

Application of SAFT-AC Model to Refrigerant Systems

BY

Ahsan Kamil

A Thesis 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

MASTER OF SCIENCE

In

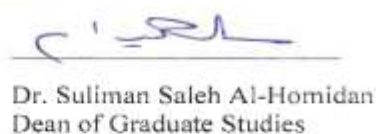
CHEMICAL ENGINEERING

DECEMBER 2023

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN- 31261, SAUDI ARABIA
DEANSHIP OF GRADUATE STUDIES

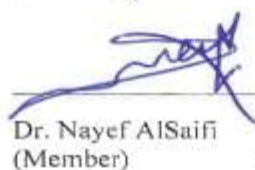
This thesis, written by **Ahsan Kamil** under the direction of his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN CHEMICAL ENGINEERING**.

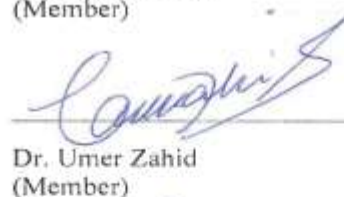

Dr. Nassan M. Baaqeel
Department Chairman

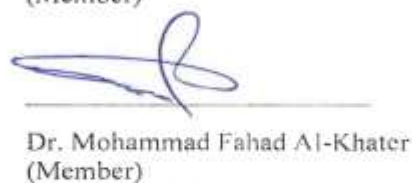

Dr. Suliman Saleh Al-Homidan
Dean of Graduate Studies

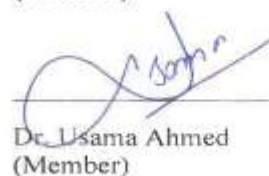
Date


Dr. Wael Ahmed Fouad
(Advisor)


Dr. Nayef AlSaifi
(Member)


Dr. Umer Zahid
(Member)


Dr. Mohammad Fahad Al-Khater
(Member)


Dr. Usama Ahmed
(Member)



© Ahsan Kamil

2023

This work is dedicated first to myself, the patience of my parents & family, KFUPM Chemical Engineering department and to all process engineers in the industry.

ACKNOWLEDGMENTS

Thanks to Allah Pak for giving me the strength, courage, and patience. All my heartiest thanks to Professor Dr. Wael Ahmed Fouad for his supervision of my research work and moral support. In fact, this degree belongs to him because of his generous guidance. Thanks to Professor Dr. Nayef Al-Saifi for guidance. Lecturer Farukh Shehzad for guidance and support. Dr. Umer Zahid for helping morally, Dr. Olivier Guy for his guidance. My mentors, family, parents, colleagues, and Chemical Engineering department for complete research support and facilities.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	VII
TABLE OF CONTENTS.....	VIII
LIST OF TABLES.....	X
LIST OF FIGURES.....	XI
LIST OF ABBREVIATIONS.....	XIV
ABSTRACT	XV
ملخص الرسالة	XVII
CHAPTER 1 INTRODUCTION.....	1
1.1 SAFT-Activity coefficient model	1
1.2 Phase Equilibrium of Cross Associating Mixtures	4
CHAPTER 2 LITERATURE REVIEW	7
2.1 SAFT-Activity Coefficient Model	7
2.1.1 Vapor-Liquid Equilibrium (VLE)	13
2.1.2 Solid-Liquid Equilibrium (SLE)	13
2.1.3 Butler’s Equation.....	14
2.1.4 MIXTURE DATA SELECTION AND DATA ANALYSIS METHODOLOGY	15
2.2 THERMODYNAMIC MODELING	16
2.2.1 Polar PC-SAFT equation of state	16

2.2.2	UNIQUAC activity coefficient model	20
2.2.3	Redlich-Kister activity coefficient model	23
CHAPTER 3 RESULTS AND CONCLUSION		25
3.1	Solubility of HFOs in PECs.....	25
3.2	Solubility of HFOs in Vegetable Oils	30
3.3	Refrigerant Blends	34
3.3.1	Surface Tension Estimation of Refrigerant Blends	35
3.4	Phase Equilibrium of CO ₂ Refrigerant blends	39
3.5	Solid Liquid Equilibrium (SLE) of refrigerant blends.....	41
3.6	Phase Equilibrium of Cross Associating Mixtures	42
CHAPTER 4 CONCLUSION.....		50
REFERENCES.....		53
VITAE.....		61
APPENDIX		62

LIST OF TABLES

Table 2.1. 1 Pure component molecular parameters for refrigerants and lubricants	12
Table 2.2.1. 1 Polar PC-SAFT Equation of State Pure component molecular parameters for Oxygenated solvents and Haloalkanes	17
Table 2.2.1. 2 Solvation parameters for chloroform and halothane binary mixtures	19
Table 2.2.2. 1 Surface and volume parameters for UNIQUAC[92]	21
Table 2.2.2. 2 Coefficients used to calculate Redlich-Kister binary interaction parameters	22
Table 2.2.2. 3 Coefficients used to calculate UNIQUAC binary interaction parameters.	23
Table 3.1. 1 Temperature independent binary interaction parameters of PEC containing systems used in SAFT-AC calculations	29
Table 3.2. 1 Pure component properties and binary interaction parameters used for R-744 containing systems in SAFT-AC calculations.....	40

LIST OF FIGURES

Figure 3.1. 1 Isothermal PT_x phase diagrams for R-1234ze(<i>E</i>) in (a) PEC5, (b) PEC7 and (c) PEC9 at different temperatures. Symbols represent experimental data[1], [2] and lines represent SAFT-AC correlations.	26
Figure 3.1. 2 Isothermal PT_x phase diagrams for R-1234yf in (a) PEC5, (b) PEC7 and (c) PEC9 at different temperatures. Symbols represent experimental data [3], [4] and lines represent SAFT-AC correlations.	27
Figure 3.1. 3 Isothermal PT_x phase diagrams for R-600a in (a) PEC5, (b) PEC7 and (c) PEC9 at different temperatures. Symbols represent experimental data [1][2] and lines represent SAFT-AC correlations.	27
Figure 3.2. 1 Isothermal PT_x phase diagrams for (a) R-1234ze(<i>E</i>) and (b) R-1234yf in ISO VG32 at different temperatures. Symbols represent experimental data [95] and lines represent SAFT-AC predictions	30
Figure 3.2. 2 Isothermal PT_x phase diagrams for R-290 in (a) ISO VG32 and (b) ISO VG22 at different temperatures. Symbols represent experimental data [96, 97] and lines represent SAFT-AC predictions	30
Figure 3.2. 3 Isothermal VLE of R-23 containing binary mixtures. (a) R-116 with $k_{ij} = 0$, (b) R-170 with $k_{ij} = 0.035$ and (c) R-32 with $k_{ij} = -0.03$. Symbols represent experimental data [96-99] and lines represent SAFT-AC correlations.	32
Figure 3.3. 1 Isothermal VLE of R-32 containing binary mixtures. (a) R-134a, (b) R-125, (c) R-1234yf and (d) R-1234ze(<i>E</i>). Symbols represent experimental data [98-102] and lines represent SAFT-AC predictions ($k_{ij} = 0$)	34
Figure 3.3. 2 Surface tension of R-32 containing binary mixtures. (a) R-134a, (b) R-125, (c) R-1234yf and (d) R-1234ze(<i>E</i>). Symbols represent experimental data [98, 103] and lines represent SAFT-AC predictions ($k_{ij} = 0$)	35
Figure 3.3. 3 Surface tension of R-125 containing binary mixtures. (a) R-134a, (b) R-143a and (c) R-152a. Symbols represent experimental data [103] and lines represent SAFT-AC predictions ($k_{ij} = 0$)	36
Figure 3.3. 4 Surface tension of R-134a containing binary mixtures (a) R-152a, (b) R-143a, (c) R-1234yf and (d) R-1234ze(<i>E</i>). Symbols represent experimental data [103, 104] and lines represent SAFT-AC predictions ($k_{ij} = 0$)	37
Figure 3.3. 5 Isothermal VLE for R-744 containing binary mixtures. (a) R-32, (b) R-152a, (c) R-143a and, (d) R-134a. Symbols represent experimental data [14, 105-107] and lines represent SAFT-AC correlations.	39
Figure 3.5. 1 SLE for R-744 containing binary mixtures. (a) R-152a, (b) R-134a, (c) R-143a, (d) R-32 and (e) R-125. Symbols represent experimental data [108, 111-115] and lines represent SAFT-AC predictions	41

Figure 3.6. 1 Phase behavior of acetone + chloroform binary mixture. (a) isothermal VLE at 308.32 K, (b) activity coefficients at 308.32 K, and (c) excess enthalpy at 298.15 K. Symbols represent experimental data [119, 120], solid curves represent Polar PC-SAFT, dashed curves represent UNIQUAC, and dash-dotted curves represent Redlich-Kister	43
Figure 3.6. 2 Phase behavior of methyl acetate + chloroform binary mixture. (a) isothermal VLE at 298.15 K, (b) activity coefficients at 298.15 K, and (c) excess enthalpy at 308.15 K. Symbols represent experimental data [121, 122], solid curves represent Polar PC-SAFT, dashed curves represent UNIQUAC, and dash-dotted curves represent Redlich-Kister	43
Figure 3.6. 3 Phase behavior of MTBE + chloroform binary mixture. (a) isothermal VLE at 303.15 K, (b) activity coefficients at 303.15 K, and (c) excess enthalpy at 300.05 K. Symbols represent experimental data [123, 124], solid curves represent Polar PC-SAFT, dashed curves represent UNIQUAC, and dash-dotted curves represent Redlich-Kister	44
Figure 3.6. 4 Phase behavior of diethyl ether + chloroform binary mixture at 298.15 K. (a) isothermal VLE, (b) activity coefficients, and (c) excess enthalpy. Symbols represent experimental data [125, 126], solid curves represent Polar PC-SAFT, and dashed curves represent UNIQUAC	45
Figure 3.6. 5 Phase behavior of tetrahydrofuran + chloroform binary mixture. (a) isothermal VLE at 303.15 K, (b) activity coefficients at 303.15 K, and (c) excess enthalpy at 298.15 K. Symbols represent experimental data [127, 128], solid curves represent Polar PC-SAFT, dashed curves represent UNIQUAC, and dash-dotted curves represent Redlich-Kister	45
Figure 3.6. 6 Phase behavior of acetone + halothane binary mixture. (a) isothermal VLE at 308.15 K, (b) activity coefficients at 308.15 K, and (c) excess enthalpy at 298.15 K. Symbols represent experimental data [129, 130], solid curves represent Polar PC-SAFT, dashed curves represent UNIQUAC, and dash-dotted curves represent Redlich-Kister	47
Figure 3.6. 7 Phase behavior of methyl acetate + halothane binary mixture. (a) isothermal VLE at 308.15 K, (b) activity coefficients at 308.15 K, and (c) excess enthalpy at 298.15 K. Symbols represent experimental data [129, 130], solid curves represent Polar PC-SAFT, dashed curves represent UNIQUAC, and dash-dotted curves represent Redlich-Kister	47
Figure 3.6. 8 Phase behavior of MTBE + halothane binary mixture. (a) isothermal VLE at 308.15 K, (b) activity coefficients at 308.15 K, and (c) excess enthalpy at 298.15 K. Symbols represent experimental data [129, 130], solid curves represent Polar PC-SAFT, dashed curves represent UNIQUAC, and dash-dotted curves represent Redlich-Kister	49

Figure 3.6. 9 Phase behavior of tetrahydrofuran + halothane binary mixture. (a) isothermal VLE at 308.15 K, (b) activity coefficients at 308.15 K, and (c) excess enthalpy at 298.15 K. Symbols represent experimental data [129, 130], solid curves represent Polar PC-SAFT, dashed curves represent UNIQUAC, and dash-dotted curves represent Redlich-Kister 49

LIST OF ABBREVIATIONS

SAFT	:	Statistical Associating Fluid Theory
VLE	:	Vapor Liquid Equilibrium
SLE	:	Solid Liquid Equilibrium
GWP	:	Global Warming Potential
EOS	:	Equation of State
ACR	:	Auto-cascade Refrigeration
HFCs	:	Hydrofluorocarbons
VG	:	Vegetable Oil
AC	:	Activity Coefficient
ULT	:	Ultra-low Temperature

ABSTRACT

Full Name : [Ahsan Kamil]

Thesis Title : [Predicting the VLE, SLE and surface tension of refrigerant systems using a SAFT-based activity coefficient model and phase equilibrium predictions of cross-associating mixtures using association theory-based Polar PC-SAFT Equation of State]

Major Field : [Chemical Engineering]

Date of Degree : [December 2023]

A molecular activity coefficient model that is based on the statistical associating fluid theory (SAFT-AC) is applied to predict the vapor-liquid equilibria (VLE), solid-liquid equilibria (SLE), and surface tension of binary refrigerant mixtures. In comparison to traditional activity coefficient models, SAFT-AC is able to explicitly account for multiple polar and hydrogen bonding (association) interactions among molecules. The model is consistent with the bulk equations of state, in this case the polar and perturbed chain form of SAFT, but calculations are done at a significantly faster rate. The model is used to fully predict the solubility of hydrocarbons and hydrofluoroolefins (HFOs) in commercial polyol ester lubricants and the VLE of hydrofluorocarbon (HFC) and HFO containing binary mixtures without the need of any adjustable parameters. The application of SAFT-AC is also extended to predict the interfacial tension of refrigerant systems under consideration using Butler's method. The solubility of dry ice (solid carbon dioxide) in HFC solvents is also examined to study the eutectic behaviour at cryogenic applications. Overall, results were found to be in excellent agreement with experimental data across a wide range of conditions. Taking advantage of the molecular nature of the activity coefficient model, a

discussion on the effect of refrigerant molecular structure on the phase behaviour was made for each of the systems considered in this work.

