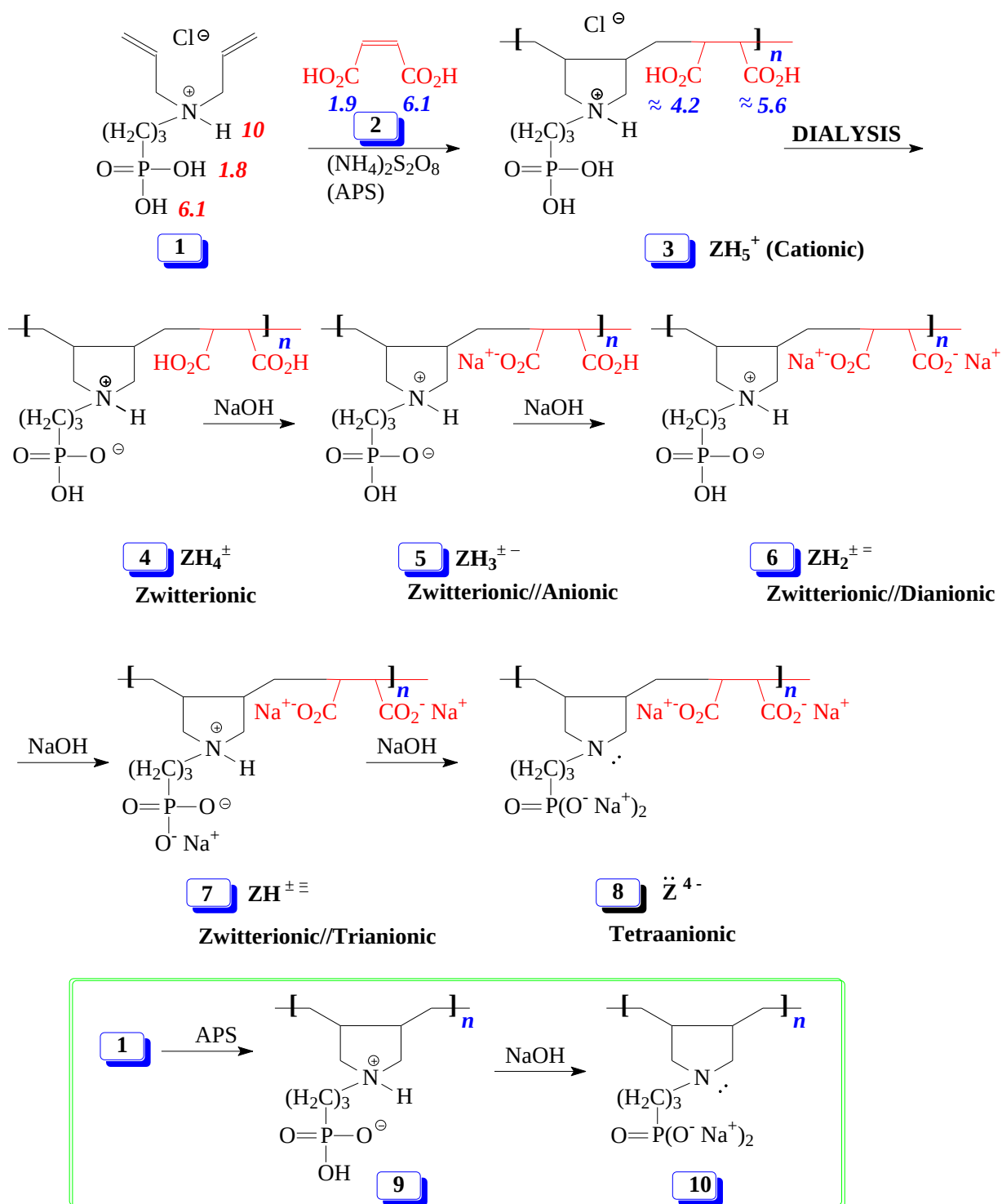
2.2 Introduction

Butler's cyclopolymerization protocol [1,8] using diallylammonium salt monomers has etched an important place in the synthesis of a variety of ionic polymers of remarkable industrial significance [2,3,96]. This industrially important protocol is known to lead to the formation of a pyrrolidine ring-embedded backbone considered to be the eighth most important architecture for high polymers [2,9]. Butler's cyclopolymer poly(diallyldimethylammonium chloride) has numerous publications and patents (> 1000) [1]; millions of pounds of poly(diallyldimethylammonium chloride) are sold annually for water treatment [1]. The polymers from diallylamine salts $[(CH_2=CH-CH_2)_2NH^+R Cl^-]$, bearing pH-responsive backbone nitrogens and functionalities in the pendants (R), undergo pH-induced transformation to polymers having charges of both algebraic signs in the chains [3,6,97]. The bio-mimicking polyampholytes (+ -) [98,99] and polyzwitterions ($\pm$) [100] have found applications in the field of biotechnology, medicine, oil industry, hydrometallurgy and desalination [5].

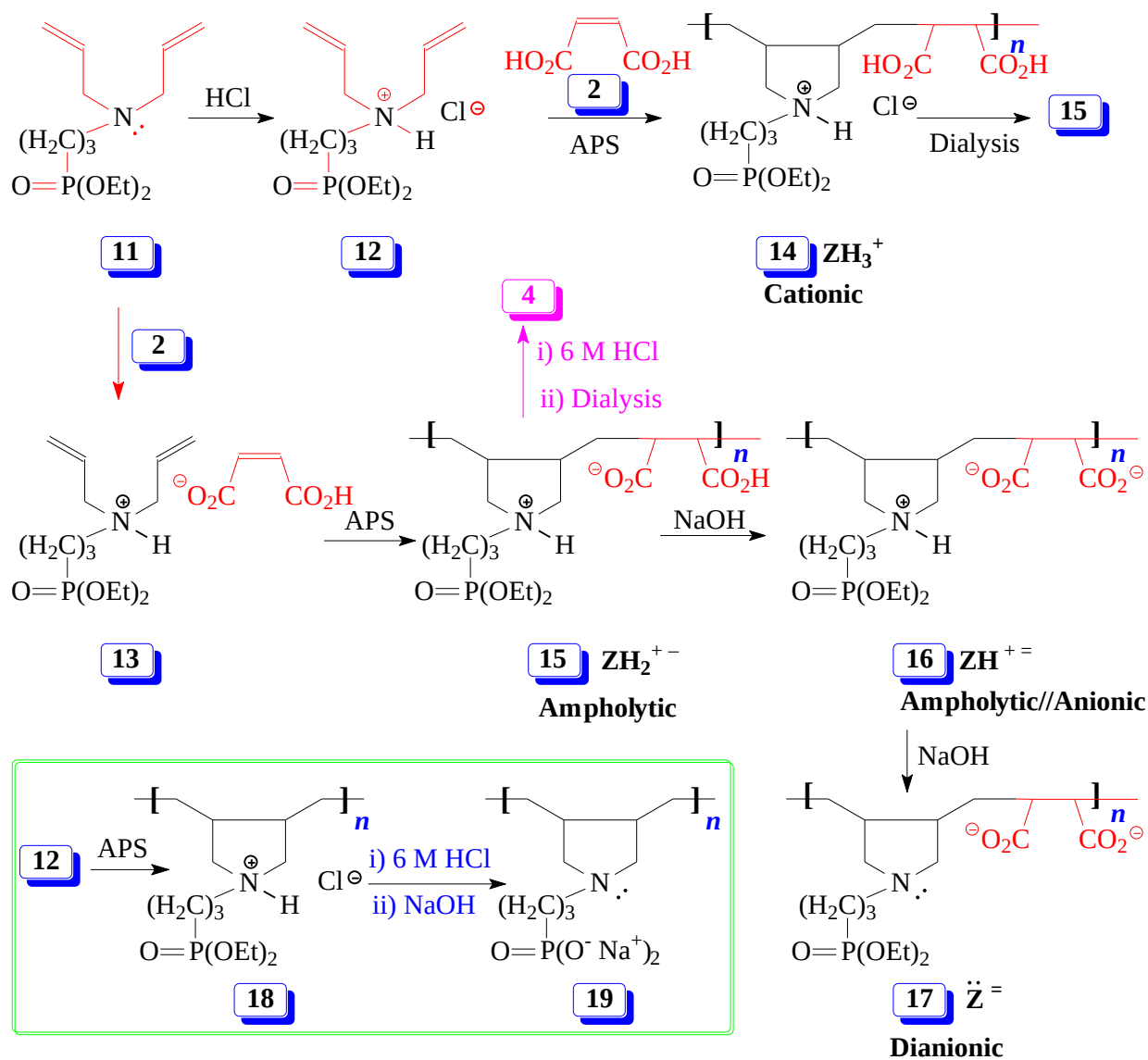
The effectiveness of a desalination process depends on the mitigation of scale formation leading to membrane fouling. In reverse osmosis (RO) membrane desalination, as the concentration of salts, such as calcium sulfate, calcium carbonate, barium sulfate and strontium sulfate, etc., exceeds their saturation levels, the crystallization (i.e., scale formation) on membrane surfaces results in the decline of permeate flux. The feed passages are also often plugged by the scale. There are three commonly employed methods of scale control: acidification, ion exchange softening and antiscalant addition. Antiscalants are surface-active materials that interfere with precipitation reactions to keep the scaling salts in supersaturated state [101]. As a crystal begins to grow, an antiscalant is adsorbed on its

surface thereby disrupting the crystal growth and leading to a soft non-adherent distorted scale. An antiscalant can act as a dispersant; upon adsorption onto a crystal surface, it imparts high anionic charges to keep the crystals separated. The active ingredients in commercial antiscalants are mostly proprietary mixtures of various polycarboxylates and polyacrylates, condensed polyphosphates and organophosphonates [101-103].

Herein, with judicious choice of monomers, Butler cyclopolymerization protocol is utilized to decorate the repeating units with both the carboxylate and phosphonate motifs, which are potent functionalities to impart antiscalant behavior. Thus, we report, for the first time, the copolymerization of **1**, **11** and **12** (containing phosphonate pendants) with maleic acid (**2**) to pH-responsive alternate copolymers (Schemes 2.1 and 2.2). The study would examine the mechanism of alternation, the pH-induced transformation and the efficacy of the copolymers as antiscalants.



Scheme 2.1 Synthesis of alternate copolymers from monomer **1**/maleic acid **2** using cyclopolymerization protocol.



Scheme 2.2 Synthesis of alternate copolymers from monomer **12**/maleic acid **2** and monomer complex **13** using cyclopolymerization protocol.

2.3 Experimental

2.3.1 Materials

Ammonium persulfate (APS), 2,2'-azobis(2-methylpropionamidine) dihydrochloride (AMPH) from Sigma-Aldrich, and maleic acid from BDH Chemicals Ltd., Poole, England, were used as received. Trivalent amine **11** and its hydrochloride salt **12** were prepared as described [104,94]. 3-(*N,N*-Diallylamino)propanephosphonic acid (**1**) was obtained by means of hydrolysis of **11** following the reported procedure [102]. The molar mass of **1** was determined to be 277 g mol⁻¹ using ¹H NMR integration of several non-overlapping signals of the monomer and a known concentration of ethanol. It is difficult to remove the strenuous HCl present in the sample. Note that the calculated molar mass of **1** is 255.68 g mol⁻¹. As such, in subsequent polymerization, the monomer is considered to have a purity of 92%. Spectra/Por membrane with molecular weight cut-off (MWCO) of 6000-8000 Da, was purchased from Spectrum Laboratories Inc. was used for dialysis.

2.3.2 Physical Methods

A Perkin Elmer Elemental Analyzer Series 11 Model 2400 (Waltham, Massachusetts, USA) was employed to determine elemental composition. A Thermo scientific FTIR spectrometer (Nicolet 6700, Thermo Electron Corporation, Madison, WI, USA) was used to record IR spectra. ³¹P, ¹H and ¹³C NMR spectra of the polymers were measured in D₂O on a JEOL LA 500 MHz spectrometer. ³¹P NMR was referenced with 85% H₃PO₄ in DMSO. The residual HOD signal of D₂O at δ 4.65 ppm, and dioxane ¹³C resonance at δ 67.4 were used as internal references. However, the position of residual proton resonance of D₂O depends on the solution pH; in such cases the chemical shifts were referenced with

sodium 3-trimethylsilylpropionate-2,2,3,3-d₄ (TSP-deuterated) having ¹H signal at δ 0.0 ppm. An Ubbelohde viscometer (Viscometer Constant = 0.005718 cSt/s) was utilized for viscosity measurements. An SDT analyzer (Q600: TA instruments, USA) was utilized for thermogravimetric analyses (TGA) in the range 20–800 °C increasing at rate of 15 °C/min using N₂ flowing at a rate of 50 cm³/min.

2.3.3 Polymer Synthesis

2.3.3.1 Copolymerization of 3-(N,N-diallylamino)propanephosphonic Acid (1) and Maleic Acid (2)

The alternate polymerizations were performed under the conditions described in [Table 2.1](#). In one such case ([entry 2, Table 2.1](#)), APS was added at 98 °C in two equal portions (2×200 mg) with an interval of 5 min to a stirred mixture comprised of monomer **1** (2.77 g, 10 mmol) and maleic acid (**2**) (1.28 g, 11 mmol) in water (1.74 g; monomers/water wt ratio is 70:30) in a RB flask fitted with a condenser under N₂. After 20 min at 98 °C, the polymer solution was cooled and dialyzed against deionized water. Note that initial polymer **3** became cloudy when diluted with H₂O and clear in dilute HCl. During dialysis against distilled water, a thick cloudy jelly material settled at the bottom of the dialysis tube within an hour. At this stage, dialysis was continued against a 0.3M HCl which rendered the polymer mixture clear and ensured the removal unreacted maleic acid. On further dialysis against distilled water, the mixture became cloudy and a gel settled at the bottom of the dialysis tube. Afterward (48 h), both the supernatant and the jelly material were subjected to freeze drying to give copolymer **4** (2.5 g, 75%). (Found: C 46.2; H 6.8; N 4.1%. C₁₃H₂₂NO₇P requires C 46.57; H 6.61; N 4.18%); δ_P (200 MHz, 2 M NaCl in D₂O): 23.08 (m, 1P); δ_P (200 MHz, in D₂O in the presence of 4 equivs NaOH): 20.33 (major, 98%, s,

1P), 26.23 (m, minor, 2%); $\nu_{\max}$ (KBr): 3566 (broad), 2958, 2925, 1717, 1458, 1233, 1122, 1029, 906, 704, 669, 537, and 474 cm^{-1} . The peak assignments of the signals in the ^1H and ^{13}C NMR spectra are displayed in [Figure 2.1](#) and [Figure 2.2](#), respectively.

Table 2.1 Cyclocopolymerization^a of monomers **1**, **12** and **13** with maleic acid **2**

Entry	Monomer (mmol)				Initiator (APS) (mg)	Yield ^b (%)	[η] ^c (dL g ⁻¹)
	1	11	12	2			
1	5.0	—	—	5.5	400	4 : 55 (90)	0.0614 ^d
2	5.0	—	—	5.0	300	4 : 75 (85)	0.0872 ^d
3	5.0	—	—	5.5	300	4 : 72 (93)	0.0581 ^d
4	5.0	—	—	11.0	300	4 : 66 (91)	0.0611 ^d
5	—	—	5.0	5.5	300	14 : 66 (98)	0.0178
6	—	10.0	—	11.0	400	15 : 73 (90)	0.0618
7 ^e	—	5.0	—	5.5	300	15 : 82 (94)	0.0253
8 ^f	—	5.0	—	5.5	60 (AMPH)	15 : 45 (60)	0.0657

^aCopolymerization reactions were carried out in aqueous solution of two monomers (70 w/w% monomers) in the presence of ammonium persulfate (APS) or (AMPH) at 98 °C for 20 min.

^bPolymer obtained is written in bold followed by isolated yields; the percent conversion determined by ^1H NMR analyses of the crude reaction mixture are written in parentheses.

^cViscosity of 1-0.25 % polymer solution in 0.1 N NaCl at 30 °C was measured with Ubbelohde Viscometer ($K = 0.005317 \text{ mm}^2 \text{ s}^{-2}$).

^din the presence of 1 equiv NaOH.

^e Polymerization carried out in the presence of 5.0 mmol NaCl.

^f Polymerization was run for 48 h at 80 °C.

2.3.3.2 Copolymerization of N,N-diallyl-3-(diethylphosphonato) Propylamine (11) and Maleic Acid (2) through Ion pair 13

For the experiment under [entry 6, Table 2.1](#), a mixture of trivalent amine **11** (2.76 g, 10.0 mmol), and maleic acid **2** (1.28 g, 11.0 mmol) in water (1.74 g; monomers/water wt ratio is 70:30) was stirred at 98 °C under a positive atmosphere of N₂ in a RB flask attached to a condenser. Then, initiator (APS) was added in two equal portions (2×200 mg) with an interval of 5 min. Exothermic polymerization ensued with the increase in viscosity. After stirring at 98 °C (15 min), the mixture was dialyzed against deionized water for 24 h. The dialyzed mixture was then freeze-dried affording alternating copolymer, polyampholyte **15** as a white powder (2.85 g, 73%). δ P (200 MHz, D₂O): 23.60 (s, minor 10%, 1P), 31.19 (s, major 90%); (Found: C 51.8; H 7.9; N 3.4%. C₁₇H₃₀NO₇P requires C 52.17; H 7.73; N 3.58. ν_{max} (KBr): 3455 (broad), 2984, 2941, 1712 (s), 1640 (s), 1575 (s), 1451, 1395, 1214, 1051, 1023, 968 and 790 cm⁻¹. The peak assignments of the signals in the ¹H and ¹³C NMR spectra are displayed in [Figure 2.1](#) and [Figure 2.2](#), respectively.

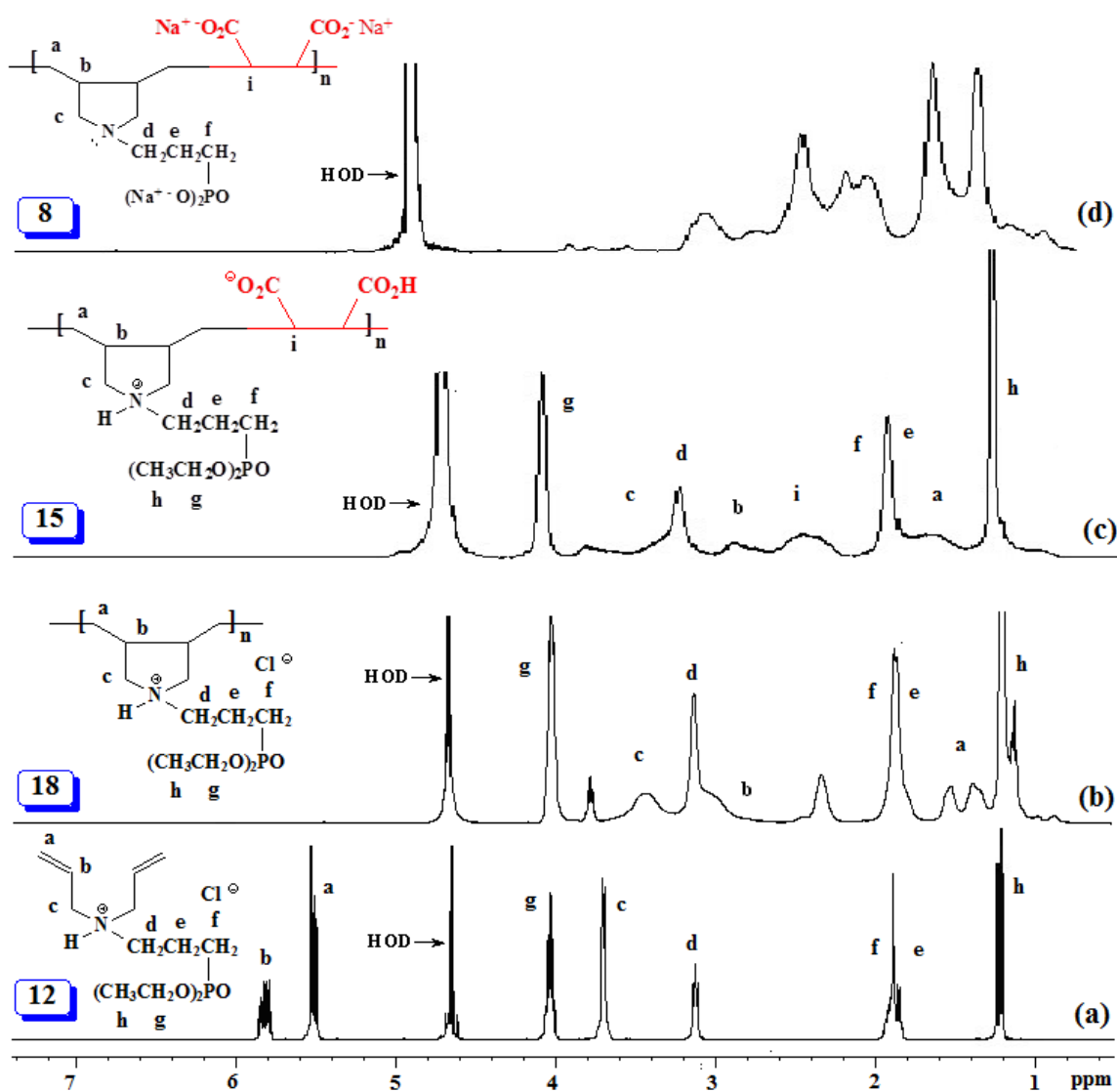


Figure 2.1 ^1H NMR spectrum of (a) 12, (b) 18, (c) 15, and (d) 8 in D_2O

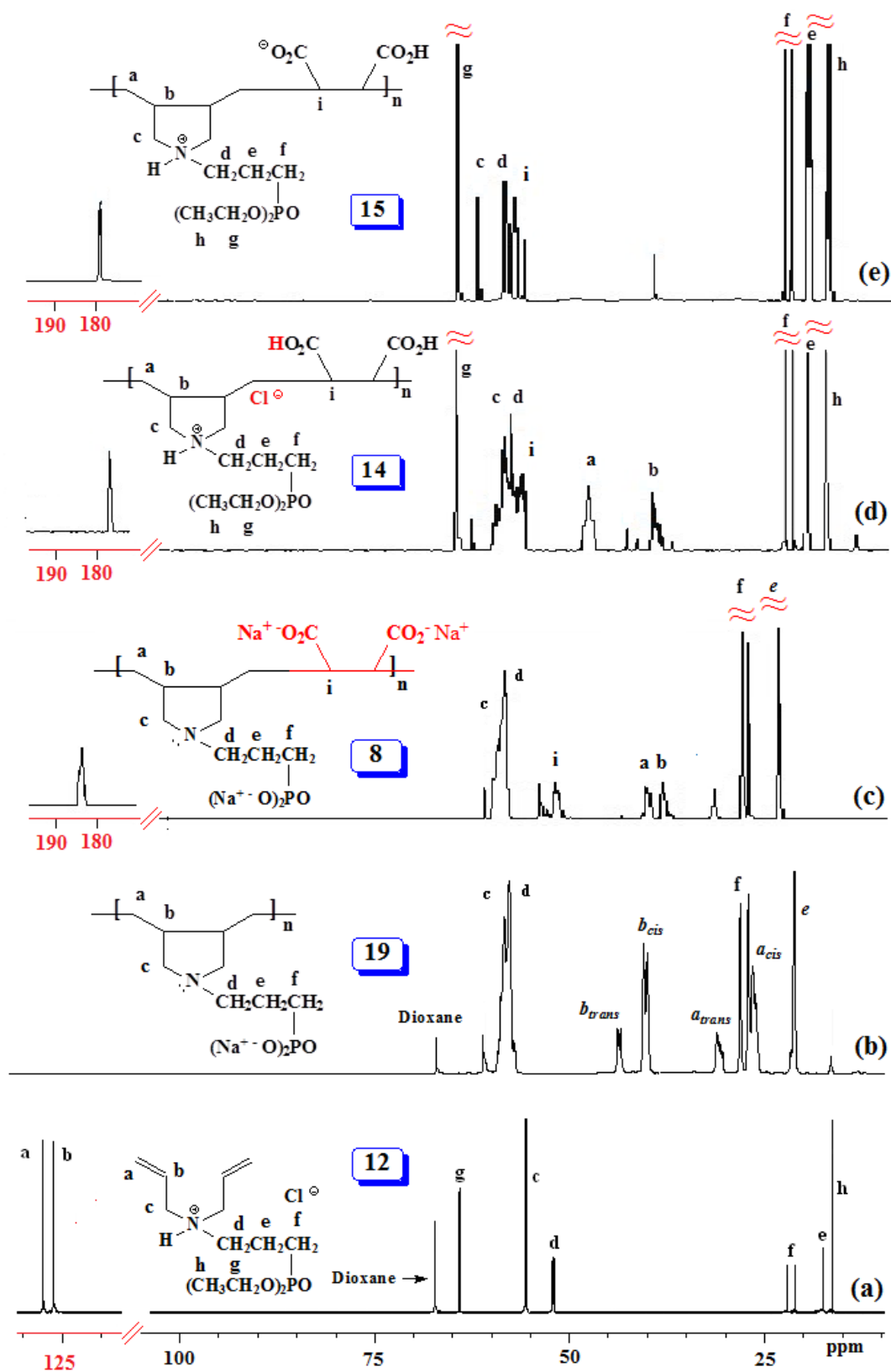


Figure 2.2 ^{13}C - NMR spectrum of (a) 12, (b) 19, (c) 8, (d) 14, and (e) 15 in D_2O

2.3.3.3 Copolymerization of Hydrochloride Salt **12** and Maleic Acid (**2**)

For the experiment under [entry 5, Table 2.1](#), a mixture of hydrochloride salt **12** (1.56 g, 5.0 mmol) and **2** (0.640 g, 5.5 mmol) in water (0.94 g; monomers/water wt ratio: 70:30) was stirred at 98 °C in a RB flask attached to a condenser and maintained under a positive atmosphere of N₂. Then, initiator (APS) was added in two equal portions (2×200 mg) with an interval of 5 min. Exothermic polymerization ensued to give a viscous solution. After stirring at 98 °C for 15 min, the mixture was cooled and dialyzed against 0.1 M HCl for 24 h and subsequently against deionized water. The dialyzed mixture was treated with concentrated HCl (0.50 g, 37%, 5.0 mmol) and freeze-dried to obtain alternate cationic copolymer **14** as a white powder (1.29 g, 66%). (Found: C 47.4; H 7.5; N 3.4%. C₁₇H₃₁ClNO₇P requires C 47.72; H 7.30; N 3.27. δ P (200 MHz, D₂O): 25.85 (m, minor, 5%, 1P), 31.16 (m, major, 95% 1P); ν_{max} (KBr): 3483 (broad), 3208, 3082, 2990, 2939, 2703, 1724, 1639 (very weak), 1612, 1452, 1399, 1201, 1027, 966, 801, 704 and 610 cm⁻¹. The peak assignments of the signals in the ¹H and ¹³C NMR spectra are displayed in [Figure 2.1](#) and [Figure 2.2](#), respectively.

2.3.3.4 Ester Hydrolysis of Polyampholyte **15** to Polyzwitterion **4**

A solution of polyampholyte **15** (obtained from [entry 6, Table 2.1](#)) (1.5 g, 3.83 mmol) in 6 M HCl (20 cm³) was stirred at 90 °C under N₂ for 24 h. The solution of the resulting cationic polymer **3** upon depletion of HCl during dialysis (24 h) against deionized water gave PZ **4**. Initially polymer **3** was soluble in the presence of HCl, however as the dialysis was continued PZ **4** started separating out within 1 h as a jelly material. The heterogeneous mixture was freeze-dried to obtain **4** (1.22 g, 95%). The polymer thus obtained is spectrally (IR, NMR) similar to **4** obtained *via* copolymerization of **1** and **2** (*vide supra*).

2.3.4 Potentiometric Titrations

The basicity or protonation constants (K) of several basic centers in the synthesized polymers were determined in CO_2 -free water using procedures reported elsewhere [35,105] as described in Tables 2.2 and 2.3. A certain number of mmole of a repeating unit of PA **15** ($\text{ZH}_2 + -$) or PZ **4** ($\text{ZH}_2^\pm$) in water (200 cm^3) was titrated by stepwise addition of 0.05–0.15 mL of $\approx 0.1 \text{ M}$ NaOH or HCl. Because of water-insolubility, PZ **4** ($\text{ZH}_2^\pm$) was first dissolved using 1–1.5 mL of 0.09594 M NaOH, then the titration was continued. Log K_{is} were calculated using the pH values and the Henderson–Hasselbalch equation (Eq. 2; Scheme 3). While all three log K_{is} ($i = 2, 3, 4$) associated with the protonation of PDA (=) **17** were determined, two (log K_1 and log K_5) of the five log K_{is} associated with the protonation of basic centers in PTA (=) **8** could not be determined. Log K_5 , associated with the equilibrium: **4** ($\text{ZH}_4^\pm$) + $\text{H}^+ \rightleftharpoons (\text{ZH}_5^+) \text{3}$, was not determined since PZ ($\pm$) **4** was water-insoluble, while log K_1 involving ($: \text{Z} =$) **8** + $\text{H}^+ \rightleftharpoons \text{7} (\text{ZH}^\pm \equiv)$ would require a large amount of NaOH to generate a meaningful concentration of ($: \text{Z} =$) **8**.

2.3.5 Antiscalant Behavior of the Synthesized Polymers

A solution containing Ca^{2+} (2598 mg L^{-1}) and SO_4^{2-} (6300 mg L^{-1}), which is supersaturated with respect to CaSO_4 , was used to investigate scale formation at $40 \pm 1^\circ\text{C}$ as described [106] using its supersaturated solution in the presence of antiscalants **4** (derived from hydrolysis of polymer **15** from entry 6, Table 2.1) and **15** (Table 2.1, entry 6). Stock solution of antiscalant **4** was prepared by dissolving it in the presence of minimum quantity of NaHCO_3 . At a certain time, called induction time, the conductivity decreased

suddenly as a result of scale formation (Table 2.4). Any turbidity is confirmed by visual inspections.

2.4 Results and Discussion

2.4.1 Synthesis of Alternate Copolymers

The results of the alternate cyclopolymerization of diallyl amine salts **1**, trivalent amine **11** and amine salt **12** with maleic acid **2** are given in Table 2.1. Cationic monomer **1**/maleic acid **2** copolymerization afforded polycation (PC) (+) **3** which was changed to polyzwitterion (PZ) ($\pm$) **4** during dialysis as a result of depletion of HCl (Scheme 2.1). Changing 1:1 monomer stoichiometry (i.e., changing the feed ratio) did not change the composition of polymer **4** as indicated by its identical IR and NMR spectra (*vide supra*) as well as elemental analyses (entries 1-4, Table 2.1), which indicated the formation of alternate copolymers.

Similar homopolymerization of *N*-alkyldiallylammonium chloride as well as its copolymerization with maleic acid in aqueous solution using 5 mol-% 2,2'-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide] (VA086) as initiator for 48 h at 75 °C have been reported to give polymers in low yields (typically below 20%) [106,107]. High initiator concentrations (up to 5 mol-%) were necessary to obtain the polymers, while the use of other initiators (ammonium persulfate, hydrogen peroxide) did not improve the yields [106,107]. It is interesting to note in the current work, the use of ammonium persulfate ($\approx$ 10 mol%) at higher polymerization temperature (98 °C) for a short duration (20 min) afforded the alternate PZ **4** in very good isolated yields ($\approx$ 70%) (Entries 1-4, Table 2.1).

Note that the monomer conversions were $\approx 90\%$ as determined by ^1H NMR analyses; during dialysis, however, low MW molecules left the dialysis tube.

The reactivity ratios for diallylamines / maleic acid copolymerization are very much close to zero, thereby indicating a perfect alternating copolymerization [107]. Several reports suggested that the alternating incorporation of the amine and maleic acid monomers may be attributed to the formation of ions pairs (akin to **13**, Scheme 2.2) in solution and their polymerization [108,109]. In the current work, both the monomers **1** and **2** are fully protonated, and the extent of ionization in a highly concentrated solution (70:30 wt. ratio of monomer/water) is rather low. This led us to believe that as in the case of the alternating copolymer of styrene and maleic anhydride, the copolymerization described here points towards a preferential combination of electron-rich **1** and electron-poor **2** monomers. Similar argument might as well be put forward against the formation of monomer ion-pair for the cyclopolymerization of **2/12** (Scheme 2.2). The stronger binding ability of Cl^- for the positive nitrogen would preclude the formation of ion-pair involving maleate anion $\text{HO}_2\text{CCH}=\text{CHCO}_2^-$.

The polymerization of **11/2** monomer-pair as depicted by structure **13** (Entries 6-8, Table 2.1) as well as copolymerization of **12** and **2** (Entry 5, Table 2.1) afforded the same polyampholyte (PA) **15** (Scheme 2.2). The copolymerization under entry 5 was even run in the presence of NaCl, which has excellent ability to bind to positive nitrogen, thereby preventing the maleate to be a part of the ion-pair. The results thus indicate that ion-pair formation is not necessary to form alternate copolymers, rather it is the result of near zero reactivity ratios of the monomers. Note that while the initiator APS afforded copolymers in 20 min reaction-time in very good yields (entries 1-7), the azo initiator AMPH gave

polymer **15** in lower yield even after carrying out the polymerization for a duration of 48 h at 80 °C (entry 8).

The isolated yields of the polymers as obtained after dialysis are given in Table 2.1. However, the actual percent conversion (written in parentheses, Table 2.1) was determined by ¹H NMR analyses (as described below) of the crude reaction mixture. The area **A** under δ 5.5-6 ppm accounts for 6 olefinic protons of unreacted monomer **12** or **13**, while its remaining 20 H would appear in the range δ 1.2-4.1 ppm accounting for an area of **B** [i.e., (A/6)×20] (Fig. 2.1a). The total integrated area **C** in the range δ 1.0-4.1 ppm would belong to area integration of 28 H (26 H from repeating unit of **12** and 2 H from maleic acid **2**) of polyzwitterion **15** (Fig. 2.1c) and 20 H of unreacted monomer **12**. The area **D** of the polymer alone would then equate to (**C**-**B**). The percent conversion was then calculated using integration of 1 H of the polymer **15** and monomer **12** as: $100 \times (\mathbf{D}/28)/[(\mathbf{D}/28) + \mathbf{A}/6]$. In a similar fashion, the percent conversion to **4** was determined.

2.4.2 Solubility Behavior

Unlike the majority of electroneutral polymers, PA (+ -) **15** was found to be water-soluble. A possible rationale could be that both the positive nitrogens as well as the negative charge centers on the carboxyl are in a crowded environment, thus preventing them from intragroup, intra- and inter-chain associations required for the manifestation of ampholytic interactions [8]. The relatively large separation between the charge centers and their difficulty in transiting to a curled conformation are expected to increase the dipole moment (μ) of the ampholytic motifs. Increased dipole moment would lead to increased hydrophilicity and solubility [110,29].

Polyzwitterion ($\pm$) **4**, however, was found to be water-insoluble. pK_1 of PO_3H_2 in (+) **3** and pK_1 of CO_2H in (+) **14** is expected to be < 2 and ≈ 4 , respectively (*vide infra*). As a result, PO_3H^- in ($\pm$) **4** has more dispersed charge than CO_2^- in (+) **15**, thereby making the former motifs less hydrated and hence more capable of manifesting zwitterionic interactions with the positive nitrogens [33]. Polyzwitterion **4** was insoluble in salt free water both at room and elevated temperatures (40-70 °C). At 4 wt. % in 0.5 M NaCl, PZ **4** was soluble at 0 °C, but became cloudy while heating (50 °C). The lower critical solution temperature (LCST) was determined to be 27 °C. As expected, the PZ was found to be soluble in the presence of NaOH to generate polymers **5-8** (Scheme 2.1). In the presence of HCl (0.1 M), PZ **4** is transformed to cationic **3** which was found to be water-soluble.

2.4.3 TGA Curves, FT-IR and NMR Spectra

The PZ **4** was found to be more stable than PA **15** according to their TGA curves (Fig. 2.3). For PZ **4**, a 6% weight loss up to 200 °C was accounted for the removal of moisture. An additional 7% loss in the range 200-270 °C resulted from the elimination of water as a result of formation of cyclic anhydrides from two neighboring CO_2H groups. A loss of $\approx 23\%$ in 275-400 °C range is attributed to the release of maleic anhydride units from the polymer backbone [111,113]. The total loss up to 400 °C was found to be 36%, while the maleic acid units' accounts for 34.6% thus giving credence to the described losses mentioned above. A further loss of 36% in the 400-800 °C range is linked to the detachment of phosphonate pendants.

The IR spectra of ($\pm$) **4**, (+) **14** and (+) **15** revealed a strong absorption band at $\approx 1720\text{ cm}^{-1}$ attributed to C=O stretch of CO_2H group. While the absorption peak for CO_2^- ions in **15** appeared at 1575 cm^{-1} [33], the corresponding peak was absent in the spectrum of **14**.

Fig. 2.1 and 2.2 display the NMR spectra of several polymers. The absence of any signal for residual alkene protons at δ 5.5-6 ppm or carbons at $\approx$ δ 125 ppm suggested the degradative chain transfer [107] by abstraction of allylic hydrogens or coupling process for the termination reaction. As compared to homopolymer **18** [114] (Scheme 2.2) (Fig. 2.1b), the spectrum of copolymer (+ -) **15** (Fig. 2.1c) is broadened presumably as a result of its compact coil conformation and hydrophobic association in aqueous solution [101]. The presence of a peak near 180 ppm proves the incorporation of maleic acid in the copolymer (Fig. 2.2c,d,e). Note that the ^{13}C NMR signals attributed to the carbons in the polymer backbone marked 'a' and 'b' are missing in the spectrum of (+ -) **15** (Fig. 2.2e), while the carbons away from the polymer backbone give well resolved signals. This behavior is characteristic of many polymerized surfactant, pointing to an immobilization of the polymer backbone. Note that the ester carbons marked 'h' and 'g' (Fig. 2.2a,d,e) are absent in the NMR spectra of the hydrolyzed polymers (Fig. 2.2b,c).

The ^{13}C NMR spectra shed some light on the monomer sequence of repeating units in the current polymers. The backbone carbon marked 'a' for homopolymer **19** around δ 27 ppm (Fig. 2.2b) is shifted downfield in the copolymers' spectra (Fig. 2.2c,d); the absence of any residual signal around δ 27 ppm points toward a perfect alternation of the repeating units.

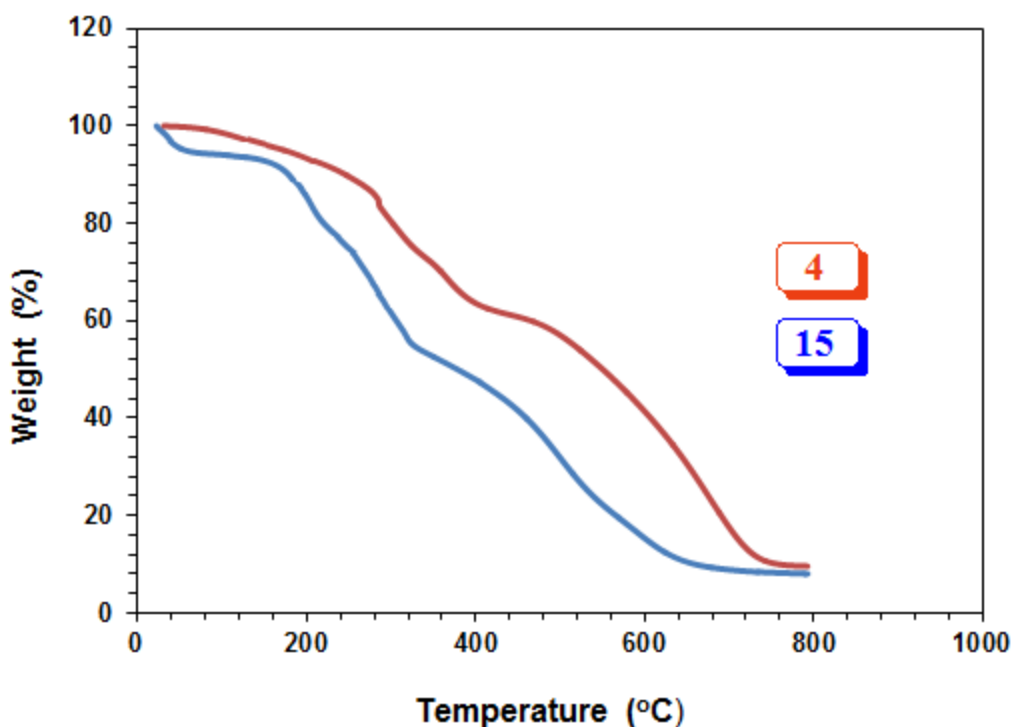


Figure 2.3 TGA curves of **4** and **15**

2.4.4 Viscosity Measurement

The viscosity values of PA (+ −) **15** (entry 6, Table 2.1) are presented in Fig. 2.4. The antipolyelectrolytic [112] behavior of the polyampholyte is demonstrated as evinced by the direct proportionality of the viscosity with the NaCl concentrations (cf. Fig. 2.4d-f). The ampholytic dipole may not be electroneutral; a residual negative charge on the dipole is a consequence of greater neutralization of N^+ by Cl^- as compared to the binding ability of CO_2^- by Na^+ [23,115-116]. The magnitude of excess negative charge on a dipole increases with increasing salt concentrations, thereby leading to increasing repulsion among the dipole centers and increasing viscosity.

The pH-induced changes in the polymer backbone of **14-17** are illustrated in Scheme 2.3. In 0.1 M HCl, PA (+ -) **15** becomes CPE (+) **14**; increased hydrodynamic volume as a result of repulsion among positive charges leads to the increase in the viscosity (Fig. 2.4c). PA (+ -) **15** is transformed to polyampholyte/anion (+ =) **16** and polydianion (=) **17** upon treatment with one and two equivalents of NaOH, respectively. As expected, the viscosity increases in the presence of NaOH (Fig. 2.4a and b), the larger charge imbalance in (=) **17** makes it more viscous.

In order to correlate the viscosity values of polyphosphonate ester and polyphosphonic acid, PA (+ -) **15** (entry 6, Table 2.1) is converted to PZ ($\pm$) **4** having identical degree of polymerization. Viscosity plots for PZ ($\pm$) **4** are shown in Fig. 2.5. The pH-induced changes in the polymer backbone of **4-8** are illustrated in Schemes 2.1 and 2.4. In the presence of one, two, three and four equivalents of NaOH (per repeating unit), PZ ($\pm$) **4** is expected to generate polyzwitterion/anion (PZA) ($\pm$ -) **5**, polyzwitterion/dianion (PZDA) ($\pm$ =) **6**, polyzwitterion/trianion (PZTA) ($\pm$ $\equiv$) **7**, polytetraanion (PTA) (= =) **8**, respectively, as the dominant species involved in mobile equilibria with other species. With the increase in NaOH concentrations, the imbalance in favor of negative charges increases, thereby forcing the polymer backbone to adapt more extended conformation to minimize repulsion. This would result in the increase of viscosity values in the order: (= =) **8** > ($\pm$ $\equiv$) **7** > ($\pm$ =) **6** > ($\pm$ -) **5** as determined experimentally (cf. Fig. 2.5a-d). PZ ($\pm$) **4** is insoluble in salt-free water; however, its viscosity plot in 1.0 M NaCl is shown in Fig. 2.5f. The viscosity plot for PZ ($\pm$) **4** in 0.1 M HCl is found to be concave upward, presumably as a result of increasing dissociation to (PZA) ($\pm$ -) **5** with dilution (Fig. 2.5e).

The increase in charge imbalance in a polymer backbone leads to an increase in excluded volume, which has been used to rationalize the solution properties of ionic polymers [23,115-117]. Polyzwitterion/anion (PZA) ($\pm -$) **5** and polyampholyte/anion ($+ =$) **16**, having identical degree of polymerization, were generated by treating ($\pm$) **4** and ($+ -$) **15**, respectively, with one equivalent NaOH. Ionic polymers ($\pm -$) **5** and ($+ =$) **16** having similar imbalances in favor of negative charges were found to have intrinsic viscosity $[\eta]$ of 0.131 dL g⁻¹ (Fig. 2.5d) and 0.0928 dL g⁻¹ in 0.1 M NaCl (Fig. 2.4b). Likewise, polyphosphonic acid derivative polyzwitterion/dianion (PZDA) ($\pm =$) **6** was determined to have higher $[\eta]$ value of 0.168 dL g⁻¹ (Fig. 2.5c) than the $[\eta]$ value of 0.120 dL g⁻¹ of diester derivative polydianion ($=$) **17** having identical DP and charge imbalances (Fig. 2.4a). The lower $[\eta]$ values for the ester polymers **16/17** could be attributed to the greater hydrophobic character owing to the presence of ethyl groups in the pendants.