The polar and perturbed chain form of statistical associating fluid theory (Polar PC-SAFT) and the universal quasi-chemical (UNIQUAC) excess Gibbs free energy model were used to model the VLE and excess properties of solvating mixtures. Mixtures of chloroform and halothane with oxygenated solvents were selected for which good quality data were found in the literature. The phase behavior of these systems is characterized by a strong negative deviation from Raoult's law due to cross-association between the oxygenated solvents' lone pairs of electrons and the hydrogen bond donor haloalkane molecule. The impact of such cross-association is reflected on the activity coefficients of oxygenated solvents in chloroform and halothane at low concentrations. Results show that UNIQUAC was unable to properly capture the highly non-linear function of the activity coefficient curves which resulted in overall poor infinite dilution estimates. Moreover, the model was unable to simultaneously fit the VLE and excess enthalpy for many of these systems accurately. On the contrary, and through the explicit modeling of association using Wertheim's first order thermodynamic perturbation theory (TPT1), Polar PC-SAFT was able to capture well the distribution of hydrogen bonds found in these systems which resulted in good prediction of both VLE and excess properties. Furthermore, the symmetry and asymmetry found in the excess enthalpy of mixtures forming 1:1 and 1:2 complexes, respectively, was successfully reproduced by the molecular model.

ملخص الرسالة

الاسم الكامل: إحسن كامل

عنوان الرسالة: التنبؤ بـ VLE و SLE والتوتر السطحي لأنظمة التبريد باستخدام نموذج معامل نشاط SAFT وتنبؤات توازن الطور للمخاليط المترابطة باستخدام معادلة الحالة Polar PC-SAFT القائمة على نظرية الارتباط

التخصص: الهندسة الكيميائية

تاريخ الدرجة العلمية: جمادي الآخر ١٤٤٥ هجري

تم تطبيق نموذج معامل النشاط الجزيئي الذي يعتمد على نظرية ربط السوائل الإحصائية (SAFT-AC) للتنبؤ بتوازن البخار والسائل (VLE)، وتوازن السائل الصلب (SLE)، والتوتر السطحي لمخاليط التبريد الثنائية. بالمقارنة مع نماذج معامل النشاط التقليدية، فإن SAFT-AC قادر على الحساب الواضح لتفاعلات (ارتباطات) الروابط القطبية والهيدروجينية المتعددة بين الجزيئات. يتوافق النموذج مع مجموعة معادلات الحالة، وهي في هذه الحالة تتمثل في السلسلة القطبية والمضطربة لـ SAFT، ولكن تتم الحسابات بمعدل أسرع بكثير. يتم استخدام النموذج بشكل كامل للتنبؤ بقابلية ذوبان الهيدروكربونات والهيدروفلوروليفينات (HFOs) في مواد التشحيم التجارية من البوليول إستر و VLE للهيدروفلوروكربون (HFC) و HFO التي تحتوي على مخاليط ثنائية دون الحاجة إلى أي معلمات تعديل. تم أيضًا توسيع تطبيق SAFT-AC للتنبؤ بالتوتر السطحي لأنظمة التبريد قيد النظر باستخدام طريقة بتلر. يتم أيضًا فحص قابلية ذوبان الثلج الجاف (ثاني أكسيد الكربون الصلب) في مذيبات مركبات الكربون الهيدروفلورية، لدراسة السلوك اليوكيني في التطبيقات التي تتطلب برودة عالية. وبشكل عام، وجد أن النتائج تتفق بشكل ممتاز مع البيانات التجريبية عبر مجموعة واسعة من الظروف. من خلال الاستفادة من الطبيعة الجزيئية لنموذج معامل النشاط، تم إجراء مناقشة حول تأثير التركيب الجزيئي لغاز التبريد على سلوك الطور لكل من الأنظمة التي تم النظر فيها في هذا العمل.

تم استخدام شكل السلسلة القطبية والمضطربة لنظرية الموائع المرتبطة الإحصائية (Polar PC-SAFT) ونموذج الطاقة الحرة الزائدة شبه الكيميائية (UNIQUAC) لنموذج Gibbs لنمذجة الـ VLE والخصائص الزائدة لمخاليط الذوبان. تم اختيار مخاليط الكلوروفورم والهالوثان مع المذيبات المؤكسدة والتي تم العثور على بيانات جيدة عنها في الأبحاث السابقة. يتميز سلوك الطور لهذه الأنظمة بانحراف سلبي قوي عن قانون راوالت بسبب الارتباط المتقاطع بين أزواج الإلكترونات الوحيدة للمذيبات المؤكسدة وجزيء الهالوكين المانح لرابطة الهيدروجين. وينعكس تأثير هذا الارتباط المتبادل على معاملات نشاط المذيبات المؤكسدة في الكلوروفورم والهالوثان بتركيزات منخفضة. أظهرت النتائج أن UNIQUAC لم يكن قادرًا على التقاط الوظيفة غير الخطية للغاية لمنحنيات معامل النشاط بشكل صحيح مما أدى إلى تقديرات التخفيف اللانهائية الضعيفة بشكل عام. علاوة على ذلك، لم يكن النموذج قادرًا على ملائمة VLE والمحتوى الحراري الزائد للعديد من هذه الأنظمة بدقة في نفس الوقت. على العكس من ذلك، ومن خلال النمذجة الواضحة للارتباط باستخدام نظرية الاضطراب الديناميكي الحراري من الدرجة الأولى لـ Wertheim (TPT1)، تمكنت Polar PC-SAFT من التقاط توزيع روابط الهيدروجين الموجودة في هذه الأنظمة بشكل جيد مما أدى إلى تنبؤ جيد لكل من VLE والفائض. علاوة على ذلك، فإن التماثل وعدم التماثل الموجود في المحتوى الحراري الزائد للمخاليط التي تشكل مجمعات 1:1 و 1:2، على التوالي، تم إعادة إنتاجه بنجاح بواسطة النموذج الجزيئي.

CHAPTER 1

INTRODUCTION

1.1 SAFT-Activity coefficient model

The demand for ultra-low temperature (ULT) refrigeration has skyrocketed in the past few years mostly due to the rapid growth seen in industries related to biomedical sample storage and electronic information technology. ULT refrigeration refers to the preservation of materials at temperatures between 163 K and 233 K [1, 2]. Such temperature range was never included in the 2016 Kigali Amendment to the Montreal Protocol to phase down the production and consumption of hydrofluorocarbons (HFCs) [3]. This can be attributed to the limited number of low global warming potential (GWP) alternatives that can replace existing working fluids found in the market. Furthermore, many of the newly proposed low GWP refrigerants require higher compression ratios at such ULT conditions, which in return lowers the system's coefficient of performance and reduces the miscibility of the refrigerant and lubricating oil mixture.

Cascade or auto-cascade refrigeration (ACR) cycles are commonly employed to achieve temperatures below 213 K [4]. In comparison to a typical cascade refrigeration cycle with multiple compressors, the ACR configuration adopts a single compressor design with a set of zeotropic mixtures. The cascade effect between the high boiling point and low boiling point component is achieved through a series of phase separators and evaporative condensers. In

addition, the phase separators ensure the effective recycle of the lubricating oil which in return maintains the system's heat transfer performance [2, 5].

Extensive efforts have been made to study the performance, optimization, and selection of refrigerants for different ACR systems. The application of HFC blends in ACR was first introduced by Martin Ruhemann [6] in 1946 using chlorotrifluoromethane (R-13) + chlorodifluoromethane (R-22) binary mixtures to achieve a temperature of 200 K. A lower temperature of 117 K was later achieved by Fuderer Andrija [7] in 1965 using methane (R-50) + dichlorodifluoromethane (R-12) binary mixtures. The use of chlorofluorocarbons (CFCs) and hydrofluorochlorocarbons (HCFCs) was later banned by the 1987 Montreal Protocol [8] due to their ozone depleting potential. Since then, several HFC blends were explored in the literature to achieve a higher refrigeration capacity and a lower cooling temperature. Currently, 1,1,1,2-tetrafluoroethane (R-134a) + trifluoromethane (R-23) and R-134a + R-23 + tetrafluoromethane (R-14) are the most commonly studied blends for two- and three-stage ACR systems, respectively [5, 9]. However, alternative working fluids with GWP of less than 150 are now preferred to better align with current environmental regulations applied in the high temperature region (above 233 K). These alternative fluids should also possess other equally important properties such as low flammability, non-toxicity, and low cost.

Calm [10] proposed the use of hydrofluoroolefins (HFOs) as alternatives for R-134a in ACR systems. Fluoromethane (R-41), an HFC with lower GWP, and light hydrocarbons were proposed as alternatives for R-23. To date, there are no alternatives for R-14. The cycle characteristics using trans-1,3,3,3-tetrafluoropropene (R-1234ze(E)) + difluoromethane (R-32) binary mixture [11] was studied for two-stage ACR systems, and using propane (R-290)

+ R-23 + R-14, propylene (R-1270) + ethane (R170) + R14, 2,3,3,3-tetrafluoropropene (R-1234yf) + R-41 + R-14, R-1234yf + R-170 + R-14 and R-1234yf + R-23 + R-14 ternary mixtures for three-stage AC systems [2, 12].

Still, the high flammability of many of the aforementioned low GWP blends limit their use in some applications [5]. For such cases, carbon dioxide (R-744), a natural non-flammable refrigerant with a sublimation temperature of -78°C , is suggested. Di Nicola et al. [13] proposed the use of an HFC refrigerant with a low melting temperature to act as a solvent for solid carbon dioxide (dry ice) below its triple point. A variety of refrigerants were studied including R-41, R-32, and several fluorinated derivatives of ethane. R-32 was recommended due to its good thermophysical properties and relatively low GWP.

However, experimental data available in the literature on the phase behavior of refrigerants at ULT conditions are scarce [14]. Consequently, the industry relies on process simulations to predict and optimize the cycle characteristics as a function of working fluid type and composition. Owing to their simplicity, activity coefficient models are commonly used to model nonidealities in the liquid phase at such conditions. These models assume no change in volume upon mixing which is most accurate at low temperatures and pressures.

Nevertheless, conventional activity coefficient models such as the universal quasi-chemical model (UNIQUAC) [15, 16] and the non-random two-liquid model (NRTL) [17] lack the physics to explicitly describe molecular interactions such as polarity, molecular size, and shape. Consequently, Chapman and Fouad [18, 19] have recently developed the statistical associating fluid theory activity coefficient model (SAFT-AC) which offers the user a systematic, fast, and simple approach to incorporate molecular interactions in a fundamental manner that is based on statistical mechanics. As part of our continuous efforts to study the

bulk, interfacial and transport properties of refrigerant systems [20-28], we apply the SAFT-AC model to predict the solubility of refrigerants in polyol ester (POE) lubricants as well as the solubility of solid carbon dioxide in refrigerant solvents. In addition, the application of SAFT-AC to predict the interfacial properties of binary systems is explored for the first time through the use of Butler's method [29].

1.2 Phase Equilibrium of Cross Associating Mixtures

Accurate modeling of fluid phase equilibrium is of great importance for an effective process design and simulation of various separation processes found in the industry. Thermodynamic frameworks for modeling of phase equilibrium are typically based on activity coefficients or equations of state which provide for mixture nonidealities. As pointed out by Palmer[30], complex formation such as association and solvation have the most impact on mixture nonidealities followed by difference in size and shape of molecules. Current activity coefficient models in chemical engineering practice, such as the universal quasi-chemical model (UNIQUAC)[15] and the non-random two-liquid model (NRTL)[17], are based upon the local composition approach and this approach relies upon non-polar non-associating interactions between molecules.

It was pointed out by Asprion et al.[31] that UNIQUAC model is unable to correctly model the composition dependence of activity coefficients as well as heat of mixing of alcohol and alkane mixtures. Subsequently, Fouad et al.[32] showed that UNIQUAC exhibited a false liquid-liquid phase split and an inaccurate composition dependence for the activity coefficients of 1-alcohol + n-alkane binary mixtures. The phase behavior of these mixtures is characterized

by its strong deviation from Raoult's law due to self-association of alcohols in a non-polar fluid leading to large non-idealities. The ability of Wertheim association theory[33-36] based equation of state models[37-39] in predicting accurate VLE of 1-alcohol + n-alkane mixtures was previously shown using different versions of the statistical associating fluid theory (SAFT)[37-39] equation of state including: the original version[40-43], the perturbed chain version of SAFT (PC-SAFT)[44-47], the polar versions of SAFT as implemented by Jog and Chapman[48-54], the simplified version of PC-SAFT[55-60], the Chen and Kregleqski version of SAFT (CK-SAFT)[61-63], the group contribution versions of SAFT[64-67] and the cubic plus association (CPA)[68-72]. Moreover, comparison with spectroscopic measurements[73] and molecular dynamics (MD) simulation[32, 74] also showed the SAFT model to work well for hydrogen bonding distribution in these mixtures for un-associated monomer concentration[32].

In this paper, we extend the previous comparisons to an entirely different set of mixtures for species that form solvation complexes, usually of 1:1 and 1:2 association scheme leading to negative deviations from ideality[75]. In this article, we first describe the Polar PC-SAFT model that we have utilized as an example of association theory-based models. We also provide details of the UNIQUAC model which has been utilized as an example of the local composition models. We then describe the mixture data selection methodology used to narrow down the systems to mixtures of chloroform and halothane with oxygenated solvents. We further present the mixture data modeling methodology. Emphasis is placed not only on the activity coefficients for vapor-liquid equilibrium (VLE) but also on modeling the excess enthalpy to provide temperature dependency of activity coefficients using the Gibbs-Helmholtz

equation[75]. In particular, accurate description of the activity coefficient at low concentrations is essential for optimum design of separation equipment[76].