As reported earlier [111] and found in the current work, the molar masses of the polymers could not be obtained by GPC presumably owing to the strong interaction of the materials in the GPC column with the amine and carboxy motifs of the polymers. The lower intrinsic viscosity values, however, suggest lower molar masses of the polymers because of using higher doses of initiator and a higher temperature of ≈ 100 °C. Moreover, the degradative chain transfer involving abstraction of allylic hydrogen in the diallylamine salts also lowers the molar masses [118].

The molecular weights of the polyzwitterion ($\pm$) **4** was estimated from the viscosity data by Mark-Houwink equation ($[\eta] = KMv^a$) [119], using $K = 1.12 \times 10^{-4}$ dL g⁻¹ and $a = 0.82$, which are given for poly(diallyldimethylammonium chloride) for a temperature of 25 °C in 1 M NaCl [120]. The $[\eta]$ of ($\pm$) **4** was determined to be 0.0324 dL g⁻¹ (Fig. 2.5f) which

translates into a viscosity average molecular weight $M_v \approx 16,640 \text{ g mol}^{-1}$ corresponding to a degree of polymerization of approximately 99 (i.e., number of structural units).

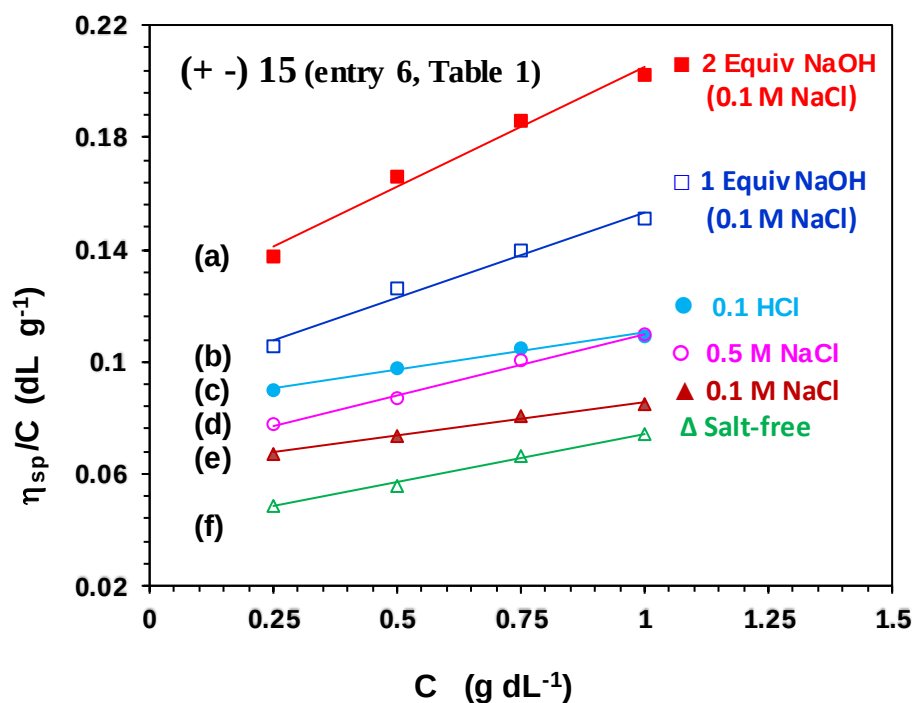


Figure 2.4 The viscosity behavior at 30 °C of polyampholyte **15** (entry 6, Table 2.1) (a) ■ in the presence of 2equiv NaOH in 0.1 M NaCl, (b) □ in the presence of 1 equiv NaOH in 0.1 M NaCl, (c) ● in 0.1 M HCl, (d) ○ in 0.5 M NaCl, (e) ▲ in 0.1 M NaCl, and (f) Δ in salt-free water

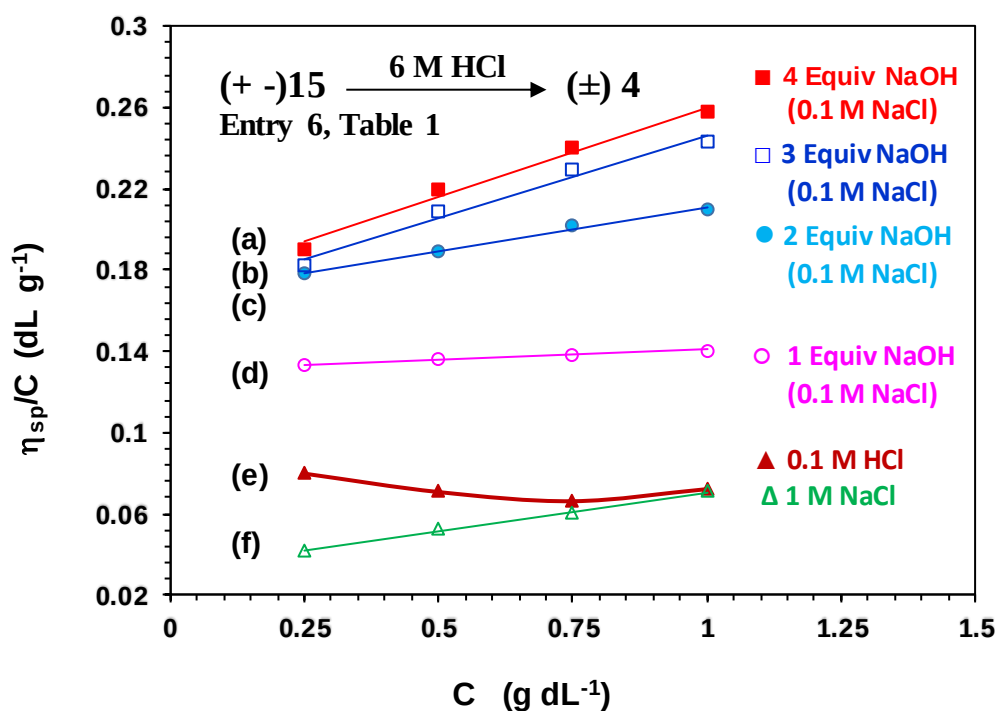


Figure 2.5 The viscosity behavior at 30 °C of polyzwitterion **4** (prepared by acid hydrolysis of **15** from entry 6, Table 2.1) (a) ■ in the presence of 4 equiv NaOH in 0.1 M NaCl, (b) □ in the presence of 3 equiv NaOH in 0.1 M NaCl, (c) ● in the presence of 2 equiv NaOH in 0.1 M NaCl, (d) ○ in the presence of 1 equiv NaOH in 0.1 M NaCl, (e) ▲ in 0.1 M HCl, and (vi) Δ in 1.0 M NaCl

2.4.5 Basicity Constant

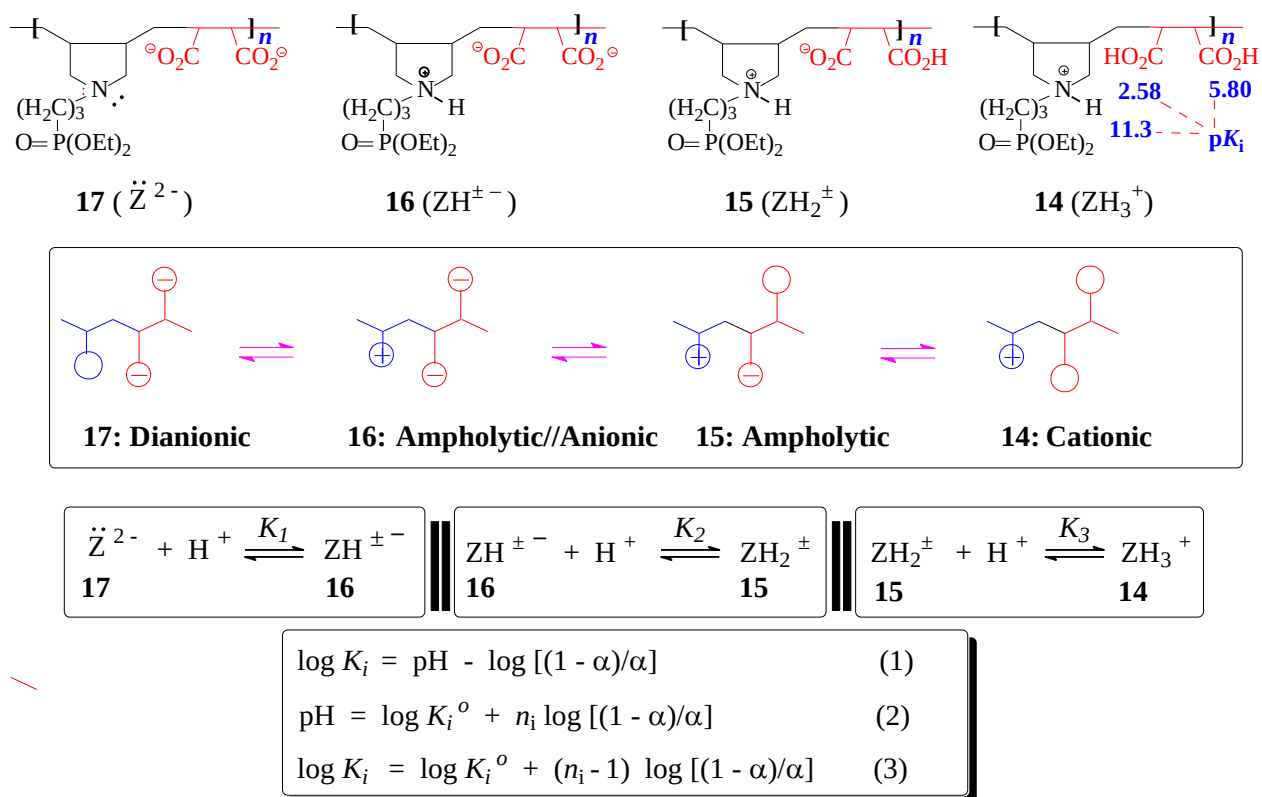
The apparent basicity constant (K) of several functional centers in polymer (=) **17** and (=) **8** is described by Eq. (3) (Scheme 2.3) where $\log K^0 = \text{pH}$ at $\alpha = 0.5$ and $n = 1$ observed for basicity constant of small molecules. The slope and intercept of the straight-line plot of pH vs. $\log [(1-\alpha)/\alpha]$ gave the values of ' n ' and $\log K^0$, respectively. In salt-free water, basicity constant $\log K^0_1$, $\log K^0_2$ and $\log K^0_3$ were determined to be 11.3, 5.80 and 2.58, respectively, with the corresponding n_1 , n_2 and n_3 values of 1.71, 2.38 and 0.41 (Table 2.2).

The n values >1 or < 1 reflects the “apparent” nature of the basicity constant since the basicity constant changes with the degree of protonation [121,122]. A measure of the polyelectrolyte index n is shown in (Fig. 2.6) displaying variation of K with α signifying a polyelectrolyte effect. With increasing α , a gradual decrease of $\log K^0_1$ [involving (Z^-) **17** + $H^+ \rightleftharpoons (ZH^+^-)$ **16**] and $\log K^0_2$ [involving (ZH^+^-) **16** + $H^+ \rightleftharpoons (ZH_2^{+-})$ **15**] is a result of decreasing overall negative charges that induces protonation. The n values $>$ or < 1 confirm the consequence of entropy effects [121,123]. PDA (=) **17** having greater charge imbalance is more hydrated than $(+ =)$ **16** which in turn is more hydrated than $(+ -)$ **15**. With each protonation, water molecules are released from the hydration shell of the repeating unit that is being protonated. With increasing α , the excess average negative charge in the polymer backbone decreases as does the average number of water molecules in the hydration shell of a repeating unit. Therefore, there will be release of lesser and lesser number of water molecules from the polymer backbones with increasing α , and the associated entropy change dictates the decrease of K with increasing α . The exothermic ΔH^0 has been reported to be independent of α , the ΔG^0 is thus controlled by the entropy term [123].

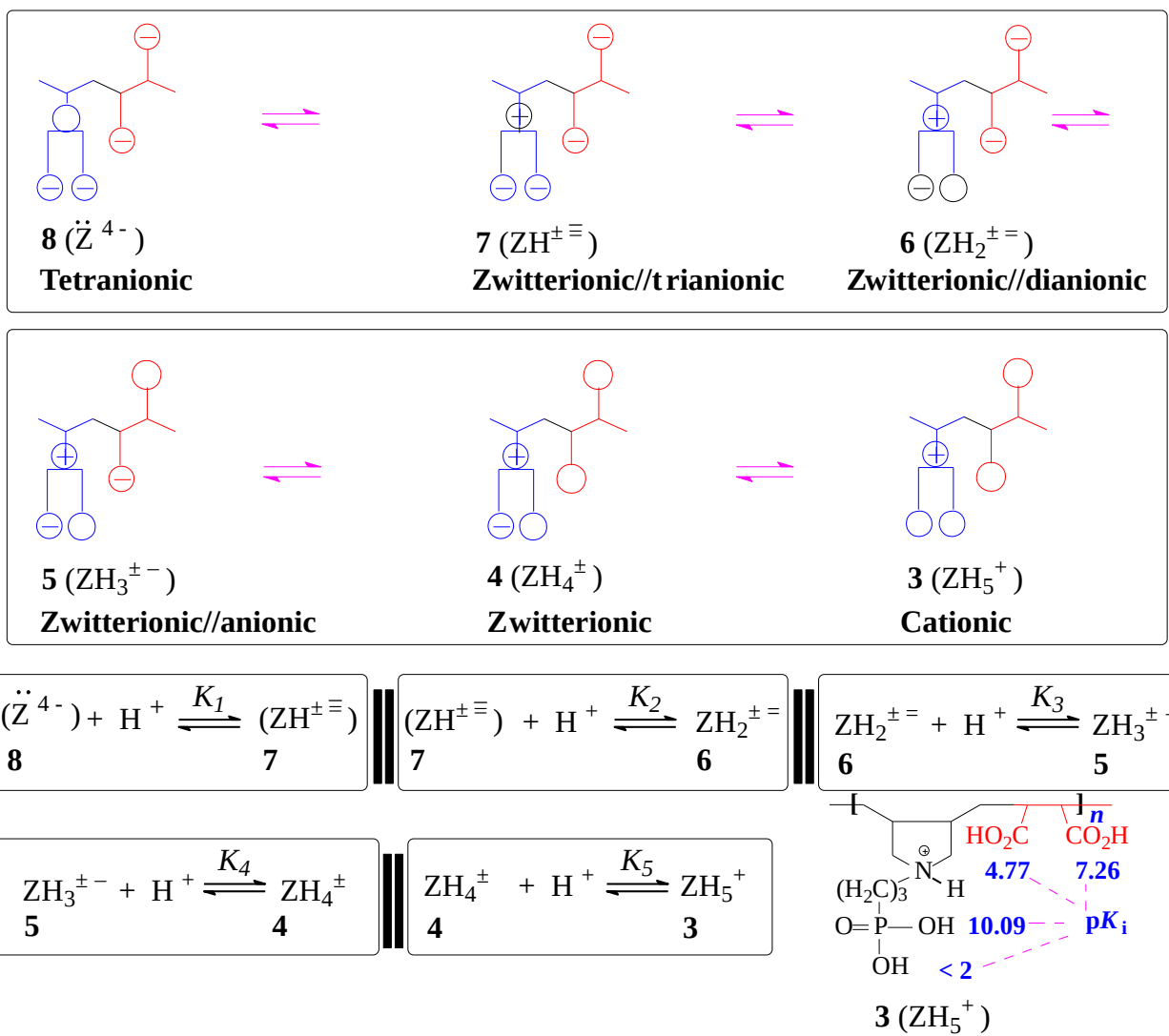
The n_3 value associated with $\log K^0_3$ [involving (ZH_2^{+-}) **15** + $H^+ \rightleftharpoons (ZH_3^+)$ **14**] was found to be 0.41. The n value < 1 is characteristic of a compact conformation arising out of the presence of ampholytic and zwitterionic motifs. The approach of protons towards (ZH_2^{+-}) **15** becomes easier with the increasing degree of protonation [124,40]. The protonation constant $\log K_3$ increases progressively with increasing α (Fig. 2.6a). The macromolecular coil expands as a result of a decrease in the density of the ampholyte motifs (*cf. viscosity curves Fig. 2.4c versus e*), thereby exposing the polymer backbone for easier access to protonation. With each protonation, the imbalance in favor of positive charges on the

backbone increases. Increased hydration, as a result, leads to entropically favorable release of a greater number of hydrated molecules during protonation.

For polytetraionic (= =) **8**, $\log K^0_2$, $\log K^0_3$ and $\log K^0_4$ were determined to be 10.09, 7.26 and 4.77, respectively with the corresponding n values of 1.27, 1.62 and 0.99. Note that the pK_a of an acid (HA) is the $\log K_b$ (i.e., $\log$ [basicity constant]) of its conjugate base (A^-). For the pentaprotic acid (ZH_5^+) **3** and triprotic acid (ZH_3^+) **14**, the pK s of several protic centers are shown in Schemes 2.3 and 2.4. The values of pK_1 and pK_5 were not determined for the reasons mentioned in the experimental, however, the pK_1 of (ZH_5^+) **3** (Schemes 2.1 and 2.4) is estimated to have a value of < 2 since methanephosphonic acid itself is known to have pK_1 value of 2.12. The considerable difference is observed in the acidity of the first carboxylic acid groups in **14** (with pK value 2.58) [involving (ZH_3^+) **14** $\rightleftharpoons$ (ZH_2^{+-}) **15** + H^+] (Scheme 2.3) and **4** (with pK value of 4.77) [involving ($ZH_4^{\pm}$) **4** $\rightleftharpoons$ ($ZH_3^{\pm-}$) **5** + H^+] (Scheme 2.4). While the higher acidity of the first CO_2H in (ZH_3^+) **14** is attributable to the electrostatic attraction [33,121,122] associated with polyampholyte motifs (ZH_2^{+-}) in its conjugate base **15**, the difficulty associated with the removal of a proton from ($ZH_4^{\pm}$) **4** involves the transformation of a zwitterionic motif to an energetically less favorable zwitterion/anion ($ZH_3^{\pm-}$) **16**. (Ampholytic/anion (ZH^{+-})).



Scheme 2.3 pH Induced changes in the charge types and densities in the backbone of **14 -17**.



Scheme 2.4 pH Induced changes in the charge types and densities in the backbone of **3-8**.

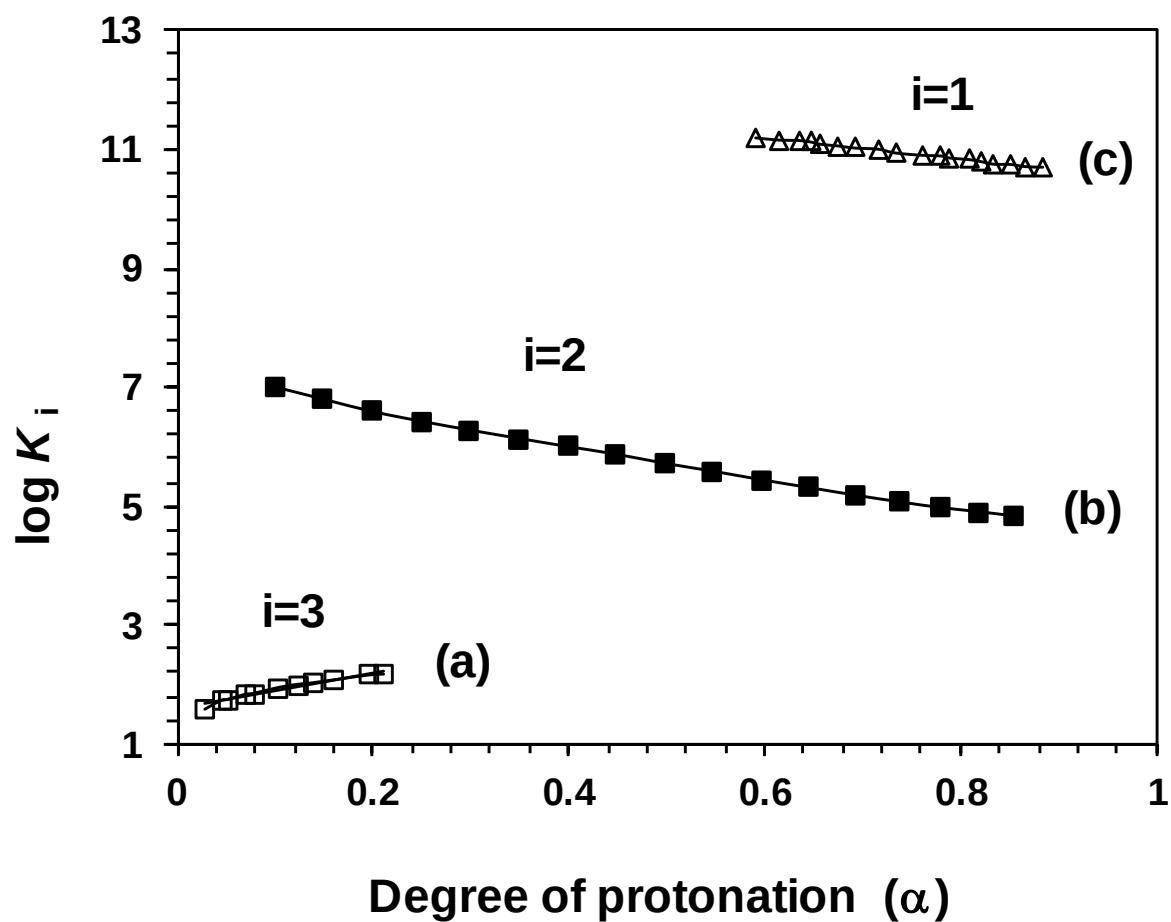


Figure 2.6 Plot for the apparent $\log K_i$ versus degree of protonation (α) in salt-free water (a) $\square$ ($\log K_3$, run 1, Table 3), (b) $\blacksquare$ ($\log K_2$, run 3, Table 3) and (c) $\triangle$ ($\log K_3$, run 3, Table 3).

Table 2.2 Protonation of polymer **15** ($\text{ZH}_2^\pm$) at 23 °C

run	$\text{ZH}_2^\pm$ (mmol)	C_T^a (mol dm ⁻³)	α -range	pH-range	Points ^b	Log K_i^o ^c	n_i ^c	R^2 , ^d
1	0.2554 ($\text{ZH}_2^\pm$)	+0.1222	0.03-0.21	3.09-2.75	11	2.54	0.36	0.9916
2	0.2812 ($\text{ZH}_2^\pm$)	+0.1222	0.05-0.21	3.08-2.81	12	2.57	0.42	0.9887
3	0.3193 ($\text{ZH}_2^\pm$)	+0.1222	0.06-0.18	3.09-2.85	07	2.59	0.40	0.9934
Average						2.58 (3)	0.41 (4)	
Log $K_3^e = 2.58 - 0.59 \log [(1-\alpha)/\alpha]$ For the reaction: $\text{ZH}_2^\pm + \text{H}^+ \xrightleftharpoons{K_1} \text{ZH}_3^+$								
1	0.2554 ($\text{ZH}_2^\pm$)	-0.09594	0.87-0.14	3.74-7.74	17	5.82	2.43	0.9989
2	0.3193 ($\text{ZH}_2^\pm$)	-0.09594	0.88-0.10	4.01-8.10	19	5.83	2.33	0.9964
3	0.3831 ($\text{ZH}_2^\pm$)	-0.09594	0.85-0.20	4.06-7.20	17	5.74	2.37	0.9965
Average						5.80 (5)	2.38 (5)	
Log $K_2^e = 5.80 + 1.38 \log [(1-\alpha)/\alpha]$ For the reaction: $\text{ZH}^{\pm-} + \text{H}^+ \xrightleftharpoons{K_2} \text{ZH}_2^\pm$								
1	0.2554 ($\text{ZH}_2^\pm$)	-0.09594	0.91-0.58	9.65-11.06	17	11.29	1.71	0.9911
2	0.3193 ($\text{ZH}_2^\pm$)	-0.09594	0.90-0.56	9.78-11.17	17	11.36	1.68	0.9964
3	0.3831 ($\text{ZH}_2^\pm$)	-0.09594	0.88-0.59	9.83-11.04	18	11.31	1.73	0.9967
Average						11.31 (4)	1.71 (3)	
Log $K_1^e = 11.31 + 0.71 \log [(1-\alpha)/\alpha]$ For the reaction: $\text{Z}^- + \text{H}^+ \xrightleftharpoons{K_1} \text{ZH}^{\pm-}$								

^a Titrations with NaOH and HCl are described by (-)ve and (+)ve values, respectively.^b Data points used.^c Parentheses include the standard deviations in the last digit.^d R = Correlation coefficient.^e $\log K_i = \log K_i^o + (n_i - 1) \log [(1 - \alpha)/\alpha]$.

Table 2.3 Protonation of polymer **4** ($\text{ZH}^\pm$) at 23 °C

run	$\text{ZH}_2^\pm$ (mmol)	Cr^a (mol dm ⁻³)	α -range	pH-range	Points ^b	$\log K_1^{o\ c}$	n_1^c	$R^2,^d$
Polymer 4								
1	0.2416 ($\text{ZH}_4^\pm$)	-0.09594	0.54–0.09	4.65–5.72	7	4.76	0.99	0.9842
2	0.2701 ($\text{ZH}_4^\pm$)	-0.09594	0.52–0.08	4.68–5.66	9	4.80	1.03	0.9902
3	0.2982 ($\text{ZH}_4^\pm$)	-0.09594	0.51–0.11	4.74–5.62	9	4.74	0.96	0.9965
Average						4.77 (3)	0.99 (4)	
$\log K_4^e = 4.77 - 0.01 \log [(1-\alpha)/\alpha]$ For the reaction: $\text{ZH}_3^{\pm-} + \text{H}^+ \xrightleftharpoons{K_4} \text{ZH}_4^\pm$								
1	0.2416 ($\text{ZH}_4^\pm$)	-0.09594	0.89–0.10	6.00–8.71	9	7.27	1.59	0.9845
2	0.2701 ($\text{ZH}_4^\pm$)	-0.09594	0.87–0.12	6.05–8.65	11	7.31	1.64	0.9907
3	0.2982 ($\text{ZH}_4^\pm$)	-0.09594	0.86–0.18	6.11–8.28	8	7.21	1.62	0.9827
Average						7.26 (3)	1.62 (3)	
$\log K_3^e = 7.26 + 0.62 \log [(1-\alpha)/\alpha]$ For the reaction: $\text{ZH}_2^{\pm=} + \text{H}^+ \xrightleftharpoons{K_3} \text{ZH}_3^{\pm-}$								
1	0.2416 ($\text{ZH}_4^\pm$)	-0.09594	0.87–0.37	9.17–10.43	10	10.15	1.22	0.9982
2	0.2701 ($\text{ZH}_4^\pm$)	-0.09594	0.85–0.35	9.18–10.42	12	10.20	1.29	0.9894
3	0.2982 ($\text{ZH}_4^\pm$)	-0.09594	0.81–0.30	9.19–10.45	9	9.93	1.31	0.9913
Average						10.09 (14)	1.27 (5)	
$\log K_2^e = 10.09 + 0.27 \log [(1-\alpha)/\alpha]$ For the reaction: $\text{ZH}^{\pm=} + \text{H}^+ \xrightleftharpoons{K_2} \text{ZH}_2^{\pm=}$								

^a Titrations with NaOH is described by (-)ve values.^b Data points used.^c Parentheses include the standard deviations in the last digit.^d R = Correlation coefficient.^e $\log K_i = \log K_i^o + (n_i - 1) \log [(1 - \alpha)/\alpha]$.

2.4.6 Scale Inhibition Study

The inlet feed water in a Reverse Osmosis (RO) process produces product water and rejects brine. The supersaturation of any of the dissolved salts in the reject brine stream leads to its precipitation. The percent scaling inhibition (PSI) is calculated using [Eq. \(4\)](#):

$$PSI = \frac{[Ca^{2+}]_{inhibited(t)} - [Ca^{2+}]_{blank(t)}}{[Ca^{2+}]_{inhibited(t_0)} - [Ca^{2+}]_{blank(t)}} \times 100 \quad (4)$$

Where $[Ca^{2+}]$ describes concentration at time zero and t, in the presence (inhibited) and absence (blank) of antiscalant.

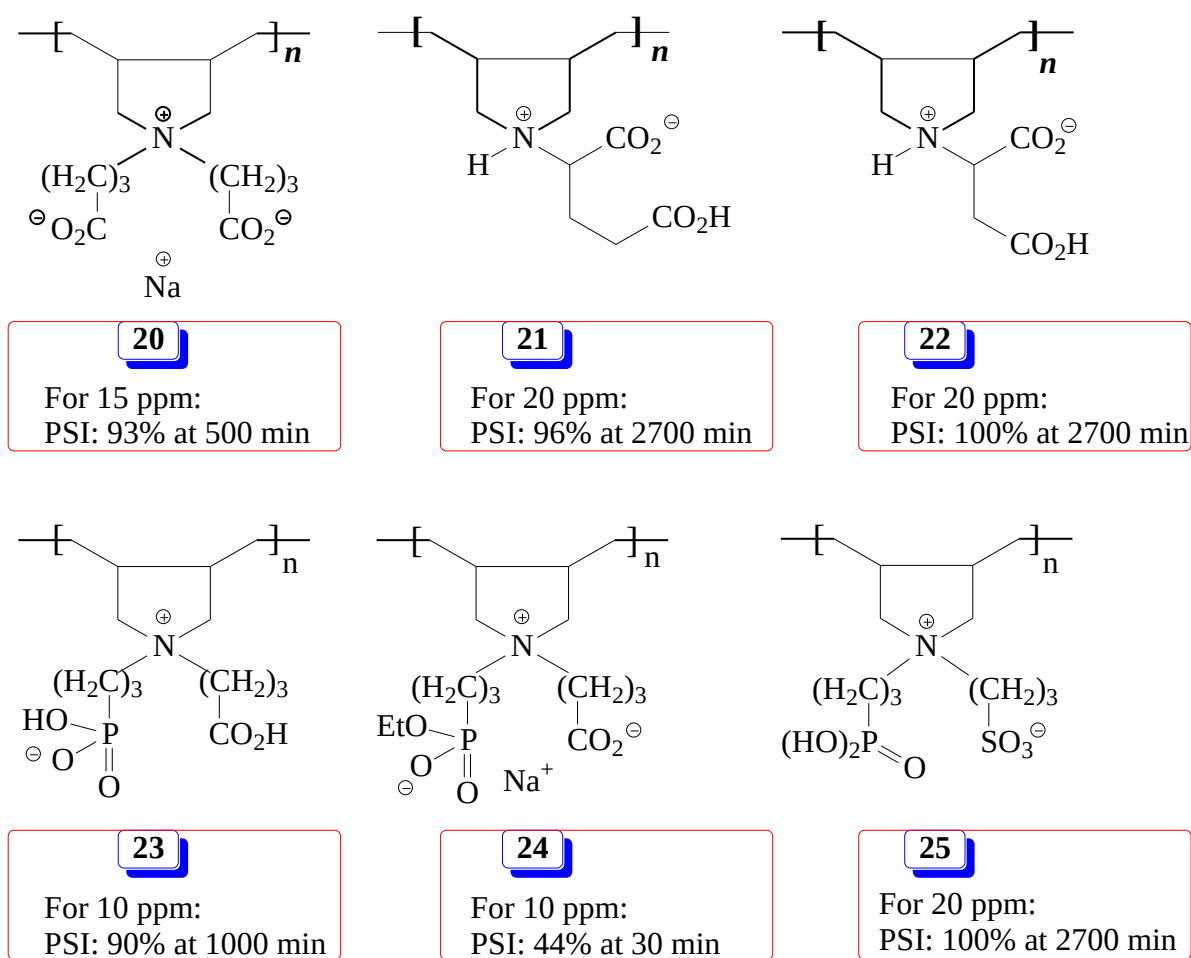
The scaling behavior of a supersaturated solution of $CaSO_4$ containing Ca^{2+} (2598 ppm) and SO_4^{2-} (6300 ppm) in the presence of synthesized polymers **4** and **15** was investigated. These are three times the concentration of Ca^{2+} and SO_4^{2-} found in the reject brine denoted as 1 CB (i.e., concentrated brine) from a RO plant [\[123\]](#). The PSI by **4** and **15** at various concentrations of the antiscalants is given in [Table 2.4](#). The onset of $CaSO_4$ precipitation is marked by a sudden drop in the conductivity ([Fig. 2.7](#)). To our satisfaction, the presence of a small concentration (5 ppm) of **4** registered a 99 % scale inhibition for about 120 min. In the presence of 10, 15 and 20 ppm of the antiscalant, it registered a PSI of $\approx 100\%$ for 2000 min. It is indeed astonishing to observe that the antiscalant **4**, at a concentration of 15 or 20 ppm, PSI remains $\approx 100\%$ even after 14000 min (i.e., 9.7 days). An antiscalant needs to be effective at least for a minimum period of ≈ 30 min which is the residence time for the brine in the osmosis chamber. Note that PA **15** containing ester motifs was ineffective as an antiscalant ([Fig. 2.7](#)). ([Table 2.4](#)); the precipitation of $CaSO_4$ occurred within 10 min as confirmed by a large drop in conductivity. The current PZ **4** has even much superior

antiscalant efficacy than its corresponding homopolymer **9** or **10** (Scheme 2.1) [114]. As shown in Fig. 2.7, the onset of precipitation occurs after an induction period. A sharp drop in conductivity is attributed to an accelerated growth of CaSO_4 crystals. At a concentration of 5 and 10 ppm, the induction time was observed to be 170 and 2100 min, respectively. For a duration of 14000 min, induction time was not observed in the presence PZ **4** (15 and 20 ppm). The antiscalant inhibits the crystal growth by complex formation with metal cations, thereby altering the crystal morphology at the time of nucleation [124,40]. The precipitation of gypsum, i.e., CaSO_4 in mineral form, is an undesirable occurrence in several processes like sea water desalination, water distillation, industrial water recovery and hydrometallurgical operations [125]. PZ **4** is remarkably efficient in prolonging the induction period, and thus has the potential to mitigate the membrane fouling as a result of scale formation.

In comparing the antiscalant activity of **4**, **15**, **9** or **10**, note that polymer **15** with ester motifs cannot bear negative charges on the phosphonate pendants and as such cannot effectively interfere with the positive Ca^{2+} during nucleation [126-128]. The repeating unit in **4** has a greater negative charge density than its homopolymer **9** or **10**. The greater negative charges in **4** not only disturb the nucleation process by adsorption onto the developing crystal, they also prevent the agglomeration (i.e., scale formation) by repulsion among the distorted crystals bearing excessive negative charges. The above rationale clearly accounts for the remarkable antiscalant activity of PZ **4**.

Some polyzwitterions (PZs) synthesized via cyclopolymerization and their effectiveness as antiscalants in terms of percent scale inhibition (PSI) under conditions like the current work are presented in Scheme 2.5. Note that PZ **23** performed much better than its

counterpart **24** having a monoethyl ester group, thereby confirming the necessity of the presence of the completely hydrolyzed phosphonate motifs to be a better antiscalant [129]. Glutamic acid-based PZ **21** [130], aspartic acid-based PZ **22** [131] and PZ **25** [3] containing phosphonate and sulfonate pendants as well as **20** [132] containing carboxyl group in both pendants performed very well imparting similar PSIs. However, the current PZ **4** with greater negative charge density outperformed all the other PZs presented in Scheme 2.5.



Scheme 2.5 Percent scale inhibition (PSI) of some antiscalants synthesized via cyclopolymerization protocol.

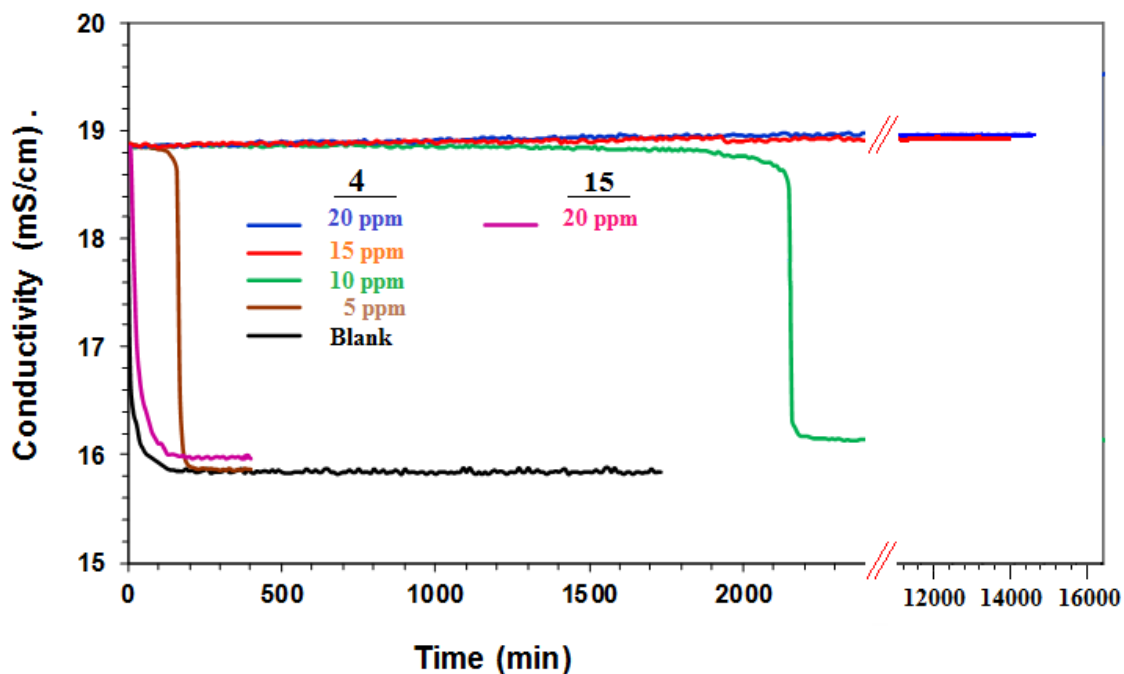


Figure 2.7 Conductivity of a supersaturated solution of CaSO_4 in the presence (5,10,15,20 ppm) of **4** and **15** (20 ppm) and in the absence (blank) of antiscalant.

Table 2.4 Percent scale inhibition in the presence of PZ **4** and PA **15** in 3 CB^b supersaturated CaSO_4 solution at 40 °C.

Entry	Sample (ppm)	Percent inhibition at times (min) of						Induction time (min)
		30	60	120	1000	2000	14000	
Polymer 4								
1	5	100	100	99	—	—	—	170
2	10	100	100	100	100	100	—	2100
3	15	100	100	100	100	100	100	— ^a
4	20	100	100	100	100	100	100	— ^a
Polymer 15								
5	20	19	5	—	—	—	—	10

^a No induction time was observed.

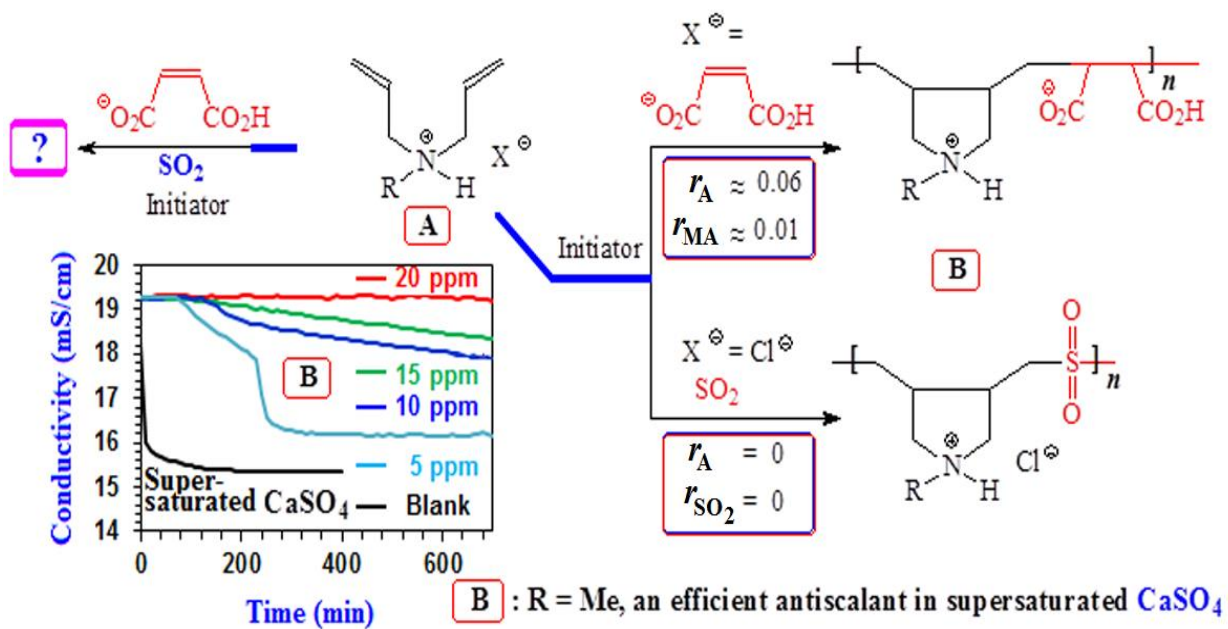
^b Three times the concentration of Ca^{2+} and SO_4^{2-} found in the concentrated brine of an RO plant.

2.5 Conclusion

Maleic acid has been copolymerized with diallylammionium monomers **1** and **12** using Butler's cyclopolymerization protocol to give alternate copolymers PZ **4** and CPE **14** having three-carbon spacer separating the phosphonate and amine motifs. Likewise, ion-pair generated by treating *N,N*-Diallyl-3-(diethylphosphonato)propylamine **11** with maleic acid underwent copolymerization to give alternate PA **15**. To correlate the solution properties of **4** and **15**, diester groups in **15** were hydrolysed by 6 M HCl to generate **4**. The pH-induced changes of backbone charges in pH-responsive tetraprotic **4** and diprotic **15** having identical degree of polymerization were investigated in detail by viscometric technique. Several protonation constants (or pK_a) of the CO_2^- (or CO_2H) and trivalent nitrogen (or protonated NH^+) in **4** and **15** have been determined by potentiometric titrations. Evaluation of the antiscalant properties using supersaturated solution of CaSO_4 revealed that PZ **4** is remarkably effective in inhibiting the formation of calcium sulfate scale for days at 40 °C. The superiority of phosphonic acid motifs in **4** over the phosphonate ester motifs in **15** in scale inhibition is demonstrated as the latter is found to impart no scale inhibition.

CHAPTER 3

SCOPE OF SULFUR DIOXIDE INCORPORATION IN ALKYLDIALLYLAMINE-MALEIC ACID-SO₂ TERCYCLOPOLYMERIZATION



Graphical Abstract

3.1 Abstract

Alternate copolymerization of diallylamine derivatives $[(\text{CH}_2=\text{CH}-\text{CH}_2)_2\text{NR}]$; $\text{R} = \text{Me}$, $(\text{CH}_2)_3\text{PO}(\text{OEt})_2$, and $\text{CH}_2\text{PO}(\text{OEt})_2$ (**I**)-maleic acid (MA) and (**I.HCl**)- SO_2 pairs have been carried out thermally using ammonium persulfate initiator as well as UV radiation at λ of 365 nm. The reactivity ratios of ≈ 0 for the monomers in each pair **I**-MA and **I.HCl**- SO_2 ensured their alternation in each copolymer. However, numerous attempted terpolymerization of **I**-MA- SO_2 failed to entice MA to participate to any meaningful extent. In contrast to reported literature, only 1-2 mol% of MA was incorporated into the polymer chain mainly consisting of poly(**I-alt-SO**₂). Quaternary diallyldialkylammonium chloride $[(\text{CH}_2=\text{CH}-\text{CH}_2)_2\text{N}^+\text{R}_2 \text{Cl}^-]$; $\text{R} = \text{Me}$, Et] (**II**) also, did not participate in **II**-MA- SO_2 terpolymerizations. Poly(**I**, $\text{R}=\text{Me}$)-*alt*- SO_2) **III** is a stimuli-responsive polyampholyte; its transformation under pH-induced changes to cationic, polyampholyte-anionic, and dianionic polyelectrolytes has been examined by viscosity measurements. The pK_a of two carboxylic acid groups and NH^+ in **III** has been determined to be 2.62, 5.59, and 10.1. PA **III**, evaluated as a potential antiscalant in reverse osmosis plants, at the concentrations of 5 and 20 ppm, imparted $\approx 100\%$ efficiency for CaSO_4 scale inhibition from its supersaturated solution for over 50 and 500 min, respectively, at 40 °C. The synthesis of PA **III** in excellent yields from cheap starting materials and its very impressive performance may accord PA **III** a prestigious place as an environment-friendly phosphate-free antiscalant.

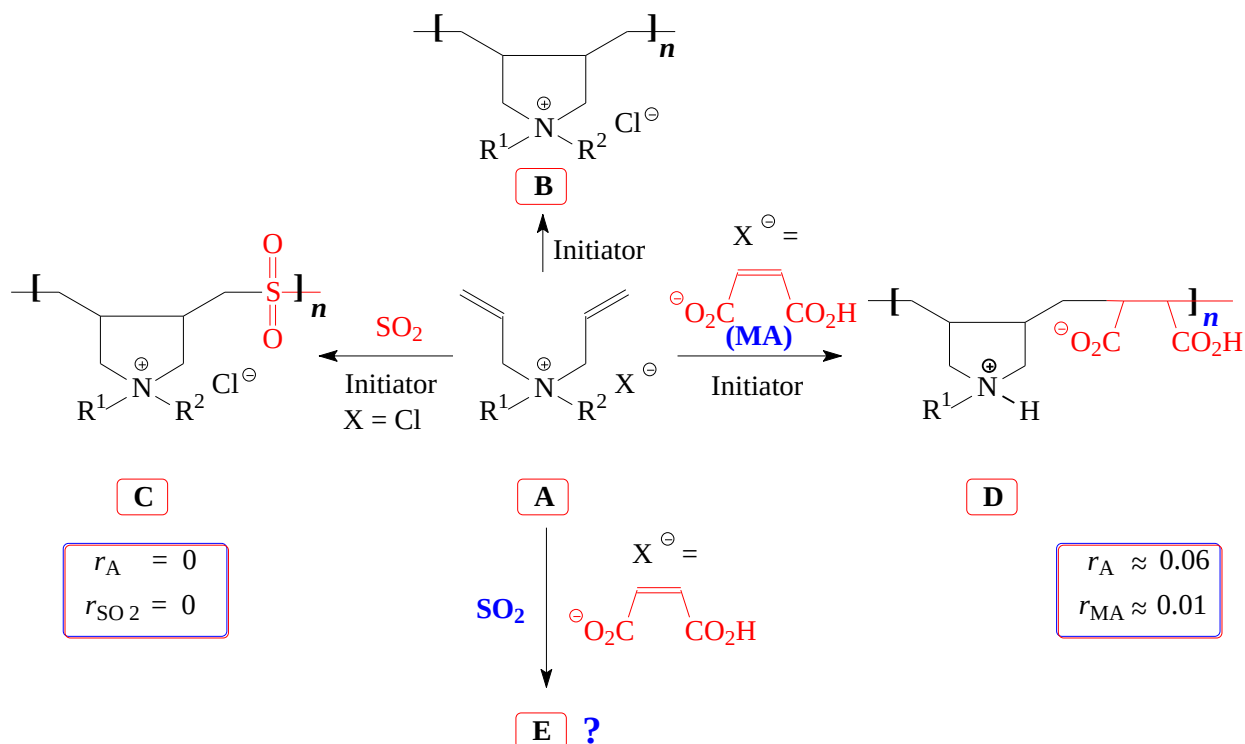
Keywords: pH-responsive polymers; diallylamine salts; alternate cyclopolymerization; polyampholyte; maleic acid; antiscalant.

3.2 Introduction

Butler's cyclopolymerization protocol [1] has etched a place of distinction in the synthesis of polymers of tremendous technological importance [2,96,133]. Free radical-initiated polymerization of diallylammonium salts **A** led to **B** having pyrrolidine rings embedded into the macromolecules (Scheme 3.1). The macromolecule **B** represents the eighth most important architecture among synthetic high polymers [8,9]. Poly(diallyldimethylammonium chloride) **B** ($R^1=R^2=Me$), alone accounting for over 1000 patents and publications, has been produced to the tune of millions of pounds for a variety of industrial applications including water treatment [1]. Sulfur dioxide has been extensively used to synthesize alternate cyclocopolymers **C** having numerous applications [134,135]. The reactivity ratios of amine (salt) (r_A) and r_{SO_2} being zero led to the alternation in **C**. Likewise, the almost zero reactivity ratios of r_A and maleic acid (MA) (r_{MA}) led to the exclusive formation of alternate copolymer **D** from alkyldiallylamine/MA ion pair **A** [35,136]. Interestingly, diallyldimethylammonium chloride (**A**) – MA – SO_2 is reported in several patents [137-139] to give terpolymers in respective ratios of 50:25:25 [137] and 70:25:5 [139]. However, the patents do not describe any micro-structural analysis. To our knowledge, no journal article has appeared to date to describe such terpolymerization involving **A** – maleic acid – SO_2 to give **E** (Scheme 3.1).

Amino-carboxylate and -phosphonate are important antiscalant and metal chelation motifs; as such, the decoration of repeating units with a high density of these potent functional groups is expected to impart, for instance, an antiscalant behavior. Looking at the zero reactivity ratios for both the monomer pairs: $r_A \approx r_{SO_2} \approx 0$ and $r_A \approx r_{MA} \approx 0$ (Scheme 3.1), we do fancy the success of the terpolymerization to pave the way to a great many interesting

tripolymers **E**. Herein, we report a systematic study involving the cyclopolymerization of **A**, **A-SO₂**, **A-MA**, and **A-MA-SO₂** to investigate the course of action of an amine terminal radical $\text{—A}\bullet$, whether it adds exclusively or preferentially onto SO_2 or MA or both.



Scheme 3.1 Synthesis of homocyclopolymer and alternate copolymers from monomeric pairs: **A/maleic acid** and **A/SO₂**.

3.3 Experimental

3.3.1 Materials

Paraformaldehyde was purchased from Fluka Chemie AG. Diallylamine from Merck Schuchardt OHG, ammonium persulfate (APS), azobisisobutyronitrile (AIBN) and maleic acid from Sigma-Aldrich were used as received. Diallyldimethylammonium chloride (**15a**) from Sigma-Aldrich, obtained as 65 wt% solution, was freeze-dried and crystallized from methanol/acetone. Phosphonate ester **1a** [94], **1b** [6], and **5** [102] were prepared as described. For dialysis, Spectra/Por membrane (MWCO: 6000-8000) from Spectrum Laboratories Inc. was utilized.

3.3.2 Physical Methods

Elemental analysis was carried out in a Perkin Elmer Elemental Analyzer Series 11 Model 2400 (Waltham, Massachusetts, USA). IR spectra were recorded on a Thermo scientific FTIR spectrometer (Nicolet 6700, Thermo Electron Corporation, Madison, WI, USA). ^1H and ^{13}C NMR spectra of the polymers were measured in D_2O on a JEOL LA 500 MHz spectrometer. The residual HOD signal of D_2O at δ 4.65 ppm and dioxane ^{13}C resonance at δ 67.4 were used as internal and external references, respectively. Viscosities were measured using an Ubbelohde viscometer (Viscometer Constant = 0.005718 cSt/s). An SDT analyzer (Q600: TA instruments, USA) was utilized for thermogravimetric analysis (TGA) under N_2 flowing at a rate of $50\text{ cm}^3/\text{min}$. For photoinitiated polymerization, the samples were irradiated at 365 nm using UV Lamp 365 nm/254 nm SPECTROLINE (Model: ENF-240C) from Spectronic Corp., Westbury, NY, USA, with LONGLIFE Filter

to ensure highest UV intensity and Fluorescence Analysis Cabinet SPECTROLINE CM-10A.

3.3.3 Synthesis of Methyldiallylamine (7) and its Hydrochloride Salt 8

The procedure for the methylation of amines is adapted from the literature [140]. Formic acid (35 g, 85%, 0.646 mol) was added slowly (30 min) onto an ice-cold diallylamine (1) (49 g, 0.506 mol) in a 1 L RB flask under stirring. Paraformaldehyde (18.3 g, 0.613 mol) and water (33 mL) were added to the flask. The mixture in the flask, fitted with a long condenser, was stirred at 75 - 77 °C during which CO₂ evolution happened (30 min). Thereafter, the reaction mixture was heated to 90 °C; after the gas evolution stopped (15 min), the reaction mixture was cooled and saturated with the addition of a solution of NaOH (30 g, 0.75 mol) in water (30 mL). The separated organic layer of amine 7 was dried over NaOH and distilled at 107 °C (Lit. [141] b.p.109 °C) to obtain 7 as a colorless liquid (49 g, 87%).

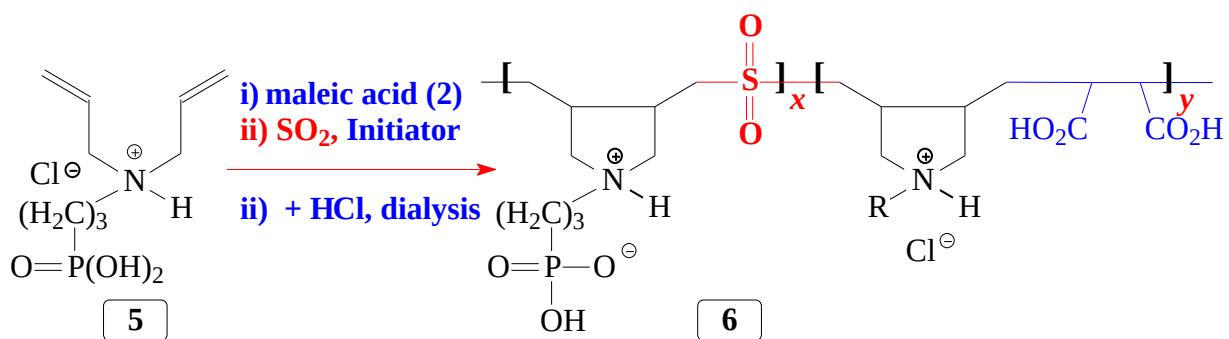
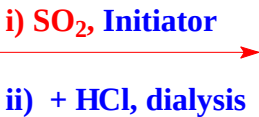
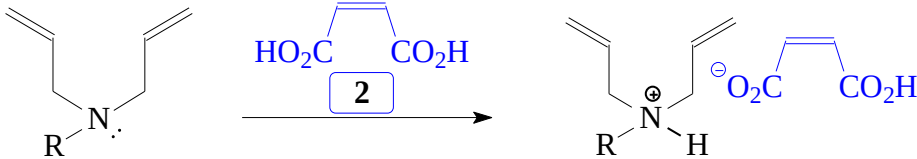
A dry HCl gas was passed to a solution of methyldiallylamine (7) (25 g, 0.225 mol) in ether (150 mL) at 0° C. Immediate precipitation of white salt 8 occurred. The passage of HCl was continued until the supernatant liquid becomes clear instead of cloudy. After filtration, the white salt was dried under vacuum to obtain 8 (30 g, 90%). δ_{H} (D₂O) 2.70 (3H, s), 3.65 (4H, d, *J* 7.3 Hz), 5.50 (4H, m), 5.82 (2H, m); δ_{C} (D₂O) 39.57 (1C, Me), 58.30 (2C, NCH₂), 126.60 (2C, =CH), 127.33 (2C, =CH₂). The ¹³C spectral assignments was supported by DEPT 135 NMR analysis.

3.4 Polymer Synthesis

3.4.1 Procedure for 1 or 5/2/SO₂ Terpolymerization

[Table 3.1](#) describes the polymerizations conditions ([Scheme 3.2](#)). For experiment under entry 1, SO₂ (705 mg, 11 mmol) was absorbed in a solution of monomer **1a** (1.38 g, 5.0 mmol) and MA **2** (0.70 g, 6.0 mmol) in DMSO (2.6 g) in an RB flask (10 mL). After purging the mixture with N₂, initiator APS (0.260 g) was added to the stirring mixture in the closed flask at 21 °C for 24 h. The polymer mixture was dialyzed against 0.2 M HCl for 24 h with frequent change of 0.2 M HCl. Finally, the polymer solution was dialyzed against distilled water for 6 h. The dialyzed solution was acidified with concentrated HCl (1.0 mL) and freeze-dried to obtain **4a**. Note that the acidification was intended to keep the nitrogens and carboxyls protonated. The FTIR and NMR spectra of the polymers resembled with the spectra of **1a**•HCl/SO₂ and **1b**•HCl/SO₂ copolymers **4a** [\[94\]](#) and **4b** [\[6\]](#) ($y \approx 0$), respectively.

For the polymerization involving monomer **5** [\[102\]](#), the crude reaction mixture was dialyzed against 2 M HCl followed by deionized water. Polymer **6**, precipitated out during dialysis, was dried under vacuum. The spectral analysis revealed the identical nature of the material **6** ($y \approx 0$) described elsewhere [\[142\]](#).



69

Table 3.1 Attempted cycloterpolymerization^a of monomers **1a**, **1b** and **5** with maleic acid **2** and SO₂.

Entry	Amine 1 (mmol)	MA 2 (mmol)	SO ₂ mmol	Initiator ^c (mg)	Temp (°C)	Yield ^b	[η] ^c (dL g ⁻¹)
1	1a : 5	6	11	APS (260)	21	4a : 39 (67)	0.0721
2	1a : 5	6	11	APS (70)	45	4a : 34 (68)	0.0562
3	1a : 5	6	11	APS (260)	45	4a : 48 (86)	0.0571
4	1a : 5	10	16	APS (260)	45	4a : 62 (90)	0.0462
5	1a : 5	6	11	APS (96)	65	4a : 11 (72)	0.0401
6	1a : 5	6	11	APS (210)	65	4a : 53 (60)	0.0454
7	1a : 5	6	11	APS (250)	65	4a : 48 (81)	0.0228
8	1a : 5	6	11	AIBN (46)	65	4a : Trace (28)	–
9	1a : 5	6	11	AIBN (100)	65	4a : 27 (60)	0.0211
10	1b : 5	6	11	APS (140)	65	4b : 49 (72)	0.0355
11	5 : 5	6	11	APS (200)	65	6 : 61 (67)	0.532 ^e
12	5 : 5	6	11	AIBN (50)	65	6 : 67 (71)	0.519 ^e
13	–	6	5	APS (140)	45	No Polymer	–
14	–	6	5	TBHP (100)	Temp ^d	No Polymer	–

^a Copolymerization reactions were carried out in DMSO (2.6 g) in the presence of ammonium persulfate (APS) or azoisobutyronitrile (AIBN) or *tert*-butylhydroperoxide for 48 h;

^b Polymer obtained is written in bold followed by isolated yields; the percent conversion determined by ¹H NMR analyses of the crude reaction mixture are written in parentheses;

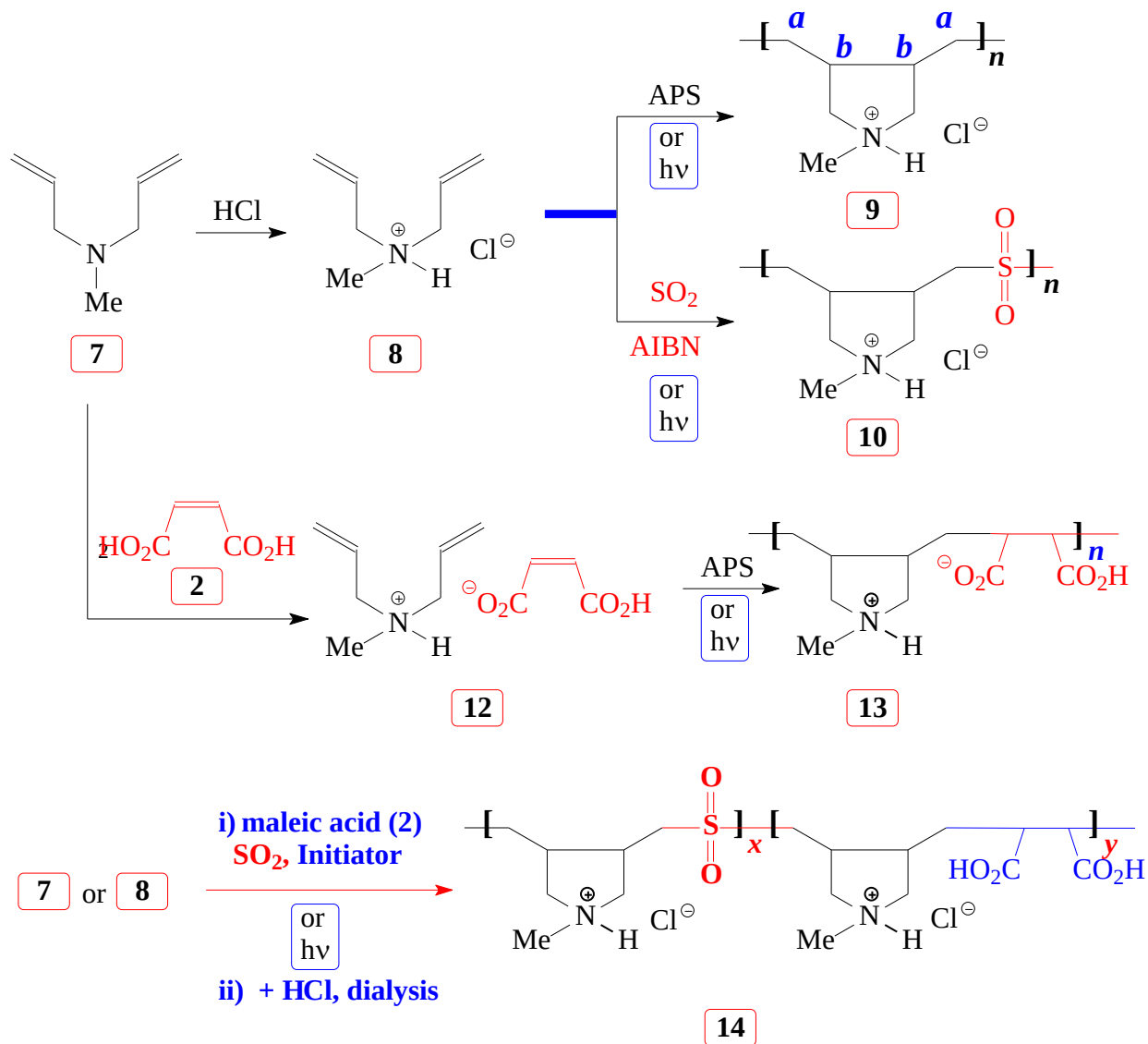
^c Viscosity of 1-0.25 % polymer solution in 0.1 M NaCl at 30 °C was measured with Ubbelohde Viscometer ($K = 0.005317 \text{ mm}^2 \text{ s}^{-2}$);

^d at -10 °C for 2 days, then at 0 and 25 °C for 2 days each.

^e in 0.1 N NaCl.

3.4.2 Free Radical Polymerization of Monomer **8**

A solution of salt **8** (8.86 g, 60 mmol) in water (3.5 g) and concentrated HCl (36 wt%) (0.5 g) in an RB flask (50 mL) fitted with a condenser was degassed with N₂ and then heated to 100 °C. APS was added in three portions (3×250 mg) with intervals of 3 min (Scheme 3.3). The temperature of the exothermic polymerization rose to 110 °C. The reaction mixture was continued to stir at the oil bath temperature of 100 °C for an additional 30 min. The product mixture was then dialyzed against distilled water and freeze-dried to obtain polymer **9** (7.7 g, 87%) as a white powder. (Found: C 56.7; H 9.58; N 9.4%. C₇H₁₄ClN requires C 56.94; H 9.56; N 9.49%); ν_{max} (KBr): 3500 (broad), 2946, 2724, 1649 (H₂O bending), 1461, 1107, 1053, 973, 909, 628, and 483 cm⁻¹. $[\eta]$ 0.0805 dL g⁻¹ at 30 °C in 0.1 M NaCl.



Scheme 3.3 Synthesis of homopolymer from **8**, alternate copolymers from **7/MA**, **8/SO₂** and terpolymers from **7** or **8/MA/SO₂**.

3.4.3 Photo-Chemical Initiated Polymerization of Monomer **8**

A sample of monomer **8** (200 mg, 1.4 mmol) in a vial was exposed to UV radiation at room temperature for 4 days. No polymerization occurred as indicated by ^1H NMR spectrum. Likewise, a solution of monomer **8** (295 mg, 2.0 mmol) in water (120 mg) was exposed to UV radiation at room temperature for 4 days giving **9** only in 5 % yield as revealed by ^1H NMR spectrum. The yield was improved to 7.6% after further irradiation for 2 days.

3.4.4 Copolymerization of **8** with SO_2

To a solution of monomer **8** (5.02 g, 34 mmol) in DMSO (8.4 g) was absorbed SO_2 (2.18 g, 34 mmol). After adding initiator AIBN (200 mg), the reaction mixture was heated at 65 °C inside a closed vessel for 24 h. The resultant polymer mixture was dialyzed against distilled water. The dialyzed solution was treated with 2.0 g concentrated HCl (37%, 20 mmol) and then freeze-dried to obtain a white powder of copolymer **10** (6.7 g, 93%). $[\eta]$ 0.276 dL g $^{-1}$ at 30 °C in 0.1 M NaCl. (Found: C 39.4; H 6.8; N 6.5%. $\text{C}_7\text{H}_{14}\text{ClNO}_2\text{S}$ requires C 39.71; H, 6.67; N 6.62%); ν_{max} (KBr): 3452 (broad), 2955, 2719, 1636 (H_2O bending), 1466, 1413, 1304, 1128, 1036, 963, 856, 773, and 517 cm^{-1} .

3.4.5 Methyldiallylamine (**7**) and Maleic Acid (**2**) Ion Pair **12**

Maleic acid **2** (1.16 g, 10.0 mmol) was added to a biphasic mixture of amine **7** (1.11 g, 10.0 mmol) in water (8 mL) and stirred at 25 °C for 30 min. Exothermic neutralization led to a homogeneous solution which was freeze-dried to obtain ion pair **12** as a colorless liquid in quantitative yield. ν_{max} (neat): 3496 (strong), 3375 (strong and broad), 3031, 2962, 2656 (R_3NH^+), 2516 (R_3NH^+), 2356 (R_3NH^+), 1704, 1623, 1581, 1477, 1363, 1202, 1082, 988, 869, 710, 653, and 568 cm^{-1} . δ_{H} (D_2O) 2.55 (3H, s), 3.43 (2H, ABX, J 7.5, 13.4 Hz), 3.57

(2H, ABX, J 7.0, 13.4 Hz), 5.35 (4H, m), 5.67 (2H, m), 6.08 (2H, s); δ_C (D₂O) 39.37 (1C, Me), 58.07 (2C, NCH₂), 126.37 (2C, =CH), 127.19 (2C, =CH₂), 135.09 (CH=CH), 171.14 (C=O). The ¹³C spectral assignments were supported by DEPT 135 NMR.

3.4.6 Copolymerization of 7 and MA 2

Amine **7** (2.22 g, 20.0 mmol) and MA **2** (2.54 g, 22.0 mmol) mixture in water (2.04 g) in an RB flask fitted with a condenser was stirred at 100 °C under a positive atmosphere of N₂. Initiator APS was added (2×200 mg) over 4 min. The exothermic polymerization started, and the mixture was stirred at 100 °C (10 min), cooled, dialyzed against deionized water, and freeze-dried to obtain a white powder of alternate polyampholyte (PA) **13** (3.68 g, 81%). The crude mixture revealed the monomer conversion of 86% as indicated by ¹H NMR spectrum. (Found: C 57.8; H 7.7; N 6.0 %. C₁₁H₁₇NO₄ requires C 58.14; H 7.54; N 6.16%). $\nu_{\max}$ (KBr): 3455 (broad), 2949, 2729, 2357, 1714, 1635, 1574, 1464, 1391, 1207, 1053, 810, 661 and 566 cm⁻¹.

3.4.7 Procedure for 7 or 8/2/SO₂ Terpolymerization

Table 3.2 describes the polymerizations conditions. The polymerizations were carried out as described under section 3.4.1. After completion of the polymerization, the crude mixture was dialyzed against 0.2 M HCl with frequent change of the 0.2 M HCl for a duration of 24 h, and finally, dialyzed against distilled water for 6 h. The resulting solution was acidified with concentrated HCl (1.0 mL) and freeze-dried to obtain polymer **14**. Note that the acidification was carried out to keep the nitrogens and carboxyls protonated. The FTIR and NMR spectra of the polymer **14** resembled with the spectra of **7**•HCl/SO₂ copolymer **10**, thereby implying the value of $y \approx 0$.

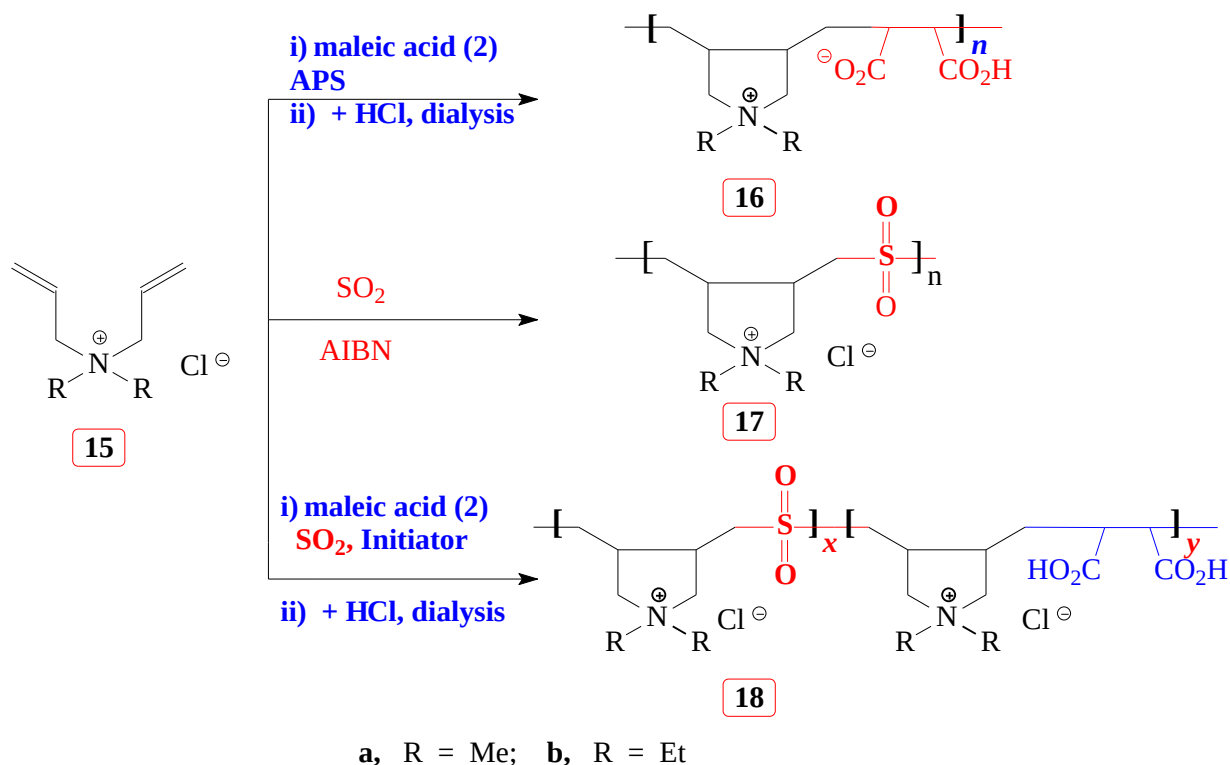
Table 3.2 Attempted cycloterpolymerization of monomer **7** or **8** with SO₂ and maleic acid **2**.

Entry	7 or 8 (mmol)	MA 2 (mmol)	SO ₂ (mmol)	DMSO (g)	Initiator (mg)	Temp (°C)	Time (h)	Yield ^a	[η] ^b (dL g ⁻¹)
1 ^c	7 : (5)	6	11	2.3	APS: 85	45	72	14 :21 (63)	0.141
2 ^c	7 : (5)	6	11	2.3	APS: 150	45	72	14 :31 (57)	0.125
3	7 : (5)	11	16	2.3	APS: 85	45	72	14 :23 (63)	0.121
4	7 : (5)	11	16	2.3	APS 175	45	48	14 :47 (60)	0.182
5	7 : (5)	11	16	2.3	APS 260	65	24	14 :32 (83)	0.129
6	7 : (5)	22	31	2.8	APS 260	65	24	14 :62 (85)	0.172
7 ^c	7 : (5)	6	11	2.3	AIBN 75	65	36	14 :0 (10)	–
8 ^d	8 : (1)	10	25	4.6	APS:360	45	48	14 :51 (67)	–
9 ^d	8 : (5)	5	5	0	Dark	23	24	14 :0 (0)	–
10 ^d	7 : (5)	5	6	0	UV	23	168	14 :26 (43)	0.278
11 ^e	8 : (5)	5	10	0	UV	23	24	14 :45 (62)	0.329
12 ^e	8 : (5)	5	10	0	UV	–15	4	14 :43 (67)	0.273
13 ^e	8 : (5)	5	10	1.0	UV	23	24	14 :43 (83)	0.471
14	8 : (5)	5	10	MeOH:1.0	UV	–10	6	14 :15 (35)	0.192
15	8 : (5)	0	4.5	0	UV	23	24	10 :54 (72)	0.836
16	8 : (5)	0	0	H ₂ O:0.3	UV	23	144	9 : – (7.6)	–

^a Isolated yields is followed by the percent conversion written in parentheses as determined by ¹H NMR analyses of the crude reaction mixture; ^b Viscosity of 1-0.25 % polymer solution in 0.1 M NaCl at 30 °C was measured with Ubbelohde Viscometer ($K = 0.005317 \text{ mm}^2 \text{ s}^{-2}$); ^c Cloudy reaction mixture after 4 h; ^d MA remained partially soluble; ^e solidified.

3.4.8 Procedure for 15/2/SO₂ co- and Terpolymerization

Table 3.3 describes the polymerizations conditions (Scheme 3.4). The polymerizations of monomers **15** were carried out as described under section 2.4.1. After the elapsed time, the reaction mixture (involving MA) was dialyzed against 0.5 M HCl for 24 h with frequent change of the 0.5 M HCl to remove excess MA, followed by dialysis against distilled water for 6 h. The resulting solution was acidified with concentrated HCl (1.0 mL) and freeze-dried to obtain polymers **16** and **18**. (Acidification was carried out to keep the carboxyl groups protonated). In the case where MA was not involved, the polymer **17** was simply purified by dialysis against distilled water. The FTIR and NMR spectra of the polymer **18** resembled with the copolymer **17**, thereby implying the value of $y \approx 0$.



Scheme 3.4 Synthesis of alternate copolymers from **15/MA** and **15/SO₂** and terpolymers from **15/MA/SO₂**.

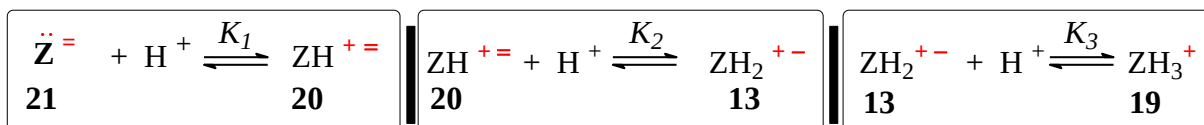
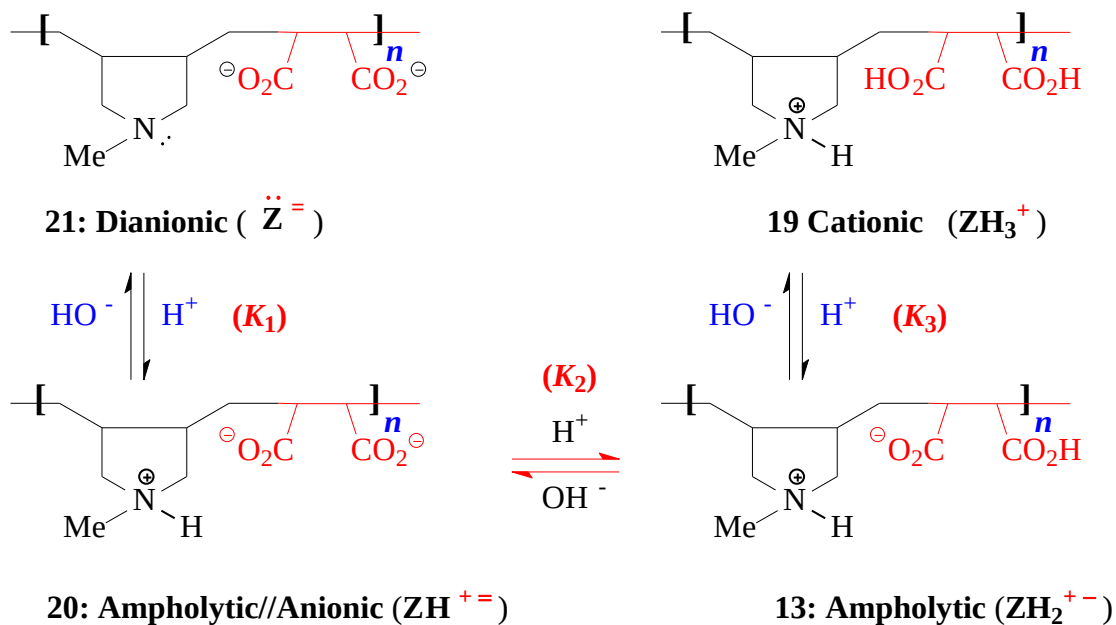
Table 3.3 Attempted cycloterpolymerization of monomers **15** with SO₂ and maleic acid **2**.

Entry	15 (mmol)	MA 2 (mmol)	SO ₂ (mmol)	DMSO (g)	Initiator (mg)	Temp (°C)	Time (h)	Yield (%)	[η] ^a (dL g ⁻¹)
1	15a:5	6	–	H ₂ O (1.0)	APS:250	100	0.25	16a:27 ^b	0.102
2 ^c	15a:5	–	6	0	UV	23	48	17a:80	1.86
3	15a:5	6	11	3.0	APS:215	55	24	18a:87	0.317
4	15a:5	6	6 ^{d,e}	0	UV	23	48	18a:71	1.67
5	15b:5	–	6	2.6	APS:250	55	2	17b:96	0.552
6	15b:5	–	6	2.6	AIBN:29	55	72	17b:87	0.253
7	15b:5	6	10	2.8	APS:125	55	48	18b:88	0.401

^a Viscosity of 1-0.0625 % polymer solution in 0.1 N NaCl at 30 °C was measured with Ubbelohde Viscometer ($K = 0.005317 \text{ mm}^2 \text{ s}^{-2}$); ^b 98% conversion as revealed by ¹H NMR of crude mixture; ^c white solid mixture in the beginning and no phase change throughout; ^d Not been able to add more SO₂; ^e slightly turbid in the beginning but hardened towards the end.

3.5 Determination of Basicity Constant by Titration

The basicity constant (K) of the three basic centers in PA **13** were determined using reported procedures [5,104,136]. The basic centers in PA **13** ($\text{ZH}_2^+^-$) (0.31-0.53 mmol repeating unit) in water (200 cm³) were titrated by stepwise addition of 0.05–0.15 mL of $\approx$ 0.1 M NaOH or HCl (Table 3.4). Log K 's were calculated using the Henderson–Hasselbalch equation (Eq. 2; Scheme 3.5).



$$\log K_i = \text{pH} - \log [(1 - \alpha)/\alpha] \quad (1)$$

$$\text{pH} = \log K_i^o + n_i \log [(1 - \alpha)/\alpha] \quad (2)$$

$$\log K_i = \log K_i^o + (n_i - 1) \log [(1 - \alpha)/\alpha] \quad (3)$$

Scheme 3.5 pH induced changes in the charge types in the backbone of 13, 19-21.

Table 3.4 Protonation of polymer **13** ($\text{ZH}_2^\pm$) at 23 °C.

run	$\text{ZH}_2^\pm$ (mmol)	C_T^a (mol dm ⁻³)	α -range	pH-range	Points ^b	Log $K_I^{o,c}$	n_I^c	$R^2,^d$
1	0.3080 ($\text{ZH}_2^\pm$)	+0.1222	0.13-0.58	3.05-2.57	22	2.65	0.47	0.9927
2	0.4400 ($\text{ZH}_2^\pm$)	+0.1222	0.064-0.65	3.15-2.51	25	2.63	0.45	0.9895
3	0.5280 ($\text{ZH}_2^\pm$)	+0.1222	0.087-0.65	3.13-2.47	26	2.59	0.52	0.9939
Average						2.62 (3)	0.48 (4)	
Log $K_3^e = 2.62 - 0.52 \log [(1-\alpha)/\alpha]$ For the reaction: $\text{ZH}_2^\pm + \text{H}^+ \xrightleftharpoons{K_3} \text{ZH}_3^+$								
1	0.3080 ($\text{ZH}_2^\pm$)	-0.09594	0.82-0.13	4.08-7.22	13	5.63	2.16	0.9907
2	0.4400 ($\text{ZH}_2^\pm$)	-0.09594	0.82-0.13	4.01-7.45	18	5.55	2.21	0.9978
3	0.5280 ($\text{ZH}_2^\pm$)	-0.09594	0.87-0.13	3.87-7.45	22	5.58	2.20	0.9971
Average						5.59 (4)	2.19 (3)	
Log $K_2^e = 5.59 + 1.19 \log [(1-\alpha)/\alpha]$ For the reaction: $\text{ZH}^{\pm-} + \text{H}^+ \xrightleftharpoons{K_2} \text{ZH}_2^\pm$								
1	0.3080 ($\text{ZH}_2^\pm$)	-0.09594	0.89-0.27	9.10-10.65	11	10.09	1.13	0.9883
2	0.4400 ($\text{ZH}_2^\pm$)	-0.09594	0.87-0.36	9.07-10.33	12	10.08	1.14	0.9924
3	0.5280 ($\text{ZH}_2^\pm$)	-0.09594	0.90-0.27	9.05-10.63	08	10.19	1.18	0.9945
Average						10.12 (6)	1.15 (3)	
Log $K_1^e = 10.12 + 0.15 \log [(1-\alpha)/\alpha]$ For the reaction: $\text{Z}^- + \text{H}^+ \xrightleftharpoons{K_1} \text{ZH}^{\pm-}$								

^a Titrations with NaOH and HCl are described by (-)ve and (+)ve values, respectively.^b Data points used.^c Parentheses include the standard deviations in the last digit.^d R = Correlation coefficient.^e $\log K_i = \log K_i^o + (n_i - 1) \log [(1 - \alpha)/\alpha]$.

3.6 Use of Synthesized PA 13 as an Antiscalant

The inhibition of CaSO_4 scale formation from its supersaturated solution was examined in the presence of various concentrations of PA **13** in an aqueous solution containing Ca^{2+} (2600 mg L⁻¹) and SO_4^{2-} (6300 mg L⁻¹) at 40 ± 1 °C as described [5]. The conductivity decreased suddenly after an induction time, owing to the formation of scale as confirmed by visual inspections.

3.7 Results and Discussion

3.7.1 Polymer Synthesis

The results of APS-initiated terpolymerization of monomers **1a** or **1b** or **5** with SO₂ and MA **2** are given in Table 3.1 (Scheme 3.2). The attempted copolymerization of MA-SO₂ was unsuccessful (entries 13 and 14). Terpolymerization of **1a**-MA-SO₂ was conducted under various conditions using APS or AIBN initiator. The polymer **4a** was isolated after extensive dialysis against aqueous HCl to remove unreacted MA and replace the maleate anion with Cl⁻ ions. The spectral (NMR and IR) analysis revealed that terpolymer **4a** resembled the **1a**-SO₂ copolymer **4a** (y = 0) [5], except a minor ¹³C C=O peak at $\approx$ δ 180 ppm (*vide supra*) and a minor vibration at $\approx$ 1728 cm⁻¹ attributed to C=O of CO₂H in the IR spectrum. The absence of alkene carbons at δ 135 ppm excluded the presence of MA either as a free acid or the maleate ions; however, the presence of minor C=O signals suggests the incorporation of maleic acid into the polymer backbone. The MA does undergo propagation, but the addition is reversible as indicated by the presence of fumaric acid (FA) (*trans*-HO₂CC=CHCO₂H) in the unreacted reaction mixture, in addition to its original *cis*-counterpart MA in a $\approx$ 1:4 ratio. The radical having MA terminal: R-CH(CO₂H)-CH(CO₂H)• may undergo quick reversion to give R• and MA as well as FA. Likewise, **1b**-MA-SO₂ (entry 10) and **5**-MA-SO₂ (Table 3.1, entries 11, 12) terpolymerizations afforded **4b** and **6**, respectively (Scheme 3.2), whose spectra are identical to those of **4b** (y = 0) [6] and **6** (y = 0) [142], except that a very minor peak due to C=O in the ¹³C NMR and IR spectra indicate the very minor incorporation of MA.

Monomer **8** was homo- and co-polymerized with SO₂ to obtain cationic polyelectrolytes **9** and **10** in excellent yields of 87 and 93%, respectively (see Experimental) (Scheme 3.3). Homopolymerization of **8** in an aqueous solution under UV light ($\lambda=365$ nm) was very slow; after 6 days, it gave CPE **9** in a very low yield of 7.6% (entry 16, Table 3.2). The bulk photocopolymerization **8**-SO₂ (entry 15, Table 3.2) in the absence of solvent gave CPE **10** having much higher intrinsic viscosity $[\eta]$ of 0.836 dL g⁻¹ than that of the thermally initiated copolymer with a $[\eta]$ of 0.276 dL g⁻¹ (Experimental Section 3.4.4).

Terpolymerization of **7** or **8**-MA-SO₂ was extensively studied using free radical initiators APS, AIBN or UV radiation at λ 365 nm (Scheme 3.3). The results are included in (Table 3.2). Note that the isolated yields after dialysis are low as compared to the NMR conversion since the low molecular weight polymer fractions leave the dialysis bag. The ¹H and ¹³C NMR spectra of the samples from entries 1-14 dealing with the **7** or **8**-MA-SO₂ terpolymerizations afforded **14**, which is almost identical to the **8**-SO₂ copolymer **10** except the IR has very minor C=O vibrational peak at ≈ 1728 cm⁻¹ indicating the presence of MA repeating units in **14**. A series of IR spectra of copolymer **10** containing 0-5 mol% succinic acid (CH₂)₂(CO₂H)₂ helped us to estimate the proportion of MA unit in **14** as ≈ 1 -3 mol%. The strong non-overlapping IR vibrations of SO₂ unit in **10** at 1304 and 1128 cm⁻¹ and the C=O vibration of CO₂H at ≈ 1728 cm⁻¹ were used to estimate the MA mol%.

Next, we focussed our attention to the polymerization of quaternary ammonium salts **15** as outlined in Scheme 3.4; the polymerization conditions and the results are included in Table 3.3. The **15a**-MA copolymerization afforded **16a** in 27% isolated yields, while the crude mixture before dialysis indicated 98% conversion as calculated from ¹H NMR spectrum (entry 1). The spectral data matched with that reported for the polymer [143]. Bulk

copolymerization of **15a**-SO₂ under UV light [144] afforded copolymer **17a** in excellent yield (entry 2). The very high $[\eta]$ value of 1.86 dL g⁻¹ indicated the high molar mass of the polymer. The thermal **15b** [141]-SO₂ copolymerization afforded copolymer **17b** also in excellent yields (entries 5 and 6). The IR and NMR spectra of **17a,b** matched with the reported data [145,146]. The terpolymerizations: **15a**-MA-SO₂ (entries 3 and 4) and **15b**-MA-SO₂ (entry 7) gave polymers **18a** and **18b**, respectively; their NMR and IR spectra matched with those of the respective copolymers **17a** and **17b** except the minor C=O vibration at ≈ 1728 cm⁻¹ indicating the incorporation of ≈ 1 -3 mol% MA.