CHAPTER 2

LITERATURE REVIEW

2.1 SAFT-Activity Coefficient Model

The activity coefficient can be written within the SAFT-AC framework as

$$\ln \gamma_i = \ln \gamma_i^{ig} + \ln \gamma_i^{hs} + \ln \gamma_i^{chain} + \ln \gamma_i^{disp} + \ln \gamma_i^{assoc} + \ln \gamma_i^{dipolar} \quad (1)$$

where the ideal gas (*ig*) contribution to the activity coefficient is a Flory-Huggins type combinatorial term

$$\ln \gamma_i^{ig} = \ln \left(\frac{v_i^{pure}}{v^{mix}} \right) + 1 - \frac{v_i^{pure}}{v^{mix}} \quad (2)$$

where v^{mix} is the molar volume of the mixture at the mixture pressure and v_i^{pure} is the molar volume of the pure component at the pure component pressure. The soft repulsion between real molecules is described using a temperature dependent effective hard sphere segment diameter, d_i , defined in terms of the Lennard-Jones segment diameter, σ_i . Based on the hard sphere diameters of the components in the mixture, reduced densities are defined as

$$\begin{aligned} \xi_k &= \frac{\pi}{6} \rho \sum_j x_j m_j d_j^k \\ \eta = \xi_3 &= \frac{\pi}{6} \rho \sum_j x_j m_j d_j^3 \end{aligned} \quad (3)$$

where ξ_k is a reduced density and η is the packing fraction, ρ is the number density, and x_j is the mole fraction of component j.

Based on the Carnahan-Starling equation of state generalized to mixtures [77, 78], the hard sphere contribution to the activity coefficient is given by

$$\begin{aligned} \ln \gamma_i^{hs} = m_i & \left[\frac{3(d_i \xi_2 + d_i^2 \xi_1)}{(1 - \xi_3)} + \frac{3\xi_1 \xi_2 d_i^3}{(1 - \xi_3)^2} + \frac{3\xi_2^2 d_i^2}{\xi_3(1 - \xi_3)^2} + \frac{\xi_2^3(3\xi_3 - 1)d_i^3}{\xi_3^2(1 - \xi_3)^3} \right. \\ & + \left(\frac{3\xi_2^2 \xi_3 d_i^2 - 2\xi_2^3 d_i^3}{\xi_3^3} - 1 \right) \ln(1 - \xi_3) + \left(\xi_0 - \frac{\xi_2^2}{\xi_3^2} \right) \frac{d_i^3}{(1 - \xi_3)} \Big] \\ & - \frac{\rho}{\rho_i^{pure}} \bar{m} \left[\frac{\xi_3}{(1 - \xi_3)} + \frac{3\xi_1 \xi_2}{\xi_0(1 - \xi_3)^2} + \frac{3\xi_2^3 - \xi_3 \xi_2^3}{\xi_0(1 - \xi_3)^3} \right] \\ & - m_i \frac{4\eta_{pure,i} - 3\eta_{pure,i}^2}{(1 - \eta_{pure,i})^2} \end{aligned} \quad (4)$$

where $\bar{m} = \sum_i x_i m_i$ is the average chain length in the mixture and the terms in square sbrackets are evaluated at the mixture density. The mixture molar volume is estimated based on a zero excess volume assumption and can be evaluated as

$$v^{mix} = \frac{1}{\rho} = \sum_i x_i v_i^{pure} \quad (5)$$

The pure component molar volumes were evaluated in this work using the Design Institute for Physical Properties (DIPPR) database correlations [79]. For mixtures of homonuclear chains, the contribution to the activity coefficient is given by

$$\ln \gamma_i^{hc} = \left[(1 - m_i) \ln g_{ii}^{hs} + \sum_j x_j (1 - m_j) \rho \frac{\partial \ln g_{jj}^{hs}}{\partial \rho_i} - \frac{\rho}{\rho_i^{pure}} \sum_j x_j (1 - m_j) \rho \frac{\partial \ln g_{jj}^{hs}}{\partial \rho} \right] - (1 - m_i) \ln g_{ii}^{hs} \Big|_{pure} \quad (6)$$

where the term in square brackets is evaluated at the mixture density, the last term is evaluated at the pure component density, and g_{ii}^{hs} is the hard sphere radial distribution function at contact from the Carnahan-Starling equation of state generalized to mixtures[77, 78]. The activity coefficient due to dispersion from Barker and Henderson perturbation theory[80] has contributions from first order and second order terms.

$$\ln \gamma_i^{disp} = \ln \gamma_i^{disp,1} + \ln \gamma_i^{disp,2} \quad (7)$$

The contribution to the activity coefficient from the first order is given by

$$\begin{aligned} \ln \gamma_i^{disp,1} = & -2\pi\rho \left[2m_i I_1 \sum_j x_j m_j \left(\frac{\varepsilon_{ij}}{k_B T} \right) \sigma_{ij}^3 + \overline{m^2 \varepsilon \sigma^3} \sum_{k=0}^6 a_k k \eta^{k-1} \xi_{3,xi} \right. \\ & - \frac{\rho}{\rho_i^{pure}} \overline{m^2 \varepsilon \sigma^3} \left(\sum_{k=0}^6 a_k k \eta^k + I_1 \right) \\ & \left. + \overline{m^2 \varepsilon \sigma^3} (m_i - \bar{m}) \sum_{k=0}^6 \eta^k \left(\frac{1}{\bar{m}^2} a_{1k} + \frac{1}{\bar{m}^2} \left(3 - \frac{4}{\bar{m}} \right) a_{2k} \right) \right] \\ & + 2\pi\rho_i^{pure} I_1^{pure,i} m_i^2 \left(\frac{\varepsilon_{ii}}{k_B T} \right) \sigma_{ii}^3 \end{aligned} \quad (8)$$

where $\xi_{3,xi}$, and I_1 are given by

$$\xi_{3,xi} = \frac{\pi}{6} \rho m_i d_i^3 \quad (9)$$

$$I_1 = \sum_{i=0}^6 \eta^i \left(a_{0i} + \frac{\bar{m}-1}{\bar{m}} a_{1i} + \frac{\bar{m}-1}{\bar{m}} \frac{\bar{m}-2}{\bar{m}} a_{2i} \right) \quad (10)$$

The contribution to the activity coefficient from the second order is given by:

$$\begin{aligned} \ln \gamma_i^{disp,2} = & -\pi \rho \left[\left(2m_i \sum_j x_j m_j \left(\frac{\varepsilon_{ij}}{k_B T} \right)^2 \sigma_{ij}^3 \right) \bar{m} C_1 I_2 \right. \\ & + \overline{m^2 \varepsilon^2 \sigma^3} \left[C_1 I_2 (m_i - \bar{m}) + \bar{m} I_2 [C_2 \xi_{3,xi} - C_1^2 C_3 (m_i - \bar{m})] \right. \\ & + \bar{m} C_1 \sum_{k=0}^6 b_k k \eta^{k-1} \xi_{3,xi} + \bar{m} C_1 (m_i - \bar{m}) \sum_{k=0}^6 \eta^k \left(\frac{1}{\bar{m}^2} b_{1k} + \frac{1}{\bar{m}^2} \left(3 - \frac{4}{\bar{m}} \right) \right) \quad (11) \\ & + \pi \bar{m} \rho \frac{\rho}{\rho_i^{pure}} \left[C_1 \left(I_2 + \eta \sum_{k=0}^6 b_k k \eta^{k-1} \right) + \eta I_2 C_2 \right] \overline{m^2 \varepsilon^2 \sigma^3} \\ & \left. + \pi \rho_i^{pure} m_i C_1^{pure,i} I_2^{pure,i} m_i^2 \left(\frac{\varepsilon_{ii}}{k_B T} \right)^2 \sigma_{ii}^3 \right] \end{aligned}$$

where I_2 , C_1 , C_2 , and C_3 are given by

$$I_2 = \sum_{i=0}^6 \eta^i \left(b_{0i} + \frac{\bar{m}-1}{\bar{m}} b_{1i} + \frac{\bar{m}-1}{\bar{m}} \frac{\bar{m}-2}{\bar{m}} b_{2i} \right) \quad (12)$$

$$C_1 = \left(1 + \bar{m} \frac{8\eta - 2\eta^2}{(1-\eta)^4} + (1-\bar{m}) \frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{[(1-\eta)(2-\eta)]^2} \right)^{-1} \quad (13)$$

$$C_2 = -C_1^2 \left[\bar{m} \frac{(-4\eta^2 + 20\eta + 8)}{(1-\eta)^5} + (1-\bar{m}) \frac{(2\eta^3 + 12\eta^2 - 48\eta + 40)}{[(1-\eta)(2-\eta)]^3} \right] \quad (14)$$

$$C_3 = \frac{8\eta - 2\eta^2}{(1-\eta)^4} - \frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{[(1-\eta)(2-\eta)]^2} \quad (15)$$

The activity coefficient contribution due to dipolar interactions is derived based on the Jog and Chapman's Dipolar Chain Theory[48]. The residual reduced Helmholtz free energy contribution due to dipolar interactions, $a^{dipolar,res}$, written in the Pade' approximate has the following form:

$$a^{dipolar,res} = \frac{a_2}{1 - a_3/a_2} \quad (16)$$

where a_2 and a_3 are the second- and third-order terms in the perturbation expansion. The result for SAFT-AC is given by

$$\begin{aligned} \ln \gamma_i^{dipolar} = & \left(\frac{1}{1 - a_3/a_2} \right) \left(\frac{\partial A_2/Vk_B T}{\partial \rho_i} \right) \\ & + \left(\frac{1}{1 - a_3/a_2} \right)^2 \left[\left(\frac{\partial A_3/Vk_B T}{\partial \rho_i} \right) - \frac{a_3}{a_2} \left(\frac{\partial A_2/Vk_B T}{\partial \rho_i} \right) \right] \\ & - \frac{\rho}{\rho_i^{pure}} \left(\sum_i x_i \frac{\mu_i^{dipolar}}{k_B T} - a^{dipolar,res} \right) - a_i^{dipolar,res,pure} \end{aligned} \quad (17)$$

where detailed equations are provided in the work by Jog and Chapman. Expressions for the chemical potential contribution due to dipolar interactions, $\mu_i^{dipolar}$, the derivatives of second- and

third-order terms with respect to density, $\frac{\partial A_2/Vk_BT}{\partial \rho_i}$ and $\frac{\partial A_3/Vk_BT}{\partial \rho_i}$, are provided in the previous publication [19].

Table 2.1. 1 Pure component molecular parameters for refrigerants and lubricants

	MW_i (g·mol ⁻¹)	m_i	σ_i (Å)	ε_i/k (K)	x_{p_i}	μ_i (D)	Ref.
R-170	30.070	1.607	3.521	191.42			[81]
R-744	44.010	2.073	2.785	169.21	-	-	[81]
R-290	44.097	2.002	3.618	208.11	-	-	[81]
R-32	52.023	1.730	3.231	149.988	0.50	1.98	[23]
R-600a	58.124	2.262	3.757	216.530	-	-	[81]
R-152a	66.050	1.699	3.687	193.413	0.50	2.26	[20]
R-23	70.014	1.735	3.321	149.867	0.50	1.65	[28]
R-143a	84.040	1.676	3.825	168.619	0.50	2.32	[20]
R-134a	102.031	2.154	3.527	157.227	0.50	2.06	[20]
R-1234yf	114.043	2.358	3.631	179.953	0.33	2.011	[21]
R-1234ze(E)	114.043	2.811	3.369	176.935	0.33	1.440	[21]
R-125	120.021	2.399	3.451	155.244	0.50	1.54	[20]
R-116	138.012	2.880	3.294	138.420			[20]
PEC-5	472.62	10.533	3.972	261.810	-	-	[82]
PEC-7	584.84	12.104	4.141	269.990	-	-	[82]
PEC-9	697.05	12.893	4.364	284.830	-	-	[82]
VG22	540.60	8.216	4.677	321.08	-	-	This work
VG32	560.26	11.676	4.122	267.179	-	-	This work

^a $\sigma_i = 2.7927 + 10.11 \times \exp(-0.01775) - 1.417 \times \exp(-0.01146 \times T)$

2.1.1 Vapor-Liquid Equilibrium (VLE)

For vapor-liquid equilibrium (VLE), the following fundamental relationship holds for the fugacity of species i in both phases:

$$y_i \hat{\phi}_i^V p = x_i \gamma_i \phi_i^{sat} P_i^{sat} \exp \left[\frac{v_i^{pure} (p - p_i^{sat})}{RT} \right] \quad (18)$$

where x_i and y_i are the liquid and vapor phase compositions of species i , respectively, $\hat{\phi}_i^V$ is the fugacity coefficient of species i in the vapor phase using the Redlich-Kwong (RK) equation of state [83], ϕ_i^{sat} is the pure species fugacity coefficient at saturation, and P_i^{sat} is the pure species pressure at saturation using DIPPR correlations. It was assumed that v_i^{pure} is independent of pressure to simplify the Poynting correction.

2.1.2 Solid-Liquid Equilibrium (SLE)

To solve for the solid-liquid equilibrium (SLE), the following fundamental relationship holds for the fugacity of species i in both phases and is given by [84]:

$$-\ln(\gamma_i x_i) = \frac{\Delta H_{m_i}}{RT_{m_i}} \left(\frac{T_{m_i}}{T} - 1 \right) - \frac{\Delta C_p}{R} \left(\frac{T_{m_i}}{T} - 1 \right) + \frac{\Delta C_p}{R} \ln \left(\frac{T_{m_i}}{T} \right) \quad (19)$$

where ΔH_{m_i} and T_{m_i} are the solute enthalpy of fusion and melting temperature, respectively. It was assumed that the last two ΔC_p terms would cancel each other due to their opposite signs and negligible contribution to the fugacity of species i in the solid phase.