All the reactivity ratios in the pairs: amine salt-MA and amine salt-SO₂ are almost zero (*vide supra*) thereby implying that under the reaction conditions, amine salt or MA or SO₂ cannot undergo homopolymerization, instead they must give alternate copolymers as experimentally observed. MA-SO₂ reaction has been shown to give neither homo- nor copolymer (entries 13 and 14, Table 3.1). In the numerous amine salt-MA-SO₂ terpolymerizations, the extent of MA incorporation is only 1-2 mol%. In every instance, amine salt-SO₂ copolymer was obtained and no trace of amine salt-MA copolymer could be identified. The claim in the patented literatures [137-139] that the formation of terpolymer: diallyldimethylammonium chloride-maleic acid-SO₂ having repeating unit composition of 50:25:25 and 70:25:5 are doubtful. A composition ratio of 50:25:25 may indeed be a result of a mixture of two alternate copolymers of diallyldimethylammonium chloride-maleic acid and diallyldimethylammonium chloride-SO₂. The current work confirms that the amine salt-MA-SO₂ cannot be terpolymerized to any meaningful extent.

3.7.2 Solubility Behavior

Cationic polymers **4 a, b** ($y \approx 0$), **9, 10** and **14** ($y \approx 0$) are water-soluble, while the PZ **6** ($y \approx 0$) is insoluble in water but soluble in 0.8 M HCl [142]. The water-solubility of **13**, unlike most electroneutral polymers [21,20,147], could be attributed to the less effective participation of the crowded CO_2^- to undergo electrostatic associations with NH^+ for manifestation of ampholytic interactions [2]. Moreover, the hydrophilicity and solubility of the ampholytic motifs increase as a result of the increased dipole moment (μ) because of the large separation between NH^+ and CO_2^- [148,149].

3.7.3 TGA Curves and Spectroscopic Characterization

TGA plot for PA **13** revealed the weight losses at various temperature ranges (Figure 3.1). The presence of adjacent CO_2H groups would lead to the formation of anhydride motifs with the loss of water as reflected by a 14% weight loss up to 200 °C. Maleic anhydride is itself released from the polymer backbone thereby accounting for the loss of $\approx 35\%$ in 200-400 °C range [29,35]. A 35% loss in the 400-800 °C range is attributed to the removal of the amine units.

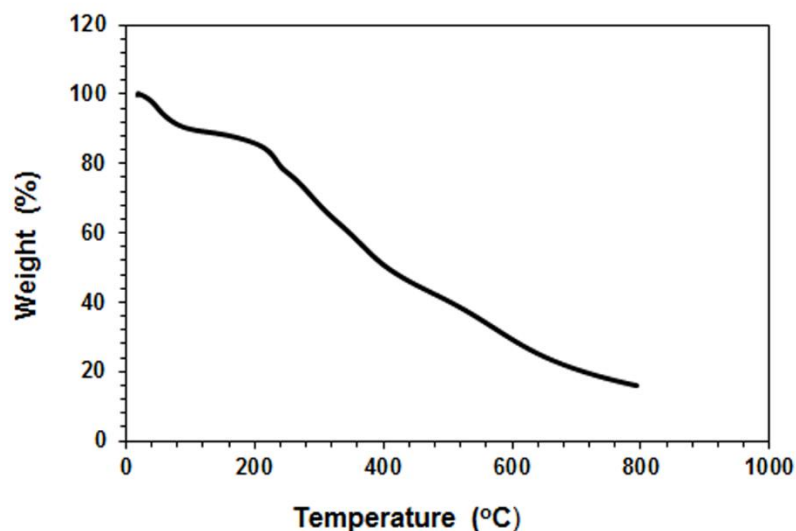


Figure 3.1 TGA curves of **13**.

The strong IR bands at 1304 and 1128 cm^{-1} were assigned to the vibrations of SO_2 unit in **10**. The absorption band at ≈ 1714 and 1574 cm^{-1} is attributed to the C=O stretch of CO_2H and CO_2^- , respectively, in (+ -) **13** [33].

The NMR spectra of several polymers are displayed in Figures 3.2 and 3.3. For the monomer pair **12**, alkene protons of the diallyl amine part and maleate motif appeared at $\delta 5.5\text{-}6$ ppm and 6.08 ppm, respectively (Figure 3.2a), while the corresponding carbons are displayed at $\delta 126.4$ (=CH), 127.2 (2C, =CH₂), and 135.1 (CH=CH) (Figure 3.3a). The low molar masses (as suggested by low viscosity values) and the absence of spectral signal for residual alkene protons or carbons of the polymers **9**, **10** and **13** are indicative of degradative chain transfer [107] involving allylic hydrogens or a termination reaction by coupling [150]. The compact coil [35] conformation of MA-copolymer (+ -) **13** is reflected in the broadened ^1H as well as ^{13}C NMR spectra (Figure 3.2d, 3.3d), whereas the spectral

signals are found to be sharp for homopolymer **9** or SO₂-copolymer **10** (Scheme 3.3) (Figure 3.2b or 3.2c). The incorporation of MA in (+ –) **13** is confirmed by the presence of a broad signal around δ 180 ppm (Figure 3.3d). Elemental analysis and the spectral data confirmed the formation of the alternate copolymer because both the reactivity ratios r_{amine} and r_{MA} , are expected to be close to zero [35,136]. Integration of the relevant carbon signals [18,151] revealed a 3:1 *cis/trans* ratio of the ring substituents at C_{b,b} (Scheme 3.3).

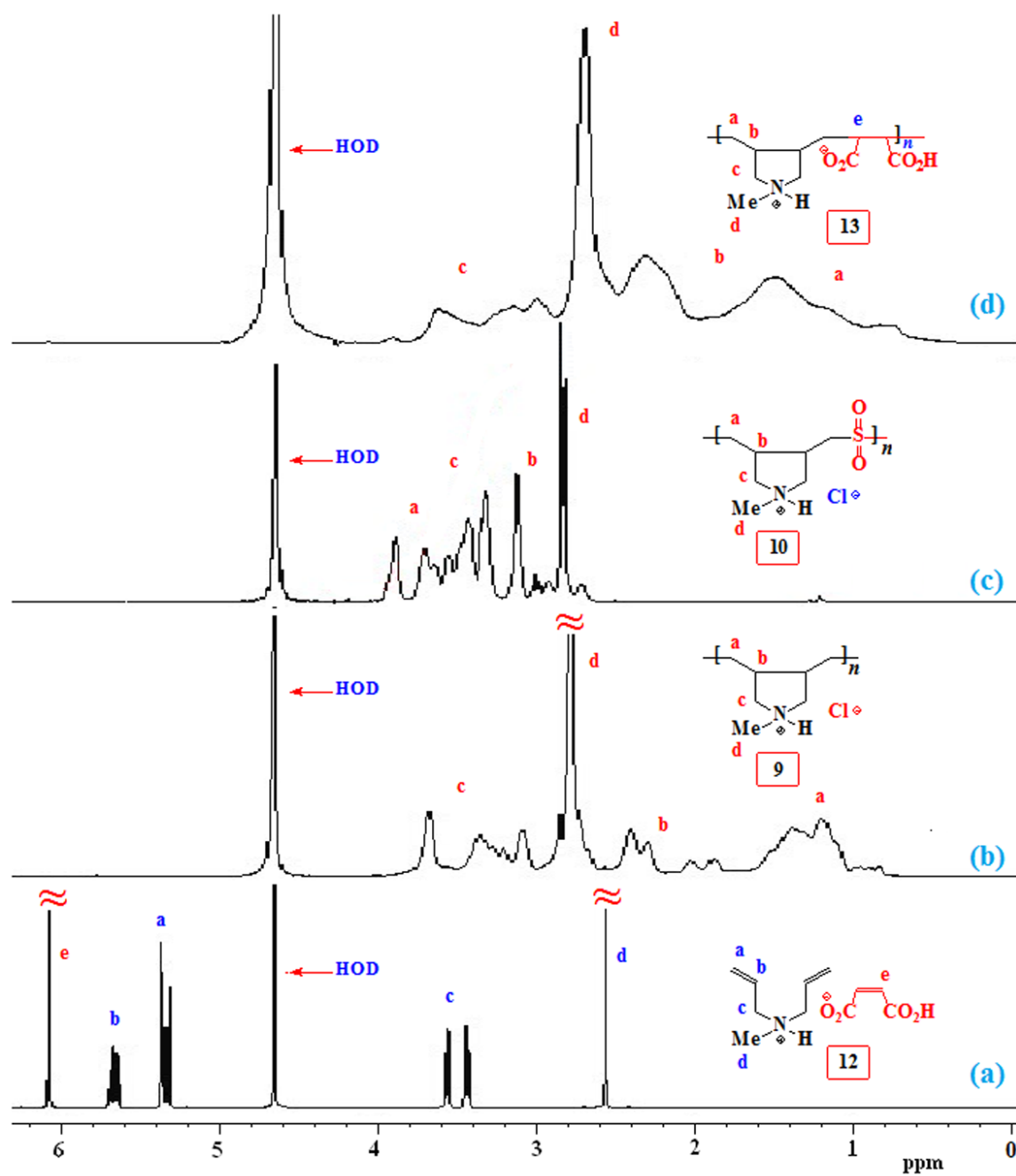


Figure 3.2 ^1H NMR spectrum of (a) 12, (b) 9, (c) 10, and (d) 13 in D_2O .

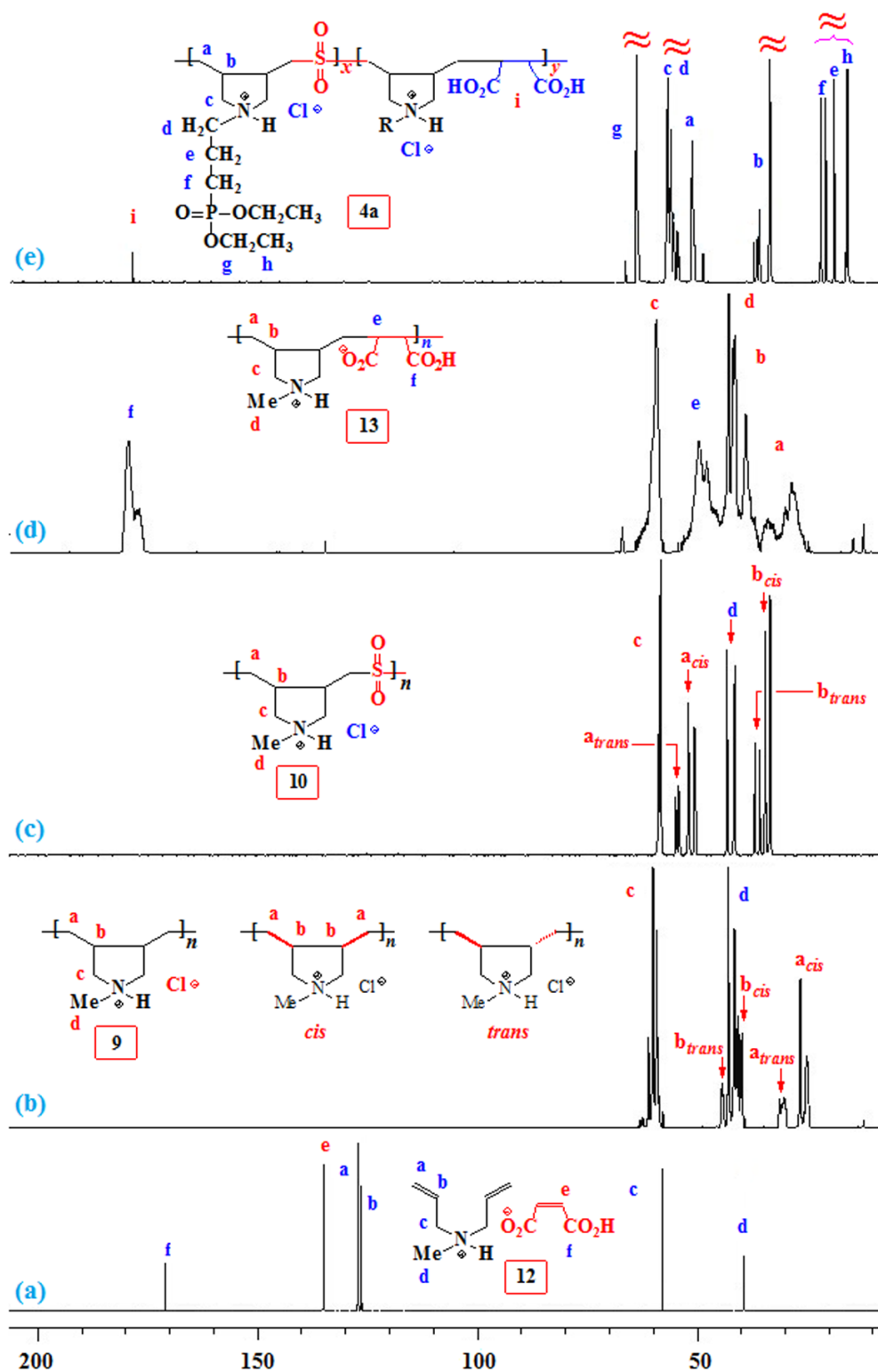


Figure 3.3 ^{13}C NMR spectrum of (a) 12, (b) 9, (c) 10, (d) 13, and (e) 4a in D_2O .

3.7.4 Viscosity Behaviors

The viscosities of PA (+ -) **13** are presented in Figure 3.4. The increase in viscosity with the increasing salt concentrations demonstrates the antipolyelectrolytic [113] nature of the polyampholyte (*cf.* Figure 3.4a-d). The ampholytic dipole is not perfectly electroneutral, rather has a residual negative charge on CO_2^- since Na^+ cannot effectively neutralize it as compared to the greater shielding of N^+ by Cl^- [112,118,152]. The magnitude of the excess negative charge, hence the viscosity, increases with salt concentrations.

PA (+ -) **13** becomes a cationic polyelectrolyte **19** by protonation of CO_2^- and as such its viscosity becomes higher in 0.1 M HCl because of repulsion among positive charges (Figure 3.4e) (Scheme 3.5). The neutralization of **13** with one or two equivalents of NaOH leads to polyampholyte/anion (+ =) **20** and polydianion (=) **21**, the greater charge imbalance in the latter makes it more viscous (Figure 3.4f and g).

Strong interactions [35] of materials of GPC columns with functional groups like amine and CO_2^- prevented the determination of molar masses of the polymers like **13**. The use of higher initiator dose along with degradative chain transfer termination process [107] led to PA **13**, having low molar mass as indicated by its lower $[\eta]$ value.

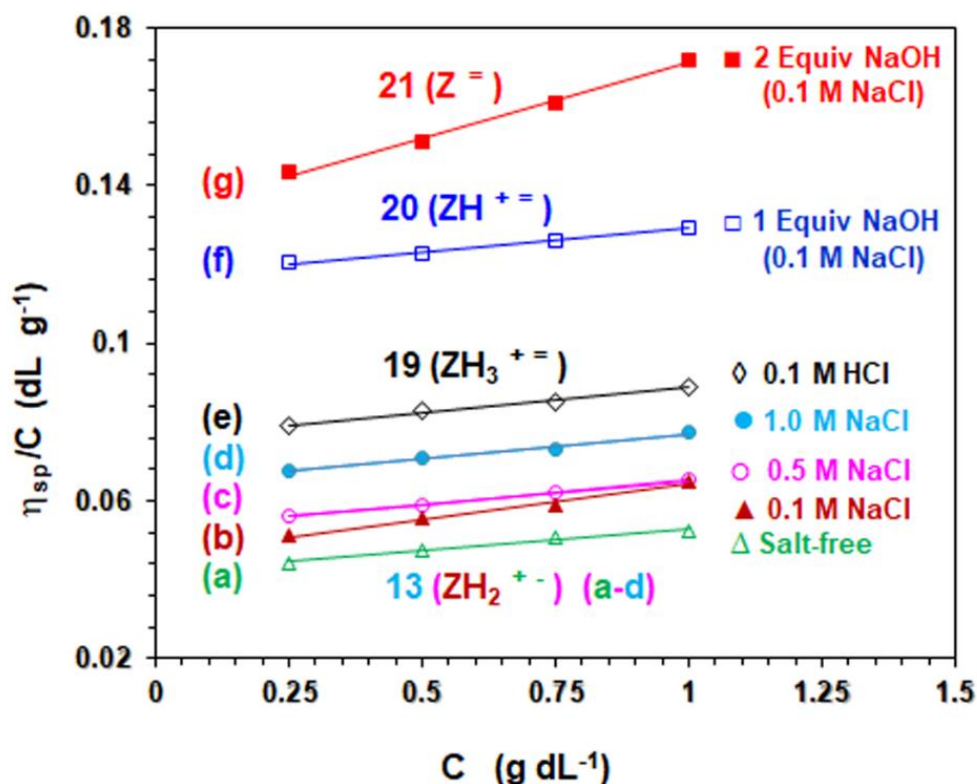


Figure 3.4 The viscosity behavior at 30 °C of polyampholyte **13** (a) $\triangle$ in salt-free water, (b) $\blacktriangle$ in 0.1 M NaCl, (c) $\circ$ in 0.5 M NaCl, (d) $\bullet$ in 1.0 M NaCl, (e) $\diamond$ in 0.1 M HCl, and (f) $\square$ in the presence of 1 equiv NaOH in 0.1 M NaCl, and (g) $\blacksquare$ in the presence of 2 equivs NaOH in 0.1 M NaCl.

3.7.5 Basicity Constant

As outlined in [Scheme 3.5](#), the protonation constant K of three basic centers in (=) **21** are calculated using Equation 3 where $\log K^0 = \text{pH}$ at α (degree of protonation) = 0.5. The variation from the true basicity constant depends on the value of n , which equals 1 for small molecules. The values of ' n ' and $\log K^0$ were extracted from the slope and intercept of the pH vs. $\log [(1-\alpha)/\alpha]$ straight-line plot. The respective $\log K^0_1$, $\log K^0_2$ and $\log K^0_3$ were determined to be 10.1, 5.59 and 2.62, with the corresponding n_1 , n_2 and n_3 values of 1.15,

2.19 and 0.48 (Table 3.4).

All the n values, especially n_2 and n_3 , are reflective of the “apparent” [119,153] nature of the K_i s which changes with the α as shown in Figure 3.5. The n value reflects a measure of the polyelectrolyte index. There are significant decrease and increase of $\text{Log } K_2$ and $\log K_3$, respectively, with increasing α , while the $\log K_1$ remains almost constant since the associated n value of 1.15 is not far from 1.

With increasing α , the equilibrium: $[(\text{ZH}^+)^- \textbf{20} + \text{H}^+ \rightleftharpoons (\text{ZH}_2^+)^- \textbf{13}]$ is shifted to the right thereby decreasing $\log K^0_2$ as a consequence of decreasing negative charge density that encourages protonation. This is in contrast to the increase of $\log K^0_3$ [involving $(\text{ZH}_2^+)^- \textbf{13} + \text{H}^+ \rightleftharpoons (\text{ZH}_3^+)^- \textbf{19}$], whereby protonation of a repeating unit also decreases the overall negative charges of the polymer chain. The n values $>$ or $<$ 1 are caused by entropy effects [119,154]. With each protonation, a repeating unit (RU) in ampholytic/anionic $(\text{ZH}^+)^- \textbf{20}$ collapses into an ampholytic RU of $(\text{ZH}_2^+)^- \textbf{13}$. Ampholytic/anionic $(\text{ZH}^+)^- \textbf{20}$ having excess negative charges is more hydrated than PA $(+)^- \textbf{13}$ as supported by the higher viscosity value of the former (cf. Figure 3.4f vs. 3.4b). The protonation of a RU leads to an entropically favorable release of water of hydration. For $(\text{ZH}^+)^- \textbf{20}$, as the α increases, the average number of water molecules per RU in a polymer chain decreases which leads to a decrease in the magnitude of the positive entropy changes. Since the exothermic ΔH^0 is independent of α , the ΔG^0 , hence K , decreases with the increasing α [154].

For the protonation of $(\text{ZH}_2^+)^- \textbf{13}$ to $(\text{ZH}_3^+)^- \textbf{19}$ (Scheme 3.5), the latter is more hydrated thus having expanded polymer chain as evinced by its greater viscosity value (cf. Figure 3.4e vs. 3.4b). The more exposed RU makes the neutralization process easier with the

increasing α (Figure 3.5, $i = 3$) [120,155]. With increasing α , increasing imbalance in favor of positive charge also increases the degree of hydration, which leads to greater entropy changes because of release of a greater number of molecules during progressive protonation.

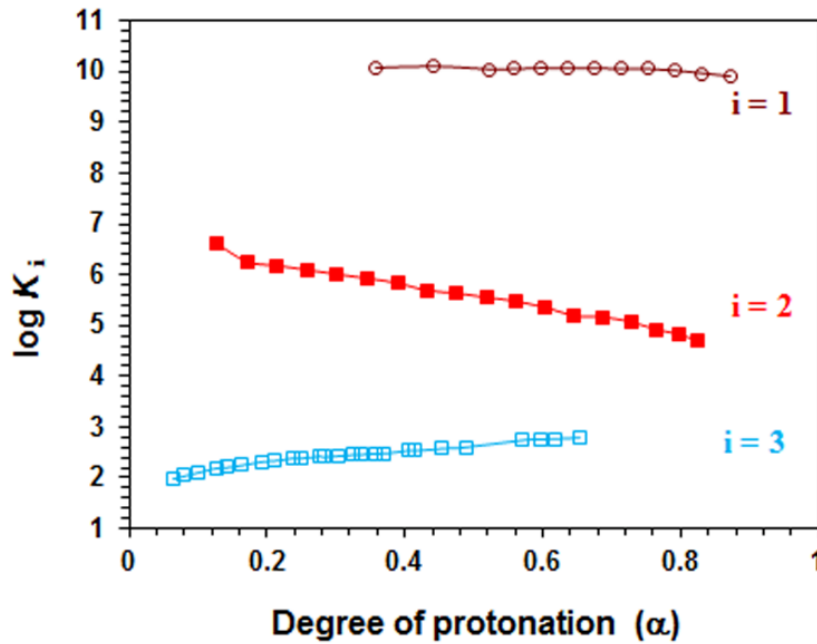


Figure 3.5 Plot for the apparent $\log K_i$ versus degree of protonation (α) in salt-free water (a) $\square$ ($\log K_3$, run 2, Table 3.4), (b) $\blacksquare$ ($\log K_2$, run 2, Table 3.4) and (c) $\circ$ ($\log K_1$, run 2, Table 3.4).

3.7.6 Scale Inhibition Study

In a Reverse Osmosis (RO) process, feed water is converted to product water and rejects brine, in which supersaturation of dissolved salts, like CaSO_4 and CaCO_3 , may lead to

precipitation, which reduces the efficacy of the membrane separation process. The percent scaling inhibition (PSI) is calculated using Equation (4):

$$PSI = \frac{[Ca^{2+}]_{inhibited(t)} - [Ca^{2+}]_{blank(t)}}{[Ca^{2+}]_{inhibited(t_0)} - [Ca^{2+}]_{blank(t)}} \times 100 \quad (4)$$

Where $[Ca^{2+}]$ concentrations are used at time zero and t. The inhibited and blank are used to describe the presence and absence of the antiscalant.

The concentration of Ca^{2+} and SO_4^{2-} , present in the reject brine of a RO plant [123], was described as 1-CB (concentrated brine). The scaling behavior in the presence of PA **13** was carried out in a supersaturated solution of $CaSO_4$ comprising 3-CB concentration of Ca^{2+} (2600 ppm) and SO_4^{2-} (6300 ppm) by conductivity measurements. A sudden drop in the conductivity indicates the onset of $CaSO_4$ scaling (Figure 3.6).

It is indeed satisfying that in the presence of 5 and 20 ppm **13**, a 100% scale inhibition was registered for about 50 and 500 min, respectively (Table 3.5). Since the reject brine usually has a residence time of ≈ 30 min in the osmosis chamber, the current antiscalant may thus be very effective in inhibiting $CaSO_4$ scaling. As shown in Figure 3.6, the onset of precipitation occurs after an induction period; an accelerated growth of $CaSO_4$ crystals is indicated by a sudden drop in conductivity. For a duration of 700 min, 20 ppm PA **13** did not show any induction time. The crystal growth starts after nucleation process, which is interfered with the complexation of the metal ions by the chelating ligands of the antiscalant [124,156]. The gypsum scale, i.e., $CaSO_4$ in mineral form, occurs during several processes involving production of water [157]. PA **13** is found to be remarkably efficient

in preventing scale formation, and as such it has the ability to mitigate the membrane fouling in RO plants.

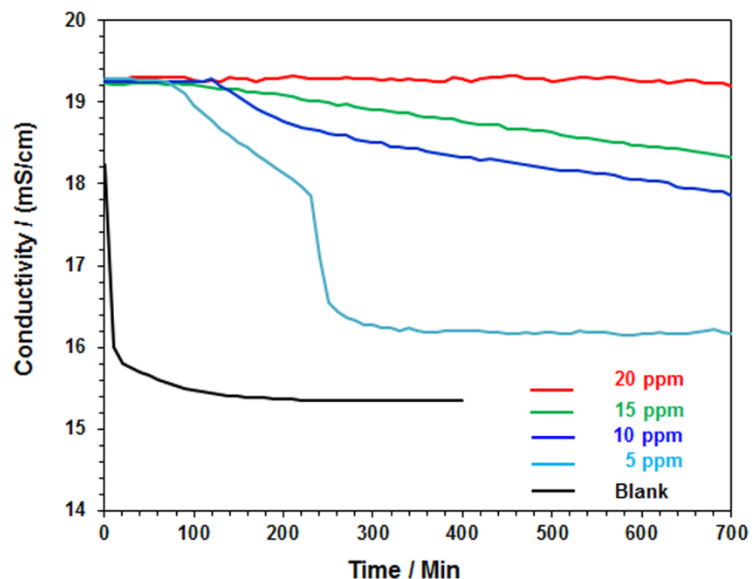


Figure 3.6 Conductivity of a supersaturated solution of CaSO_4 in the presence (5, 10, 15, 20 ppm) of **13** and in the absence (blank) of antiscalant.

Table 3.5 Percent scale inhibition in the presence of PA **13** in 3 CB^a supersaturated **CaSO₄** solution at 40 °C.

Entry	Sample (ppm)	Percent inhibition at times (min) of						
		50	100	200	300	400	500	700
1	5	100	92	71	24	22	17	17
2	10	100	100	88	81	76	71	63
3	15	100	99	96	91	88	83	75
4	20	100	100	100	100	100	100	98

^aThree times the concentration of Ca^{2+} and SO_4^{2-} found in the concentrated brine of an RO plant.

3.8 Conclusion

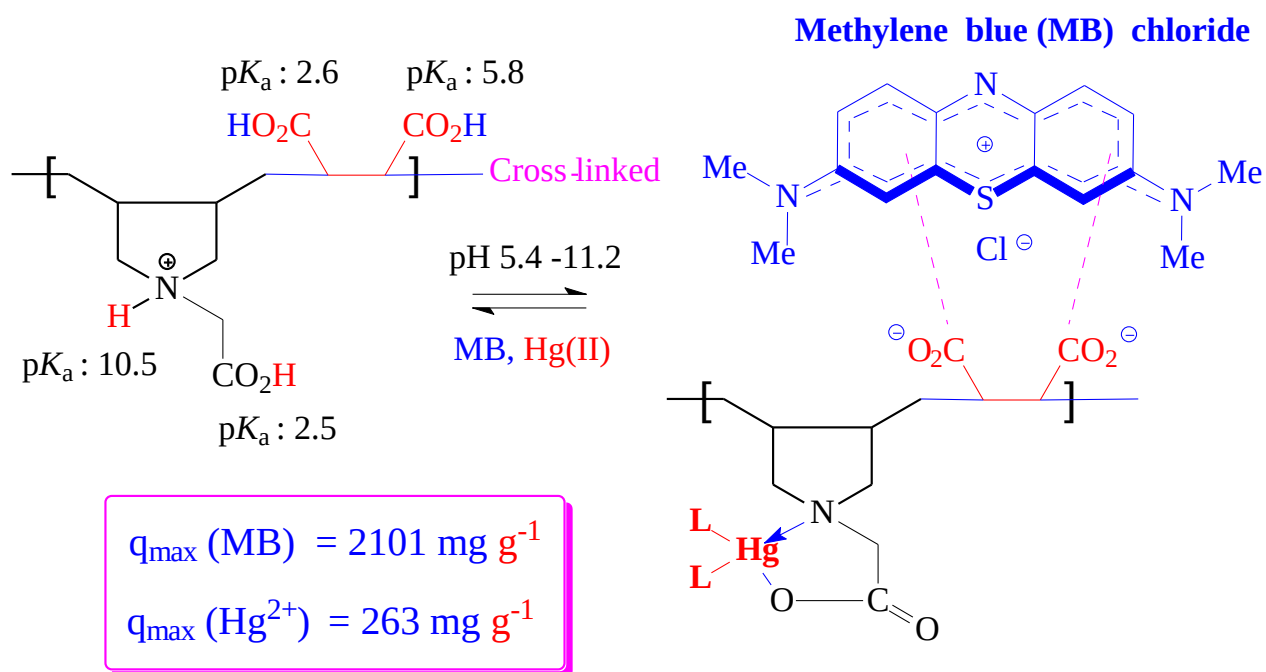
Several diallylamine derivatives **1a,b**, **5** and **7** as well as quaternary diallyldialkylammonium chlorides **15a,b** have been terpolymerized with MA and SO₂ using APS initiator or UV light at a λ of 365 nm in an attempt to obtain Amine (salt)-MA-SO₂ terpolymer. In contrast to reported literature, only 1-2 mol% of MA was incorporated into the polymer chain mainly consisting of Amine (salt)-SO₂ copolymers. The non-incorporation of MA is attributed to the far greater rate of propagation of Amine (salt)-SO₂ than either Amine (salt)-MA or MA-SO₂ under the polymerization conditions. The reactivity ratios of both monomers in the Amine (salt)-MA and MA-SO₂ pairs are ≈ 0 ; however, in a three-monomer system: Amine (salt)-MA-SO₂, the very slow reactivity of MA does not allow its incorporation into terpolymer chain to any meaningful extent.

The **1c**-MA copolymer PA **13** has been synthesized in excellent yield with an anticipation that it could be a potential antiscalant. Under pH-induced changes, stimuli-responsive polyampholyte **13** was transformed to cationic **19**, polampholyte-anionic **20**, and dianionic polyelectrolyte **21** to examine their viscosity. The viscosity values of **13** in the presence of NaCl salt confirmed its antipolyelectrolyte behaviour. The $\log K$ (i.e. $\text{p}K_a$) of two carboxylic acid groups and NH^+ in **13** has been determined to be 2.62, 5.59, and 10.1, respectively. PA **13** was evaluated as an antiscalant for potential application in reverse osmosis (RO) plants. At concentrations of 5 and 20 ppm, it demonstrated remarkable efficiency of $\approx 100\%$ for CaSO₄ scale inhibition from its supersaturated solution for 50 and 500 min, respectively. Since an antiscalant should be effective for the duration of brine's residence time (≈ 30 min) in the osmosis chamber, the synthesis of PA **13** in excellent yields from cheap starting materials and its very impressive performance may accord it a

prestigious place among many an environment-friendly phosphate-free antiscalant. Note that polyphosphate additives used for controlling scale formation, when discharged in the sea have deleterious influence over the marine biota picture [\[158\]](#).

CHAPTER 4

FAST REMOVAL OF METHYLENE BLUE AND Hg(II) FROM AQUEOUS SOLUTION USING A NOVEL SUPER-ADSORBENT CONTAINING RESIDUES OF GLYCINE AND MALEIC ACID



Graphical Abstract

4.1 Abstract

The first example of an alternate cyclopolymerization of diallylammonioethanoate $[(\text{CH}_2=\text{CHCH}_2)_2\text{NCH}_2\text{CO}_2^-]$ and maleic acid in the presence of a cross-linker afforded a cross-linked polyzwitterionic acid (CPZA) (90% yield), which upon base treatment gave the corresponding cross-linked anionic polyelectrolyte (CAPE) in quantitative yield. The novel pH-responsive resin contains a high density of CO_2^- motifs as well as the chelating motifs of glycine residues. The resin CAPE turned out to be a super-adsorbent for methylene blue (MB) removal, having a maximum uptake (q_{MB}) of 2101 mg g^{-1} . The process showed an extraordinarily fast adsorption rate; the resin (250 mg) was able to trap 69, 78 and 99.4% MB from its 3000 mg L^{-1} solution (100 mL) within 2, 3 and 30 min, respectively. The adsorption followed pseudo second-order kinetics and is found to be nearly irreversible process as suggested by the parameters obtained from Elovich kinetic model and separation factor R_L from Langmuir isotherm model. The excellent recycling efficiencies ensured the reuse of the resin. Its outstanding performance, much better than many of recently reported materials, paves the way for its potent application in remedying industrial dye-wastewater. The presence of the chelating motifs of aminocarboxylate was exploited for the removal of Hg(II) ions; the q_{Hg} was determined to be 263 mg g^{-1} from Langmuir adsorption isotherm. The resin simultaneously removed MB and Hg(II) from aqueous solution and spiked industrial wastewater with remarkable efficacy. The very impressive performance accorded the resin a prestigious place among many sorbents.

Keywords: Cyclopolymerization; Adsorption; Chelating resin; Desorption;
Methylene blue removal; Hg(II) removal.

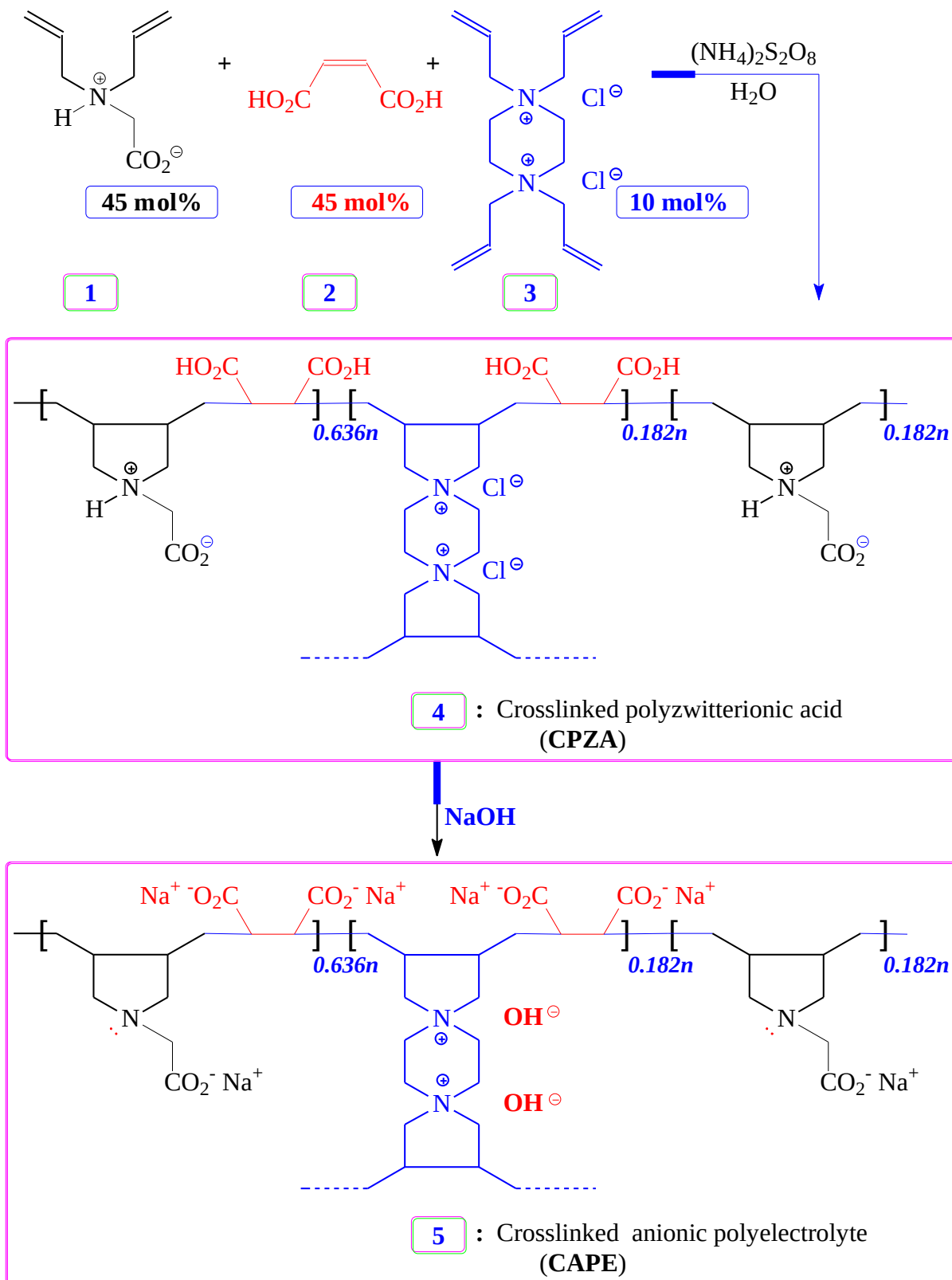
4.2 Introduction

Incontinent use of dyes and their industrial effluents cause serious water pollution and as such, their remediation becomes extremely significant for ecological environment protection. Methylene blue (MB) is a commonly used dye for coloring cotton and silk [159]. The presence of MB in the effluents of textile, paper, printing and other industries, leads to a variety of environmental problems [160] and as such, its removal from the waste streams is of great importance. A considerable fraction of $\approx 7 \times 10^5$ tons (produced annually) of commercially used dyes is discharged directly in aqueous effluent [161]. The dyes in wastewaters, when discharged into river streams, cause harm to aquatic life [162]. In addition to being carcinogenic and mutagenic (in some cases), the presence of dyes impedes the penetration of light into water, thereby affecting the photosynthetic activity and hence, the food web [163]. The low biodegradability of dyes [164] renders biological procedures [165] very inefficient in removing color [166].

Superiority over other techniques led to the extensive application of adsorption technique [167] for the removal of inorganic and organic impurities from industrial wastewater [166,168]. Adsorption kinetics and thermodynamic parameters usually provide valuable clues regarding the mechanism of the process [169]. Most of the studies dealt with the adsorption of MB mainly on activated carbons [170-172], carbon nanotubes [173], graphene hydrogels [174,175], biomimetic polydopamine [176], graphene/magnetite composite [165], chitosan-g-poly(acrylic acid)/montmorillonite nanocomposites [177] or attapulgite composite [178], metal-organic framework material, iron terephthalate [179], and metal oxide [180] as well as other adsorbents like chitosan [181], supported alumina surface [182], perlite (a glassy volcanic rock) [183], etc. Ultrasound-assisted MB

adsorption by gold nanoparticle-loaded activated carbon has been reported to give faster adsorption with high adsorption capacity [184]. Surface modification of Fe_3O_4 nanoparticles with β -cyclodextrin provided a nano-adsorbent, which was found to be efficient in the removal of MB [185]. Nanocomposite of magnetic MnFe_2O_4 and CuFe_2O_4 - 2- aminobenzoic acid – phenylenediamine has been applied for simultaneous removal of Cu(II) as well as MB [186]. A hydrogel of β -cyclodextrin/chitosan decorated graphene oxide was found to be very effective in the removal of MB [187]. The adsorptive removal of MB by a Ni-based metal-organic framework was investigated [188]. Biochars of different feedstock and pyrolysis temperature were investigated for the removal of MB [189,190]. Among various adsorbents reported for MB removal [191], the widespread use of activated carbon is limited owing to its relatively high cost, which led to the search of other potentially low-cost adsorbents like biomass, clays minerals and zeolites [163,192].

Adsorbents used for the removal of pollutants should be cheap, readily available, easy to regenerate and environment-friendly. The objective of the current work is to investigate the removal of MB (as a model basic cationic dye) and Hg(II) (as a model toxic metal ion) from industrial wastewater by a novel adsorbent **5** (Scheme 4.1). The adsorbent has been synthesized for the first time using cyclopolymerization protocol [1,8,136] involving inexpensive diallylamine salt **1** bearing residue of amino acid glycine ($\text{H}_3\text{N}^+\text{CH}_2\text{CO}_2^-$) and maleic acid (MA) **2** in the presence of cross-linker **3** (Scheme 4.1). The current study would deal with adsorption kinetics and thermodynamics, desorption, and other related factors to investigate the efficacy of the pH-responsive resin **5**. The presence of abundant CO_2^- and chelating motifs of $\text{R}_2\text{NCH}_2\text{CO}_2^-$ in **5** is anticipated to make it an extraordinary adsorbent to trap cationic dyes as well as toxic metal ions.



Scheme 4.1 Synthesis of cross-linked polyzwitterionic/anionic resins.

4.3 Experimental

4.3.1 Materials

Methylene blue trihydrate ($C_{16}H_{24}ClN_3O_3S$; MW 373.9 g mol⁻¹) and ammonium persulfate (APS) were purchased from Sigma–Aldrich. Maleic acid (MA) was purchased from BDH Chemicals Ltd., and cross-linker **3** was prepared as described in literature [193]. Experiments were carried out using Millipore water (double distilled, 18.2 MΩ·cm).

4.3.2 Physical Methods

Following instruments were used:

(1) A Perkin Elmer Series II Model 2400 for recording FTIR spectra; (2) a Perkin Elmer (16F PC) spectrometer for atomic compositions; (3) an SDT analyzer (Q600: TA Instruments) under a N₂ flow for Thermogravimetric analysis (TGA); (4) a Sartorius pH meter and an Oakton pH-meter; (5) a SEM and EDX spectroscopy to examine morphology; (6) a surface area and porosimetry analyzer (Micromeritics, USA) to characterize the resins by Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods; (7) a GENESYS 10S UV-Vis spectrophotometer (Thermo Electron Corporation, USA) to determine the concentrations of MB using absorbance at $\lambda_{\text{max}} = 665$ nm; (8) a Zetasizer (Nano-ZS, Model: ZEN2600) from Malvern Instruments and Dispersion Technology Software (DTS) were used to determine the zeta potential of resin **4**.

4.3.3 Synthesis of Monomer 1

Diallylammonioethanoate (**1**) was prepared *via* ester hydrolysis of ethyl diallylaminoethanoate [194]. In a modified procedure, a mixture of ethyl diallylaminoethanoate ($(\text{CH}_2=\text{CHCH}_2)_2\text{NCH}_2\text{CO}_2\text{Et}$) (80.0 g, 0.437 mol) and NaOH (19.3 g, 0.481 mol) in water (100 mL) was vigorously stirred at 23 °C for 6 h. The biphasic system became homogeneous after 30 min. ^1H NMR indicated the completion of the exothermic hydrolysis. After roto-vaping most of the produced ethanol, the residual mixture containing sodium diallylaminoethanoate ($(\text{CH}_2=\text{CHCH}_2)_2\text{NCH}_2\text{CO}_2\text{Na}$) was treated with concentrated HCl (37%) (50.3 g, 0.510 mol) and then freeze-dried. The residue, taken up in acetone (200 mL), was heated to boiling, quickly filtered, and the NaCl residue was washed with boiling acetone (2×200 mL). The filtrates upon evaporation afforded **1** as a white crystalline solid (65 g, 96%) which can be recrystallized from hot acetone.

4.3.4 Resin Synthesis

4.3.4.1 Terpolymerization of 1, 2, and 3 leading to Zwitterionic Resin 4

Monomer **1** (7.75 g, 50 mmol), maleic acid (**2**) (5.8 g, 50 mmol), cross-linker **3** (3.55 g, 11.1 mmol) and water (9.8 g) were taken in an RB-flask (100 mL) fitted with a condenser. The mixture thus contained monomers and water in a 65:35 wt. ratio. After heating to 100 °C under N_2 , APS (1.0 g) was added in one portion to the stirring mixture. In 2-3 min, the homogeneous mixture became cloudy and the exothermic reaction happened quickly to give the immovable resin **4**. After 10 min, the cooled resin was washed with excess water. After filtration, the resin was vacuum dried at 65 °C (15.4 g, 90%). Found: C, 54.0; H, 6.9;

N, 5.8%. The units of **1**, **2**, and **3** in a mol ratio of 0.50:0.50:0.111 ratio in resin **4** require C, 54.59; H, 6.84; N, 5.91%. A sample of 342 mg of the resin is calculated to contain 1 mmol each of repeating unit (RU) of **1** and **2**, and 0.222 mmol of **3**.

4.3.4.2 Conversion of Zwitterionic Resin **4** to Anionic Resin **5**

A sample of resin **4** (9.24 g, containing 27 mmol RU of each of **1** and **2**, and 6.0 mmol of **3**) is calculated to have 81 mmol equivalents of CO₂H and 27 mmol equivalents of protonated NH⁺. The sample is soaked in water (60 mL)/NaOH (7.0 g, 175 mmol) and stirred for 2 h in a closed flask at room temperature. The mixture was filtered and washed with methanol to remove any trace of excess NaOH. Anionic resin **5** was then vacuum dried at 60 °C (11.0 g, ≈100%). A sample of 400 mg of resin **5** is calculated to contain 1 mmol of repeating unit of **1**, 1 mmol of RU of **2** and 0.222 mmol of **3**. Found: C, 46.2; H, 5.4; N, 4.8%. The units of **1**, **2**, and **3** in a mol ratio of 0.50:0.50:0.111 ratio require C, 46.70; H, 5.21; N, 5.06%.

4.3.5 Ion Exchange Capacity (IEC)

Cross-linked anionic polyelectrolyte (CAPE) **5** (100 mg) was immersed in 0.1 M HCl (25 mL) and stirred overnight. The excess acid was determined by titrating a known aliquot of the filtrate by 0.1 M NaOH, and the IEC was calculated using Eq. (1):

$$IEC = \frac{HCl_i - HCl_f}{W} \quad (1)$$

Where the subscripts ‘i’ and ‘f’ represent initial and final amounts (mmol) of HCl and W, in grams, represents the mass of the resin. The IEC was determined to be 7.7 mmol g⁻¹.

4.3.6 Swelling Coefficient

The 20- to 30-mesh fraction of the crushed resins **4** or **5** was taken in a burette. After noting its initial volume, the resin was covered with water and the final volume of hydrated resin was noted when no more volume changes occurred. The ratio of final volume *versus* initial volume gave the swelling coefficients of 1.42 and 2.83 for zwitterionic resin **4** and its anionic counterpart **5**, respectively.

4.3.7 Adsorption of MB

Adsorption of MB from its aqueous solution (20 mL) over the concentration range 100–10,000 mg L⁻¹ onto resin **5** (50 mg) was conducted in a series of vials where the mixture was stirred at 300 rpm using a magnetic stir-bar for 12 h (to achieve equilibrium). The solution pH was adjusted to 9.5. A portion of the samples was centrifuged and the MB concentrations at equilibrium (C_e) in the clear supernatant were determined after dilution (if necessary), using a UV–Vis spectrometer at a wavelength of 665 nm. A linear regression equation, obtained by plotting a calibration curve for standard solutions of MB at pH 7.0 over a concentration range 0.1–5.0 mg L⁻¹, was used to determine the MB concentrations. To avoid pH dependency on the calibration curve, the MB concentration in various samples (after dilution to the range 0.1–5.0 mg L⁻¹) was also adjusted to pH 7. The resin's adsorption capacity (i.e. q_e) was determined using Eq. (2).

$$q_e = (C_o - C_e) \times \frac{V}{m} \quad (2)$$

Where the initial and equilibrium MB concentrations (mg L⁻¹) are denoted by C_o and C_e , V and m represent the solution volume (L) and mass of CAPE **5** (g), respectively.

The removal percentage (R) of MB was determined using Eq. (3).

$$R = \frac{(C_o - C_e)}{C_o} \times 100 \quad (3)$$

The procedure of kinetic tests at various temperatures of 288, 298, 313, and 328 K was similar to the equilibrium tests as presented above. A constant temperature bath was used. Adsorption tests were performed in RB flasks (250 mL) containing resin **5** (250 mg) and 3000 ppm MB (100 mL). At a pre-determined time, a small volume (≈ 0.2 mL) of the solution was filtered with a syringe filter (PTFE, hydrophobic, 0.25 μ m), and the dye concentration was determined after dilution using UV-Vis spectrophotometer. The adsorption capacity q_t (mg g⁻¹) at time t was obtained using Eq. (4).

$$q_t = (C_o - C_t) \times \frac{V}{m} \quad (4)$$

The q_t at various pHs was determined as above by using zwitterionic **4** (50 mg) and 1000 ppm MB (20 mL) at 298 K for 12 h. The pH of the solutions was adjusted to predefined pH using 0.1 M NaOH.

4.3.8 Adsorption/Desorption Experiment

For adsorption study, the basic resin **5** (100 mg) was stirred at 300 rpm in 40 mL MB solution (2000 ppm, pH 9.2) in a centrifuge tube for 24 h at 298 K. The absorbance value of the resultant supernatant gave the adsorption capacity of the resin. After removal of the supernatant, 1 M HCl (5 mL) was added to the MB-loaded resin at 298 K and stirred for 30 min to desorb MB. The supernatant was decanted; the loaded resin was agitated with 0.1 M HCl (5 mL) for 30 min at 297 K to remove the trace amount of leftover dye (if any)

in the resin. After the elapsed time, combined supernatants were analyzed for the desorbed MB to determine the desorption efficiency. The resin in the centrifuge tube was exposed to 1 M NaOH (10 mL) to regenerate the basic resin, and the above cycle was run in triplicate with the fixed amount of resin as ensured by centrifugation.

4.4 Results and Discussion

4.4.1 Resin Synthesis

Butler's cyclopolymerization protocol [1,8] involves polymerization of diallylammonium salts to give industrially important polymers having pyrrolidine ring embedded onto the polymer backbone. When a diallylamine salt and MA **2** undergoes copolymerization, it leads to an alternate copolymer [136]. In the current work, the APS-initiated alternate copolymerization of diallylammonioethanoate (**1**) (45 mol%), MA (45 mol%), and cross-linker **3** (10 mol%) afforded cross-linked polyzwitterionic acid (CPZA) **4** in excellent yield (90%). At such a high conversion, the feed composition is expected to match the resin composition. Keeping this in view, an approximate presentation of the resin is depicted in **4**, in which alternate sequences of **1** and **2** would be interspersed with homo sequence of monomer **1** (Scheme 4.1). This is a consequence of the presence of excess of diallyl motifs in **1** and **3** as compared to alkene motifs in MA. To our knowledge, this Butler's cyclopolymerization afforded for the first time a resin having residues of amino acid glycine and alternate sequence of monomers **1** and **2**. CPZA **4** upon treatment with NaOH gave CAPE **5** in almost quantitative yield. Resin **5**, loaded with CO₂⁻ groups as well as the chelating motifs of R₂NCH₂CO₂⁻ is expected to be a potent cation exchanger as evinced by a high IEC value of 7.7 mmol g⁻¹. The surface area of CAPE **5** was found to be 3.56 m² g⁻¹

which is comparatively large as compared to $< 0.1 \text{ m}^2 \text{ g}^{-1}$ reported for conventional ionic resins (Table 4.1) [195,196].

Table 4.1 BET surface area analysis of CAPE 5.

Parameters	Values
BET surface area	$3.56 \text{ m}^2 \text{ g}^{-1}$
Total pore volume	$0.0172 \text{ cm}^3 \text{ g}^{-1}$
Average pore diameter	2.9 nm

4.4.2 TGA Analysis of CPZA 4 and CAPE 5

For resin 5, a 9% weight loss up to 200 °C is due to the removal of moisture (Fig. 4.1a). A loss of 12% in the range 200-385 °C and a steep loss of 37% in the range 385-490 °C were observed. The 32% residue at 800 °C is attributed to the presence of sodium salts.

Basic resin 5 was found to be more stable than its acidic form 4 (Fig. 4.1a). For acidic resin 4, an 8.4% weight loss up to 240 °C is due to the elimination of water as a result of formation of succinic anhydrides. A steep loss of $\approx 54.7\%$ in 240-280 °C range is attributed to the release of anhydride and CH_2CO_2 units [29,35]. The maleic acid and CH_2CO_2 units are calculated to account for 50.9 wt% thus giving credence to the assigned loss in 240-280 °C range mentioned above. The removal of amine groups leads to a loss of 36% in the 400-800 °C range. A gradual and steep loss of 12% each were observed in the ranges 280-420 and 420-480 °C. The residue at 800 °C was found to be 7%.

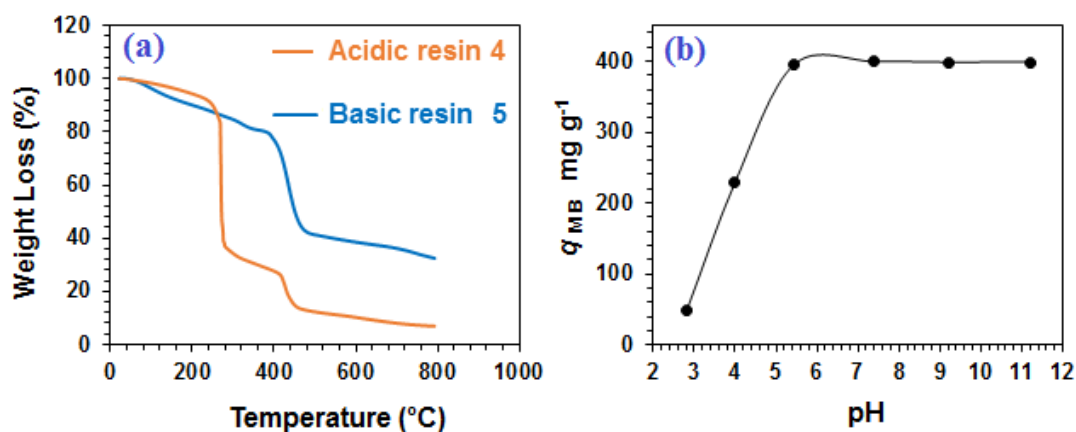
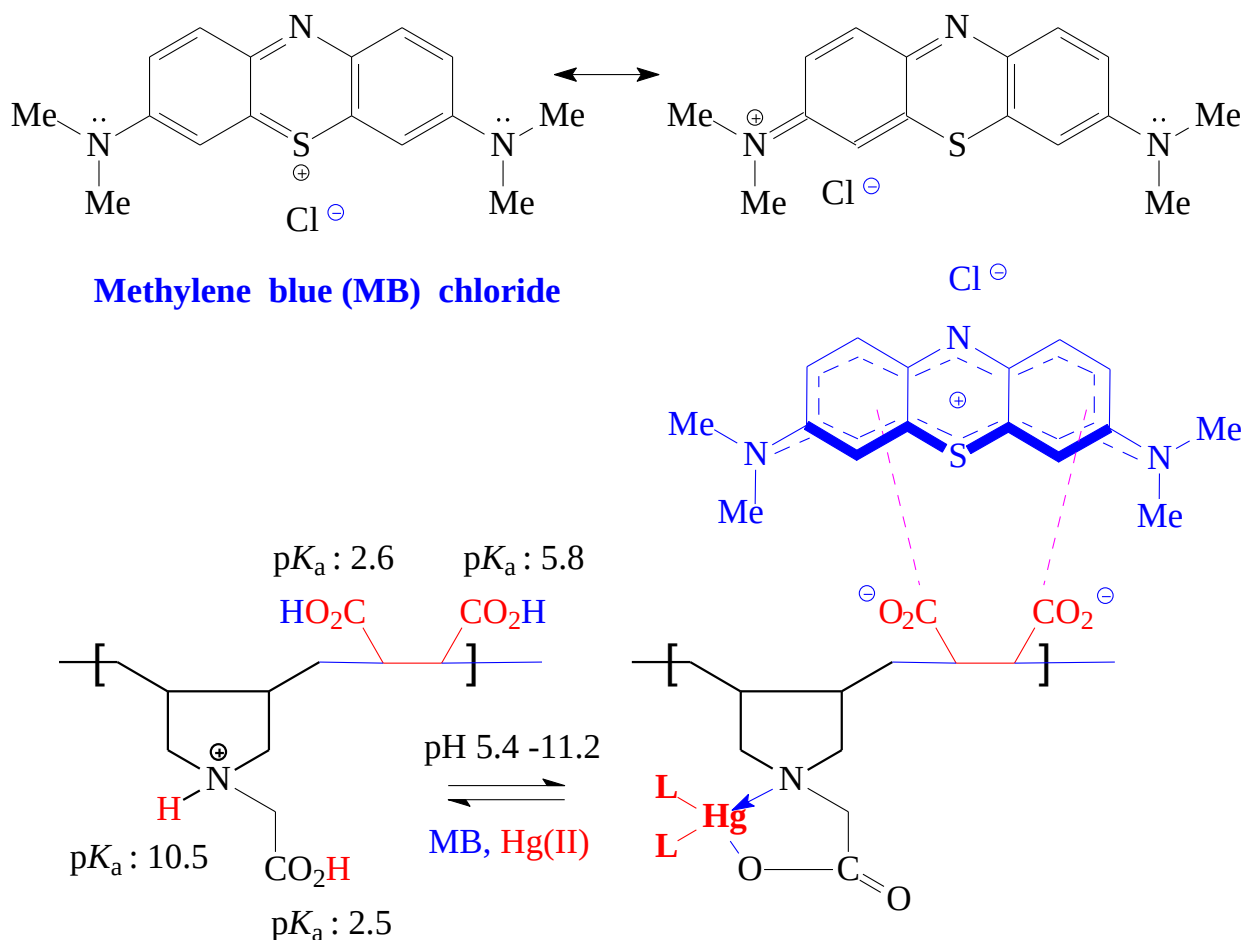


Figure 4.1 TGA analysis (a) of CPZA 4 and CAPE 5, and pH dependency (b) of adsorption capacity (q) of resin 5 for MB at various pHs.

4.4.3 pH Dependency of q_t

Adsorption capacity (q) of resin 5 for MB at various pHs is shown in Fig. 4.1b, which reveals its steep increase with increasing pH in the range 2.8-5.4, while the dye uptake remains constant over the pH-range 5.4-11.2. The pK_a of the three CO_2H groups are expected to be 2.5, 2.6 and 5.8 [136,197]. Therefore, in the pH range 5.4-11.2, all three CO_2H would remain mainly in the anionic form CO_2^- , which imparts electrostatic interaction to the cationic MB and as such the adsorption capacity remains constant in this pH range (Scheme 4.2). At lower pH values, the undissociated CO_2H groups are not capable of trapping MB, and as such q_{MB} will remain low. This finding will be helpful in carrying out adsorption and desorption at a higher and a lower pH, respectively.



Scheme 4.2 Electrostatic interaction between the resin, cationic dye and Hg(II).

4.4.4 Adsorption Kinetics at Various Temperatures

At a time of 1 min, adsorptive removal has attained the values of 41, 47, 58 and 66% at 15, 25, 40 and 55 °C, respectively, while at 10 min interval, the corresponding removal became 90, 92, 96 and 96%. Fig. 4.2 shows that the adsorption has attained its equilibrium value ($\geq 99\%$) at a time of 20 min and remained constant up to 360 min (not shown in the plot). In the beginning (1-2 min), note the faster removal at higher temperatures as dictated by the adsorption kinetics, while the exothermic nature of the process leads to a decrease in %

removal with the increasing temperatures over the time range 30-180 min as dictated by thermodynamics.

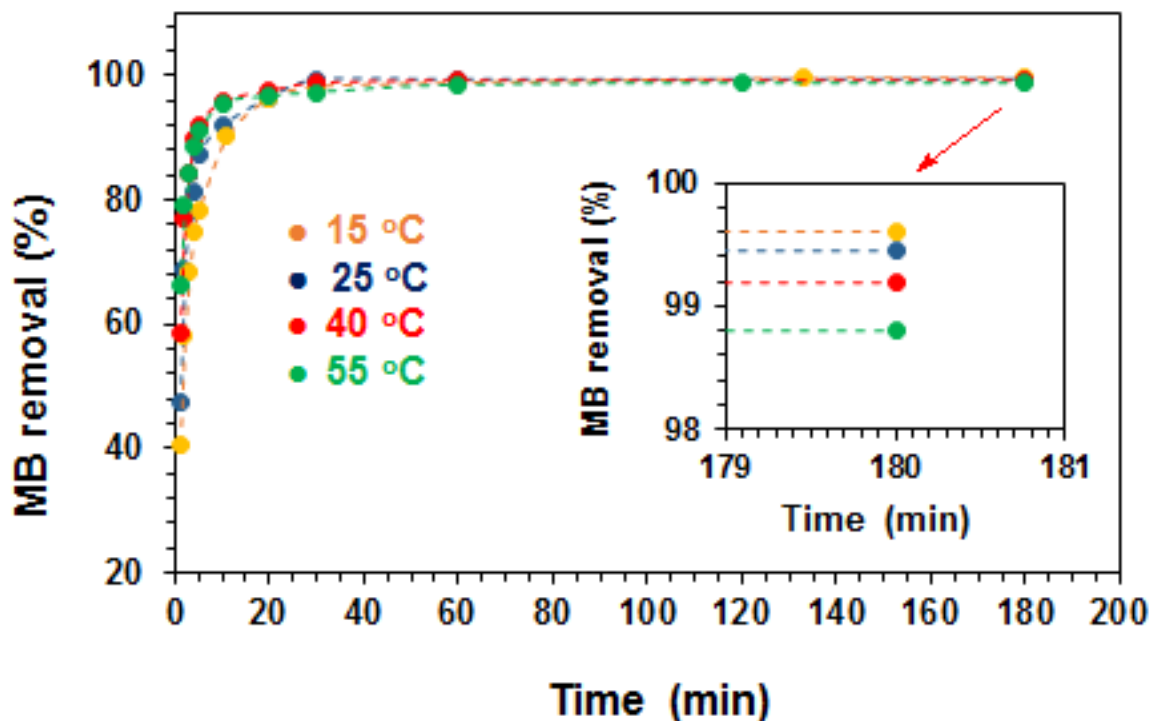


Figure 4.2 Adsorption kinetics of MB % removal at various temperatures.

The equilibrium: $\text{MB} + \text{Resin} \rightleftharpoons \text{Resin} \rightarrow \text{MB}$ is attained in a relatively short time (Fig. 4.3a). The inset, showing the equilibrium adsorption capacity q_e at a time of 6 h, reveals the continuous decrease in its value with the increase in temperature, which is diagnostic of an exothermic process.

The kinetics were explored using Lagergren first-order [Eq. (5)] [195] (Fig. 4.3b), second order kinetic [Eq. (6)] (Fig. 4.3c), and intraparticle diffusion model [Eq. (7)] (Fig. 4.3d):

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

$$q_t = x_i + k_d t^{0.5} \quad (7)$$

Where k_1 , k_2 and k_p represent the respective rate constants, while q_t and q_e represent the MB uptake at time t and at equilibrium.

The kinetic data is suggestive of a chemical adsorption process [198], since they fit second order kinetic as evinced by better R^2 values and matching of the q_{cal} and q_{exp} values (Table 4.2).

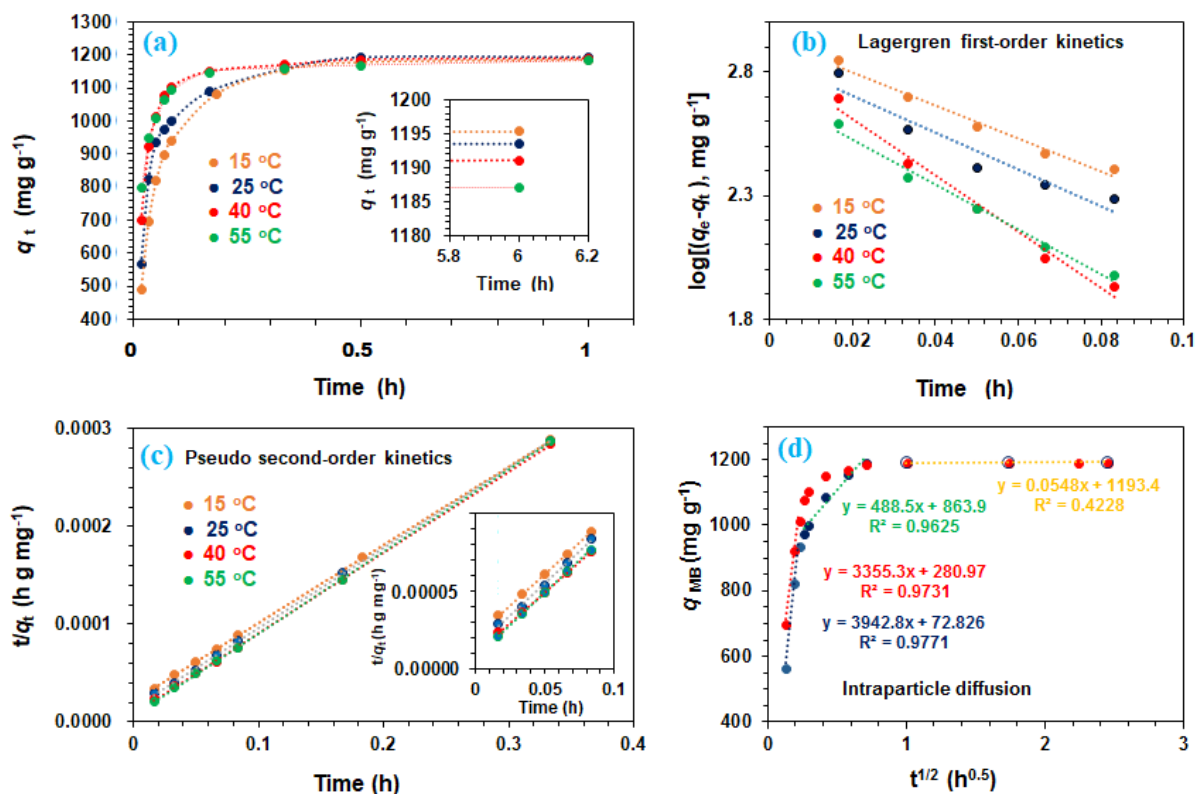


Figure 4.3 Kinetic study of MB adsorption on CAPE 5.

Usually, most of the adsorption processes involve three consecutive steps: (i) fast diffusion of adsorbate (i.e., film diffusion), (ii) followed by a slower diffusion through the resin pores (i.e., intraparticle diffusion), and (iii) finally the fast adsorption/desorption equilibrium (i.e., mass action).

A q_t versus $t^{0.5}$ plot as per Eq. (7) is expected to shed light on the rate-limiting step. A linear plot passing through the origin (i.e., $x_i = 0$) would justify the adsorption being exclusively dictated by the rate limiting intraparticle diffusion [199], while a positive or negative intercept (i.e., $x_i \neq 0$), where x_i is proportional to boundary layer thickness [200], would make the film diffusion as part of the overall rate determining step. The q_t versus $t^{0.5}$ plot (Fig. 4.3d), for instance at 25 °C, is multilinear [201]; the initial steeper section with higher slope (k_{d1}) accounts for the faster external film diffusion and instantaneous adsorption achieved in 3 min, while the second linear section with a lower slope (k_{d2}) depicts the slower intraparticle diffusion (Table 4.2) [172]. The third section parallel to the 'x'-axis represents the adsorption process at equilibrium.

The initial adsorption factor (R_i) is related to x_i and the equilibrium q_e , [Eq. (8)]:

$$R_i = 1 - \frac{x_i}{q_e} \quad (8)$$

The instantaneous adsorption and film diffusion in the q_t range 0-974 mg g⁻¹ accounts for 81.6% adsorption, while the slower portion in the q_t range 974-1193 mg g⁻¹ (i.e., 18.4% of adsorption) is dictated by the intraparticle diffusion (Fig.4.3d). The adsorption of MB at 298 K has R_i value of 0.939 [i.e., $1 - (72.8/1193)$] (Table 4.2) apparently implying that instantaneous adsorption accounts for 6.1% only. The intercept x_i of each stage depends on

the boundary layer thickness, which resists the diffusion. The decrease in intercept values in the order: $x_1 < x_2 < x_3$ means that external diffusion resistance is low in the beginning as there are not many adsorbed MB molecules to resist the mobility of the others [172].

Table 4.2 Kinetic parameters for MB adsorption on CAPE 5.

Temp (K)	$q_{e, \text{exp}}$ (mg g ⁻¹)	k_2 (h ⁻¹ g mg ⁻¹)	h^a (h ⁻¹ mg g ⁻¹)	$q_{e, \text{calc}}$ (mg g ⁻¹)	R^2	E_a (kJ mol ⁻¹)
<i>Pseudo second-order</i>						
288	1195	0.031	47438	1245	1.0000	31.5
298	1194	0.048	71225	1214	0.9999	
313	1191	0.087	127551	1208	0.9999	
328	1187	0.104	147711	1192	0.9999	
Temp (K)	$q_{e, \text{exp}}$ (mg g ⁻¹)	k_1 (h ⁻¹)		$q_{e, \text{calc}}$ (mg g ⁻¹)	R^2	
<i>Pseudo first-order</i>						
288	1195	15.4		860	0.9799	
298	1194	17.2		714	0.9164	
313	1191	26.2		688	0.9832	
328	1187	20.9		512	0.9878	
Temp (K)	K_{di} mg g ⁻¹ h ^{-1/2}	x_i (mg g ⁻¹)		R_i	R^2	
<i>Intraparticle diffusion model</i>						
298	3943 (k_{d1})	72.8 (i=1)		0.939	0.9771	
	489 (k_{d2})	864 (i=2)		–	0.9625	
	0.0548 (k_{d3})	1193 (i=3)		–	0.4228	

^aInitial adsorption rate $h = k_2 q_e^2$.

4.4.5 Infrared Spectra

An IR sample of the MB-loaded CAPE 5 was prepared by treating the resin (100 mg) with 2000 ppm MB solution (40 mL) and stirring for overnight at 25 °C. After filtration and

washing with deionized water, the loaded resin was vacuum dried at 50 °C. The IR spectra of MB, acidic resin **4**, basic resin **5**, and MB-loaded basic resin are shown in Fig.4.4. Absorption at 1716 cm⁻¹ was assigned to C=O stretch of COOH in CPZA **4**; the symmetric and antisymmetric vibrations of CO₂⁻ appeared at 1400 and 1624 cm⁻¹, respectively. In the anionic form CAPE **5**, these peaks for CO₂⁻ appeared at 1400 and 1585 (overlapping) cm⁻¹. The absorption peaks agree well with those of amino acids [202].

In the spectrum of MB.3H₂O (Fig. 4.4d), peaks at 1620 cm⁻¹ was assigned to the aromatic ring, while the peaks at 1487 and 1398 cm⁻¹ were attributed to the C–N stretching vibrations [203]. The vibration of the CH₃ group is found at 1340 cm⁻¹. Most of the peaks of MB and resin **5** (especially the C=O absorption peaks) in the spectrum of MB-loaded **5** (Fig. 4.4a) have shifted thereby indicating the interactions of the functional groups with MB. The characteristic aromatic adsorption peak of MB at 1620 cm⁻¹ is shifted to 1552 cm⁻¹ after its adsorption by CAPE **5** because of intermolecular π - π interaction between aromatic rings.

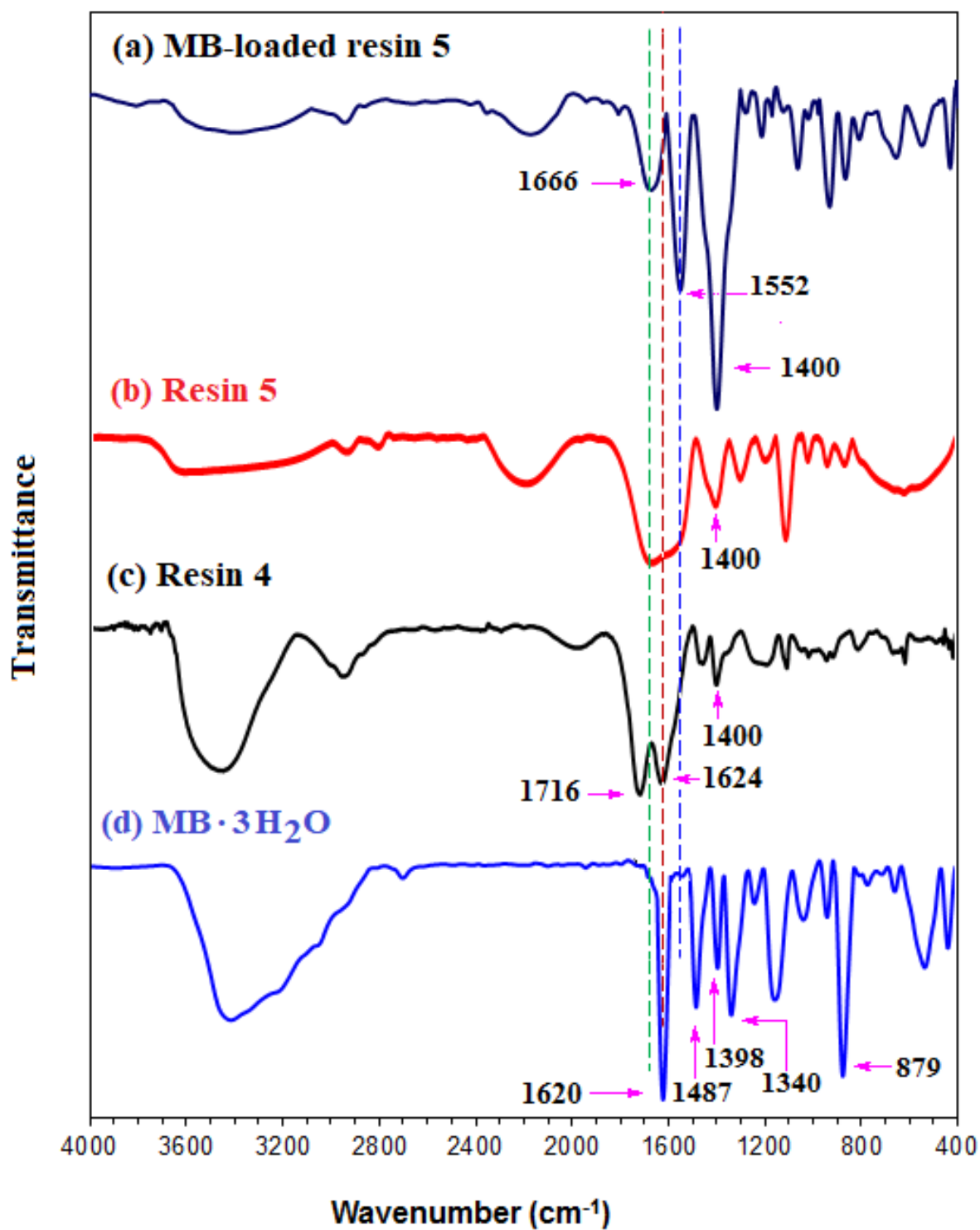


Figure 4.4 The infrared spectra of MB, acidic resin 4, basic resin 5, and MB-loaded basic resin CAPE 5.

4.4.6 Activation Energy (E_a)

E_a of 31.5 kJ mol⁻¹ for the adsorption process was determined from $\ln k_2$ versus $1/T$ plots using Arrhenius Eq. (9) (Fig. 4.5a) using second-order rate constants k_2 (Table 4.2). The relatively large E_a value indicates the process as chemisorption.

$$\ln k_2 = -\frac{E_a}{2.303RT} + \text{constant} \quad (9)$$

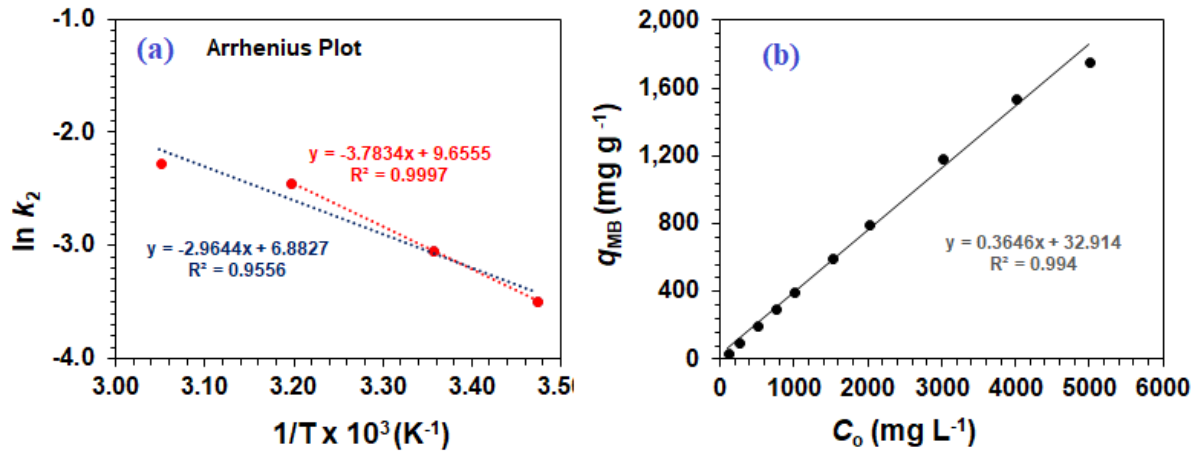


Figure 4.5 The activation energy for the adsorption process.

4.4.7 Adsorption Isotherm

Several experiments were carried out to determine equilibrium adsorption capacity q_e and concentration C_e using various initial concentration (C_o) of the dye at 298 K. The q_e versus C_o plot as displayed in Fig. 4.5b shows a linear increase of q_e with C_o , which is a consequence of shifting the equilibrium to right side with the progressive increase of free MB: $MB_{free} + Resin \rightleftharpoons MB_{ads} \rightarrow resin$.

To investigate the adsorption mechanism, following isotherm models [Eqs. (10) - (13)] relating q_e and C_e , are considered.

Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b} \quad (10)$$

Freundlich isotherm: $\log q_e = \log k_f + \frac{1}{n} \log C_e$ (11)

Temkin isotherm: $q_e = \frac{RT}{b} \ln A + \frac{RT}{b} \ln C_e = B \ln A + B \ln C_e$ (12)

Dubinin-Radushkevich (D-R) isotherm:

$$\ln q_e = \ln q_D - B_D [(RT \ln (1 + 1/C_e))]^2 = \ln q_D - B_D \epsilon^2 \quad (13)$$

where apparent energy of adsorption, $E = 1/(2B_D)^{1/2}$ (14)

The isotherm parameters from the plots Fig.4.6a-d are included in Table 4.3. Langmuir isotherm [Eq. (10)] is based on a monolayer formation where the adsorbed molecules do not interact among themselves [204]. Langmuir constant b and maximum adsorption capacity q_m are determined from the C_e/q_e vs. C_e plot (Fig. 4.6a). The outstanding performance by the resin is reflected by its q_m value of 2101 mg g⁻¹; to our knowledge, not many resins are known to surpass this staggering adsorption capacity. Note that the data obtained from the Langmuir model can be used to determine a separation factor R_L using Eq. (15):

$$R_L = \frac{1}{(1+bC_0)} \quad (15)$$

The value of $R_L > 1$, $= 1$, in the range $> 0 - < 1$, or $= 0$ diagnoses the adsorption as unfavorable, linear, favorable, or irreversible process, respectively [205].

Table 4.3 Various isotherm constants for MB adsorption on CAPE 5 at 298 K.

Langmuir		
q_m (mg g ⁻¹)	b (L mg ⁻¹)	R^2
2101	0.0387	0.9995
Freundlich		
n	k_f (mg ^{1-1/n} g ⁻¹ L ^{1/n})	R^2
1.11	142	0.9979
Temkin		
A (L g ⁻¹)	B (J mol ⁻¹)	R^2
2.94	235	0.9841
Dubinin-Radushkevich		
q_D (mg g ⁻¹)	E (kJ mol ⁻¹)	R^2
211	3.16	0.9503

The favorable nature of the process is reflected by small R_L values in the range 0.00514-0.205 (Table 4.4). The small R_L values (almost zero in most cases) seem to suggest the process as irreversible.

Table 4.4 The R_L values and % MB removal of MB on CAPE 5 at 298 K.

C_o (mg L ⁻¹)	R_L value	% MB Removal
100	0.205	99.7
250	0.0937	99.7
500	0.0491	99.7
750	0.0333	99.7
1000	0.0252	99.7
1500	0.0169	99.7
2000	0.0128	99.6
3000	0.00854	99.5
4000	0.00642	96.6
5000	0.00514	87.9
10000	—	52.4

Freundlich isotherm model [Eq. (11)] deals with heterogeneous adsorption. The plot (Fig. 4.6b) remains linear in the lower concentration (C_o) range 100-2000 ppm. The n value (1.11) in the range 1 – 10 suggests a favorable chemisorption process [204].

The adsorption data did not fit well with the Temkin [Eq. (12)] (Fig. 4.6c) and D-R isotherm model [Eq. (13)] (Fig. 4.6d); for the later, only three MB concentrations (inset: C_o = 100, 250, 500 ppm) are used to extract isotherm constants (Table 4.3). In Temkin model, B ($= RT/b$) represents the heat of adsorption. The positive B value indicates the adsorption as an exothermic process (Table 4.3) [191].

In D-R isotherm model, the free energy of sorption and isotherm constant are represented by B_D and q_D , respectively [206]. The favorability of the process is ascertained by the low value of E (3.16 kJ mol^{-1}) (Table 4.3).

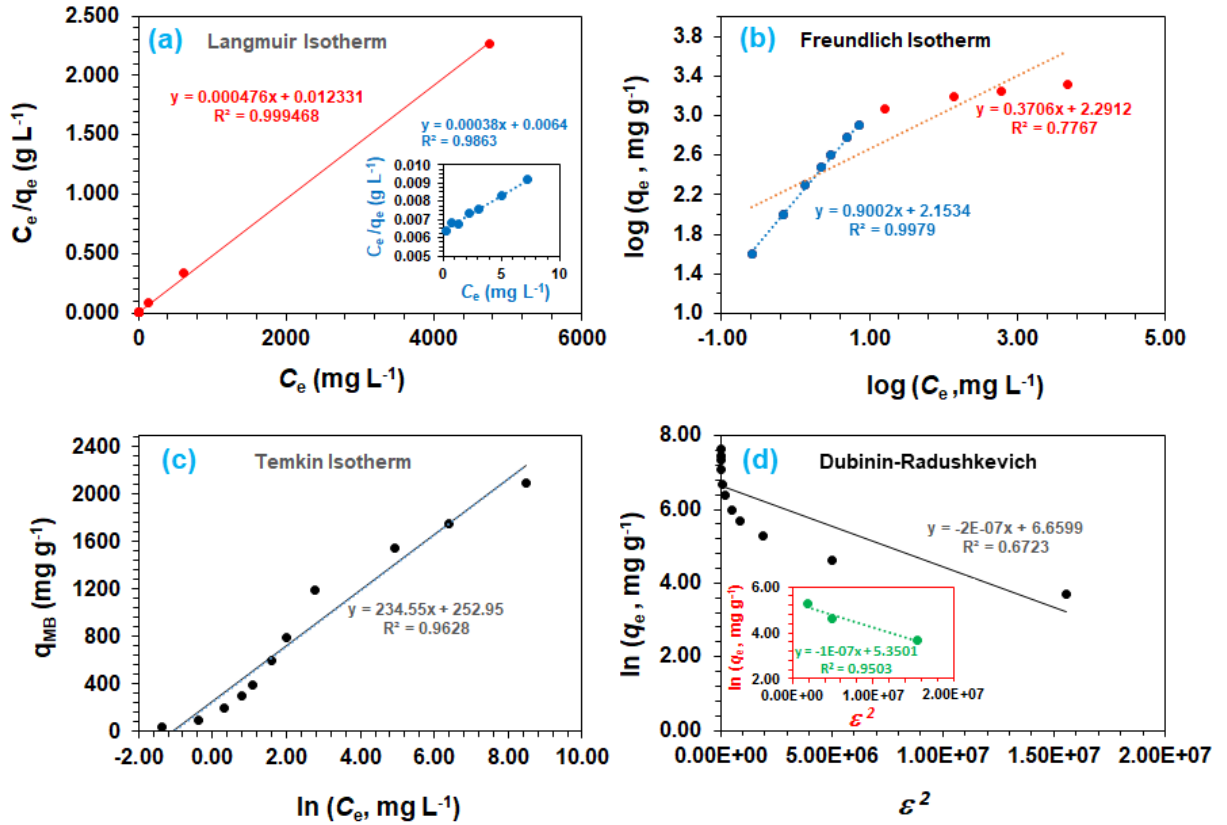


Figure 4.6 The isotherm plots of Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich.

4.4.8 Adsorption Thermodynamics

The negative slope of the q_e versus T plot confirms the adsorption as an exothermic process (Fig. 4.7a). Adsorption $\rightleftharpoons$ desorption equilibrium is shifted towards desorption at higher temperatures. The thermodynamic parameters ΔH° , ΔS° and ΔG° ($= \Delta H^\circ - T\Delta S^\circ$) [Eq. (16)]

were obtained from the Vant-Hoff plot (Fig. 4.7b). The negative ΔH° and ΔG° values indicate the adsorption process as exothermic and favorable (Table 4.5).

$$\log \left(\frac{q_e}{C_e} \right) = -\frac{\Delta H^\circ}{2.303RT} + \frac{\Delta S^\circ}{2.303R} \quad (16)$$

Table 4.5 Thermodynamic (ΔG° , ΔH° , ΔS°) data for MB adsorption on CAPE 5.

Temperature (K)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	R^2
279	-11.5	-21.0	-34.1	0.9889
288	-11.2			
298	-10.8			
313	-10.3			
328	-9.81			

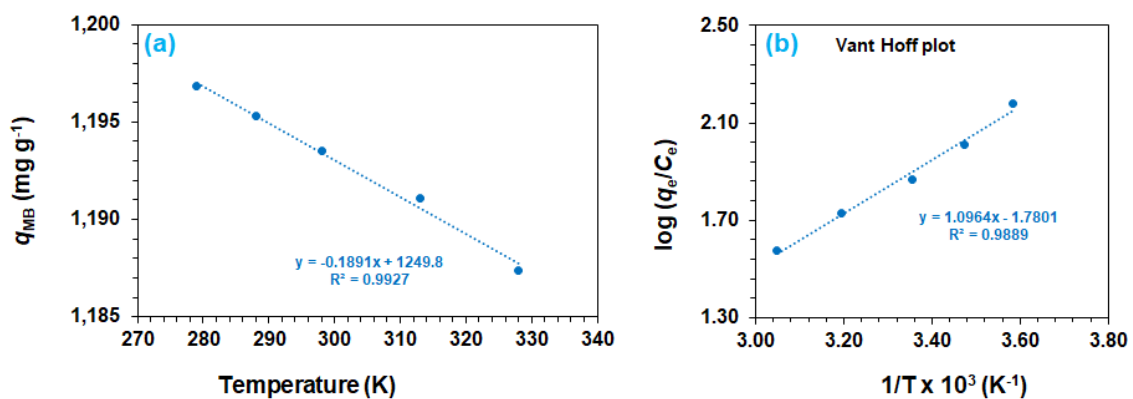


Figure 4.7 The thermodynamically Adsorption $\rightleftharpoons$ desorption process.

4.4.9 SEM Images and EDX

MB loaded - CAPE 5, prepared as described under Section 4.4.5, was sputter-coated with a thin film of gold and scanned. Note that the EDX spectrum of pristine resin revealed the presence of C, N, O, and Na as expected (Fig. 4.8a), while the presence of S and a drastic decrease in the amount of Na in the loaded resin are indicative of the exchange between cationic MB and Na^+ (Fig. 4.8b).