2.1.3 Butler's Equation

The classical Butler equation [29] is used to predict the equilibrium surface tension (σ) and surface composition ($x_{i,S}$) of binary mixtures considered in this work. To do so, pure component surface tensions (σ_i) were obtained from DIPPR and activity coefficients in the bulk and interface were calculated using SAFT-AC. The surface tension of a multicomponent mixture is given by [85]

$$\sigma = \sum_i \left(\sigma_i x_{i,B} + x_{i,B} \frac{RT}{N_A A_i} \ln \frac{\gamma_{i,S} x_{i,S}}{\gamma_{i,B} x_{i,B}} \right) \quad (20)$$

where $x_{i,B}$ is the mole fraction of species i in the bulk and the surface area of species i (A_i) is given by

$$A_i = \left(\frac{v_i^{pure}}{N_A} \right)^{2/3} \quad (21)$$

2.1.4 MIXTURE DATA SELECTION AND DATA ANALYSIS METHODOLOGY

Mixtures of oxygenated compounds, with lone pairs of electrons, and hydrogen bond donor haloalkanes were selected for which good quality data were found in the literature. An important part of our evaluation is the study of activity coefficients which as demonstrated by Van Ness and Smith [86] show more details than the TPxy diagrams. In doing so, we have focused on isothermal TPxy vapor-liquid equilibrium data along with heat of mixing measurements at nearly the same temperature. Isothermal VLE data were selected so that modeling concentration dependency of activity coefficients could be kept separate from modeling of temperature dependency of activity coefficients. Our selection of VLE data was mostly limited to those which report pure sample total pressure measurement at the temperature of interest using the same apparatus. This is important as per the recommendation of Plank et al.[87] For mixtures that form 1:1 complex, and assuming that the nonidealities are mainly due to solvation effects, symmetry of the excess enthalpy curve is also an important check. We have studied two sets of mixtures after evaluating their data for thermodynamic consistency: (a) mixtures of chloroform and oxygenated solvents and (b) mixtures of halothane and oxygenated solvents.

2.2 THERMODYNAMIC MODELING

2.2.1 Polar PC-SAFT equation of state

The SAFT equation of state describes molecules as chains of spherical segments that repel at short range and attract at long range due to van der Waals (dispersion) and polar interactions. In addition, the molecules can associate or hydrogen bond through short range attractions. The Polar PC-SAFT equation of state includes the association and chain terms of Chapman et al. [37-39], the perturbed chain segment term of Gross and Sadowski[45] and the polar term of Jog and Chapman[48, 49]. The complete equation of state in Polar PC-SAFT [53], in terms of the residual Helmholtz free energy, a^{res} , which is calculated residual to an ideal gas at the same molar volume, temperature, and composition, is given as the sum of a hard-chain contribution, a^{hc} , a dispersion contribution, a^{disp} , an association contribution, a^{assoc} and a polar contribution, a^{polar} :

$$a^{res} = a^{hc} + a^{disp} + a^{assoc} + a^{polar} \quad (22)$$

A detailed description of the Polar PC-SAFT equation of state is given in our previous publications [32, 74, 88]. Table 2.2.1. illustrates the pure component parameters used in this work. Briefly, m_i is the number of spherical segments in a molecule, σ_i is the segment diameter, and ε_i/k_B is the dispersion energy parameter. Association occurs between an electron acceptor site of one molecule and an electron donor site of another molecule. The bonding site volume, related to the entropy change due to association, is $\kappa^{A_i B_i}$. The association (or hydrogen bonding) energy, related to the enthalpy change of hydrogen bonding, is $\varepsilon^{A_i B_i}/k_B$. Oxygenated solvents also have long-range dipolar interactions where μ_{D_i} is the dipole moment and x_{p_i} is the fraction of dipolar segments.

The dipole moments were fixed to their corresponding gas phase values. Dominik et al.[53] demonstrated that the values of $m_i x_{p_i}$ were constant for any given homologous series. The latter assumption was maintained in this work to reduce the number of fitting parameters required by the molecular model. The remaining parameters were fitted to pure component saturated liquid density and vapor pressure data. The weak dipole moment of chloroform (1.0 D) was not considered in this work due its negligible influence on the phase behavior. On the other hand, dipole-dipole interactions between the moderately dipolar halothane molecule (1.4 D) and the oxygenated solvents were considered.

Table 2.2.1. 1 Polar PC-SAFT Equation of State Pure component molecular parameters for Oxygenated solvents and Haloalkanes

component	m_i	σ_i (Å)	ε_i/k_B (K)	$\kappa^{A_i B_i}$	$\varepsilon^{A_i B_i}/k_B$ (K)	μ_{D_i} (D)	$m_i x_{p_i}$	Ref.
chloroform	2.322	3.574	281.82	0.0018	1106.011	-	-	This work
halothane	2.464	3.807	250.81	0.0024	934.438	1.4	1.0	This work
acetone	2.221	3.608	259.99			2.7	0.5	[53]
THF	2.285	3.624	279.07			1.8	0.8	[53]
DEE	2.879	3.555	220.59			1.2	1.0	[53]
MTBE	2.832	3.767	236.51			1.2	1.0	This work
MAc	2.397	3.548	238.87			1.7	1.5	[53]

Chloroform and halothane were modeled in this work with two association sites, one electron acceptor site and one electron donor site. McGlashan and Rastogi [89] as well as Inglese [90] suggested that solvating mixtures that form 1:1 association complexes tend to have symmetrical excess enthalpy curves as a function of composition with a minimum at $x \approx 0.5$. On the other hand,

solvating mixtures that form 1:2 association complexes tend to have asymmetrical excess enthalpy curves that are skewed towards low mole fractions of the oxygenated solvent. Consequently, excess enthalpy data (as shown later) were used in this work to determine the number of electron donor sites that are to be assigned on each of the considered oxygenated solvents. Tetrahydrofuran (THF), diethyl ether (DEE), and methyl tert-butyl ether (MTBE) were modeled as dipolar hard chains with one electron donor site while acetone and methyl acetate (MAc) were modeled as dipolar hard chains with two electron donor sites. Furthermore, oxygenated solvents can only cross-associate with the single electron acceptor site of chloroform or halothane via a 1:1 or 1:2 solvation scheme. The cross-association parameters were fitted to VLE and excess enthalpy data and are illustrated for all mixtures in Table 2.2.1. 2. All SAFT binary interaction parameters (k_{ij}) were fixed to zero in the work of estimating phase equilibrium of binary cross-associating mixtures comprising of oxygenated solvents and haloalkanes.

Table 2.2.1. 2 Solvation parameters for chloroform and halothane binary mixtures

i	j	solvation ($i:j$)	$\kappa^{A_i B_j}$	$\varepsilon^{A_i B_j}/k_B$ (K)
chloroform	THF	1:1	0.081	1216.466
chloroform	DEE	1:1	0.038	1342.416
chloroform	MTBE	1:1	0.041	1325.508
chloroform	acetone	1:2	0.063	981.992
chloroform	MAc	1:2	0.144	855.462
halothane	THF	1:1	0.095	1190.898
halothane	MTBE	1:1	0.032	1469.904
halothane	acetone	1:2	0.065	972.495
halothane	MAc	1:2	0.097	877.616

2.2.2 UNIQUAC activity coefficient model

Within the UNIQUAC framework [15], the activity coefficient of species “ i ” in a mixture is calculated as the sum of a combinatorial contribution, γ_i^C , and a residual contribution, γ_i^R :

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (23)$$

The combinatorial term is determined based on the Stavermann-Guggenheim equation [91] to account for non-sphericity and is calculated as following:

$$\ln \gamma_i^C = \ln \left(\frac{\Phi_i}{x_i} \right) + \frac{z}{2} q_i \ln \left(\frac{\theta_i}{\Phi_i} \right) + l_i - \frac{\Phi_i}{x_i} \sum_j x_j l_j \quad (24)$$

Where l_i is defined in terms of the coordination number, z , the pure relative van der Waals volume, r_i , and the pure relative surface area, q_i as:

$$l_i = \frac{z}{2} (r_i - q_i) + 1 - r_i \quad (25)$$

The volume fraction of species “ i ” in the mixture, Φ_i , is defined as:

$$\Phi_i = \frac{r_i}{\sum_j x_j r_j} \quad (26)$$

The surface fraction of species “ i ” in the mixture, θ_i , is defined as:

$$\theta_i = \frac{q_i}{\sum_j x_j q_j} \quad (27)$$

Table 2.2.2. 1 presents the structural parameters used for UNIQUAC in this work.

Table 2.2.2. 1 Surface and volume parameters for UNIQUAC[92]

component	r_i	q_i
chloroform	2.870	2.410
halothane	3.568	3.160
THF	2.941	2.720
DEE	3.395	3.016
MTBE	4.068	3.632
acetone	2.573	2.336
MAc	2.804	2.576

The residual contribution corrects for molecular interactions between unlike species upon mixing and is calculated as follows:

$$\ln \gamma_i^R = q_i \left(1 - \ln \sum_j \theta_j \tau_{ji} - \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \right) \quad (28)$$

Since VLE measurements are often limited to TPx measurements with the possibility that the gas phase concentration may have higher uncertainties, higher standard deviations were assumed for the latter and this is consistent with the Barker methodology [87]. Calculations using the local composition model were initially carried out only with vapor-liquid equilibrium data using two adjustable parameters. In the second set of runs, excess enthalpies were added, and four adjustable parameters were utilized for the UNIQUAC model. Two different forms of temperature dependency of adjustable parameters in the UNIQUAC model were utilized and then results for the best form are reported here. The temperature dependency was expressed using Equation 29 as:

$$\ln \tau_{ij} = a_{ij} + \frac{b_{ij}}{T} + c_{ij} \ln T \quad (29)$$

where τ_{ij} is the UNIQUAC binary interaction parameter between unlike species and coefficients a_{ij} , b_{ij} , and c_{ij} are the adjustable parameters for the temperature dependency.

For analysis of consistency of TPxy data, we utilized the Redlich-Kister expansion [86] (refer to Appendix) along with PC-SAFT equation of state and pure component and mixture parameters for the gas phase nonidealities. Parameters of the vapor pressure equation utilized were adjusted to make sure of exact match with the reported pure sample total pressures as recommended by Plank et al.[87] Table 2.2.2. 2 presents coefficients fitted in this work for Equations A.3 and A.4. VLE data utilized in this study, in general, are found to be of good quality with minor inconsistencies which we are assuming to be in the gas phase concentrations. Activity coefficients from experimental data as well as activity coefficients from the consistency fit were both utilized in our comparisons of Polar PC-SAFT and the local composition model.

Table 2.2.2. 2 Coefficients used to calculate Redlich-Kister binary interaction parameters

i	j	A_{ij} (K)	B_{ij} (K)
THF	chloroform	-495.121	32.703
DEE	chloroform	-359.405	-20.606
MTBE	chloroform	-377.694	21.214
acetone	chloroform	-274.122	15.082
MAc	chloroform	-320.231	42.844
THF	halothane	-544.479	69.047
MTBE	halothane	-507.689	-6.420
acetone	halothane	-428.079	34.594
MAc	halothane	-405.744	66.136

The temperature dependency of τ_{ij} was calculated using Equation 1 and coefficients a_{ij} , b_{ij} , and c_{ij} for all mixtures considered in this work are reported in above Table 2.2.2. 2. Note that for MTBE containing binary mixtures, the lowest standard deviation from experimental data was

obtained when both a_{ij} and c_{ij} were set to zero. On average, four adjustable parameters were required to fit the VLE and excess enthalpy using UNIQUAC while only two adjustable parameters were required using Polar PC-SAFT.

For gas phase nonidealities in conjunction with the UNIQUAC activity coefficients model we also utilized the Polar PC-SAFT model and the pure component parameters, discussed earlier.

Table 2.2.2. 3 Coefficients used to calculate UNIQUAC binary interaction parameters

i	j	a_{ij}	b_{ij} (K)	c_{ij}
THF	chloroform	-303.128	92013.122	0
chloroform	THF	-388.763	117955.946	0
DEE	chloroform	2.959	0	-0.509
chloroform	DEE	5.048	0	-0.823
MTBE	chloroform	0	-80.254	0
chloroform	MTBE	0	162.382	0
acetone	chloroform	-0.708	373.107	0
chloroform	acetone	0.140	-101.591	0
MAc	chloroform	-0.423	272.073	0
chloroform	MAc	0.052	-45.231	0
THF	halothane	-0.306	294.399	0
halothane	THF	-0.504	141.706	0
MTBE	halothane	0	187.940	0
halothane	MTBE	0	-15.937	0
acetone	halothane	-0.409	343.107	0
halothane	acetone	-0.262	-39.876	0
MAc	halothane	0.432	92.034	0
halothane	MAc	-1.492	309.286	0

2.2.3 Redlich-Kister activity coefficient model

The expansion is described by Otto Redlich and A. T. Kister [93] the algebraic polynomial equation (30) for multicomponent systems is given in form of power series below for a binary system. This equation can be used for fitting activities in an aqueous solution over the entire

concentration range to calculate molecular level activities and the thermodynamic properties of aqueous solution.

$$G^{Excess} = x_1 x_2 \sum_{i=0}^n A_i (x_2 - x_1)^i \quad (30)$$

Where x_1, x_2 are component 1 and 2 mole fractions in a binary mixture, n is the degree of polynomial, A is the constant parameter found by fitting the experimental VLE data. The activity coefficient of each component is calculated by partial derivative of Excess Gibbs free energy at constant temperature, pressure and numbers of moles as shown in below in equation (31).

$$\ln \gamma_i = \left[\frac{\partial G^{Excess}}{\partial n_i} \right]_{P, T, n_j} \quad (31)$$

More details of Redlich-Kister expansion are available in Appendix.

CHAPTER 3

RESULTS AND CONCLUSION

3.1 Solubility of HFOs in PECs

Figures 3.1.1-3 exhibit the solubility of R-1234ze(E), R-1234yf and isobutane (R-600a) in three linear chained pentaerythritol tetraalkyl esters, respectively. In reference to below Table 3.1. 1, temperature independent binary interaction parameters (k_{ij}) are used to correlate the VLE. In comparison, up to four adjustable parameters are needed to adequately correlate these systems using NRTL [94]. Overall, results indicate that the solubility of refrigerants in POE lubricants is weakly dependent on the length of the tetraalkyl chains of the pentaerythritol ester. A detailed analysis reveals that systems under consideration exhibit strong negative deviations from Raoult's law at low to moderate refrigerant compositions. The strength of these negative deviations increases with increasing the length of the tetraalkyl chain. Consequently, it can be deduced that unlike dispersion (van der Waals) interactions dominate the phase behaviour at such conditions. On the other hand, positive deviations from Raoult's law are exhibited at high refrigerant compositions. Interestingly, R-1234ze(E) and R-1234yf are structural isomers that differ only in the position of the fluorine atoms. In R-1234yf, all fluorine atoms are placed on one side of the π -bond which in return creates a considerable increase in dipole moment relative to R-1234ze(E). It can be seen that positive deviations in R-1234yf binary mixtures are stronger than these in R-1234ze(E). The weakest positive deviations are exhibited by binary mixtures containing R-600a,

a non-polar hydrocarbon refrigerant. Consequently, it can be deduced that long-range dipolar interactions among refrigerant molecules dominate the phase behaviour at high compositions.