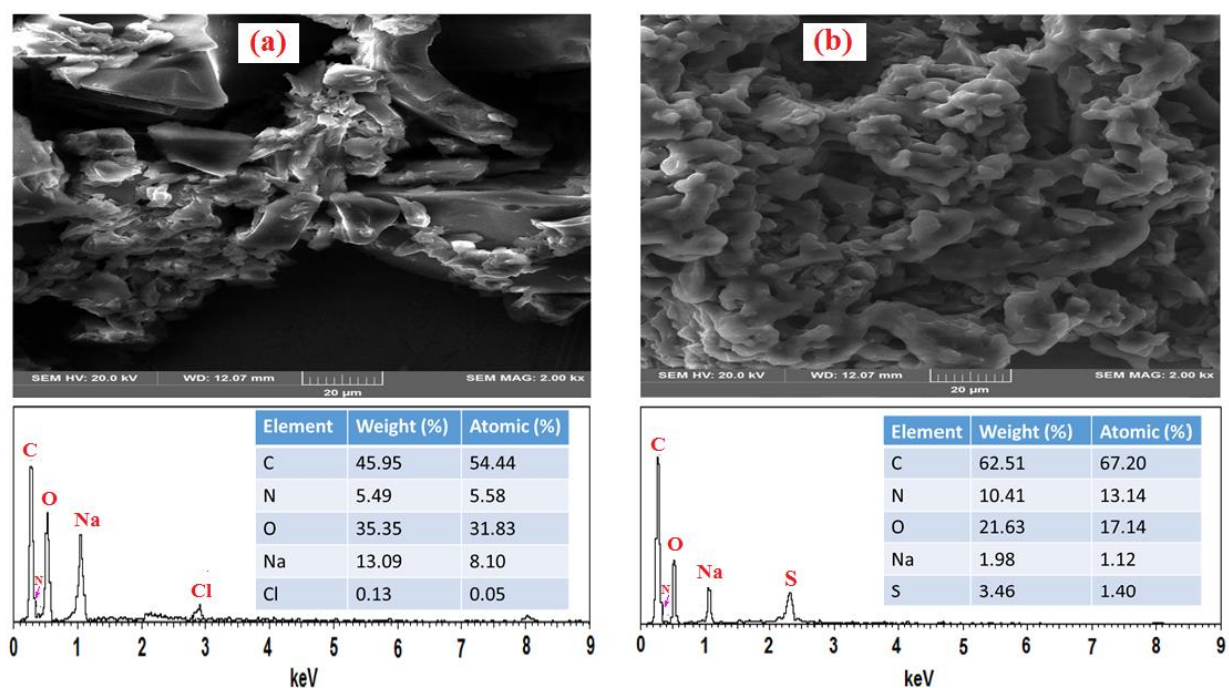


Figure 4.8 The SEM and EDX images of MB loaded - CAPE 5.

4.4.10 Effect of added Salt NaCl on the MB Uptake

The presence of salts in industrial dye wastewater has a bearing on the adsorption; as such the effect of added NaCl on the dye removal was examined. Fig. 4.9a displays the dependency of q_e on the molarity of NaCl. The Na^+ ions would compete with the cationic dye molecules for the anionic sites on the resin. The increase of NaCl concentration enhances the shielding of the negative charges in the resin, thereby weakening the electrostatic interaction between MB and the resin. The presence of NaCl in the aqueous media is thus expected to be detrimental to the adsorption efficiency. For an initial MB concentration (C_o) of 2000 ppm, its removal in the presence of 0, 0.1, 0.5 and 1 M NaCl was found to be 99.6, 93.7, 92.1, and 88.9%, respectively. For a C_o of 1000 ppm, however, removal efficiency becomes 99.7, 96.3 and 24.1% at 0, 0.1 and 0.5 M NaCl. Overall it can be seen that, under the current dye concentration range 100-2000 ppm in 0.1 M NaCl, the removal efficiency does not change significantly.

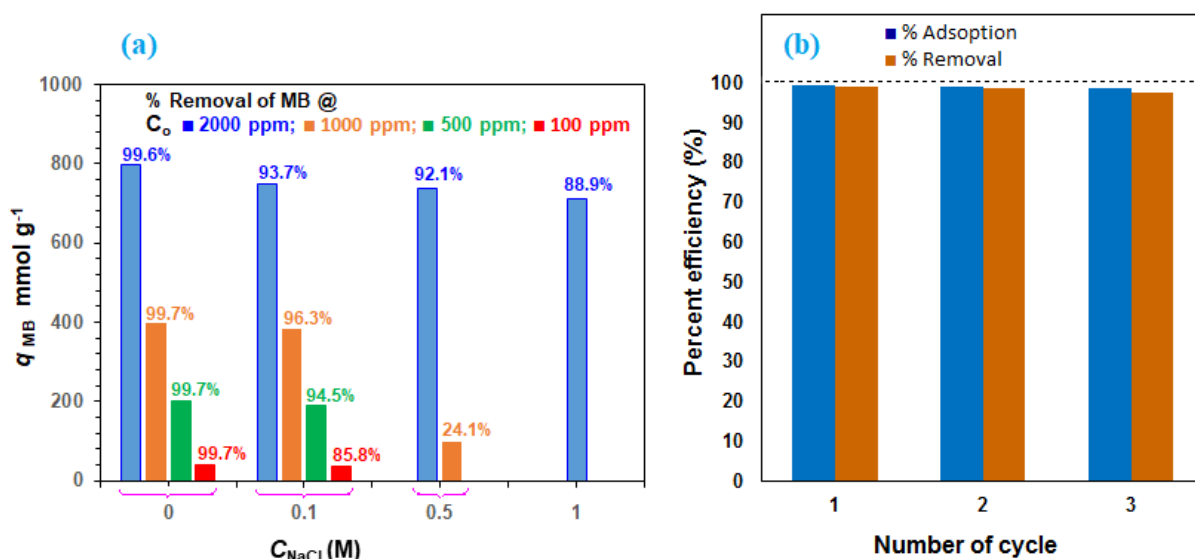


Figure 4.9 The % removal efficiency of MB in the presence of NaCl and % recovery efficiency.

4.4.11 Regeneration and Reuse of Resin

Adsorption/desorption cycle repeated three times gave efficiencies of $\approx 99\%$ for both the adsorption and desorption processes. The resin thus shows excellent recovery with stable efficiency for the subsequent cycles as shown in Fig.4.9b.

4.4.12 Immobilization Mechanism

The Elovich model [Eq. (17)] shows reasonable fit ($R^2 = 0.9582 - 0.9969$) of the kinetic data at various temperatures, which points towards a chemical adsorption process (Fig. 4.10a). The α values, which correspond to the initial adsorption rate, were found to be 9.64×10^4 , 1.48×10^5 , 2.59×10^5 , and 9.04×10^5 $\text{mg g}^{-1} \text{h}^{-1}$ at 15, 25, 40 and 55 °C, respectively. The corresponding β values, which correspond to the desorption rate, were 0.00349, 0.00367, 0.00393, and 0.00546 g mg^{-1} . The high values of α and low β thus make the adsorption as essentially an irreversible process [172]. Pseudo second-order kinetics also support the process as chemical adsorption. The small values of R_L (almost zero in most cases) seem to suggest the process as irreversible (Table 4.6).

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (17)$$

Table 4.6 The R_L values and % MB removal of MB on CAPE 5 at 298 K.

C_o (mg L ⁻¹)	R_L value	% MB Removal
100	0.205	99.7
250	0.0937	99.7
500	0.0491	99.7
750	0.0333	99.7
1000	0.0252	99.7
1500	0.0169	99.7
2000	0.0128	99.6
3000	0.00854	99.5
4000	0.00642	96.6
5000	0.00514	87.9
10000	—	52.4

The pH-dependent surface charge of the resin was determined by zeta potential measurement. A sample (50 mg) of resin **4** was dispersed in 0.05 M NaCl (5 mL) by stirring for 3 h, followed by an addition of 0.1 M HCl or 0.1 M NaOH as necessary to adjust the pH (2-12). Before the zeta potential measurement, the dispersed samples were equilibrated for 24 h at 25 °C. The pH of the point of zero charge (pH_{PZC}) for resin **4** was found to be 3.0 (Fig. 4.10b). At $pH > 3$, the resin is expected to have excess negative charges. Therefore, the MB adsorption carried out at much higher pH values (*vide supra*), would involve electrostatic attraction among the cationic MB molecules and anionic centers on the resin. Desorption of MB from MB-loaded resin by water or ethanol was unsuccessful, thus indicating the sorption of the dye onto the sorbent by a stronger force of chemisorption rather than physisorption. A strong acid such as HCl was able to dislodge the dye, its

attachment to the resin may thus be attributed to ion exchange or electrostatic attraction. FTIR data also supported strong adsorbate-adsorbent interaction.

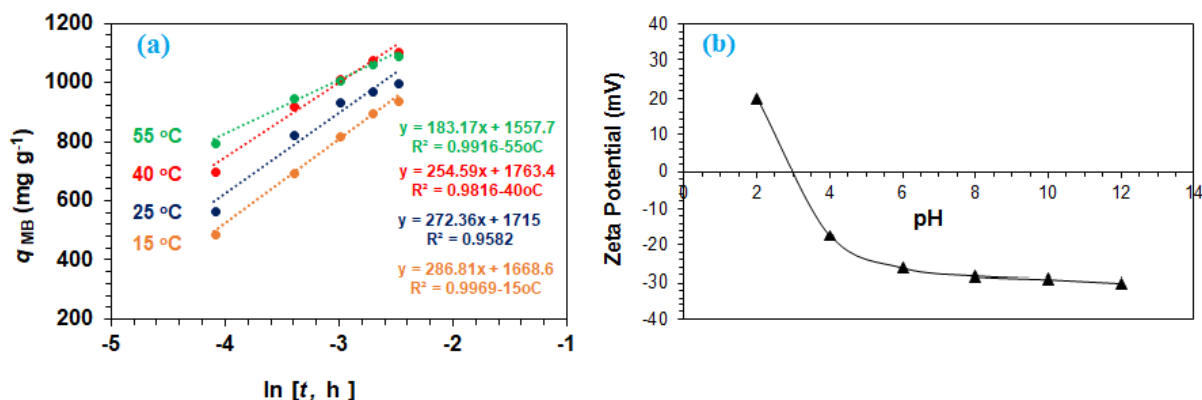


Figure 4.10 The irreversibility process of MB towards a chemical adsorption and the pH-dependent surface charge of the resin via zeta potential measurement.

4.4.13 Removal of Hg(II)

A stock solution of Hg(II) ions was prepared using Hg(NO₃)₂. Adsorption capacities for Hg(II) were determined using various concentration of Hg(II) ions in the range 100-2000 ppm at pH 5.3 using experimental conditions similar to that for the removal of MB. The concentration of Hg(II) ions was determined by ICP-MS (Model: ICP-MS XSERIES-II). Plot Fig. 4.11a for Langmuir isotherm [Eq. (10)] gave the q_m of 263 mg g⁻¹. The favorable nature of interactions is reflected by the small R_L values in the range 0.0733-0.388. The Langmuir model gives a better fit to the experimental data better than Freundlich model (not shown), thereby indicating a monolayer adsorption. Fig. 4.11b reveals the increase of metal uptake with increasing Hg(II) concentrations.

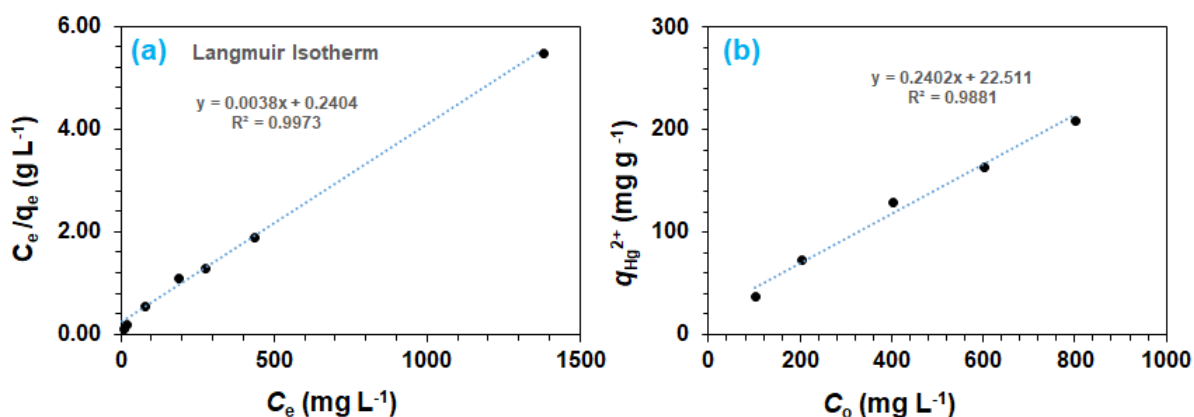


Figure 4.11 The Langmuir model for removal of Hg(II).

4.4.14 Removal of Anionic Dye Methyl Orange (MO) and Simultaneous Removal of MB and Hg(II) from Aqueous Solution

Resin **4** was quite successful in simultaneous removal of cationic MB and Hg(II) from their aqueous mixture at pH 5.3 (Table 4.7). We have also attempted to remove anionic dye such as methyl orange (MO). At pH 5.3, the nitrogens in **4** are protonated; as such the protonated nitrogens are expected to interact with negatively charged MO. However, the removal efficiency of the anionic dye was found to be modest; the resin removed only 30% MO from its 200 ppm solution.

Table 4.7 Hg(II), MB and methyl orange removal from aqueous solution (20 mL) at pH 5.3 by CPZA **4** (50 mg) at 298 K.

Original sample	Initial concentration (mg L ⁻¹)	Removal (%)
Hg(II) + MB	10 (Hg(II)) + 10 (MB)	98 (Hg(II)); 72 (MB)
MO	200	30

4.4.15 Treatment of Industrial Wastewater

The current resin was employed to remove pollutants from an industrial wastewater matrix (pH: 5.5). Resin 5 (50 mg) was exposed to the wastewater (20 mL) after spiking with 0.0 and 10 mg L⁻¹ each of MB and Hg(II) ions at 298 K for overnight. The concentration of toxic metal ions, especially Hg(II) ions, was reduced to sub-ppb level in the non-spiked sample. For the spiked samples, MB and Hg(II) concentrations are also drastically reduced (Table 4.8).

Table 4.8 Metal ions and MB concentrations in wastewater before and after treatment with CAPE 5 at 298 K.

Metal/Dye	Original sample (µg L ⁻¹)	After treatment (µg L ⁻¹)	
		Original sample treated with CAPE 5	Original sample spiked with Hg(II) (10,000 µg L ⁻¹) and MB (10,000 µg L ⁻¹) and then treated with CAPE 5
Cr	1.48	0.48	0.78
Fe	22.4	1.24	1.38
Co	1.30	0.19	0.37
Ni	2.10	0.32	0.53
Cu	7.68	1.09	0.79
Al	23.7	2.16	1.45
Pb	2.34	0.93	0.45
Hg	1.61	0.15	723.4
MB	—	—	1465

4.5 Conclusion

A resin loaded with carboxylate motifs has been prepared in excellent yield. To our knowledge, alternate polymerization involving diallyl amine salt has been carried out to obtain the novel resin for the first time. The resin bearing the residue of amino acid glycine is made from inexpensive starting materials and its synthesis can easily be scaled up.

The equilibrium experimental data fit with the Langmuir isotherm. The resin turned out to be a super-adsorbent for MB, used as a model cationic dye, having a q_m of 2101 mg g⁻¹. The process shows an extraordinarily fast adsorption rate; in a 3000 mg L⁻¹ MB solution, the resin achieved 69, 78 and 99.4% MB removal within 2, 3 and 30 min, respectively, at 298 K because of the absence of internal diffusion resistance. Its outstanding performance, better than many recently reported materials ([Table 4.8](#)), paves the way for its potent application in remedying industrial dye-waste water. The MB adsorption follows pseudo second-order kinetics. The remarkable adsorption/desorption efficiencies ensured the recycling of the resin. The very impressive performance accords the resin a prestigious place among many sorbents in recent works.

CHAPTER 5

A RESIN CONTAINING MOTIFS OF MALEIC ACID AND GLYCINE: A SUPERABSORBENT FOR ADSORPTIVE REMOVAL OF BASIC DYE PARAROSANILINE HYDROCHLORIDE AND Cd(II) FROM WATER

5.1 Abstract

The cyclocopolymerization of *N,N*-diallylglycine and maleic acid in the presence of 1,1,4,4-tetraallylpiperazinium dichloride afforded a cross-linked polyzwitterionic acid (CPZA) which upon treatment with NaOH gave the corresponding cross-linked anionic polyelectrolyte (CAPE) in quantitative yield. The pH-responsive resins contained a high density of CO₂⁻ motifs as well as the chelating motifs of glycine residues. The resin CAPE was found to be a super-adsorbent for the removal of pararosaniline hydrochloride (PRH) from aqueous solution; having a maximum adsorption capacity $q_{\max}$ of 1534 mg g⁻¹ as determined by nonlinear Langmuir adsorption isotherm. The adsorption process followed pseudo second-order kinetics and found to be nearly irreversible process as suggested by parameters obtained from Elovich kinetic model. The resin demonstrated excellent adsorption/desorption efficiencies thereby ensuring its recycling and reuse in potent application like remediation of industrial dye-waste water. The resin's chelating motifs was also efficient in adsorptive removal of Cd(II) ions with a maximum $q_{\text{Cd(II)}}$ of 248 mg g⁻¹. The resin also demonstrated remarkable efficiency in simultaneous trapping of Cd(II) and the dye from industrial waste water. The resin's impressive performance accords it a

prestigious place among many sorbents in recent works.

Keywords

Adsorption; Pararosaniline; Basic fuchsin; Maleic acid; Cyclopolymerization; Aminocarboxylate resin.

5.2 Introduction

Estimated annual discharge of more than $1.5 \times 10^8 \text{ m}^3$ of colored effluents causes serious water pollution because of suspected to be carcinogenic and mutagenic nature [207] of most of the 10,000 different organic dyes with an worldwide annual production over 7×10^5 tons [208,209]. The harmful dyes bring toxicity in human beings, fish species and microorganisms, hence their remediation remains a matter of the utmost importance for ecological environment protection [210]. The presence of dye reduces sunlight penetration and thus influences the photosynthetic activities of aquatic flora which are the food source of aquatic organisms [211].

Even while acknowledging the dyes' contribution to the world economy, we must seriously consider their toxicity [212]. Cationic dye Basic fuchsin (BF), also known as pararosaniline hydrochloride (PRH), is widely used in industries, such as textile, printing, paper, cosmetic and leather [213]. It is also used as a biological stain and as a tracking dye for certain proteins [214]. In addition to posing a great threat to aquatic organisms, it is harmful to humans as it can burn the eyes and irritate the skin [215,216]. Poorly biodegradable basic fuchsin has been listed as a suspected carcinogen [217,218]. Among a plethora of techniques used for the removal of dyes [219,220], Adsorption has been established as the

most efficient, simple, and low cost method [221, 222]. Even though traditional adsorbents such as activated carbon have excellent adsorption removal capacities for organic dyes, the water treatment systems demand the development of cheaper as well as more efficient adsorbents.

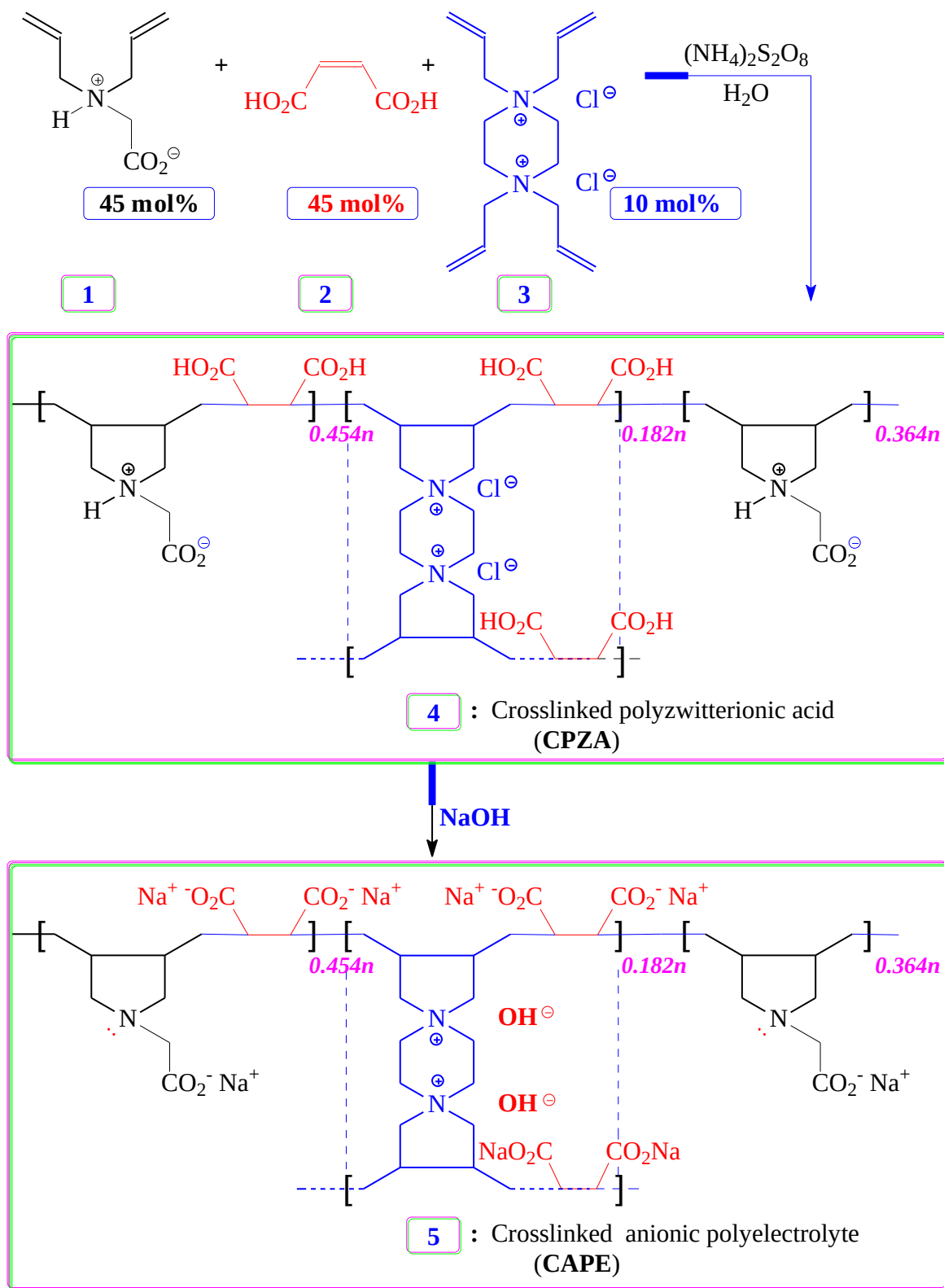
Only a few adsorbents have been developed till now for the removal of PRH [223]. A composite of Graphene/ β -cyclodextrin (GNS/ β -CD) has been reported to remove basic fuchsin with saturated adsorption capacity (q_m) of 425.8 mg g⁻¹ [224]. Magnetic ZnFe₂O₄@chitosan encapsulated in graphene oxide has shown to have a q_m value of 244 mg g⁻¹ [225]. Loess clay, modified by surface grafting copolymerization of acrylamide and sodium *p*-styrene sulfonate, is reported to remove BF with a rate of 98.4% in 40 min at 25 °C and a q_m of 130 mg g⁻¹ [226]. Polyacrylamide/graphene oxide aerogels have demonstrated remarkable efficiency for BF removal with a q_m value of 1034 mg g⁻¹ [227].

Adsorbents used for the removal of pollutants should be cheap, readily available, easy to regenerate and environment-friendly. The overall goal of this study was to examine the ability and mechanism of PRH removal by adsorbent **4** synthesized using Butler's alternate cyclopolymerization protocol [1,8,136]. Involving monomer **1**, containing motifs of amino acid glycine, maleic acid (MA) **2** and cross-linker **3** (Scheme 5.1). The current study would involve the investigation of the adsorption kinetics, isotherms, thermodynamics, desorption, and other factors such as pH and ionic strength on the adsorption behavior of PRH from aqueous solution onto the pH-responsive resin **5**. The resin, loaded with CO₂⁻ and chelating motifs of R₂NCH₂CO₂⁻, is expected to be an efficient sorbent in separate or simultaneous removal of cationic dyes (like PRH) as well as priority toxic metal ions (Cd(II) as a model case).

Note that both PRH and the resin are pH-responsive since the valency on the nitrogens is unquenched. The charge density and its type on the polymer backbone is pH-dependent.

In the presence of unquenched nitrogen valency, both PRH and the resin are pH-responsive.

In addition, the resin has the ionizable CO₂H groups which upon dissociation would change the charge density on the polymer backbone. For effective electrostatic attraction, the adsorption study has to be carried out at pH values which permits sizeable dissociation of the COOH groups and at the same time keeping the PRH dye in the cationic form without neutralizing its HCl.



Scheme 5.1 Synthesis of Cross-linked Polyzwitterionic/Anionic Resin.

5.3 Experimental

5.3.1 Materials

Ammonium persulfate (APS), maleic acid from Sigma-Aldrich were used as received. Pararosaniline hydrochloride (PRH) (also known as basic fuchsin, BF) ($C_{19}H_{18}ClN_3$ with a molar mass of 323.8 g mol^{-1}) from Aldrich was crystallized from $H_2O/MeOH$. Cross-linker 1,1,4,4-tetraallylpiperazinium dichloride (**3**) was prepared as described [193]. Monomer (**1**) was prepared as described [194]. The adsorption study was carried out using Double distilled Millipore water ($18.2 \text{ M}\Omega \cdot \text{cm}$).

5.3.2 Physical Methods

FTIR spectra were recorded in a Perkin Elmer (16F PC) spectrometer. An SDT analyzer (Q600: TA Instruments, New Castle, USA) was utilized to carry out thermogravimetric analysis (TGA) in the range $20\text{--}800^\circ\text{C}$ under a N_2 flow of 100 mL/min . An Oakton pH-meter (Thermo Fisher Scientific) was used to monitor the sample solution pH in the range of 0.00 to $14.00 (\pm 0.01)$.

The resin's morphology was examined and its elemental analysis carried out using Scanning electron microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDX). A micromeritics Tristar surface area and porosimetry analyzer (Micromeritics, USA) was used to measure the BET surface area, pore size, and volumes of the the resin as described. [228]. The concentrations of PRH dye were analyzed spectroscopically by GENESYS 10S UV-Vis spectrophotometer (Thermo Electron Corporation, USA), and 1-cm path-length quartz cuvette cell was used to monitor the absorbance at $\lambda_{\text{max}} = 540 \text{ nm}$ ($\text{pH} = 6.0$), at which the maximum absorbance occurred. Natural pH of PRH solution is known to be 5.91.

5.3.3 Synthesis of the Resins

The resin was prepared as described [228]. Briefly, a mixture of **1** (5.43 g, 35 mmol), maleic acid (**2**) (4.1 g, 35 mmol), cross-linker **3** (2.49 g, 7.77 mmol) and water (6.9 g) in an RB-flask fitted with a condenser was heated to 100 °C under N₂, then initiator APS (0.8 g) was added in one portion. After the exothermic polymerization (10 min), the immovable resin **4** was washed with water and dried under vacuum at 65 °C to a constant weight (10.5 g, 88%). Amount of (**1-HCl**), **2** and **3** in resin **4** (342 mg) was calculated to be 1.0, 1.0 and 0.222 mmol, respectively. Resin **4** was converted into resin **5** by treatment with NaOH as described [228]. Amount of (**1-HCl**), **2** and **3** in resin **5** (400 mg) was calculated to be 1.0, 1.0 and 0.222 mmol, respectively.

The IEC of CAPE **5** was determined using as described and found to be 7.65 mmol g⁻¹. CAPE **5** was found to have BET surface area, total pore volume and average pore diameter of 3.23 m² g⁻¹, 1.77 × 10⁻² cm³ g⁻¹ and 3.1 nm, respectively

5.3.4 PRH Adsorption

Aqueous solutions of PRH in the range 200–4,000 mg/ were taken in a series of vials each containing resin **5** (50 mg) and stirred at 300 rpm using a magnetic stir-bar at 300 rpm for 12 h at 298 K. Adsorption of PRH from its aqueous solution (20 mL) over the concentration range 200–4,000 mg/L onto resin **5** (50 mg) was conducted in a series of vials where the mixture was stirred using a magnetic stir-bar at 300 rpm for 12 h at 25°C (to achieve equilibrium). At the beginning of the experiments, the pH of the solutions was fixed at ≈ 6.4 by addition of 0.160 g of 1.035 M HCl. A portion of the samples was centrifuged, and the concentrations of PRH at equilibrium (*C_e*) in the supernatant were determined after dilution and adjusting the pH at 6.0 using a UV–Vis spectrometer at a wavelength of 540

nm. A calibration curve for standard solutions of PRH (0.1-5.0 mg L⁻¹) (pH = 6.0) was used to calculate the PRH concentrations in the test samples. The amount of PRH (i.e. q_e) adsorbed onto resin 5 was calculated according to Eq. (1):

$$q_e = (C_o - C_e) \times \frac{V}{m} \quad (1)$$

Where the initial and equilibrium concentrations of PRH (mg/L) are denoted as C_o and C_e , while V and m are the volume of the solution (L) and the mass of the adsorbent (g), respectively.

The removal percentage of methylene blue was calculated according to Eq. (2):

$$R (\%) = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

The kinetic tests using a constant temperature bath were carried out at 298, 313, and 328 K in RB flasks (250 mL) containing a stirred (300 rpm) mixture of 2000 mg L⁻¹ PRH solution (99.2 mL), resin 5 (250 mg) and 1.035 M HCl (0.8 g). [Firstly, the acidified PRH solution was heated to the specified temperature, then the resin was added]. Samples of solution ($\approx$ 0.1 mL) were collected at specified intervals from the top of the mixture (after stopping stirring for 10 s) using a syringe filter (PTFE, hydrophobic, 0.25 μ m). The concentrations of PRH after appropriate dilutions were determined spectrometrically after adjusting the pH to 6.0.

The amount of adsorption at time t , q_t (mg g⁻¹), was calculated using Eq. (3):

$$q_t = (C_o - C_t) \times \frac{V}{m} \quad (3)$$

The of adsorption capacity dependency on pH was determined as above by stirring a mixture of **5** (50 mg) and 2000 ppm PRH (20 mL) at 25 °C for 12 h. The pH of the solutions was controlled by the addition of 0.1 M NaOH or 0.1 M HCl. All adsorption experiments were performed in duplicates and in some cases triplicates; the relative error of all the results was in the range 1-3%.

5.3.5 Adsorption/Desorption of PRH

For adsorption study, the basic resin **5** (100 mg) in 2000 ppm rosaniline solution (40 mL) in a centrifuge tube was stirred using a magnetic stir-bar for 12 h at 298 K. At the beginning of the experiment, the pH of the solutions was fixed at ≈ 6.4 by addition of 1.0 M HCl. The absorbance value of the resultant supernatant, as determined by spectrophotometrically at a λ of 540 nm, was used to calculate the concentration of non-adsorbed PRH in the solution (pH 6.0), hence the adsorption efficiency of the resin.

The PRH-loaded resin in the centrifuge tube was then treated with 1 M HCl (5 mL) at 298 K for 30 min to desorb the dye. The washing process was repeated with 0.1 M HCl (5 mL). The concentrations of the desorbed PRH in the combined washings was then determined to calculate the desorption efficiency.

The resin left in the centrifuge tube was washed with deionized water followed by an exposure to 1 M NaOH (20 mL) to regenerate the basic resin; the adsorption/desorption procedure was repeated four times. Centrifugation, instead of filtration, ensured no loss of the resin. Note that ethanol and acetone were used to desorb the rosaniline from the resin, and was found to be unsuccessful.

5.4 Results and Discussion

5.4.1 Resin Synthesis

Cyclopolymerization of diallylammonium salts, pioneered by Butler [1,8], generated a variety of industrially important polymers whose backbones are embedded with five membered pyrrolidine rings (Scheme 5.1). It is the eighth most important architecture for synthetic macromolecules [9]. Cyclopolymerization in the presence of maleic acid leads to alternate copolymer [136]. Our objective was to synthesize a cross-linked polymer containing a high density of carboxylate (CO_2^-) which can be utilized for adsorptive removal cationic dyes by electrostatic attraction between the charges of opposite algebraic signs. Thus monomers **1** (45 mol%), **2** (45 mol%) and cross-linker **3** (10 mol%) in the presence of APS as the initiator afforded, in excellent yield (88%), the cross-linked polyzwitterionic acid (CPZA) **4**, having alternate disposition of the monomers **1** and **2** (Scheme 5.1). The resin composition is expected to match the feed composition as depicted in the Scheme because of such a high conversion to the resin. The alternate sequences of **1** and **2** are interspersed with homo sequence of monomer **1**, since diallyl motifs in **1** and **3** are in excess as compared to alkene motifs in maleic acid (**2**). Butler's cyclopolymerization afforded the new resin having residues of amino acid glycine and alternate sequence of **1** and **2**. Treatment of CPZA **4** with NaOH gave cross-linked anionic polyelectrolyte (CAPE) **5** (quantitative yield). Resin **5** contained a large density of CO_2^- groups and its cation exchange ability was assured by its high ion exchange capacity (IEC) value of 7.7 mmol g^{-1} . The surface area of CAPE **5** was found to be relatively large ($3.56 \text{ m}^2 \text{ g}^{-1}$) as compared to conventional ionic resins ($< 0.1 \text{ m}^2 \text{ g}^{-1}$) [195,229].

5.4.2 TGA Analyses

The TGA curves of resin **4**, **5** and the PRH-loaded resin, displayed shown in (Fig. 5.1a), show all three samples remained stable up to 200 °C, whereby $\approx 5\%$ is attributed to the loss of moisture. Basic resin **5** was found to be more stable than its acidic form **4** because the acid form allows the removal of water to form anhydride from two neighboring CO_2H groups, while the basic forms cannot form the anhydride. For resin **4**, A steep loss of $\approx 54.7\%$ in 240-280 °C range is attributed to the release of maleic anhydride units and CH_2CO_2 units from the polymer backbone [35,29]. The TGA curve for the PRH-loaded resin **5** was found to be like that of resin **5** except that wt% loss for the loaded resin is higher because of the associated loss of PRH. The residues at 800 °C were found to be 34% and 21% for resin **5** and the PRH-loaded resin **5**, respectively, the greater loss for the loaded resin **5** is attributed to the loss of PRH.

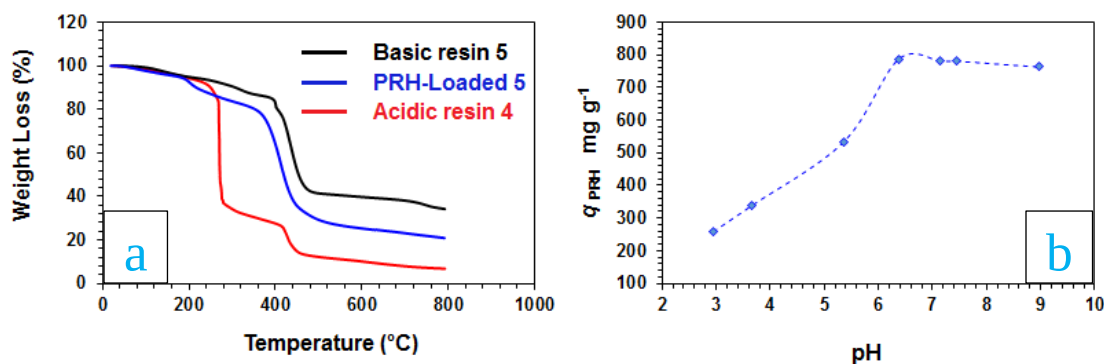
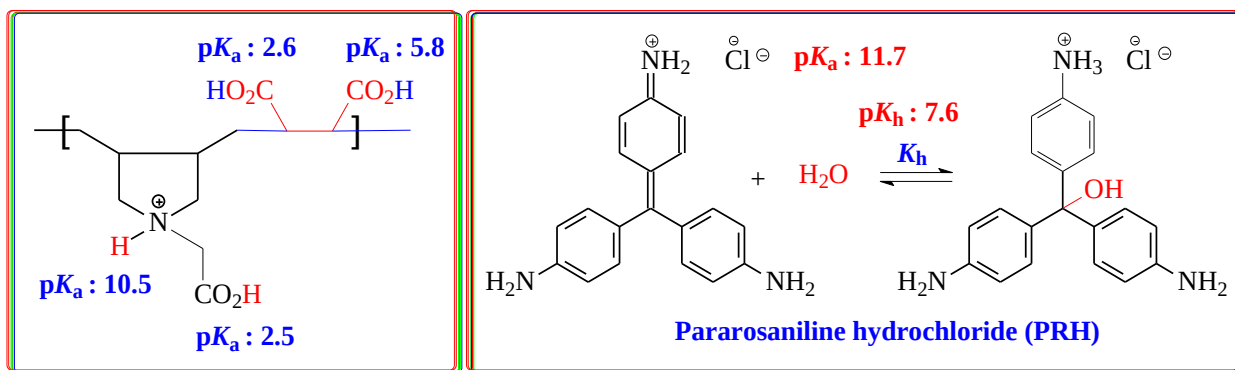


Figure 5.1 TGA (a) resin **4**, **5** and the PRH-loaded resin. Plots (b) of q_{PRH} versus pH at 298 K. [Experimental conditions: amount of resin **4**: 50 mg, volume of medium: 20 mL, initial PRH concentrations C_0 : 2000 ppm].

5.4.3 Effect of pH on Adsorption

pH versus adsorption capacity (q) plot, shown in (Fig. 5.1b), reveals the steep increase of q with increasing pH in the range 3.0-6.4. Over the pH-range 6.4-9.0, the dye uptake reaches maximum at a pH of 6.4, thereafter it decreases very slowly with the increase of pH. In the pH range 6.4-9, all three CO_2H , expected to be in the anionic form CO_2^- [136,197]. (Scheme 5.2), are involved in the electrostatic interaction with cationic PRH and as such the adsorption capacity remains constant in the pH range. The structure of PRH changes in an alkaline environment, which affects the color as well λ_{max} of adsorption. Hydrolysis constant $\text{p}K_{\text{h}}$ and $\text{p}K_{\text{a}}$ of PRH are reported [230] to be 7.6 and 11.7, respectively. Its $\text{p}K_{\text{h}}$ value of 7.6 shows that in an acidic medium of pH 6.37 or 6.0, it exists almost entirely in the non-carbinol cationic form (Scheme 5.2).



Scheme 5.2 $\text{p}K_{\text{a}}$ and $\text{p}K_{\text{h}}$ values of several acidic centers.

However, a slight decrease of adsorption capacity (q) at the higher pH values may be attributed to the decrease of cationic species of PRH. At lower pH values, the undissociated CO_2H groups are not capable of trapping PRH, and as such q_{PRH} will remain low.

5.4.4 Adsorption Kinetics

5.4.4.1 Lagergren First- and Pseudo-Second Order Kinetics, and Intraparticle Diffusion Model

The pH of the solution was measured during the adsorption process; an increase in pH in the range 5.55-6.37 was observed as it inches towards the equilibrium at 25°C. pH of natural PRH is 5.91; upon adsorption, neutral NaCl is released and the acidic motifs of PRH^+ becomes a part of insoluble resin, thereby increasing the pH of the system.



At 60 min interval, the PRH removal efficiencies have become 77, 80 and 78% at 298, 213 and 228 K, respectively, while the adsorption process reached equilibrium at around 120 min (Figure 5.2). At 360 min the equilibrium removal values become 98, 97 and 96% at 25, 40 and 55 °C. The faster kinetics for the adsorption process is observed at higher temperatures, while the equilibrium %removal decreases with increasing temperatures because of the thermodynamics of the process (see the inset showing the expanded view of the %removal at the time of 7 h.

Similar pattern is observed in the adsorption capacity q_t versus time plots (Fig. 5.3a). The q_t increases with time and attains equilibrium: $\text{PRA} + \text{Resin} \rightleftharpoons \text{Resin} \rightarrow \text{PRA}$ in a relatively short time. The inset, shows the equilibrium q_e value's continuous decrease with the increase in temperature. The kinetics of the adsorption process were examined using Eq. (4) (Fig. 5.3b), Eq. (5) (Fig. 5.3c), and Eq. (6) (Fig. 5.3d):

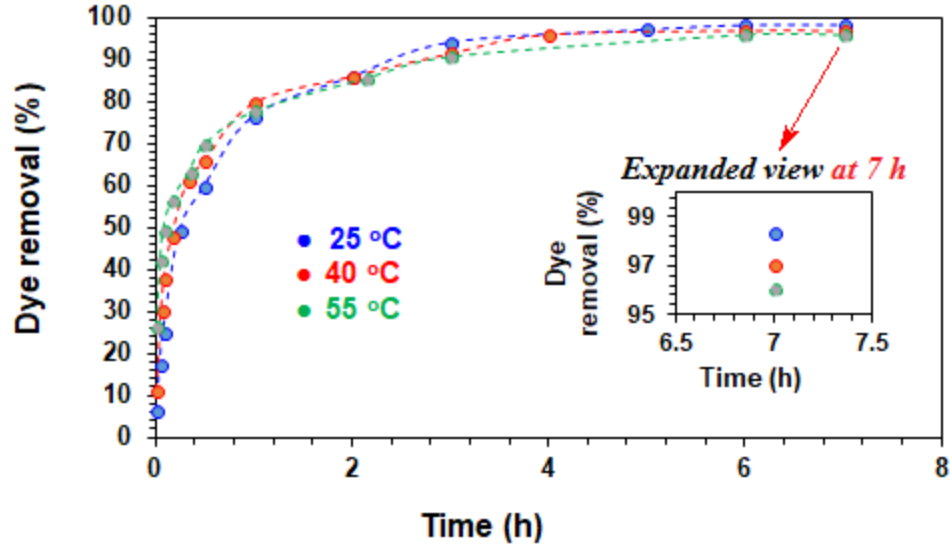


Figure 5.2 Percent PRH removal by resin 5 versus time at various temperatures. [Experimental conditions: amount of resin 5: 250 mg, volume of medium: 100 mL, initial PRH concentrations C_0 : 2000 ppm, pH 6.37].

Lagergren first order:
$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (4)$$

Pseudo – second order:
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (5)$$

Intraparticle diffusion:
$$q_t = x_i + k_d t^{0.5} \quad (6)$$

Where k_1 , k_2 and k_p represent the respective rate constants, while the adsorption capacities at time t and at equilibrium are denoted by q_t and q_e , respectively. As evinced by the R^2 values and matching of the q_{cal} and q_{exp} values, the kinetic data fit the second order model better thereby suggesting chemical nature of the adsorption process [231] (Table 5.1).

Besides fast film diffusion of the adsorbate to the sorbent, the adsorption process traverses through a slower intraparticle diffusion in the resin pores. A q_t versus $t^{0.5}$ plot as per Eq. (6)

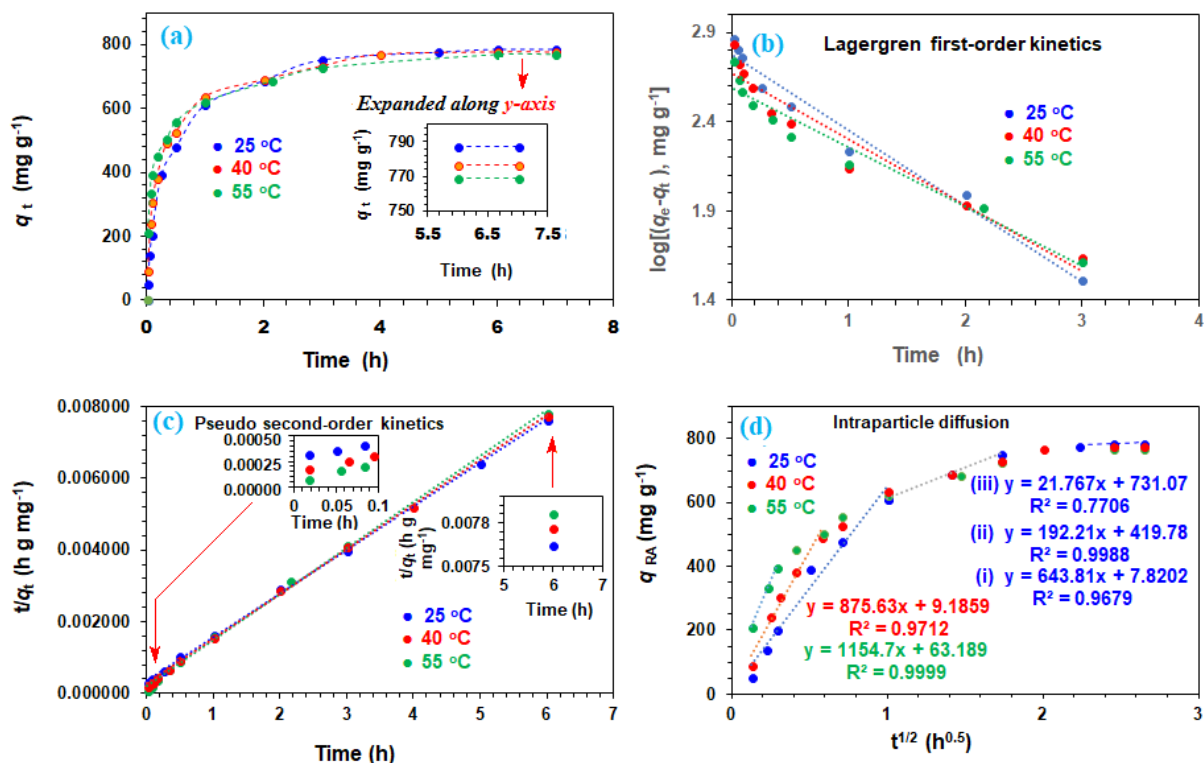


Figure 5.3 Adsorption from 2000 ppm PRH Solutions (100 mL) at pH 6.37 onto CAPE 5 (250 mg) at ●25, ●40, and ●55 °C: (a) Adsorption Capacity Versus Time Plots; Kinetic Plots of (b) First-order, (c) Pseudo second-order, and (d) Intraparticle Diffusion.