In R-1234yf, all fluorine atoms are placed on one side of the π -bond which in return creates a considerable increase in dipole moment relative to R-1234ze(E). It can be seen that positive deviations in R-1234yf binary mixtures are stronger than these in R-1234ze(E). The weakest positive deviations are exhibited by binary mixtures containing R-600a, a non-polar hydrocarbon refrigerant. Consequently, it can be deduced that strong long-range dipolar interactions among refrigerants dominate the phase behaviour at high compositions.

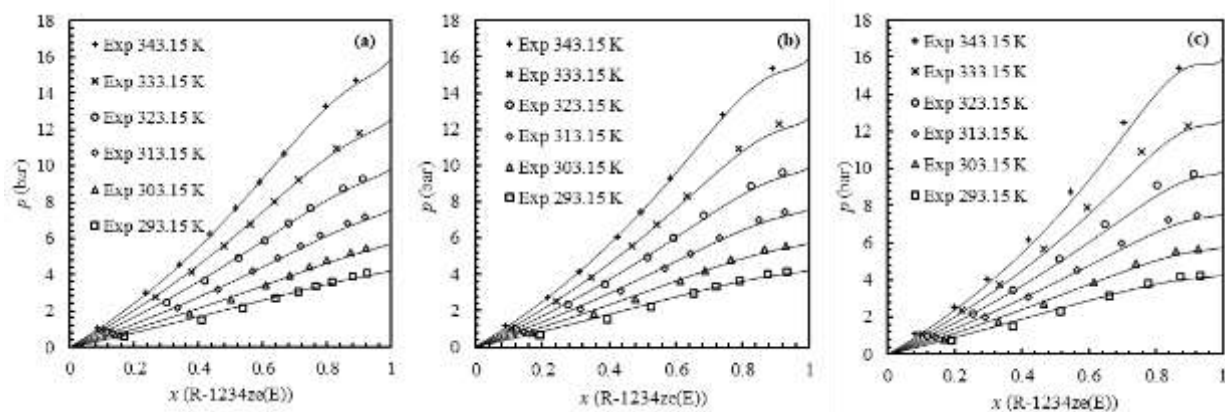


Figure 3.1. 1 Isothermal PTx phase diagrams for R-1234ze(E) in (a) PEC5, (b) PEC7 and (c) PEC9 at different temperatures.

Symbols represent experimental data[1], [2] and lines represent SAFT-AC correlations.

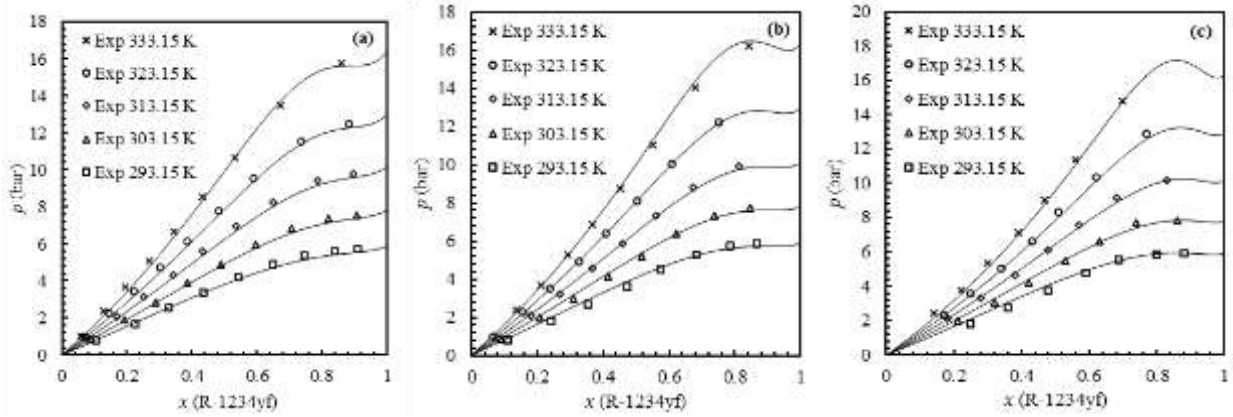


Figure 3.1. 2 Isothermal PTx phase diagrams for R-1234yf in (a) PEC5, (b) PEC7 and (c) PEC9 at different temperatures.

Symbols represent experimental data [3], [4] and lines represent SAFT-AC correlations.

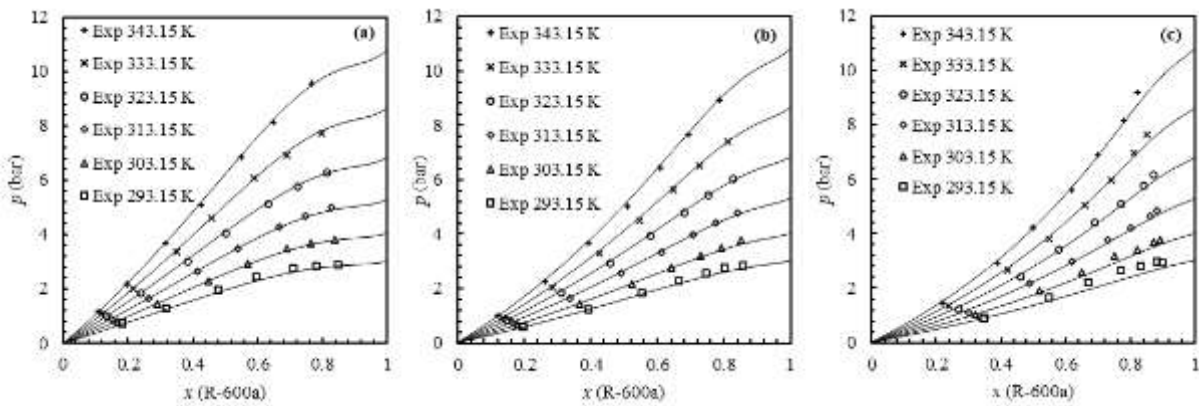


Figure 3.1. 3 Isothermal PTx phase diagrams for R-600a in (a) PEC5, (b) PEC7 and (c) PEC9 at different temperatures.

Symbols represent experimental data [1][2] and lines represent SAFT-AC correlations.

In reference to Table 3.1. 1, a linear correlation that is a function of PEC molecular weight is developed for each of the three refrigerants. Figure 3.2. 1 depicts the solubility of R-1234ze(*E*) and R-1234yf in ISO VG32, a synthetic polyol ester lubricant of known molecular weight (560.26 g.mol⁻¹). Data available in the literature on the chemical and thermodynamic properties of commercial lubricants tend to be limited. Therefore, we assume that ISO VG32 is composed of a mixture of linear PECs that can be modeled as a single pseudo-component via a simple lumping scheme. SAFT parameters for ISO VG32 are calculated using molecular weight dependent correlations developed by Fouad and Vega [25]. Required binary interaction parameters were estimated using the aforementioned developed correlations. Predictions shown in Figure 3.2. 1 are in excellent agreement with experimental data up to 348 K and 6 bars. A similar methodology was followed in Figure 3.2. 2 to predict the solubility of R-290 in ISO VG32 and VG22, respectively. SAFT parameters for ISO VG22 are calculated using its known molecular weight of 540.60 g.mol⁻¹. Up to our knowledge, the literature lacks data on the solubility of R-290 in linear PECs. Consequently, required binary interaction parameters were approximated to be equal to those of R-600a. Again, predictions are found to be in good agreement with experimental data up to 352 K and 24 bars.

Table 3.1. 1 Temperature independent binary interaction parameters of PEC containing systems used in SAFT-AC calculations

	R-1234ze(E)	R-1234yf	R-600a
	k_{ij}		
PEC 5	0.0043	-0.015	0.025
PEC 7	0.022	0	0.020
PEC 9	0.040	0.016	0.020
	$k_{ij} = A MW_{POE} + B$		
A	-0.00519	-0.00007	-0.0000223
B	-0.0712	-0.0473	0.0347

For R-1234ze + PEC

$$k_{ij} = -0.00519MW_{POE} - 0.0712$$

For R-1234yf + PEC

$$k_{ij} = -0.00007MW_{POE} - 0.0473$$

For R-600a + PEC

$$k_{ij} = -0.0000223MW_{POE} + 0.0347$$

3.2 Solubility of HFOs in Vegetable Oils

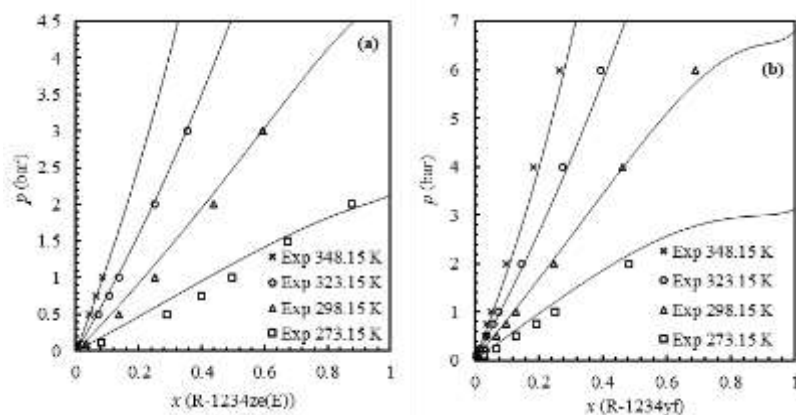


Figure 3.2. 1 Isothermal PTx phase diagrams for (a) R-1234ze(E) and (b) R-1234yf in ISO VG32 at different temperatures.

Symbols represent experimental data [95] and lines represent SAFT-AC predictions

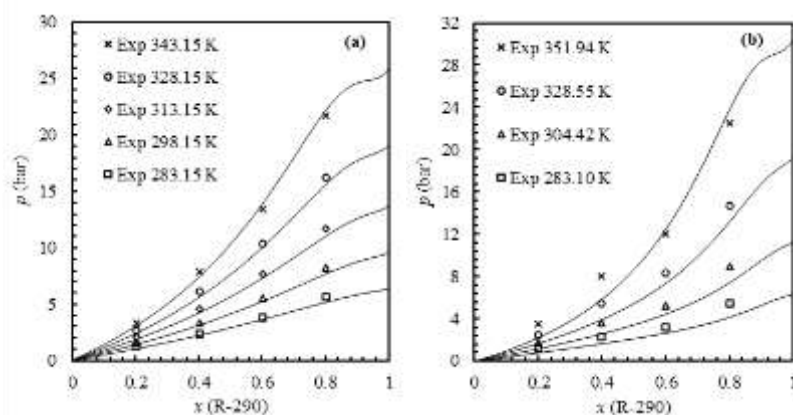


Figure 3.2. 2 Isothermal PTx phase diagrams for R-290 in (a) ISO VG32 and (b) ISO VG22 at different temperatures. Symbols

represent experimental data [96, 97] and lines represent SAFT-AC predictions

Below Figure 3.2. 3 (a) demonstrates predictions made using SAFT-AC for the azeotropic phase behavior of R-23 + hexafluoroethane (R-116) binary mixture. The strong positive deviation from Raoult's law indicates weak intermolecular interactions between the polar R-23 molecule and the non-polar R-116 molecule. Increasing the temperature leads to a shift in the azeotropic composition towards the left-hand side of the phase diagrams (pure R-116). A similar phenomenon can be observed in Figure 3.2. 3 (b) for R-23 + R-170 binary mixture. It appears that replacing all fluorine atoms found in R-116 with hydrogen atoms (R-170) creates a slight shift in the position of the azeotrope towards lower R-23 compositions. The model was able to correlate well the experimental data up to 10 bars. Deviations can be seen at higher system pressures due to compressibility effects and their negligence by all activity coefficient models. On the contrary, a near ideal solution behavior can be seen in Figure 3.2. 3 (c) when R-23 is mixed with R-32. This can be attributed to the similarity in molecular size and interactions between both molecules. Still, it is worth noting that replacing one of the fluorine atoms in R-23 with a hydrogen atom (R-32) enhances symmetry in the molecular structure which increases the dipole moment significantly. The latter explains the large difference in vapor pressures between both molecules. Again, the model was able to correlate well the experimental data up to high temperatures and pressures.

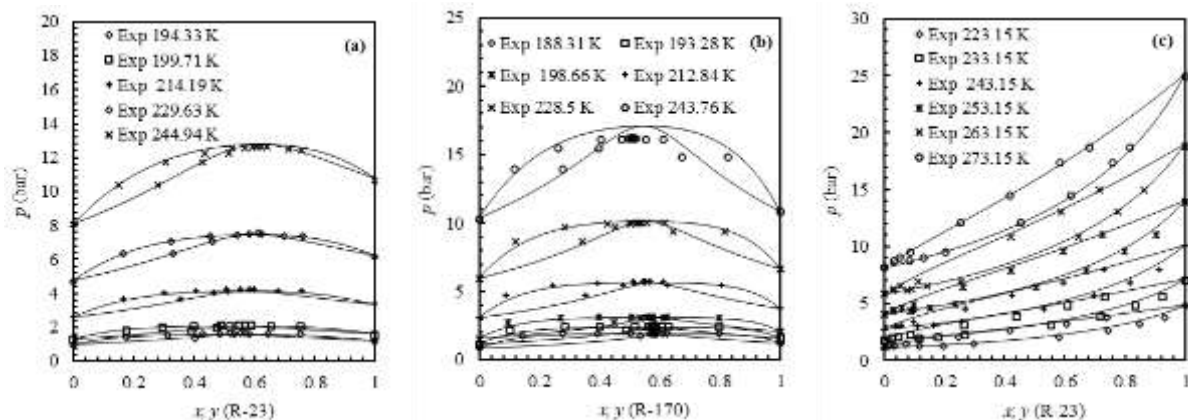


Figure 3.2. 3 Isothermal VLE of R-23 containing binary mixtures. (a) R-116 with $k_{ij} = 0$, (b) R-170 with $k_{ij} = 0.035$ and (c) R-32 with $k_{ij} = -0.03$. Symbols represent experimental data [96-99] and lines represent SAFT-AC correlations.

below Figure 3.3. 1 depicts predictions made using SAFT-AC for the VLE of R-32 containing binary mixtures. All binary interaction parameters are indicated or written in description of figures. Excellent agreement was obtained in comparison to experimental data over a temperatures range of 283-323 K. A near ideal solution behavior is exhibited when R-32 is mixed with R-134a, R-1234yf and R-1234ze(E). Interestingly, the three refrigerants share the same number of fluorine atoms. Figure 3.3. 1(a) depicts a slight negative deviation from Raoult's law which can be attributed to dipole-dipole interactions between R-32 and R-134a molecules. Adding an extra methyldene group ($=CH_2$) to R-134a's structure results in a slight positive deviation from Raoult's law as shown in Figure 3.1. 1 (c) for R-1234yf. The S-shape of the dew curve indicates that the system is thriving to form an azeotrope. It seems that placing all fluorine atoms on one side of the HFO π -bond leads to the formation of strong repulsive interactions with the structurally symmetrical HFC molecule. Changing the position of one fluorine atom in R-1234yf results in the formation of a near ideal solution behavior as demonstrated in Figure 3.3. 1 (d) for R-1234ze(E). In reference to Figure 3.3. 1 (b), a positive azeotrope is exhibited when R-

32 is mixed with R-125. The azeotropic behavior can be attributed to similarity in vapor pressure between both molecules. Strong dipole interactions, and possibly self-association, among R-32 molecules results in a significant decrease in the pure component vapor pressure, which closely resembles that of R-125. In this regard, the application of SAFT-AC is extended to predict the interfacial tension of R-32 containing binary mixtures using Butler's method. In reference to Figure 3.3. 2, predictions made using Butler's method are in good agreement with experimental data. In consistency with their bulk phase behavior, an ideal interfacial behavior with a linear dependence on composition is found for mixtures of R-32 with R-134a, R-1234yf and R-1234ze(E). In addition, mixtures with R-134a and R-1234yf exhibit weak dependence on composition. On the other hand, the surface tension of R-32 + R-125 binary mixture exhibits a non-linear dependence on composition which is a reflection to the presence of a positive azeotrope in the bulk.

3.3 Refrigerant Blends

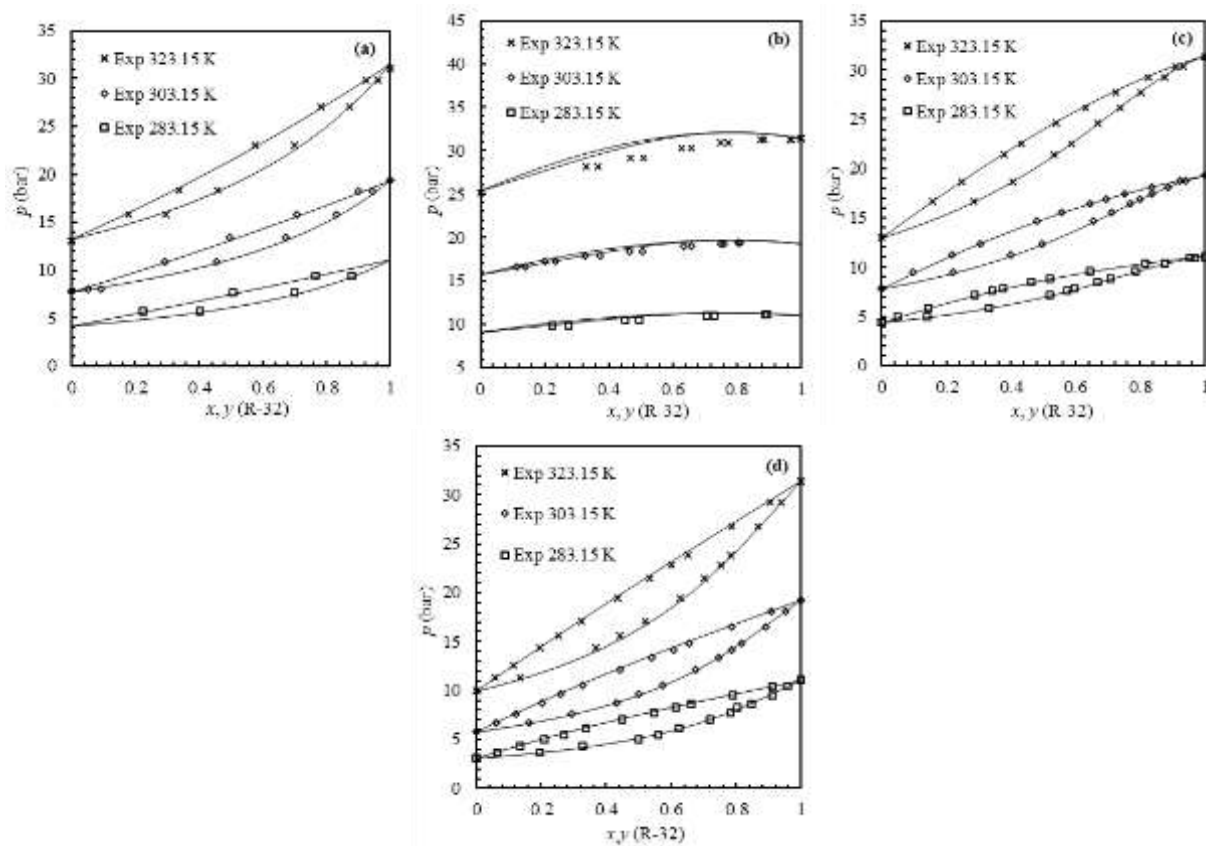


Figure 3.3. 1 Isothermal VLE of R-32 containing binary mixtures. (a) R-134a, (b) R-125, (c) R-1234yf and (d) R-1234ze(E).

Symbols represent experimental data [98-102] and lines represent SAFT-AC predictions ($k_{ij} = 0$)

In consistence with their bulk phase behavior, an ideal interfacial behavior with a linear dependence on composition is found for mixtures of R-32 with R-134a, R-1234yf and R-1234ze(E). In addition, mixtures with R-134a and R-1234yf exhibit weak dependence on composition at high temperatures. The non-linear dependence of surface tension on composition for R-32 + R-125 binary mixture is a reflection to the presence of a positive azeotrope in the bulk.

3.3.1 Surface Tension Estimation of Refrigerant Blends

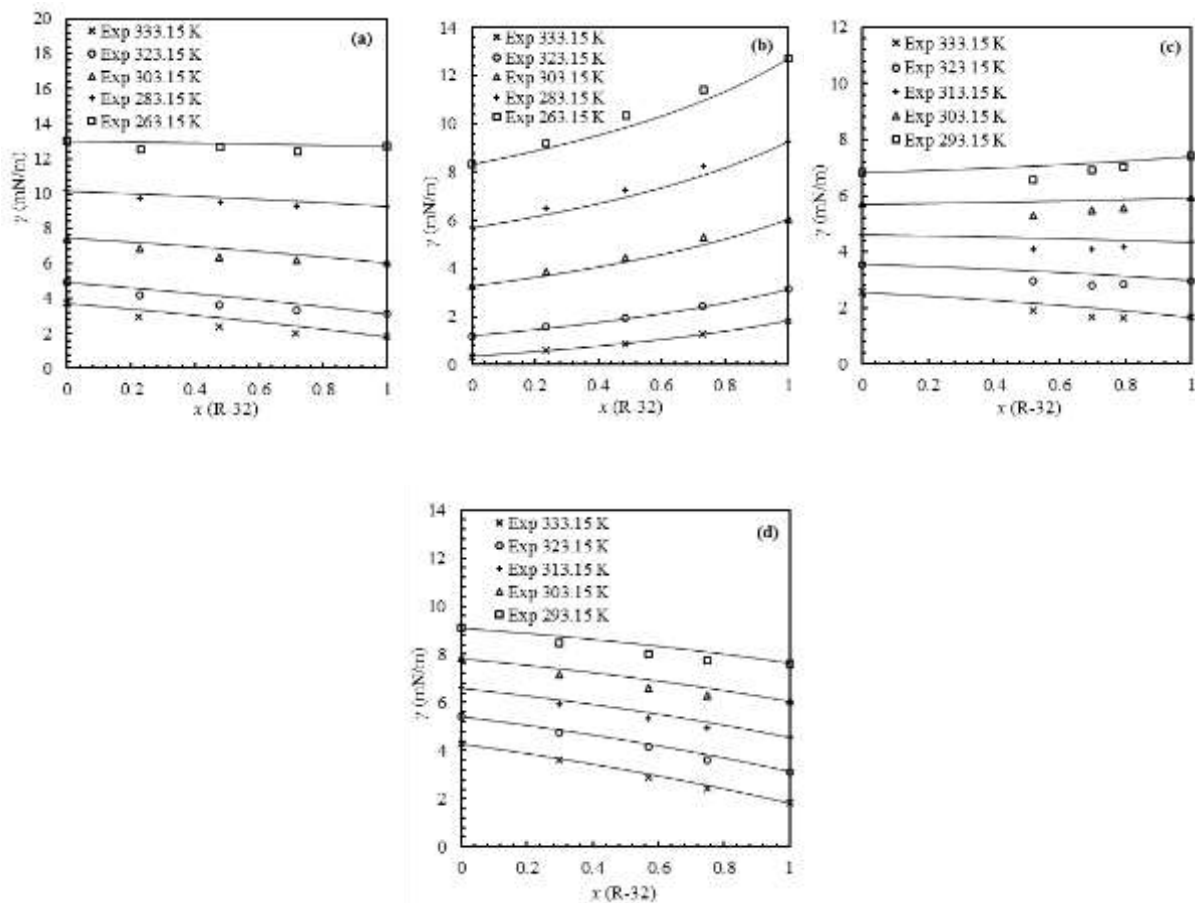


Figure 3.3. 2 Surface tension of R-32 containing binary mixtures. (a) R-134a, (b) R-125, (c) R-1234yf and (d) R-1234ze(E).

Symbols represent experimental data [98, 103] and lines represent SAFT-AC predictions ($k_{ij} = 0$)

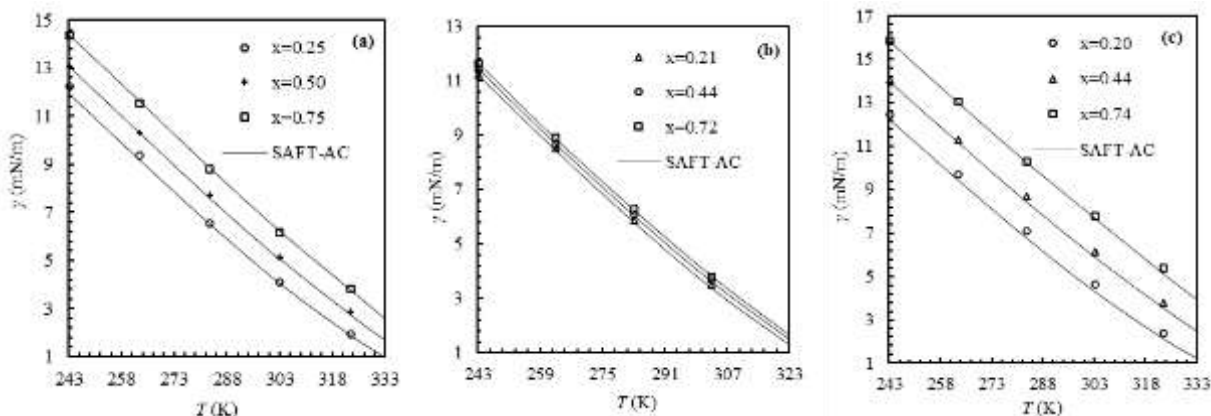


Figure 3.3. 3 Surface tension of R-125 containing binary mixtures. (a) R-134a, (b) R-143a and (c) R-152a. Symbols represent experimental data [103] and lines represent SAFT-AC predictions ($k_{ij} = 0$)

Figure 3.2. 2 and Figure 3.3. 3 demonstrate the temperature dependence of the surface tension of R-125 and R-134a containing binary mixtures, respectively. All binary interaction parameters were fixed to zero for mixtures in above Figure 3.3. 3. Predictions are in good agreement with experimental data across a temperature range of 243-333 K and a wide range of compositions. In reference to Figure 3.3. 2 (b), the surface tension of R-125 + R-143a binary mixture shows weak dependence on composition. A similar weak dependence on composition is also shown in Figure 3.3. 3 (a) for R-134a + R-152a binary mixtures.

These can be attributed to the large similarity in vapor pressure between molecules found in both mixtures, which lead to the formation of a near azeotropic phase behavior across the phase diagrams of both mixtures. Having all fluorine atoms placed on one side of the R-143a or R-152a molecule leads to the formation of a considerable dipole moment which increases the specific gravity of both gases to match that of R-125 and R-134a, respectively.