- is expected to shed light on the rate-limiting step, whereby a linear plot with a zero-intercept value would confirm the intraparticle diffusion as the rate-determining step [199, 200]. The multilinear [201] plot (Fig. 5.3d) at 298 K comprises the initial faster instantaneous adsorption (and film diffusion) with higher slope (k_{d1}), while the second linear section represents the intraparticle diffusion with a lower slope (k_{d2}) where x_i is proportional to boundary layer thickness (Table 5.1) [200, 172]. Thus, both film and intraparticle diffusion control the kinetics of the adsorption process.

Table 5.1 Lagergren Kinetic Model and Intraparticle Diffusion Model Parameters for Pararosaniline Adsorption on Resin 5 at Different Temperatures.

Temp (K)	$q_{e, \text{ exp}}$ (mg g ⁻¹)	k_2 (h ⁻¹ g mg ⁻¹)	h^a (h ⁻¹ mg g ⁻¹)	$q_{e, \text{ calc}}$ (mg g ⁻¹)	R^2	E_a (kJ mol ⁻¹)
<i>Pseudo second-order</i>						
298	787.2	0.00416	2812	822	0.9995	20.1
313	776.8	0.00630	4000	797	0.9991	
328	768.8	0.00873	5252	776	0.9981	
Temp (K)	$q_{e, \text{ exp}}$ (mg g ⁻¹)	k_1 (h ⁻¹)		$q_{e, \text{ calc}}$ (mg g ⁻¹)	R^2	
<i>Pseudo first-order</i>						
298	787.2	0.977		595	0.9532	
313	776.8	0.971		495	0.9614	
328	768.8	0.767		392	0.9479	
Temp (K)	k_{di} mg g ⁻¹ h ^{-1/2}	x_i (mg g ⁻¹)		R_i	R^2	
<i>Intraparticle diffusion model</i>						
298	644 (k_{d1})	7.82 (i=1)		0.990	0.9679	
	192 (k_{d2})	420 (i=2)		—	0.9988	
	21.8 (k_{d3})	731 (i=3)		—	0.7706	

^aInitial adsorption rate $h = k_2 q_e^2$.

Eq. (7) describes the relationship between initial adsorption factor (R_i), x_i and q_e .

$$R_i = 1 - \frac{x_i}{q_e} \quad (7)$$

The instantaneous adsorption and adsorption by film diffusion in the q_t range 0-613 mg g⁻¹

¹ accounts for 78% (i.e., 100×613/787) adsorption since the equilibrium q_e is 787 mg g⁻¹,

while the slower second linear portion in the q_t range 613-754 (i.e., 18 % of overall

adsorption) is controlled by the intraparticle diffusion process (Fig.5.3d). The adsorption of PRH, for instance at 298 K, has R_i value of 0.99 [i.e., $1 - (7.82/787)$], implying that instantaneous adsorption accounts for a negligible 1% only (Table 5.1).

5.4.5 Infrared Spectra

An IR sample of the PRH-loaded CAPE 5 was prepared by stirring a mixture of the resin (100 mg) with 2000 ppm PRH solution (40 mL) for 24 h at 298 K. After filtration and washing with deionized water, the loaded resin was dried under vacuum at 50 °C. Fig.5.4 displays the IR spectra of PRH, acidic resin 4, basic resin 5, and MB-loaded basic resin. While the absorption at 1716 cm^{-1} was due to C=O stretch of COOH in CPZA 4, the absorption bands at 1400 and 1624 cm^{-1} were attributed to the symmetric and antisymmetric stretching of COO^- in the dipolar motifs of 4, respectively. In CAPE 5, the COO^- appeared at 1400 and 1585 (overlapping) cm^{-1} . The absorption peaks agree with those observed for simple amino acids [202].

In the spectrum for PRH (Fig. 5.4d), peaks at 1580 cm^{-1} is attributed to the vibration of the aromatic ring, while the absorption band at 1456 and 1360 cm^{-1} could be assigned to the C–N stretching vibrations. Even though the characteristic absorption peaks of PRH are not shifted to any significant extent, C=O absorption peak in the spectrum of PRB-loaded 5 (Fig. 5.4a) have shifted to 1650 cm^{-1} indicating the interactions of the anionic carboxyl groups with cationic PRH.

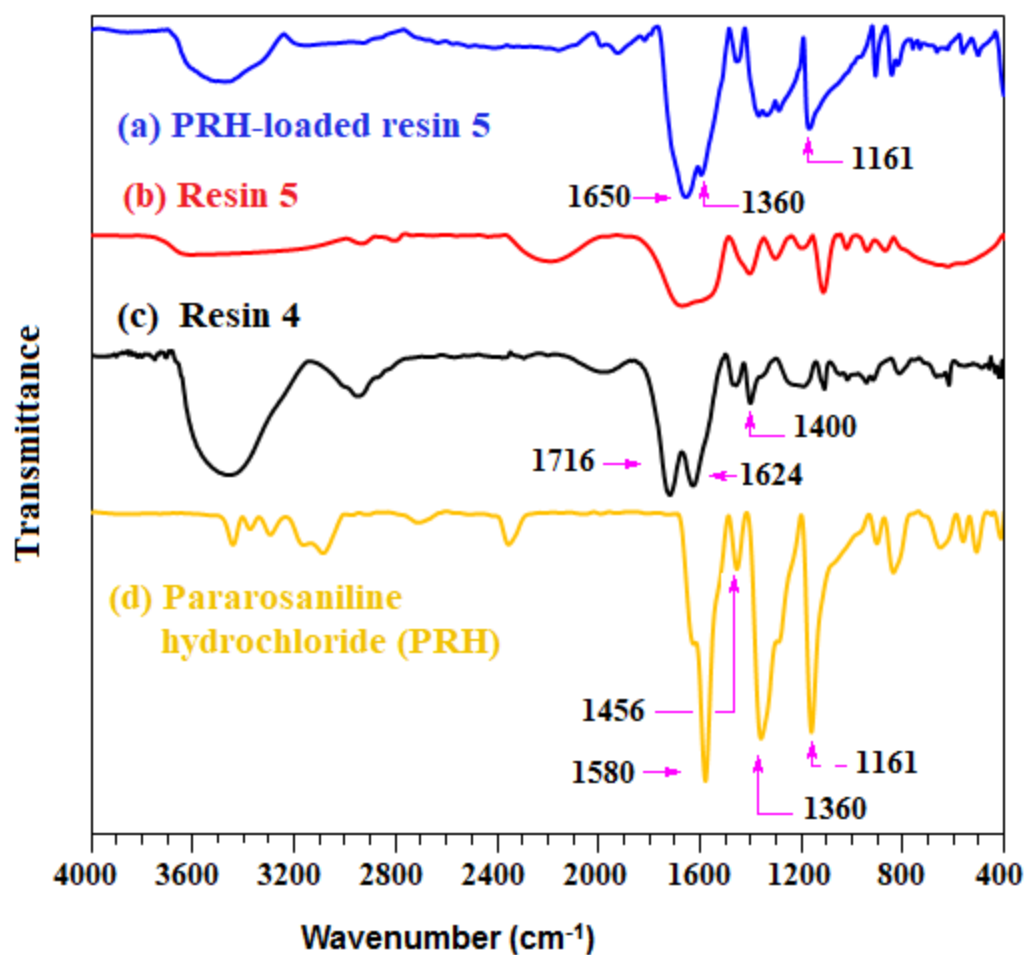


Figure 5.4 IR Spectra of (a) PRH-loaded Resin 5, (b) Resin 5, (c) Resin 4, and (d) PRH.

5.4.6 Energy of Activation

Arrhenius plot of $\ln k_2$ versus $1/T$ using Eq. (8) (Fig. 5.5a) gave the activation energy (E_a) of 20.1 kJ mol⁻¹ for the adsorption process (Table 5.1). The relatively smaller E_a value indicates the adsorption as a favorable process.

$$\ln k_2 = - \frac{E_a}{2.303RT} + \text{constant} \quad (8)$$

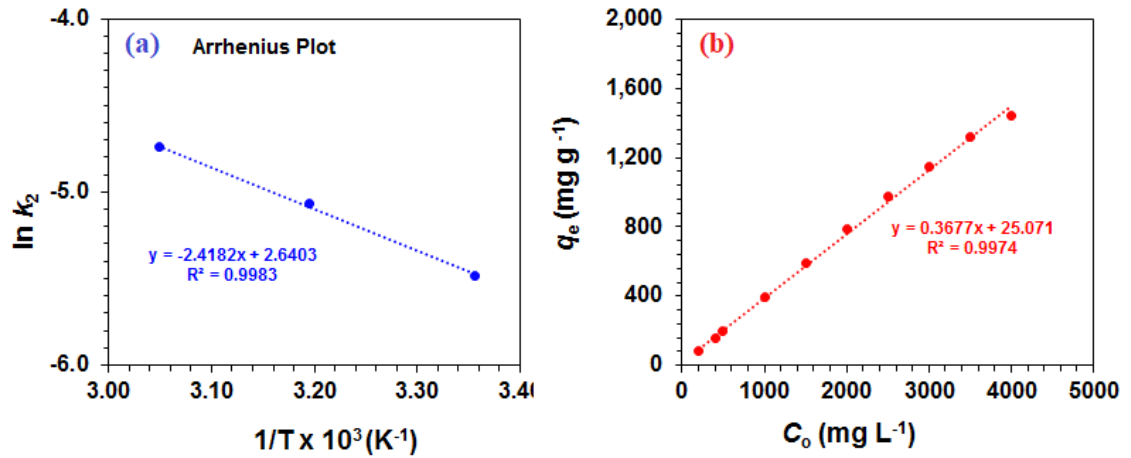


Figure 5.5 Arrhenius plot (a) and Initial Concentration (b) Versus Equilibrium Adsorption Capacity of Resin 5 for PRH at pH 6.37 at 298 K.

5.4.7 Thermodynamics of Adsorption

Several q_e and C_e were determined using various initial concentration (C_0) of the dye at 288, 298, 313, and 328 K. The Fig. 5.5b, depicting the q_e versus C_0 plot, shows a linear increase of q_e with C_0 , which is a consequence of shifting the equilibrium to right side of the equilibrium with the progressive increase of free PRH: $PRH_{free} + Resin \rightleftharpoons PRH_{ads} \rightarrow resin$.

The mechanism of the adsorption process was further explored using nonlinear isotherm models as described by Eqs. (9) - (11) involving the relationship between q_e and C_e , are considered.

$$\text{Langmuir isotherm: } q_e = \frac{q_{\max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (9)$$

$$\text{Freundlich isotherm: } q_e = K_f \cdot C_e^{1/n} \quad (10)$$

$$\text{Temkin isotherm: } q_e = B \cdot \ln (A \cdot C_e), \text{ where, } B = RT/b_T \quad (11)$$

where K_L is the Langmuir equilibrium constant ($L\ mg^{-1}$), and q_{max} is the maximum adsorption capacity of the PRH ($mg\ g^{-1}$). K_f represents Freundlich isotherm constant ($mg\ g^{-1}$), n denotes adsorption intensity. A_t , b_T and B represents Temkin isotherm equilibrium binding constant ($L\ g^{-1}$), Temkin isotherm constant and constant related to heat of sorption ($J\ mol^{-1}$), respectively.

The dimensionless thermodynamic equilibrium constant K_e° at various temperatures were determined using nonlinear isotherm plots at various temperatures, where the equilibrium constant K_L ($L\ mg^{-1}$) from Langmuir nonlinear plots must become dimensionless as described by Eq. (12) [228, 232, 233].

$$K_e^\circ = \frac{(1000 \cdot K_L \cdot M_w) \cdot [PRH]^\circ}{\gamma} \quad (12)$$

where the coefficient of activity was represented by dimensionless γ , $[PRH]^\circ$ is the standard PRH concentration ($1\ mol\ L^{-1}$) and M_w the molecular weight of the PRH ($323.8\ g\ mol^{-1}$).

Microcal Origin software (Version 7.5) were used for the nonlinear adsorption isotherm fitting and statistical analyses. The nonlinearized Langmuir isotherm plots were shown in Fig. 5.6. The R^2_{Adj} values of 0.9914, 0.9941, 0.9926 and 0.9917 at 288, 298, 313 and 328 K, respectively, indicates the excellent fitting of the experimental data to Langmuir isotherm model. The extracted parameters from the relevant nonlinear Langmuir plots (Fig.5.6a-d) are given in Table 5.2. As evident from the R^2 values, Langmuir plots fitted better than Temkin and Freundlich plots (Table 5.2). The small ΔH° value $24.8\ kJ\ mol^{-1}$ of reveals the exothermic and the physical nature of the adsorption process [234]. The negative ΔG° ensures the favorability of the adsorption process (Table 5.3).

Table 5.2 Langmuir, Freundlich, and Temkin, Isotherm Model Constants for Rosaniline Adsorption on CAPE 5 at 298 K.

Langmuir isotherm model		
$Q_{\max}$ (mg g ⁻¹)	K_L (L mg ⁻¹)	R^2
1534	0.0283	0.9954
Freundlich isotherm model		
n	k_f (mg ^{1-1/n} g ⁻¹ L ^{1/n})	R^2
2.74	180	0.9380
Temkin isotherm model		
A (L g ⁻¹)	B (J mol ⁻¹)	R^2
0.475	276	0.9830

Langmuir isotherm model (Eq. (9)) is based on the formation of a monolayer on a homogeneous sorbent surface where there are no interactions among the adsorbed molecules [204]. The outstanding performance by the resin is reflected by its q_m value of 1534 mg g⁻¹ at 298 K; not many resins are known to surpass this staggering adsorption capacity. In Temkin isotherm, the positive B ($= RT/b$) value of 276 J mol⁻¹ indicates the adsorption as an exothermic process (Table 5.2) [191].

The q_e versus T plot (Fig. 5.7a) reveals the decrease of q_e with increasing T . The thermodynamic parameters ΔH° , ΔS° and ΔG° ($= -RT \ln K_e^\circ$) were obtained from the Vant-Hoff plot (Eq. (13)) (Fig. 5.7b).

$$\ln (K_e^\circ) = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (13)$$

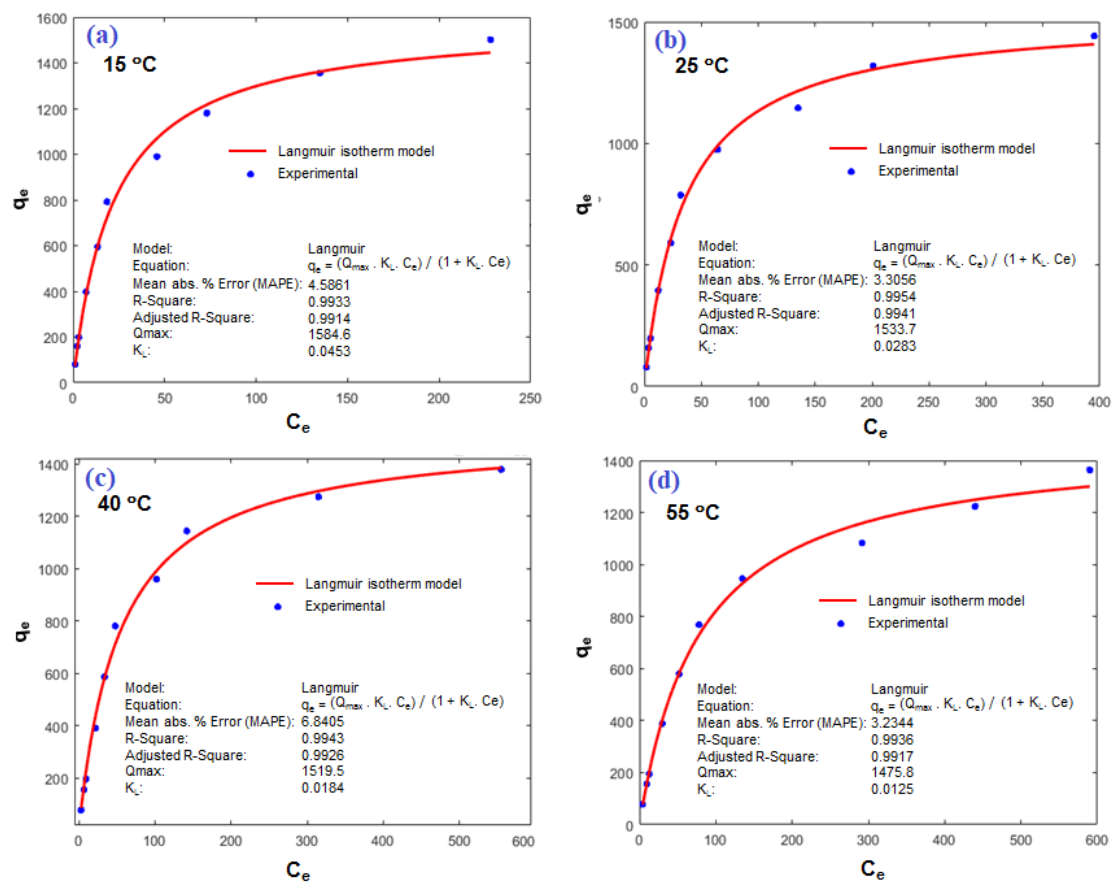


Figure 5.6 Nonlinearized Langmuir isotherm plots.

Table 5.3 Thermodynamic (ΔG^0 , ΔH^0 , ΔS^0) data for PRH adsorption on CAPE 5.

Temperature (K)	K_L^a (L mg ⁻¹)	$K_e^{o\ b}$ (unit less)	$\Delta G^0\ ^c$ (kJ mol ⁻¹)	ΔH^0 (kJ mol ⁻¹)	ΔS^0 (J mol ⁻¹ K ⁻¹)	R^2
288	0.0453	14668	-22.84	-24.8	-6.8	0.9903
298	0.0283	9163.5	-22.77			
313	0.0184	5957.9	-22.67			
328	0.0125	4047.5	-22.57			

^aLangmuir equilibrium constants from nonlinear isotherms; ^bMade dimensionless using Eq (16); ^c $\Delta G^0 = -RT \ln K$

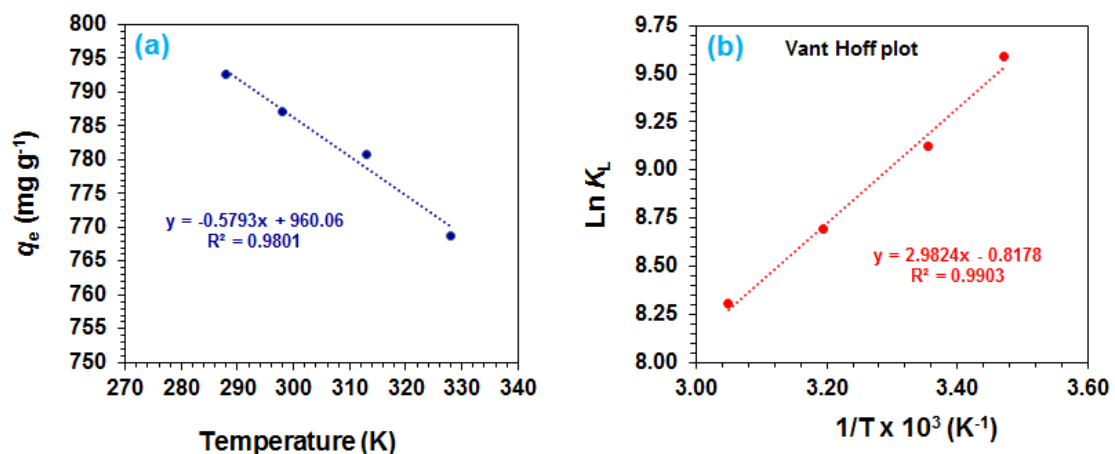


Figure 5.7 (a) Equilibrium adsorption capacity of CAPE 5 versus temperature, (b) Vant Hoff plot. [Experimental conditions; amount of resin: 50 mg, volume of medium: 20 mL, initial RA concentration: 2000 ppm; pH: 5.37].

5.4.8 SEM Images and EDX

The EDX spectrum PRH-loaded CAPE 5 (Fig. 5.8b), prepared as described for the preparation for IR sample, revealed the increase in the amount of C and N, and drastic decrease in Na and O as compared to those of the unloaded resin (Fig. 5.8a), thereby confirmed the chemical exchange between cationic PRH and Na⁺ (Fig. 5.8b).

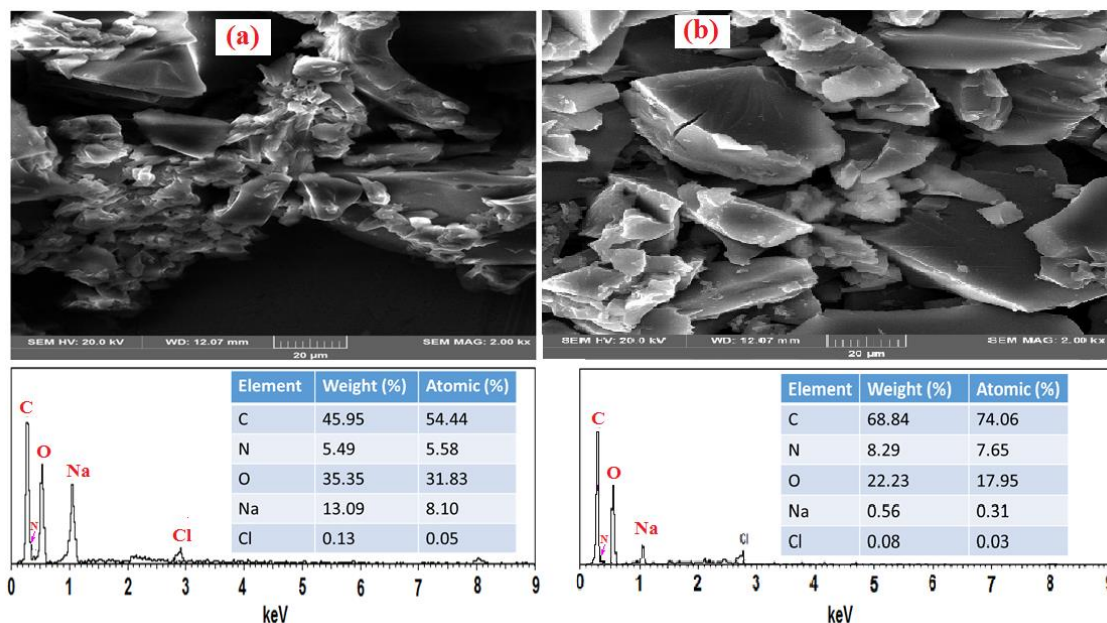


Figure 5.8 SEM and EDX Analysis for CAPE 5 (a) Unloaded and (b) Loaded with PRH.

5.4.9 Mechanism of Adsorption

The Elovich model Eq. (14) excellent fit ($R^2 = 0.9906 - 0.9970$) of the kinetic data at various temperatures, indicating that the process occurs by chemical adsorption (Fig. 5.9a). The initial adsorption rate represented by α values were found to be 9.26×10^3 , 1.57×10^4 and 5.77×10^4 $\text{mg g}^{-1} \text{h}^{-1}$ at 25, 40 and 55 °C, respectively. The corresponding desorption rates (i.e β values) were 0.00720, 0.00793 and 0.0103 g mg^{-1} . The high and low values of α and β thus make the adsorption as essentially an irreversible process [172]. Pseudo second-order kinetics also support the process as chemical adsorption. The small values of R_L (almost zero in most cases) seem to suggest the process as irreversible (Table 5.4).

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (14)$$

Desorption studies can help elucidating the mechanism of an adsorption process. Desorption by water indicates that the attachment of the dye onto the adsorbent is by weak bonds. If a strong acid such as HCl can dislodge the dye, its attachment to the resin may be attributed to ion exchange or electrostatic attraction.

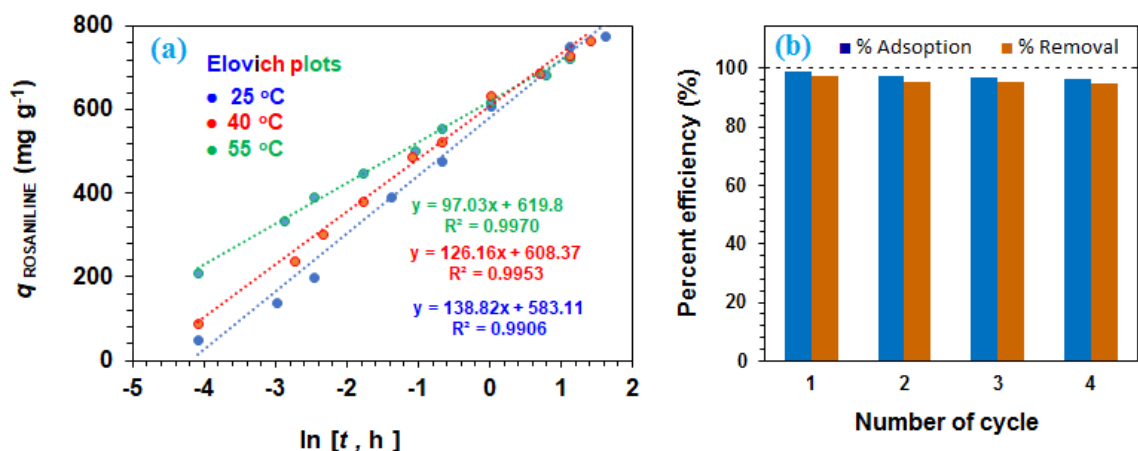


Figure 5.9 (a) Linear fits of Elovich kinetic model to the PRH adsorption at concentrations of 2000 ppm (100 mL) pH 6.37 in the presence of resin 5 (250 mg) at 25, 40 and 55 °C, (b) Adsorption/desorption repeated cycles of PRH onto resin 5. [Experimental conditions: amount of resin 5: 100 mg, volume of medium: 40 mL, initial PRH concentrations C_0 : 2000 ppm, pH 6.4].

5.4.10 Recycling

The four cycles of adsorption/desorption revealed the efficiencies of $\approx 95\%$ (Fig. 5.9b), thereby showing excellent recovery with stable efficiency.

5.4.11 Removal of Cd(II) and Simultaneous Removal of PRH and Cd(II) from Aqueous Solution

The release of heavy metal ions from various industrial effluents to water bodies poses the greatest danger to the environment and their inherent toxicity poses formidable health

problems to various living organisms [235]. The toxicity of cadmium in human body leads to various diseases [236,237], and its threshold level stipulated by WHO in drinking water is 0.003 mg/L [64]. Adsorption capacities for Cd(II) were determined for various concentration of Cd(II) ions (prepared using Cd(NO₃)₂) in the range 100-1000 ppm at pH 5.3 using resin 4 (50 mg) and Cd(II) solution (20 mL). ICP-MS (Model: ICP-MS XSERIES-II) was utilized to determine the concentration of Cd(II) ions. Langmuir isotherm plot (Eq. 10) gave the q_m of 248 mg g⁻¹ (Fig. 5.10a). Cd(II) uptake was found to increase with increasing Cd(II) concentrations (Fig. 5.10b).

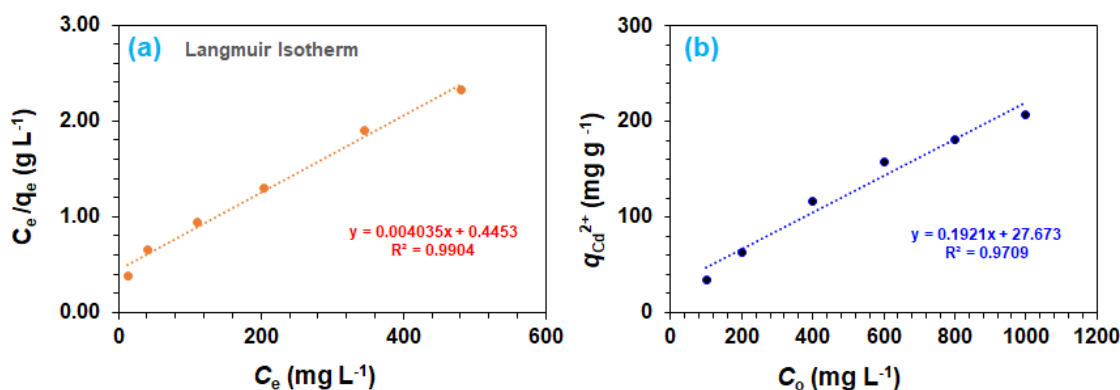


Figure 5.10 (a) Langmuir isotherm of the adsorption of Cd²⁺ ions on resin 4 at 298 K, (b) Initial concentration versus equilibrium adsorption capacity of resin 4 for Cd²⁺ ions at 298 K. [Experimental conditions; amount of resin: 50 mg, volume of medium: 20 mL, temperature: 298 K, initial Cd²⁺ concentrations: 100, 200, 400, 600, 800, and 1000 ppm], pH 5.3].

5.4.12 Industrial Wastewater Remediation

An industrial wastewater matrix (pH: 5.5) (20 mL) was treated with Resin 5 (50 mg) at 298 K in the absence and presence of Cd(II) (10,000 µg L⁻¹) and PRH (10,000 µg L⁻¹) for overnight. The concentrations of priority toxic metals like Hg(II) and Pb(II) were reduced

to sub-ppb levels. For the spiked samples, PRH and Cd(II) concentrations are also drastically reduced (Table 5.4). Resin 4 was also able to trap simultaneously both PRH and Cd(II) quite successfully (Table 5.4).

Table 5.4 Comparison of Cd²⁺ and Rosaniline (RA) Dye Concentrations in Wastewater and Deionized Water Samples Before and After the Treatment with Resin 4 or 5 at 298 K.

Metal/Dye	Original Sample (µg L ⁻¹)	After Treatment (µg L ⁻¹)	
		Original Sample Treated with Resin	Original Sample Spiked with Cd ²⁺ (10,000 µg L ⁻¹) and RA (10,000 µg L ⁻¹) and then Treated with Resin
Wastewater having pH 5.5 Treated with Resin 5			
Cr	1.46	0.32	0.66
Fe	22.1	1.31	1.54
Co	1.28	0.26	0.43
Ni	1.99	1.14	1.21
Cu	8.26	1.22	1.48
Al	22.5	8.23	10.2
Pb	3.08	0.98	1.22
Hg	1.49	0.47	0.64
Cd	88.4	1.01	798
PRH	0	0	889
Deionized water Cd ²⁺ (10,000 µg L ⁻¹) and RA (10,000 µg L ⁻¹) treated with Resin 4 at pH 5.5			
Cd	—	—	400
PRH	—	—	1790

Table 5.5 A comparative Adsorption Capacities (q_m) of Resin 5 for PRH (or Basic Fuchsin) with other Types of Adsorbents.

Adsorbents	q_m (mg/g)	Ref.
Euryale ferox Salisbury seed shell	19.5	[17]
Graphene/ β -cyclodextrin composite	426	[48]
Magnetic ZnFe_2O_4 @chitosan encapsulated in graphene oxide	244	[19]
Acrylamide copolymer grafted on Loess clay	130	[20]
Anionic polyacrylamide/graphene oxide aerogels	1034	[21]
Magnetic and non-magnetic modified sugarcane bagasse	419	[51]
Modified peat-resin particle	280	[52]
KMnO_4 modified Typha orientalis activated carbon	145	[53]
Activated carbon/ferrospinel composite	101	[14]
Tubular structured ordered mesoporous carbon	1403	[54]
Sodium sulfite modified cation exchange resin	127	[7]
Aminocarboxylate/maleic acid resin	1534	This work

5.5 Conclusion

A resin loaded with carboxylate motifs has been prepared in excellent yield using cyclopolymerization reaction. The resin is made from inexpensive starting materials and its synthesis can easily be scaled up. The equilibrium experimental data fit perfectly with the Langmuir isotherm. The resin turned out to be a superadsorbent for PRH, used as a model cationic dye, having a maximum adsorption capacity of 1534 mg g^{-1} . The resin outperforms many a recently reported material (Table 5.5), and hence becomes a potent candidate for the remediation of industrial waste water. The PRA removal mechanism involves pseudo second-order kinetics. The negative ΔH° and ΔG° values ensured the favorability of the exothermic adsorption process. The adsorption/desorption efficiencies were excellent to

ensure the recycling and reuse of the resin. The very impressive performance accorded the resin a prestigious place among many sorbents in recent works. The ultrahigh adsorption capacity (*vide infra*) for PRH, (used as the model basic cationic dye because of its extensive use in various industries) suggests that the resin has great potential and a promising future to remove dyes from industrial dye-wastewater. The presence of numerous CO_2^- in **5** is anticipated to make it a superadsorbent to trap cationic dyes. Note that the current resin has successfully removed dye and Cd(II) pollutants from an industrial wastewater matrix (pH: 5.5).

CHAPTER 6

CONCLUSION AND FUTURE WORK

6.1 Conclusion

The diallylammionium monomers **1** and **12** (Chapter 2) have been copolymerized successfully using maleic acid **2** via alternate cyclopolymerization resulting in to polyzwitterion PZ **4** ($\text{ZH}_2^{\pm}$). While monomer **1** with maleic acid **2** upon treatment with concentrated HCl afforded alternate cationic polyelectrolyte copolymer CPE **14**. polyampholyte **15** have been synthesized by an exothermic polymerization of monomers **11** with Maleic acid **2**. The diester groups in **15** were hydrolysed by using 6 M HCl to generate **4** in order to correlate the solution properties of **4** and **15**. The successful formation of these synthesized polymers in term of functional groups, bonds, and stage of thermal stability and dissociation was proven qualitatively by ^1H -NMR, ^{13}C -NMR, IR, spectroscopy and TGA.

In order to compare the degree of homopolymerization of monomer **1** and copolymerization between **1** and Maleic acid **2** using different imitators in aqueous solution found that homopolymerization of **1** as well as its copolymerization with maleic acid **2** using AIBN as initiator have been reported to give polymers in low yields (typically below 20%) and it observed that the High initiator concentrations (up to 5 mol-%) were necessary to obtain the polymers while the use of APS initiator (≈ 10 mol%) at higher polymerization temperature ($98\text{ }^\circ\text{C}$) for a short duration (20 min) afforded the alternate PZ **4** in very good isolated yields ($\approx 70\%$).

The solubility behavior of synthesized polymers have been tested and it's showed that unlike the majority of electroneutral polymers. For instance, PA (+ -) **15** was found to be water-soluble. A possible point behind that could be that both the positive nitrogens as well as the negative charge centers on the carboxyl are in a crowded environment, hence preventing them from intragroup, intra- and inter-chain associations required for the appearance of ampholytic interactions.

To investigate the degree of polymerization in pH-responsive tetraprotic **4** and diprotic **15**, a pH-induced changes of backbone charges have been studied in detail by viscometric technique and it showed having identical degree of polymerization.

The potentiometric titrations have been applied in polymers **4** and **15** to determined protonation constants (or pK_a) of the CO_2^- (or CO_2H) and trivalent nitrogen (or protonated NH^+).

The antiscalant properties using supersaturated solution of CaSO_4 have been Evaluation for PZ **4** it implied a remarkably effective in inhibiting the formation of calcium sulfate scale for days at 40 °C.

Several diallylamine derivatives **1a,b**, **5** and **7** as well as quaternary diallyldialkylammonium chlorides **15a,b** has been terpolymerized with MA and SO_2 using APS initiator or UV light at a wavelength of 365 nm in an attempt to obtain Amine (salt)-MA- SO_2 terpolymer (Chapter 3). The results indicated that In contrast to reported literature, only 1-2 mol% of MA was incorporated into the polymer chain mainly consisting of Amine (salt)- SO_2 copolymers. And that might due to big difference in the rate of

propagation of Amine (salt)-SO₂ than either Amine (salt)-MA or MA-SO₂ under the polymerization conditions.

The Polyampholyte **13** has been synthesized in excellent yield constructed of **1c**-MA copolymer which under pH-induced changes was transformed to cationic **19**, polampholyte-anionic **20**, and dianionic polyelectrolyte **21**. All the synthesized polymeric structures have been elucidated by ¹H-NMR, ¹³C-NMR, IR, and TGA. The solubility behavior, antiscalant, viscosity in the presence of salt NaCl, and basicity constant have been studied in details.

Alternate polymerization involving diallyl amine salt has obtained the novel resin loaded with carboxylate motifs in excellent yield for the first time (Chapter 4). The resin considered be a super-adsorbent for MB, used as a model cationic dye, having a q_m of 2101 mg g⁻¹. The experimental process showed an extraordinarily fast adsorption rate; in a 3000 mg L⁻¹ MB solution. It has exhibited an outstanding efficiency better than many a recently reported resins (Table 4.8). The recycling process of the resin has been studied and showed remarkable efficiency.

6.2 Future Work

The synthesized polymers showed very good performance in application of water treatment as scale inhibitors as well as metal ions and organic dye removal. There are some scopes for the future study to be taken in account as follows:

- The synthesized polymers could be tested as corrosion inhibitors.
- These polymers can be applicable for the separation techniques such as in the protein separation.

- Some biological study for these polymers could be performed like the toxicity because if considered them to use in separation via membranes.
- These new prepared polymers could need a further characterizations using advanced techniques such as combination of NMR and fluorescence spectroscopies and/or dynamic light scattering specially in case of study of the pH-dependent aqueous solution properties.
- The new synthesized novel resin (chapter 4) may be a good candidate represents another important family of cross-linked polyelectrolytic/anionic resins might have another applications for both academic and industrial.

CHAPTER 7

REFERENCES

- [1] G. B. Butler, Cyclopolymerization and cyclocopolymerization, Marcel Dekker, New York, (1992).
- [2] S. Kudaibergenov, W. Jaeger, A. Laschewsky, *Adv. Polym. Sci.*, (2006), **201**, 157-224.
- [3] P. K. Singh, V. K. Singh, M. Singh, *E-Polymers*, (2007), **030**, 1-34.
- [4] W. Jaeger, J. Bohrisch, A. Laschewsky, *Prog. Polym. Sci.*, (2010), **35**, 511-577.
- [5] S. A. Haladu, S. A. Ali, *J. Polym. Sci., Part A: Polym. Chem.*, (2013), **51**, 5130-5142.
- [6] O. C. S. Al-Hamouz, S. A. Ali, *J. Polym. Sci., Part A: Polym. chem.*, (2012), **50**, 3580-3591.
- [7] S. A. Ali, H. A. Al-Muallem, O. C. S.O. Al-Hamouz, M. K. Estaitie, *React., Funct. Polym.*, (2015), **86**, 80–86.
- [8]. G. B. Butler, **38**, 3451-3461. Cyclopolymerization, *J. Polym. Sci., Part A: Polym. Chem.*, (2000),
- [9] F.C. McGrew, Structure of synthetic high polymers, *J. Chem. Educ.* 35 (1958) 178–186.

- [10] S. A. Ali, Othman Charles S. Al-Hamouz, *Polymer*, (2012), **53**, 3368-3377.
- [11] Y. Umar, B. F. Abu-Sharkh, Sk. Asrof Ali, *Polymer*, (2005), **46**(24), 10709-10717.
- [12] S. A. Ali, Ahmed, S. Z. Wazeer, M. I. M. Hamad, E. Z, (1997), **38** (13), 3385-3393.
- [13] A. B. Lowe; C. L. McCormick; *Chem. Rev.*, (2002), **102**, 4177-4189.
- [14] N. Y. Abu-Thabit, H. A. Al-Muallem, S. A. Ali, *J. Appl. Polym. Sci.*, (2011), **120**, 3662-73.
- [15] W. F. Lee, C. H. Lee, *Polymer*, (1997), **38**(4), 971-979.
- [16] P. Anton, A. Laschewsky, *Makromol Chem.*, (1993), **194**, 601- 624.
- [17] D. B. Thomas, R. S. Armentrout, C. L. McCormick, *Polym Prepr.*, (1999), **40**, 275-276.
- [18] S. A. Ali, A. Rasheed, M. I. M. Wazeer, Synthesis and solution properties of a quaternary ammonium polyampholyte, *Polymer*, (1999), **40** (9), 2439-2446.
- [19] M. M. Ali, H. P. Perzanowski, S. A. Ali, *Polymer*, (2000), **41**(15), 5591-5600.
- [20] T. A. Wielema, J. B. F. N. Engberts, Zwitterionic polymers - I. Synthesis of a novel series of poly(vinylsulfobetaines). Effect of structure of polymer on solubility in water, *Eur Polym J.*, (1987), **23**, 947-950.
- [21] J. C. Salamone, W. Volksen, A. P. Olson, S. C. Israel, Aqueous solution properties of a poly(vinyl imidazolium sulfobetaine), *Polymer*, (1978), **19**(10), 1157-1162.

- [22] M. Skouri, J. P. Munch, S. J. Candau, S. Nyret, F. Candau, *Macromolecules*, (1994), **27**(1), 69-76.
- [23] P. G. Higgs, J. F. Joany, *J. Chem. Phys.*, (1991), **94**(2), 1543-1554.
- [24] S. M. Waziri, B. F. Abu-Sharkh, S. A. Ali, *Fluid Phase Equilibria*, (2003), **205**, 275-290.
- [25] A. V. Dobrynin, M. Rubinstein, *J. Phys II*, (1995), **5**, 677-695.
- [26] P. G. Higgs, JF. Joany, *J. Chem Phys.*, (1991), **94**, 1543-54.
- [27] J. C. Salamone, W. Volksen, AP. Olson, SC. Israel, *Polymer*, (1978), **19**, 1157-1162.
- [28] M. Skouri, J. P. Munch, SJ. Candau, S. Nyret, F. Candau, *Macromolecules*, (1994), **27**, 69-76.
- [29] M. Hahn, W. Jaeger, R. S. Schmolke, J. Behnisch, Synthesis of regular polyampholytes by copolymerization of maleic acid with allyl and diallyl amine derivatives, *Acta Polymerica*, (1990), **41**(2), 107-112.
- [30] A. I. Vorob'eva, G. R. Sultanova, A. K. Bulgakov, V. I. Zainchkovskii, S. V. Kolesov, *Pharmaceutical Chemistry Journal*, (2013), **46**(11), 653-655.
- [31] C. Note, J. Ruffin, B. Tiersch, J. Koetz, *Journal of Dispersion Science and Technology*, (2007), **28**, 155–164.

- [32] M. Fechner, M. Kramer, E. Kleinpeter, J. Koetz, *Colloid Polym. Sci.*, (2009) **287**, 1145–1153.
- [33] Z. E. Ibraeva, M. Hahn, W. Jaeger, L. A. Bimendina, S. E. Kudaibergenov, Solution properties and complexation of polyampholytes based on N,N-dimethyldiallylammonium chloride and maleic acid or alkyl (aryl) derivatives of maleamic acids, *Macromol. Chem. Phys.*, (2004), **205**(18), 2464–2472.
- [34] M. Fechner, J. Koetz, *Macromol. Chem. Phys.*, (2011), **212**, 2691–2699.
- [35] F. Rullens, M. Devillers, A. Laschewsky, New regular, amphiphilic poly(ampholyte)s: synthesis and characterization, *Macromolecular Chemistry and Physics*, (2004), **205**(9), 1155–1166.
- [36] F. Rullens, M. Devillers, A. Laschewsky, *J. Mater. Chem.*, (2004), **14**, 3421-3426.
- [37] A. F. Thünemann, K. Sander, and W. Jaeger, *Langmuir*, (2002), **18**(13), 5099-5105.
- [38] F. Rullens, N. Deligne, A. Laschewsky, M. Devillers, *J. Mater. Chem.*, (2005), **15**, 1668–1676.
- [39] M. Al-Shammiri, M. Safar, M. Al-Dawas. *Desalination*, (2000), **128**, No. 1, 1-16.
- [40] R. J. Davey, S. J. Jancic, E. J. De Jong, *North-Holland Publishing Co.*, (1982), **81**, 123-135.
- [41] D. Logan, J. L. Walker, Scale Control in High Temperature MSF Evaporators with Concurrent Acid and Inhibitor Treatment, Calgon Corporation, Pittsburgh, Pennsylvania. (1982)

- [42] A. Harris, *Desalination Technology*, Ed. A. Porteous, (1983), pp. 44-48.
- [43] AG. I. Dalvi, M. N. K Mohammad, S. Al-Sulami, R. Al-Rasheed, K. Sahul, *Technical Report*, (1999), No. TR 3803/APP 95001, SWCC.
- [44] S. Matsumura, S. Mada, S. Yoshikawa, *Polymer Mater. Sci. Eng.*, (1990), **62**,984.
- [45] T. Ouchi, Shiratani, M. Jinno, M. Hirao, M. Ohya, Y., *Macromol. Chem., Rapid Commun.*, (1993), **14**, 825.
- [46] T. Hayashi, M. Iwatsuki, *Biopolymers*, (1990), **29**, 549.
- [47] G. L. Jain, A. R. Ray, *Macromol. Chem.*, (1981), **182**, 2557.
- [48] T. Nakato, A. Kusono, T. Kakuchi, *J. Polym. Sci.: Part A: Polym. Chem.*, (2000), **38**, 117-122.
- [49] W. Zarges, T. Groth, W. Joentgen, A. Groschl, *USP*, (2001), 6,187,195 B1, Feb 13.
- [50] J. E. Zuback, Desalination of water containing high silica content, PCT Int. Appl., WO, (2009), 10, 2442 A1 20090820.
- [51] K. S. Rajan, J. Murase, A. E. Martell, New multidentate ligands VII. Ethylenediamine-N,N'-diacetic-N,N'-bis(methylenephosphonic) acid, (1969).
- [52] S. J. Westerback, A. E. Martell, *Nature*, (1956), **178**, 321-322.
- [53] Y. Yamashoji, T. Matsushita, T. Shono, *Technol Rep Osaka Univ.*, (1985), **35** (1800-1818): 331-337.

- [54] K. Riedelsberger, W. Jaeger, *Des. Monomers Polym.*, (1998), **1**, 387–407.
- [55] O.C.S. Al-Hamouz, S. A. Ali, *Separation and Purification Technology*, (2012), **98**, 94–101.
- [56] J. Liu, Y. Ma, T. Xu, G. Shao, *J. Hazard. Mater.*, (2010), **178**, 1021–1029.
- [57] R. Vinodh, R. Padmavathi, D. Sangeetha, *Desalination*, (2011), **267**, 267–276.
- [58] G. Camci-Unal, N. L. B. Pohl, *J. Chem. Eng. Data*, (2010), **55**, 1117–1121.
- [59] R. Kiefer, W.H. Höll, *Ind. Eng. Chem.*, (2001), **40**, 4570–4576.
- [60] H. K. Boparai, M. Joseph, D.M. O’Carroll, *Journal of Hazardous Materials*, (2011), **186**, 458–65.
- [61] S. H. Hasan, M. Talat, S. Rai, *Bioresource Technology*, (2007), **98**, 918–28.
- [62] WHO, Copper in drinking-water, guidelines for drinking-water quality. World Health Organization, Geneva, (2003).
- [63] A. Netzer, D. E. Hughes, *Water Res.*, (1984), **18**, 927-33.
- [64] WHO, Guidelines for Drinking Water Quality: Recommendations, World Health Organization, Geneva, (2008), vol. **1**, 3rd Ed.
- [65] T. J. Butter, L. M. Evison, I. C. Hancock, F. S. Holland, K. A. Matis, A. Philipson, A. I. Sheikh, A.I. Zouboulis, *Wat. Res.*, (1998), Vol.**32**, No.2, pp.400-406.

- [66] G. Garg, G. S. Chauhan and JH. Ahn, *Polym. Adv. Technol.*, (2011), **22**(12), 1794–1801.
- [67] J. Liu, Y. Ma, T. Xu, G. Shao, *J. Hazard. Mater*, (2010), **178**, 1021-9.
- [68] J. Liu, Y. Ma, Y. Zhang, G. Shao, *J. Hazard. Mater*, (2010), **173**, 438-44.
- [69] W. Liang, C. Wu, C. Hsu, P. Kuo, *J. Polym. Sci. A: Polym. Chem.*, (2006), **44**, 3444-3453.
- [70] Iqbal M.J., Ashiq M.N., Adsorption of dyes from aqueous solutions on activated charcoal, *J. Hazard. Mater*, 139 (2007) 57–66.
- [71] Al-Ghouti, M. A.; Khraisheh, M.; Allen, S. J.; Ahmad, M. N. *J Environ Manage* 2003, 69, 229.
- [72] Santos A.B., Cervantes F.J., Lier J.B., *Biores. Technol.* 98 (2007) 2369–2385.
- [73] F. A. Ozdemir et al., Adsorptive Removal of Methylene Blue from Simulated Dyeing Wastewater with Melamine-Formaldehyde-Urea Resin *Journal of Applied Polymer Science*, Vol. 112, 3442–3448 (2009).
- [74] Garg, V. K.; Amita, M.; Kumar, R.; Gupta, R. *Dyes Pigments*, 2004, 63, 243.
- [75] Pinherio H.M., Touraud E., Tomas O., *Dyes Pigments* 61(2004) 121–139.
- [76] Barka N., Assabbane A., Nounah A., Ait-Ichou Y., *J Hazard Mater* 152 (2008) 1054–1059.
- [77] Solozhenko, E. G.; Soboleva, N. M.; Goncharuk, V. V. *Wat Res*, 1995, 29, 2206.

- [78] Gregorio, C. *Bioresou Technol* 2005, 97, 1061.
- [97] Knapp, J. S.; Newby, P. S.; Reece, L. P. *Enzyme Microbiol Technol* 1995, 17, 664.
- [80] Dabrowski, A. *Adv Colloid Interface Sci*, 2001, 93, 135.
- [81] Cooper, P. J *Soc Dyers Colourists* 1993, 109, 97.
- [82] Babel, S.; Kurniawan, T.A. *J Hazard Mater* 2003, 97, 219.
- [83] Ramakrishna, K. R.; Viraraghavan, T. *Water Sci Technol* (1997), 36, 189.
- [84] Streat, M.; Patrick, J. W.; Perez, M. J. *Water Res* 1995, 29, 467.
- [85] F. Ayca Ozdemir, Birsen Demirata, R. Apak, Adsorptive Removal of Methylene Blue from Simulated Dyeing Wastewater with Melamine-Formaldehyde-Urea Resin, *Journal of Applied Polymer Science*, Vol. 112, 3442–3448, (2009).
- [86] S. Akazdam, M. Chafi, W. Yassine, B. Gourich, Removal of Acid Orange 7 Dye from Aqueous Solution Using the Exchange Resin Amberlite FPA-98 as an Efficient Adsorbent: Kinetics, Isotherms, and Thermodynamics Study, *Journal of Materials and Environmental Sciences (JMES)*, 2017, 8 (8), pp. 2993-3012.
- [87] Song Cheng et al, Removal of organic dyes from aqueous solution using waste catalyst-derived adsorbent: Isotherm modeling and kinetic studies, *Mater. Res. Express* 5 065603, 2018.
- [88] Xu et al., facile preparation of porous organic copolymer based on triptycene and crown ether for efficient organic dye adsorption, *RSC Adv.*, 2018, 8, 4963–4968.

- [89] B. A. Armitage; D. E. Bennet; H. G. Lamparski; D. F. O'Brien, *Adv. polym. Sci.*, (1996), **126**, 54.
- [90] K. S. Rajan; J. Murase; A. E. martell, *J. Am. Chem. Soc.*, (1969), **91**, 4408.
- [91] S. Westerback; A. E. Martell, *Nature*, (1956), **178**, 321.
- [92] Y. Yamashoji; T. Matsushita; T. Shono, *Technol Rep Osaka Univ.*, (1985), **35**, 331.
- [93] S. Matsumura, S. Mada, S. Yoshikawa, *polymer Mater. Sci. Eng.*, (1990), **62**, 984.
- [94] Shaikh A. Ali, N. Y. Abu-Thabit, Hasan A. Al-Muallem, *J. Polym. Sc., Part A Polym. chem.*, (2010), **48** (24), 5693-5703.
- [95] K. Riedelsberger, W. Jaeger, *Des. Monomers Polym.*, (1998), **1**, 387.
- [96] A. Laschewsky, *Polymers*, 2014, **6**, 1544-1601.
- [97] Z. A. Jamiu and Shaikh A. Ali, *RSC Adv.*, 2016, **6**, 31019-31030.
- [98] A. V. Dobrynin, R. H. Colby and M. Rubinstein, *J. Polym. Sci., Part B: Polym. Phys.*, 2004, **42**, 3513–3538.
- [99] A. Rabiee, A. Ershad-Langroudi and H. Jamshidi, *Rev. Chem. Eng.*, 2014, **30**, 501-506.
- [100] R. Kumar and G. H. Fredrickson, *J. Chem. Phys.*, 2009, **131**, 104901.
- [101] M. Turek, K. Mitko, K. Piotrowski, P. Dydo, E. Laskowska, and A. Jakobik-Kolon, *Desalination*, 2017, **401**, 180–189.

- [102] S. A. Ali, I. W. Kazi and Nisar Ullah, *Ind. Eng. Chem. Res.*, 2015, **54**, 9689–9698.
- [103] M. Chaussemier, E. Pourmohtasham, D. Gelus, N. Pecoul, H. Perrot, J. Ledion, H. Cheap-Charpentier, and O. Horner, *Desalination*, 2015, **356**, 47-55.
- [104] S. A. Ali, S. A. Haladu and H. A. Al-Muallem, *J. Appl. Polym. Sci.*, 2014, **131**, 40615.
- [105] J. E. Boothe, H. G. Flock and M. F. Hoover, *J. Macromol. Sci., Chem.*, 1970, **A4**, 1419.
- [106] J. C. Salamone, M. K. Raheja, Q. Anwaruddin and A. C. Watterson, *J. Polym. Sci., Part C: Polym. Lett.*, 1985, **23**, 655.
- [107] G. B. Butler and R. J. Angelo, Preparation and polymerization of unsaturated quaternary ammonium compounds. VIII. A proposed alternating intramolecular chain propagation, *J. Am. Chem. Soc.*, 1957, **79**, 3128–3131.
- [108] M. Galin, A. Chapoton, and J-C. Galin, *J. Chem. Soc., Perkin Trans. 2*, 1993, 545.
- [109] A.W. Lloyd, C. J. Olliff, and K.L. Rutt, *Int. J. Pharm.*, 1996, **131**, 257.
- [110] D. J. Walsh and G. L. Cheng, *Polymer*, 1984, **25**, 499.
- [111] J. C. Salamone, M. K. Raheja, Q. Anwaruddin and A. C. Watterson, *J. Polym. Sci., Part C: Polym. Lett.*, 1985, **23**, 655.

- [112] S. Morozova, G. Hu, T. Emrick and M. Muthukumar, Influence of Dipole Orientation on Solution Properties of Polyzwitterions, *ACS Macro Lett.*, 2016, **5**, 118–122.
- [113] K. Nishida, K. Kaji, T. Kanaya and N. Fanjat, Determination of intrinsic viscosity of polyelectrolyte solutions, *Polymer*, 2002, **43**, 1295-1300.
- [114] I. W. Kazi, F. Rahman, and S.A. Ali, *Polym. Eng. Sci.*, 2014, **54**, 166–174.
- [115] F. Candau and J. F. Joanny, *Polyampholytes (Properties in Aqueous Solution)*, J.C. Salamone Ed.; CRC Press: Boca Raton, FL 7, 1996, 5462-5476.
- [116] J. Wittmer, A. Johner and J. F. Joanny, *Europhys. Lett.*, 1993, **24**, 263-268.
- [117] R. Everaers, A. Johner, and J. F. Joanny, *Europhys. Lett.*, 1997, **37**, 275-280.
- [118] Z. Cao and G. Zhang, Dynamics of polyzwitterions in salt-free and salt solutions, *Phys. Chem. Chem. Phys.*, 2015,**17**, 27045-27051.
- [119] R. Barbucci, M. Casolaro, N. Danzo, V. Barone, P. Ferruti and A. Angeloni, Effect of different shielding groups on the polyelectrolyte behavior of polyamines, *Macromolecules*, 1983, **16**, 456-462.
- [120] A. Fini, M. Casolaro, M. Nocentini, R. Barbucci and M. Laus, Synthesis and thermodynamic studies on the protonation of a new polymeric amino diacid, *Makromol. Chem.*, 1987,**188**, 1959-1971.
- [121] Y. Merle, *J. Phys. Chem.*, 1987, **91**, 3092-3098.

- [122] S. Mafe, V. Garcia-Morales and P. Ramirez, *Chem. Phys.*, 2004, **296**, 29-35.
- [123] F. H. Butt, F. Rahman and U. Baduruthamal, Pilot plant evaluation of advanced vs. conventional scale inhibitors for RO desalination, *Desalination*, 1995, **103**, 189–198.
- [124] H. David, S. Hilla and S. Alexander, State of the Art of Friendly "Green" Scale Control Inhibitors: A Review Article, *Ind. Eng. Chem. Res.*, 2011, **50**, 7601–7607.
- [125] G. Mazziotti di Celso, and M. Prisciandaro, *Desalin. Water Treat.*, 2013, **51**, 1615-1622.
- [126] M. Turek, K. Mitko, K. Piotrowski, P. Dydo, E. Laskowska, and A. Jakobik-Kolon, *Desalination*, 2017, **401**, 180–189.
- [127] H. Shemer, D. Hasson, and R. Semiat, Review of the state of the art of antiscalant selection, From Mineral Scales in Biological and Industrial Systems, ed. Amjad, Zahid, *CRC Press*, 2014, 227-255.
- [128] M. Chaussemier, E. Pourmohtasham, D. Gelus, N. Pecoul, H. Perrot, J. Ledion, H. Cheap-Charpentier, and O. Horner, *Desalination*, 2015, **356**, 47-55.
- [129] S. A. Ali, S. A. Haladu, A.M Z. El-Sharif, *J. Polym. Res.*, 2016. DOI: 10.1007/s10965-016-1006-5, 2016, **23**,167.
- [130] Z. A. Jamiu, H. A. Al-Muallem, and S. A. Ali, *Des. Monomers Polym.*, 2016, **19**, 128-137.
- [131] Z. A. Jamiu, H. A. Al-Muallem, S.A. Ali, *React. Funct. Polym.*, 2015, **93**, 120–129.

- [132] S. A. Ali, S. A. Haladu, A. M. Z. El-Sharif, *Macromol. Res.*, 2016, **24**, 163-169.
- [133] Singh, P.K.; Singh, V.K.; Singh, M. Zwitterionic polyelectrolytes: a review. *e-Polymers* **2007**, *30*, 1-34.
- [134] Abu-Thabit, N.Y.; Kazi, I.W.; Al-Muallem, H.A.; Ali, S.A. Phosphonobetaine/sulfur dioxide copolymer by Butler's cyclopolymerization process. *Eur. Polym. J.* **2011**, *47*, 1113-1123.
- [135] Ali, S.A.; Rachman, I.B.; Saleh, T.A. Simultaneous trapping of Cr(III) and organic dyes by a pH-responsive resin containing zwitterionic aminomethylphosphonate ligands and hydrophobic pendants. *Chem. Eng. J.* **2017**, *330*, 663–674.
- [136] Yaagoob, I.Y.; Al-Muallem, H.A.; Ali, S.A. Synthesis and application of polyzwitterionic and polyampholytic maleic acid-alt-(diallylamino) propylphosphonates. *RSC Adv.* **2017**, *7*, 31641–31653.
- [137] Kogure, E.; Morii, N.; Makino, Y.; Hawakawa, T.; Tsukuda, K. *Jpn. Kokai Tokkyo Koho* 2007, JP 2007106920 A 20070426
- [138] Yomogida, Y.; Torigoe, H. *Jpn. Kokai Tokkyo Koho* 2012, JP 2012214539 A 20121108.
- [139] Suzuki, N.; Togashi, H.; Ito, S.; Yamazaki, Y. *Jpn. Kokai Tokkyo Koho* 2007, JP 2007238921 A 20070920.
- [140] Pine, S.H. Eschweiler-Clarke methylation of amines. An organic chemistry experiment. *J. Chem. Educ.* **1968**, *45*, 118.

- [141] Negi, Y.; Harada, S.; Ishizuka, O. Cyclopolymerization of diallylamine derivatives in dimethyl sulfoxide. *J. Polym. Sci.: Part A Polym. Chem.* **1967**, 5, 1951-1965.
- [142] Ali, S.A.; Kazi, I.W.; Rahman, F. Synthesis of a diallylammonio propanephosphonate-alt-(sulfur dioxide) copolymer and its evaluation as an antiscalant in desalination plants. *Polym. Int.* **2014**, 63, 616–625.
- [143] Vorobeveva, A.I.; Sultanova, G.R.; Bulgakov, A.K.; Zainchkovskii, V.I.; Kolesov, S.V. Synthesis and biological properties of copolymers based on N,N-diallyl-N,N-dimethylammonium chloride. *Pharmaceutical Chem. J.* **2013**, 46, 653-655
- [144] Harada, S.; Arai, K. Process for the bulk photocopolymerization of polyaminesulfones. US Patent 3585118, 1971.
- [145] Ali, S.A.; Umar Y.; Abu-Sharkh, B.F. Amphiphilic cycloterpolymers of diallyldimethylammonium chloride, diallyloctadecylammonium chloride, and sulfur dioxide. *J. Appl. Polym. Sci.* **2005**, 97, 1298-1306.
- [146] Vorobeveva, A. I.; Vasileva, E. V.; Gaisina, K. A.; Puzin, Y. I.; Leplyanin, G. V. Copolymerization of N, N-dialkyl-N, N-diallylammonium halides with sulfur dioxide. *Polym. Sci. Ser. A* **1996**, 38, 1077–1080.
- [147] Soto V.M.M.; Galin, J.C. Poly(sulfopropylbetaines). 2. Dilute solution properties. *Polymer* **1984**, 25, 254–262.
- [148] Galin, M.; Chapoton, A.; Galin, J-C. Dielectric increments, interchange distances and conformation of quaternary ammonioalkylsulfonates and

- alkoxydicyanoethenolates in aqueous and trifluoroethanol solutions. *J. Chem. Soc. Perkin Trans. 2*, **1993**, 545-553.
- [149] Lloyd, A.W.; Olliff, C.J.; Rutt, K.L. A comparison of carboxylate salts as liposomal cryoprotectants. *Int. J. Pharm.* **1996**, *131*, 257-262.
- [150] Pike, R.M.; Cohen, R.A. Organophosphorous polymers. I. Peroxide-initiated polymerization of diethyl and diisopropyl vinylphosphonate. *J. Polym. Sci.* **1960**, *44*, 531-538.
- [151] Vynck, V.D.; Goethals, E. J. Synthesis and polymerization of N,N-diallylpyrrolidinium bromide. *Macromol Rapid Commun.* **1997**, *18*, 149-156.
- [152] Gao, M.; Gawel K.; Stokke, B.T. Polyelectrolyte and antipolyelectrolyte effects in swelling of polyampholyte and polyzwitterionic charge balanced and charge offset hydrogels. *Eur. Polym. J.* **2014**, *53*, 65–74.
- [153] Bodnarchuk, M.S.; Doncom, K.E.B.; Wright, D.B.; Heyes, D.M.; Dini, D.; O'Reilly, R. K. Polyelectrolyte pK_a from experiment and molecular dynamics simulation. *RSC Adv.* **2017**, *7*, 20007-20014.
- [154] Barbucci, R.; Casolaro, M.; Ferruti, P.; Nocentini, M. Spectroscopic and calorimetric studies on the protonation of polymeric amino acids. *Macromolecules* **1986**, *19*, 1856-1861.
- [155] Barbucci, R.; Casolaro, M.; Nocentini, M.; Correzzi, S.; Ferruti, P.; Barone, V. Acid-base and metal ion complex formation properties of polymers containing amino acid residues. *Macromolecules* **1986**, *19*, 37-42.

- [156] Davey, R.J. The Role of Additives in Precipitation Processes. In *Industrial crystallization 81: Proceedings of the 8th Symposium on Industrial Crystallization*, Eds. Jancic, S.J.; de Jong, E.J. North-Holland Publishing Co.: Amsterdam, Holland, 1982; pp.123-135; 0444864024.
- [157] Mazziotti di Celso, G.; Prisciandaro, M. Wastewater reuse by means of UF membrane process: a comparison with Italian provisions. *Desalin. Water Treat.* **2013**, *51*, 1615-1622.
- [158] Shams El Din, A.M.; Aziz, Sh.; Makkawi, B. Electricity and water production in the Emirate of Abu Dhabi and its impact on the environment. *Desalination* **1994**, *97*, 373–388.
- [159] I. Tan, B. Hameed, A. Ahmad, Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon, *Chem. Eng. J.* 127 (2007) 111–119.
- [160] K. Mohanty, J.T. Naidu, B.C. Meikap, M.N. Biswas, Removal of crystal violet from wastewater by activated carbons prepared from rice husk, *Ind. Eng. Chem. Res.* 45 (2006) 5165-5171.
- [161] G. Crini, Non-conventional low-cost adsorbents for dye removal: a review, *Bioresour. Technol.* 97 (2006) 1061-1085.
- [162] T. Akar, T.A. Demir, I. Kiran, A. Özcan, A.S. Özcan, S. Tunali, Biosorption potential of *Neurospora crassa* cells for decolorization of Acid Red 57 (AR57) dye. *J. Chem. Technol. Biotechnol.* 81 (2006) 1100-1106.

- [163] C.A.P. Almeida, N.A. Debacher, A.J. Downs, L. Cottet, C.A.D. Mello, Removal of methylene blue from colored effluents by adsorption on montmorillonite clay, *J. Colloid Interface Sci.* 332 (2009) 46–53.
- [164] S. Preethi, A. Sivasamy, S. Sivanesan, V. Ramamurthi, G. Swaminathan, Removal of safranin basic dye from aqueous solutions by adsorption onto corncob activated carbon, *Ind. Eng. Chem. Res.* 45 (2006) 7627-7632.
- [165] L. Ai, C. Zhang, Z. Chen, Removal of methylene blue from aqueous solution by a solvothermal-synthesized graphene/magnetite composite, *J. Hazard. Mater.* 192 (2011) 1515– 1524.
- [166] A.N. Fernandes, C.A.P. Almeida, C.T.B. Menezes, N.A. Debacher, M.M.D. Sierra, Removal of methylene blue from aqueous solution by peat, *J. Hazard. Mater.* 144 (2007) 412-419.
- [167] M. T. Yagub, T.K. Sen, S. Afroze, H.M. Ang, Dye and its removal from aqueous solution by adsorption: A review, *Adv. Colloid Interfac.* 209 (2014) 172–184.
- [168] H. Deng, L. Yang, G.H. Tao, J.L. Dai, Preparation and characterization of activated carbon from cotton stalk by microwave assisted chemical activation—application in methylene blue adsorption from aqueous solution, *J. Hazard. Mater.* 166 (2009) 1514–1521.
- [169] E. Chibowski, A.O. Ortega, M. Espinosa-Jiménez, R. Perea-Carpio, L. Holysz, Study of the leacril dyeing process by a cationic dye from an emulsion system, *J. Coll. Interf. Sci.* 235 (2001) 283–288.

- [170] N. Kannan, M.M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study, *Dyes Pigm.* 51 (2001) 25–40.
- [171] V. Meshko, L. Markovska, M. Mincheva, A.E. Rodrigues, Adsorption of Basic Dyes on Granular Activated Carbon and Natural Zeolite. *Water Res.* 35 (2001) 3357–3366.
- [172] K.C. Bedin, A.C. Martins, A.L. Cazetta, O. Pezoti, V.C. Almeida, KOH-activated carbon prepared from sucrose spherical carbon: Adsorption equilibrium, kinetic and thermodynamic studies for Methylene Blue removal, *Chem. Eng. J.* 286 (2016) 476–484.
- [173] Y. Yan; M. Zhang, K. Gong, L. Su, Z. Guo, L. Mao, Adsorption of Methylene Blue Dye onto Carbon Nanotubes: A Route to an Electrochemically Functional Nanostructure and Its Layer-by-Layer Assembled Nanocomposite. *Chem. Mater.* 2005, 17, 3457–3463.
- [174] Z. Sui, Q. Meng, X. Zhang, R. Ma, B. Cao, Green Synthesis of Carbon Nanotube-Graphene Hybrid Aerogels and Their Use as Versatile Agents for Water Purification. *J. Mater. Chem.* 22 (2012) 8767–8771.
- [175] H. Gao, Y. Sun, J. Zhou, R. Xu, H. Duan, Mussel-Inspired Synthesis of Polydopamine-Functionalized Graphene Hydrogel as Reusable Adsorbents for Water Purification. *ACS Appl. Mater. Interfaces* 5 (2012) 425–432.

- [176] Y. Xie, B. Yan, H. Xu, J. Chen, Q. Liu, Y. Deng, H. Zeng, Highly Regenerable Mussel-Inspired Fe_3O_4 @Polydopamine-Ag Core–Shell Microspheres as Catalyst and Adsorbent for Methylene Blue Removal, *ACS Appl. Mater. Interfaces* 6 (2014) 8845–8852.
- [177] L. Wang, J. Zhang, A. Wang, Removal of methylene blue from aqueous solution using chitosan-g-poly(acrylic acid)/montmorillonite superadsorbent nanocomposite, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 322 (2008) 47–53.
- [178] L. Wang, J. Zhang, A. Wang, Fast removal of methylene blue from aqueous solution by adsorption onto chitosan-g-poly (acrylic acid)/attapulgitite composite, *Desalination* 266 (2011) 33-39.
- [179] E. Haque, J. W. Jun, S. H. Jhung, Adsorptive removal of methyl orange and methylene blue from aqueous solution with a metal-organic framework material, iron terephthalate (MOF-235), *J. Hazard. Mater.* 185 (2011) 507–511.
- [180] T. Zhu, J.S. Chen, X.W. Lou, Highly Efficient Removal of Organic Dyes from Waste Water Using Hierarchical NiO Spheres with High Surface Area, *J. Phys. Chem. C* 116 (2012) 6873–6878.
- [181] F. Wu, R. Tseng, R. Juang, Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan, *Water Res.* 35 (2001) 613–618.

- [182] I.A. Salem, M.S. El-Maazawi, Kinetics and mechanism of color removal of methylene blue with hydrogen peroxide catalyzed by some supported alumina surfaces, *Chemosphere* 41 (2000) 1173–1180.
- [183] M. Doğan, M. Alkan, A. Türkyilmaz, Y. Özdemir, Kinetics and mechanism of removal of methylene blue by adsorption onto perlite, *J. Hazard. Mater. B* 109 (2004) 141–148.
- [184] M. Roosta, M. Ghaedi, A. Daneshfar, R. Sahraei, A. Asghari, Optimization of the ultrasonic assisted removal of methylene blue by gold nanoparticles loaded on activated carbon using experimental design methodology, *Ultrason. Sonochem.* 21 (2014) 242–252.
- [185] A. Z. M. Badruddoza, G. S. S. Hazel, K. Hidajat, M.S. Uddin, Synthesis of carboxymethyl- β -cyclodextrin conjugated magnetic nano-adsorbent for removal of methylene blue, *Colloids and Surfaces A: Physicochem. Eng. Aspects* 367 (2010) 85–95.
- [186] M. H. Beyki, F. Shemirania, J. Malakootikhah, S. Minaeian, R. Khani, Catalytic synthesis of graphene-like polyaniline derivative - MFe_2O_4 (M; Cu, Mn) nanohybrid as multifunctionality water decontaminant, *React. Funct. Polym.* 125 (2018) 108–117.
- [187] Y. Liu, S. Huang, X. Zhao, Y. Zhang, Fabrication of three-dimensional porous β -cyclodextrin/chitosan functionalized graphene oxide hydrogel for methylene blue removal from aqueous solution, *Colloids and Surfaces A* 539 (2018) 1–10.

- [188] H.M. Abd El Salam, T. Zaki, Removal of hazardous cationic organic dyes from water using nickel-based metal-organic frameworks, *Inorg. Chim. Acta* 471 (2018) 203–210.
- [189] H. Lyu, B. Gao, F. He, A. R. Zimmerman, C. Ding, J. Tang, J. C. Crittenden, Experimental and modeling investigations of ball-milled biochar for the removal of aqueous methylene blue, *Chem. Eng. J.* 335 (2018) 110–119.
- [190] J. He, A. Cui, S. Deng, J. P. Chen, Treatment of methylene blue containing wastewater by a cost-effective micro-scale biochar/polysulfone mixed matrix hollow fiber membrane: Performance and mechanism studies, *J. Coll. Interface Sci.* 512 (2018) 190–197.
- [191] O. Hamdaoui, Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick, *J. Hazard. Mater.* 135 (2006) 264–273.
- [192] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, Adsorption of methylene blue on low-cost adsorbents: A review, *J. Hazard. Mater.* 177 (2010) 70–80.
- [193] S. A. Ali; S. Z. Ahmed; Z. Hamad, cyclopolymerization studies of diallyl- and tetraallylpiperazinium salts, *J. Appl. Polym. Sci.*, (1996), **61**, 1077–1085.
- [194] S. A. Ali, O. C. S. Al Hamouz, N. M. Hassan, Novel cross-linked polymers having pH-responsive amino acid residues for the removal of Cu^{2+} from aqueous solution at low concentrations, *J. Hazard. Mater.*, (2013), 248–249 47–58.

- [195] S.D. Alexandratos, Ion-Exchange Resins: A Retrospective from Industrial and Engineering Chemistry Research, *Ind. Eng. Chem. Res.* 48 (2009) 388–398.
- [196] R. Kunin, E.A. Meitzner, J.A. Oline, S.A. Fisher, N. Frisch, Characterization of amberlyst 15. macroreticular sulfonic acid cation exchange resin, *Ind. Eng. Chem. Prod. Res. Dev.* 1 (1962) 140–144.
- [197] H.A. Al-Muallem, M.I.M. Wazeer, S.A. Ali, Synthesis and solution properties of a new pH-responsive polymer containing amino acid residues, *Polymer* 43 (2002) 4285-4295.
- [198] A. Ramesh, H. Hasegawa, T. Maki, K. Ueda, Adsorption of inorganic and organic arsenic from aqueous solutions by polymeric Al/Fe modified montmorillonite. *Sep. Purif. Technol.* 56 (2007) 90–100.
- [199] F.C. Wu, R.L.Tseng, R.S. Juang, Initial behavior of intraparticle diffusion model used in the description of adsorption kinetics, *Chem. Eng. J.* 153 (2009) 1–8.
- [200] D. Kavitha, C. Namasivayam, Experimental and kinetic studies on methylene blue adsorption by coir pith carbon, *Bioresour. Technol.* 98 (2007) 14–21.
- [201] H. K. Boparai, M. Joseph, D. M. O’Carroll, Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles, *J. Hazard. Mater.* 186 (2011) 458–465.
- [202] J.F. Pearson, M.A. Slifkin, The infrared spectra of amino acids and dipeptides, *Spectrochim. Acta Part A: 28A* (1972) 2403-2417.

- [203] L. Xiong, Y. Yang, J. Mai, W. Sun, C. Zhang, D. Wei, Q. Chen, J. Ni, Adsorption behavior of methylene blue onto titanate nanotubes, *Chem. Eng. J.* 156 (2010) 313–320.
- [204] F. Haghseresht, G. Lu, Adsorption characteristics of phenolic compounds onto coal-reject-derived adsorbents, *Energy Fuel* 12 (1998) 1100–1107.
- [205] S.T. Ong, E.H. Tay, S.T. Ha, W.N. Lee, P.S. Keng, Equilibrium and continuous flow studies on the sorption of congo red using ethylenediamine modified rice hulls, *Int. J. Phys. Sci.* 4 (2009) 683–690.
- [206] J. Liu, L. Song, G. Shao, Novel zwitterionic inorganic–organic hybrids: Kinetic and equilibrium model studies on Pb^{2+} removal from aqueous solution, *J. Chem. Eng. Data* 56 (2011) 2119–2127.
- [207] A. W. M. Ip, J. P. Barford and G. McKay, A comparative study on the kinetics and mechanisms of removal of Reactive Black 5 by adsorption onto activated carbons and bone char, *Chem. Eng. J.*, 157 (2010), 434–442.
- [208] V.K. Garg, R. Kumar, R. Gupta, Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste, *Dyes Pigment* 62 (2004) 1–10.
- [209] R. Chen, W. Wang, X. Zhao, Y. Zhang, S. Wu, F. Li, *Chem. Eng. J.* 242 (2014) 226–233.

- [210] Y. Feng, F. Yang, Y. Wang, L. Ma, Y. Wu, P. G. Kerr and L. Yang, *Bioresour. Technol.*, 2011, 102, 10280–10285.
- [211] Prasad, A. L., & Santhi, T., Adsorption of hazardous cationic dyes from aqueous solution onto *Acacia nilotica* leaves as an eco friendly adsorbent, *Sustain Environ Res*, 22 (2012). 113–12.
- [212] V. Chandane and V. K. Singh, *Desalin. Water Treat.*, 57, (2016), 4122.
- [213] G. Bayramoglu, B. Altintas, M.Y. Arica, *Chem. Eng. J.* 152 (2009), 339.
- [214] Y. Tao, W. Z. Jian, J. Kui and L. Q. Jun, *Chem. Res. Chin. Univ.*, 22 (2006), 292–296.
- [215] T. A. Khan and E. A. Khan, *Appl. Clay Sci.*, 107 (2015), 70.
- [216] Y. He, H. Li, Z. Zhang, T. Lu and R. M. Wang, *Key Eng. Mater.*, 726 (2017), 345.
- [217] L.H. Huang, J.J. Kong, W.L. Wang, C.L. Zhang, S.F. Niu, B.Y. Gao, *Desalination* 286 (2012) 268.
- [218] Y. Zhou, Q. Jin, X. Hu, Q. Zhang, T. Ma, Heavy metal ions and organic dyes removal from water by cellulose modified with maleic anhydride, *J Mater Sci.*, 47 (2012), 5019–5029.
- [219] J. Ma, W. Song, C. Chen, W. Ma, J. Zhao and Y. Tang, *Environ. Sci. Technol.*, 39 (2005), 5810–5815.
- [220] L. Ai, J. Jiang, *Desalination*, 262 (2010), 134–140.

- [221] M. Rafatullah, O. Sulaiman, R. Hashim and A. Ahmad, *J. Hazard. Mater.*, 177 (2010), 70–80.
- [222] G. Zhang, Z. He and W. Xu, *Chem. Eng. J.*, 183 (2012), 315–324.
- [223] S. Kalita, M. Pathak, G. Devi, H. P. Sarma, K. G. Bhattacharyya, A. Sarmad and A. Devi, *RSC Adv.*, 7 (2017), 27248–27259.
- [224] Ping Tan, Yongyou Hu, *Journal of Molecular Liquids* 242 (2017) 181–189.
- [225] X.-L. Wu, P. Xiao, S. Zhong, K. Fang, H. Lin, J. Chen, *RSC Adv.*, 7 (2017), 28145–28151.
- [226] T. Lu, L. Wang, Y. He, J. Chen, R.-M. Wang, Loess surface grafted functional copolymer for removing basic fuchsin, *RSC Adv.*, 7 (2017), 18379–18383.
- [227] X. Yang, Y. Li, Q. Du, J. Sun, L. Chen, S. Hu, Z. Wang, Y. Xia, L. Xia, Highly effective removal of basic fuchsin from aqueous solutions by anionic polyacrylamide/graphene oxide aerogels, *Journal of Colloid and Interface Science* 453 (2015) 107–114.
- [228] S. A. Ali, I. Y. Yaagoob, M. A. J. Mazumder, H. A. Al-Muallem, Fast removal of methylene blue and Hg(II) from aqueous solution using a novel super-adsorbent containing residues of glycine and maleic acid, *J Hazard Mater.*, 369, (2019), 642–654.

- [229] R. Kunin, E.A. Meitzner, J.A. Oline, S.A. Fisher, N. Frisch, Characterization of amberlyst 15. macroreticular sulfonic acid cation exchange resin, *Ind. Eng. Chem. Prod. Res. Dev.* 1(2) (1962) 140–144.
- [230] M. G. Iogannsen, Some structural features of vital dyes, *Bulletin of Experimental Biology and Medicine*, 83 (1977), 591–595.
- [231] A. Ramesh, H. Hasegawa, T. Maki, K. Ueda, Adsorption of inorganic and organic arsenic from aqueous solutions by polymeric Al/Fe modified montmorillonite. *Sep. Purif. Technol.* 56 (2007) 90–100.
- [232] É. C. Lima, A. Hosseini-Bandegharai, J. C. Moreno-Piraján, I. Anastopoulos, A critical review of the estimation of the thermodynamic parameters on adsorption equilibria. Wrong use of equilibrium constant in the Van't Hoof equation for calculation of thermodynamic parameters of adsorption, *J Mol Liq.* 273 (2019), 425-434.
- [233] É. C. Lima, M. A. Adebayo, F. M. Machado, Chapter 3-Kinetic and Equilibrium Models of Adsorption. In: Bergmann C., Machado F. (eds) *Carbon Nanomaterials as Adsorbents for Environmental and Biological Applications. Carbon Nanostructures*, C. P. Bergmann, F. M. Machado, Editors, ISBN 978-3-319-18874-4, Springer (2015), pp 33-69.
- [234] P. S. Thue, A. C. Sophia, E. C. Lima, A. G. N. Wamba, W. S. de Alencar, G. S. dos Reis, F. S. Rodembusch, S. L. P. Dias, Synthesis and characterization of a novel

organic-inorganic hybrid clay adsorbent for the removal of Acid Red 1 and Acid Green 25 from aqueous solutions, *J. Clean. Prod.* 171 (2018) 30-44.

- [235] Srivastava, V., Weng, C.H., Singh, V.K., Sharma, Y.C., Adsorption of nickel ions from aqueous solutions by nano alumina: kinetic, mass transfer, and equilibrium studies. *J. Chem. Eng. Data.* 56 (2011), 1414–1422.
- [236] Ouadjenia-Marouf, F., Marouf, R., Schott, J., Yahiaoui, A., Removal of Cu(II), Cd(II) and Cr(III) ions from aqueous solution by dam silt. *Arab. J. Chem.* 6 (2013), 401–406.
- [237] Rao, M.M., Ramesh, A., Rao, G.P.C., Sessaiah, K., 2006. Removal of copper and cadmium from the aqueous solutions by activated carbon derived from Ceiba pentandra hulls. *J. Hazard. Mater.* B129 (2006), 123–129.
- [238] Rao, M.M., Ramesh, A., Rao, G.P.C., Sessaiah, K., 2006. Removal of copper and cadmium from the aqueous solutions by activated carbon derived from Ceiba pentandra hulls. *J. Hazard. Mater.* B129 (2006), 123–129.

VITAE

Name : Ibrahim Yahia Yaagoob Mohamed

Nationality : Sudanese

Date of Birth : 5/2/1978

Email : heema36@gmail.com, ebraheemyahia@hotmail.com

Address : Current Address: Chemistry Department, King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia Tel. +966540362139. Permanent Address: Khartoum 11111, Sudan, Tel. +249915991194

Academic Background : [Click here to enter text.](#)

2013 – 2018 Ph.D., Chemistry (Polymer: Synthesis, Characterization & Application), King Fahd University of Petroleum & Minerals (KFUPM), Kingdom of Saudi Arabia (KSA).
Dissertation: "Alternate Cyclocopolymerization: Synthesis of a Novel Class of Ionic Polymers and their Applications".

2009 – 2011 MSc., Chemistry, Sudan University of Science and Technology (SUST), the Republic of Sudan.
Dissertation: Synthesis of Some 1,2,3-Thiadiazole Derivatives.

2002 – 2006 BSc. (Hons), Chemistry, Sudan University of Science and Technology, (SUST), the Republic of Sudan.
Dissertation: "Study of Heterocyclic Compounds: Five-Membered Rings (Synthesis of Pyrazole Derivatives)".

LIST OF PUBLICATIONS

1. **Ibrahim Y. Yaagoob**, Hasan A. Al-Muallem, Shaikh A. Ali, Synthesis and application of polyzwitterionic and polyampholytic maleic acid-*alt*-(diallylamino)propylphosphonates, **RSC Adv.**, (2017), 7, 31641 – 31653.
2. **Ibrahim Y. Yaagoob**, Shaikh A. Ali, Hasan A. Al-Muallem, Mohammad A. J. Mazumder, Scope of sulfur dioxide incorporation in alkyldiallylamine-maleic acid-SO₂ tercyclopolymerization, **RSC Adv.**, (2018), 8, 38891–38902.
3. Shaikh A. Ali, **Ibrahim Y. Yaagoob**, Mohammad A. J. Mazumder, Hasan A. Al-Muallem, Fast removal of methylene blue and Hg(II) from aqueous solution using a novel super-adsorbent containing residues of glycine and maleic acid, **Journal of Hazardous Materials**, 369(2019), 642-654.
4. **Papers under review**
 - 4.1. **Ibrahim Y. Yaagoob**, Mohammad A. J. Mazumder, Shaikh A. Ali, Hasan A. Al-Muallem, A resin containing residues of glycine and maleic acid: A superabsorbent for adsorptive removal of basic dye pararosaniline hydrochloride and Cd(II) from water, **Chemical Engineering Journal**, Submitted-under review.
 - 4.2. L. K. M. O. Goni, M. A. J. Mazumder, S. A. Ali, M. A. Quraishi, H. A. Al-Muallem, **I. Y. Yaagoob**, Polymeric materials as corrosion inhibitors, **Applied Polymer Science**. Submitted-under review.

Conferences & Symposia

1. Hasan A. Al-Muallem, **Ibrahim Y. Yaagoob**, M. A. Jafar Mazumder and Shaikh A. Ali, Synthesis of a new class of alternate ionic cyclocopolymers and their potential use as antiscalants. *251st American Chemical Society National Meeting and Exposition (ACS)*, Conference Paper ID: 2402667, March 13 -17, 2016 **San Diego California (CA), USA**.
2. **Ibrahim Y. Yaagoob**, Hasan A. Al-Muallem, M. A. Jafar Mazumder and Shaikh A. Ali, Alternate Cyclocopolymerization: Synthesis of a new class of ionic polymers and their applications, *1st Research Symposium*, Chemistry Department, King Fahd University of Petroleum and Minerals (**KFUPM**), Dhahran, Saudi Arabia, 26/11/2015.
3. Shaikh A. Ali, **Ibrahim Y. Yaagoob**, *4th International Conference on Material Chemistry & Science*, **Singapore**, March 18-19, 2019.

Honors, Awards, and Distinctions

- Financial Prizes for an Excellent Academic Performance in Chemistry, the first in the class for all four academic (B.Sc.), *Years, 2002 – 2006*, Sudan University of Science and Technology (SUST), Sudan.
- The Prize of the Ministry of Higher Education and Scientific Research for an Excellent Academic Performance in Chemistry, awarded by Sudan Institute for Natural Sciences (SIFNS), *Year, 2005-2006*, Sudan.
- Graduate scholarship for distinguished graduate applicants, *Feb. 2013 – 2018*, King Fahd University of Petroleum & Minerals (KFUPM), Kingdom of Saudi Arabia.