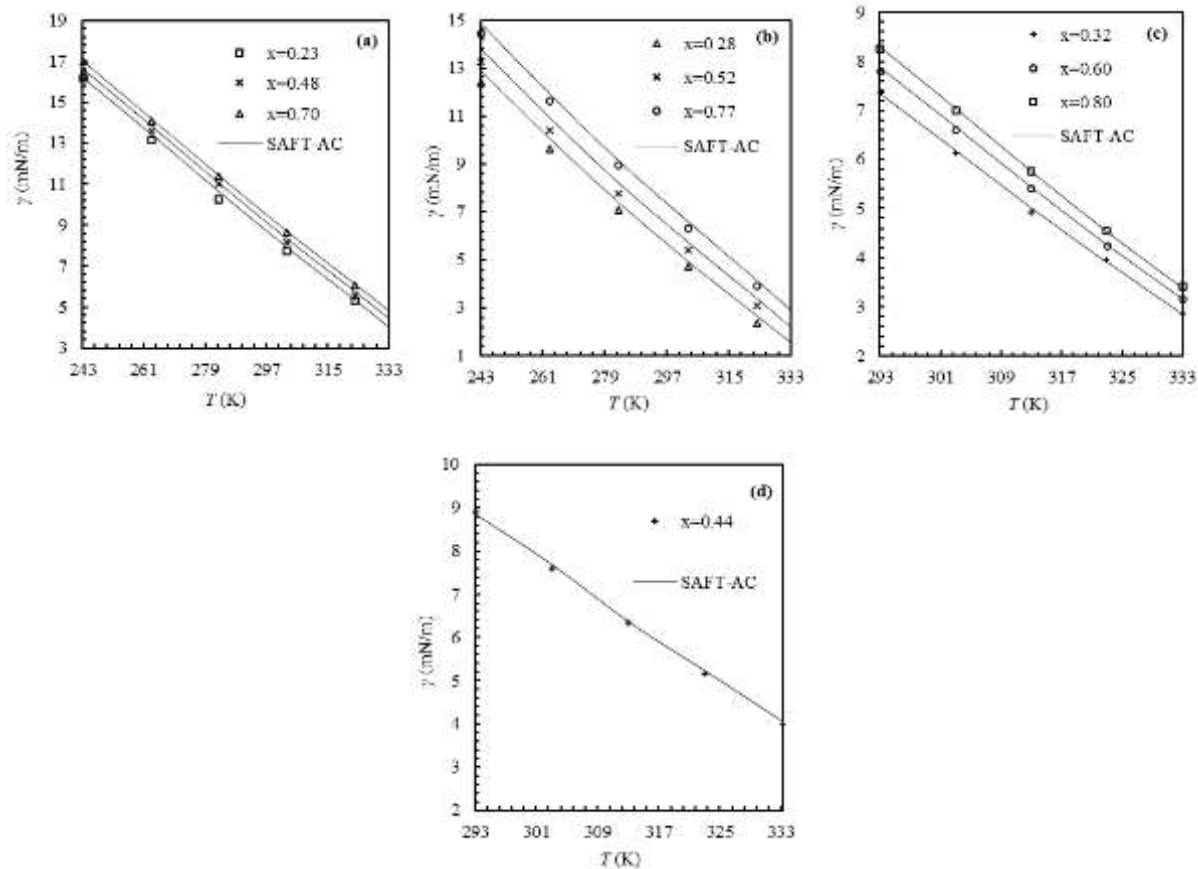


Figure 3.3. 4 Surface tension of R-134a containing binary mixtures (a) R-152a, (b) R-143a, (c) R-1234yf and (d) R-1234ze(E).

Symbols represent experimental data [103, 104] and lines represent SAFT-AC predictions ($k_{ij} = 0$)

Figure 3.3. 5 demonstrates the isothermal VLE of R-744 containing binary mixtures at subcritical temperatures. Binary interaction parameters used to correlate the phase equilibria are shown in Table 3.2. 1. Values were found to be negative which indicate that many of the interactions among unlike species are not properly considered. The contribution to the activity coefficient from quadrupolar interactions is not yet derived within the SAFT-AC framework. Our future publications will include the development and implementation of such term. Systems under consideration exhibit slight negative deviations from Raoult's law. In addition, the strength of these negative deviations increases with increasing the refrigerant dipole moment. Consequently, it can be deduced that dipole-quadrupole interactions dominate the phase behaviour. However, this work is more concerned about the application of SAFT-AC to predict the SLE of refrigerant blends at cryogenic conditions using temperature independent k_{ij} s. Figure 3.5. 1 demonstrates the excellent agreement with experimental data obtained using SAFT-AC for the eutectic behaviour of R-744 containing binary mixtures. Melting points and heats of fusion used to run the SLE calculations are illustrated in below Table 3.2. 1. The eutectic composition was found to be at around 14 mol. % R-744 and is weakly dependent on carbon and fluorine number. The latter suggests that the phase behaviour is dominated by dispersion interactions.

3.4 Phase Equilibrium of CO₂ Refrigerant blends

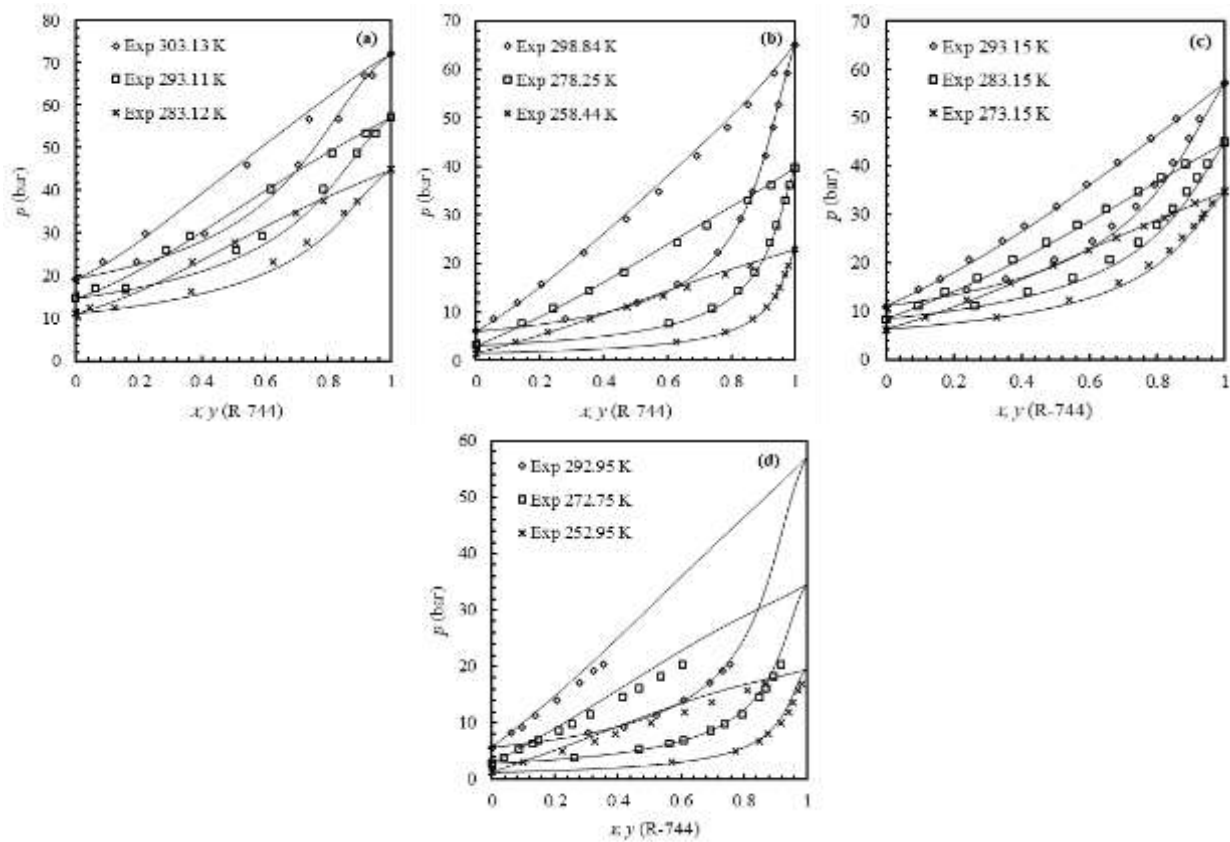


Figure 3.3. 5 Isothermal VLE for R-744 containing binary mixtures. (a) R-32, (b) R-152a, (c) R-143a and, (d) R-134a. Symbols represent experimental data [14, 105-107] and lines represent SAFT-AC correlations.

Table 3.2. 1 Pure component properties and binary interaction parameters used for R-744 containing systems in SAFT-AC calculations

Refrigerant	T_m (K)	H_m (J·mol ⁻¹)	k_{ij}	Ref.
R-744	216.56	9020	-	[108]
R-134a	169.7	6540	-0.06	[109]
R-143a	5853	161.4	-0.07	[110]
R-32	136.45	4494.27	-0.15	[111]
R-125	173.05	2249	-0.05	[112]
R-152a	154.3	1566	-0.06	[108]

3.5 Solid Liquid Equilibrium (SLE) of refrigerant blends

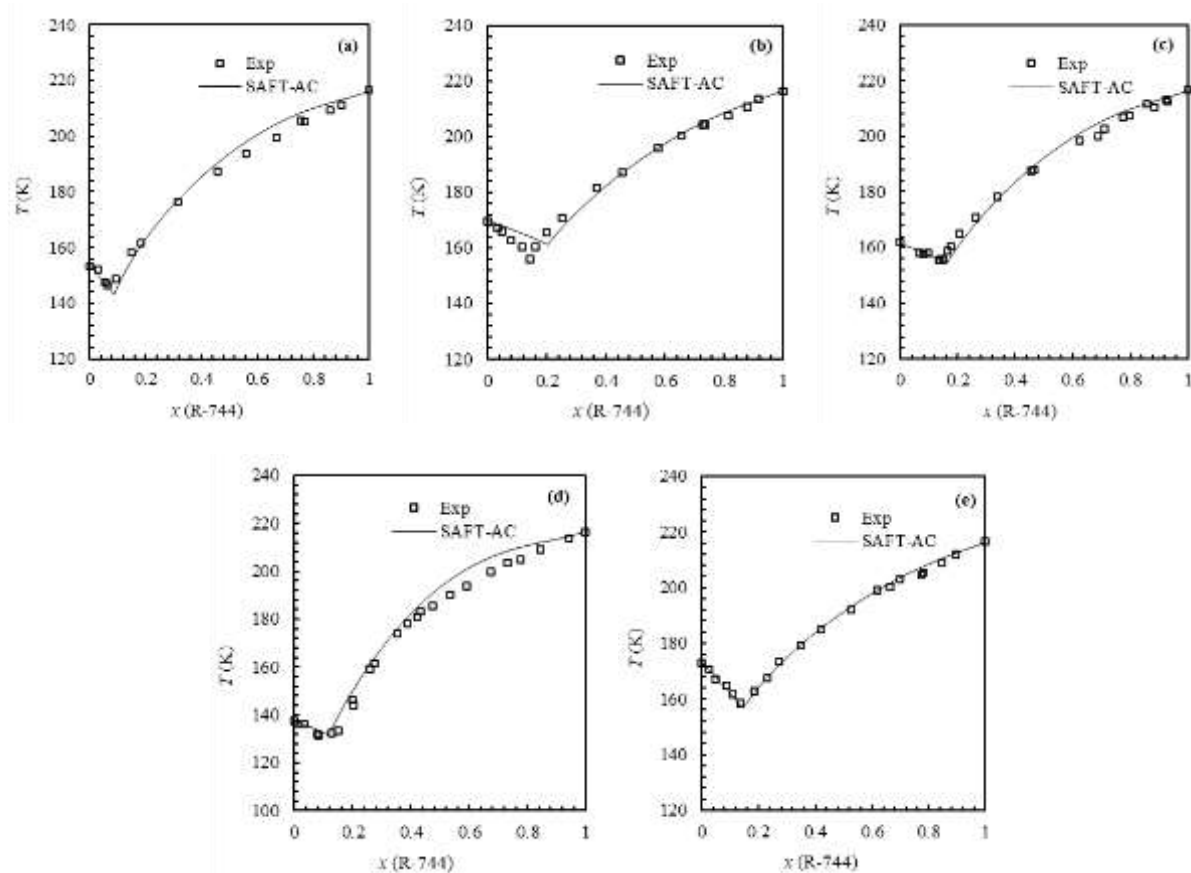


Figure 3.5. 1 SLE for R-744 containing binary mixtures. (a) R-152a, (b) R-134a, (c) R-143a, (d) R-32 and (e) R-125. Symbols represent experimental data [108, 111-115] and lines represent SAFT-AC predictions

3.6 Phase Equilibrium of Cross Associating Mixtures

Figure 3.6. 1 (a-b) show comparisons of TPxy phase diagram and liquid phase activity coefficients at 308.32 K, respectively, for acetone + chloroform binary mixture followed by a comparison of excess enthalpy at 298.15 K is shown in Figure 3.6. 1 (c). As shown in Figure 3.6. 1 (a), the azeotropic vapor pressure is well correlated by Polar PC-SAFT and UNIQUAC. However, Figure 3.6. 1 (b) depicts that UNIQUAC is unable to reproduce the shape of the activity coefficient curves at low concentrations for either component. Although there is some disagreement between Polar PC-SAFT and the activity coefficients obtained from the consistency analysis using the Redlich-Kister expansion. The shape of the activity coefficient curve is of great significance as it dictates how values would extrapolate down to infinite dilution. Polar PC-SAFT is able to exhibit the S-shape found in acetone's activity coefficient curve which is obviously due to the cross-association of species as previously discussed by Dohnal et al.[116-118]. Such behavior is also shown by the ideal chemical equilibrium theory [75], but SAFT incorporates density dependent nonidealities. Here, UNIQUAC shows a nearly linear behavior as a function of concentration. As shown in Figure 3.6. 1 (c), both models describe well the excess enthalpy including the asymmetric behavior as is expected for mixtures that form 1:2 complex[89]. Similar findings are obtained in Figure 3.6. 2 for methyl acetate + chloroform binary mixture but with Polar PC-SAFT showing superiority over UNIQUAC in correlating the mixture excess enthalpy.

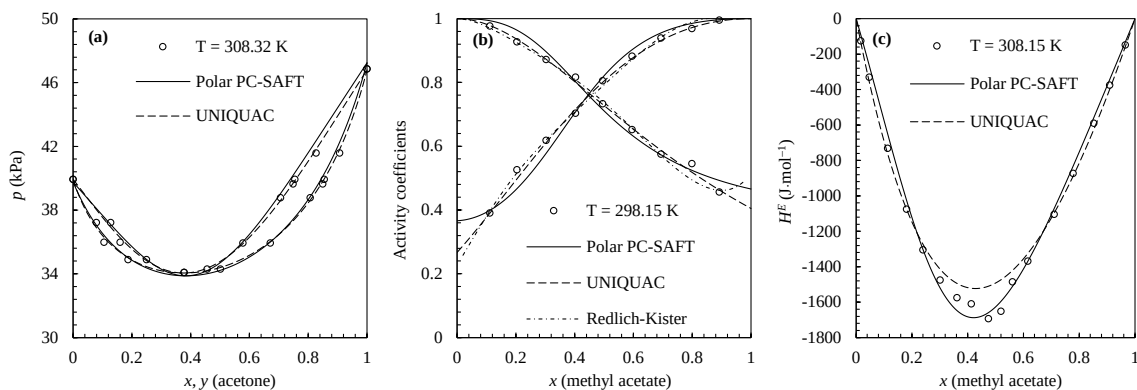


Figure 3.6. 1 Phase behavior of acetone + chloroform binary mixture. (a) isothermal VLE at 308.32 K, (b) activity coefficients at 308.32 K, and (c) excess enthalpy at 298.15 K. Symbols represent experimental data [119, 120], solid curves represent Polar PC-SAFT, dashed curves represent UNIQUAC, and dash-dotted curves represent Redlich-Kister

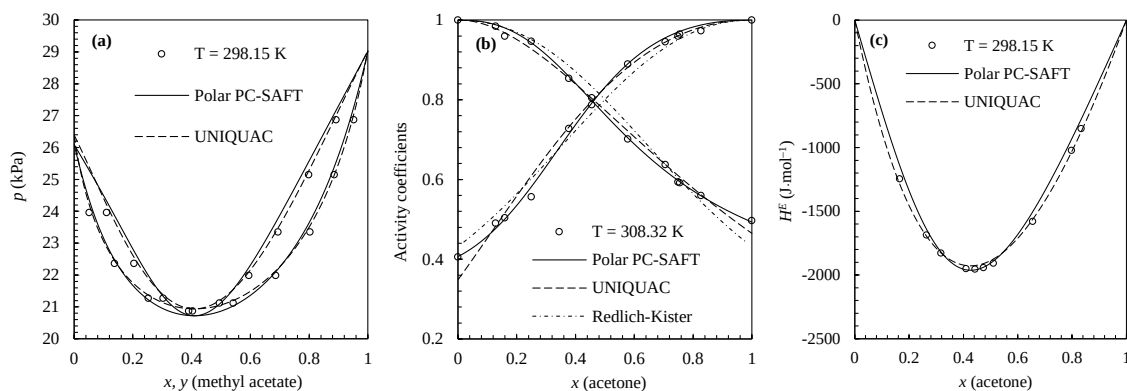


Figure 3.6. 2 Phase behavior of methyl acetate + chloroform binary mixture. (a) isothermal VLE at 298.15 K, (b) activity coefficients at 298.15 K, and (c) excess enthalpy at 308.15 K. Symbols represent experimental data [121, 122], solid curves represent Polar PC-SAFT, dashed curves represent UNIQUAC, and dash-dotted curves represent Redlich-Kister

Figure 3.6. 1-2 demonstrate the phase behavior of chloroform containing binary mixtures that forms 1:1 complex. Figure 3.6. 5(a) and Figure 3.6. 8 (a) depict that UNIQUAC is unable to correlate well the azeotropic pressure of MTBE and THF binary mixtures in comparison to Polar PC-SAFT. In reference to Figure 3.6. 1 (b) - Figure 3.6. 2 (b), Polar PC-SAFT shows the expected S-shape for

the activity coefficient curves while UNIQUAC retains its nearly linear composition dependence for activity coefficients at low concentrations. Furthermore, excellent agreement is obtained in Figure 3.6. 1 (b) and Figure 3.6. 2 (b) between Polar PC-SAFT, and activity coefficients obtained from the consistency analysis using the Redlich-Kister expansion. In reference to Figure 3.6. 4(c) - Figure 3.6. 5 (c), Polar PC-SAFT and UNIQUAC exhibit quite well the symmetric behavior in excess enthalpy that is expected for mixtures that form 1:1 complex. However, better agreement with experimental data is found using Polar PC-SAFT in comparison to UNIQUAC.

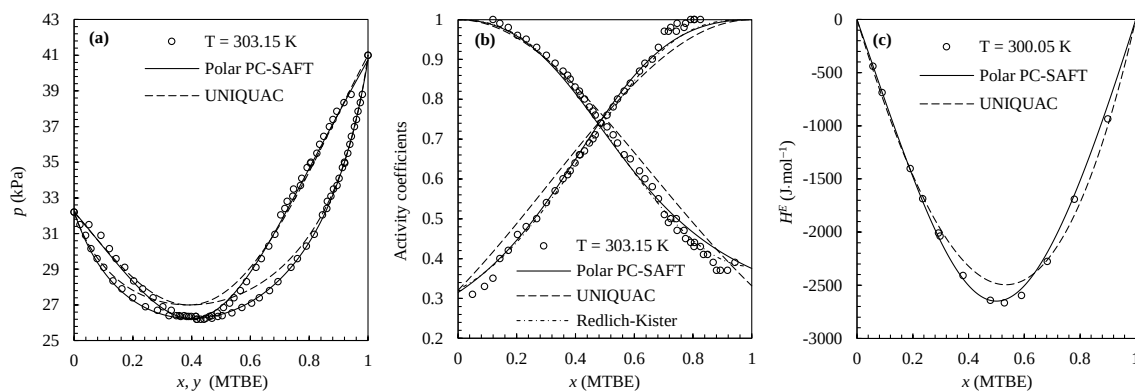


Figure 3.6. 3 Phase behavior of MTBE + chloroform binary mixture. (a) isothermal VLE at 303.15 K, (b) activity coefficients at 303.15 K, and (c) excess enthalpy at 300.05 K. Symbols represent experimental data [123, 124], solid curves represent Polar PC-SAFT, dashed curves represent UNIQUAC, and dash-dotted curves represent Redlich-Kister

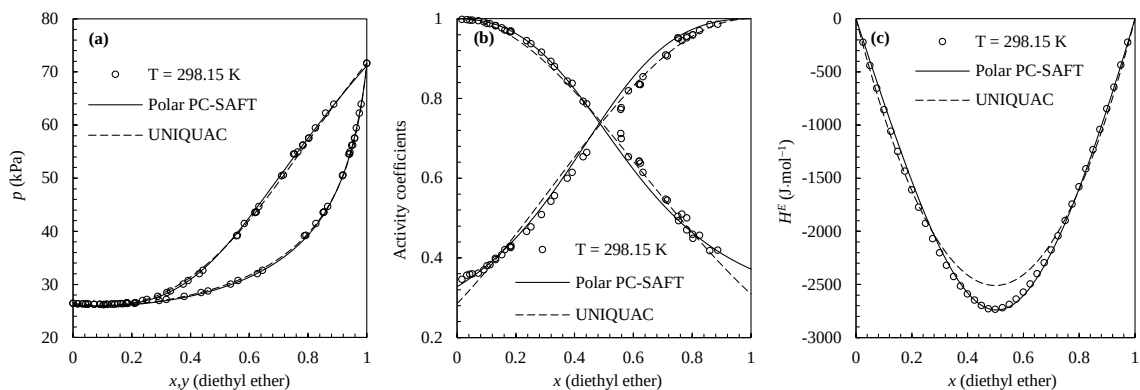


Figure 3.6. 4 Phase behavior of diethyl ether + chloroform binary mixture at 298.15 K. (a) isothermal VLE, (b) activity coefficients, and (c) excess enthalpy. Symbols represent experimental data [125, 126], solid curves represent Polar PC-SAFT, and dashed curves represent UNIQUAC

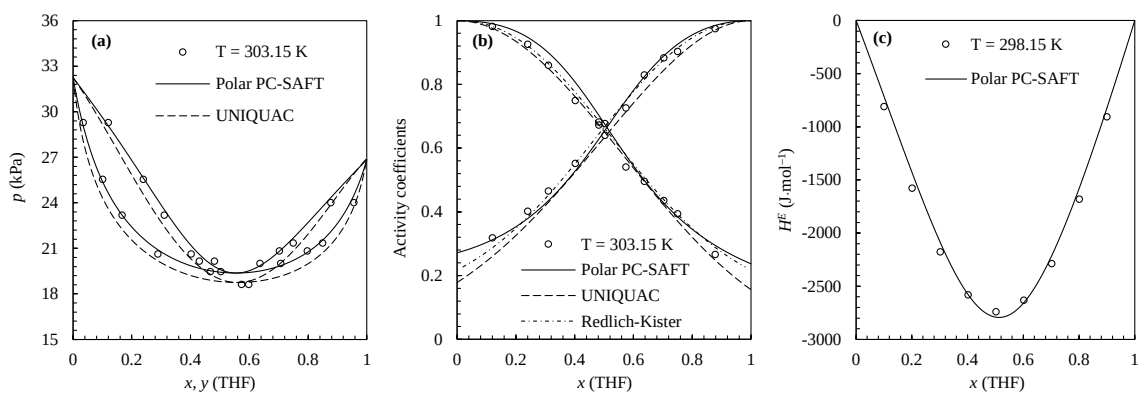


Figure 3.6. 5 Phase behavior of tetrahydrofuran + chloroform binary mixture. (a) isothermal VLE at 303.15 K, (b) activity coefficients at 303.15 K, and (c) excess enthalpy at 298.15 K. Symbols represent experimental data [127, 128], solid curves represent Polar PC-SAFT, dashed curves represent UNIQUAC, and dash-dotted curves represent Redlich-Kister

Figure 3.6. 6 (a-b) show comparisons of TP_{xy} phase diagram and liquid phase activity coefficients at 308.15 K, respectively, for acetone + halothane binary mixture followed by a comparison of excess enthalpy at 298.15 K is shown in Figure 3.6. 6 (c). As shown in Figure 3.6. 6 (a), Polar PC-SAFT provides a more accurate azeotrope than UNIQUAC. In addition, Figure 3.6. 6 (b) shows that UNIQUAC is unable to reproduce the shape of the activity coefficient curves at moderate to low concentrations for either component. Instead, UNIQUAC shows a nearly linear behavior as a function of concentration. On the contrary, Polar PC-SAFT exhibits the S-shape found in halothane's activity coefficient curve which is attributed due to the cross-association of species. Excellent agreement is also found between Polar PC-SAFT and the activity coefficients obtained from the consistency analysis using the Redlich-Kister expansion. As shown in Figure 3.6. 6 (c), both models describe well the asymmetric behavior in excess enthalpy as is expected for mixtures that form 1:2 complex but better agreement with experimental data is found using Polar PC-SAFT. Similar findings are obtained in Figure 3.6. 7 for methyl acetate + halothane binary mixture, another system that forms a 1:2 complex.

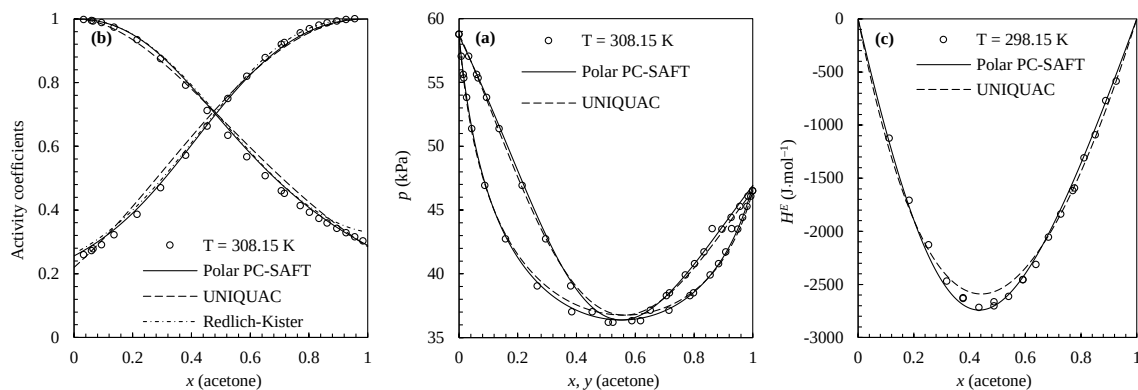


Figure 3.6. 6 Phase behavior of acetone + halothane binary mixture. (a) isothermal VLE at 308.15 K, (b) activity coefficients at 308.15 K, and (c) excess enthalpy at 298.15 K. Symbols represent experimental data [129, 130], solid curves represent Polar PC-SAFT, dashed curves represent UNIQUAC, and dash-dotted curves represent Redlich-Kister

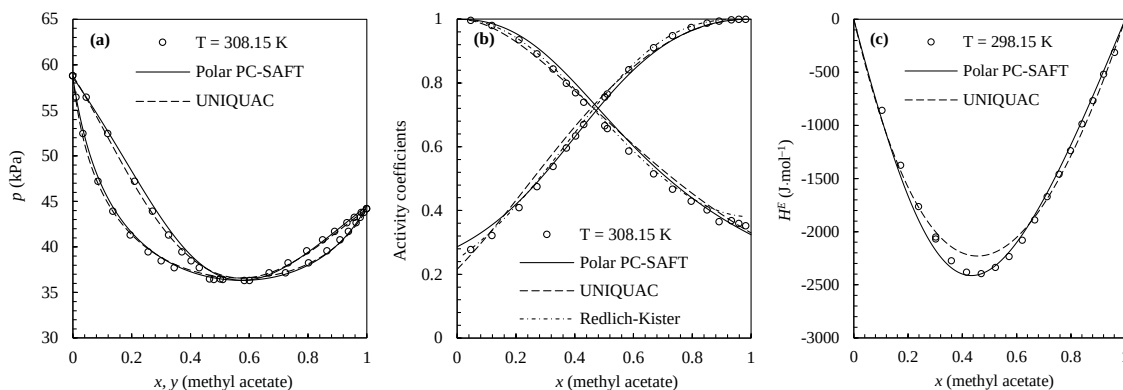


Figure 3.6. 7 Phase behavior of methyl acetate + halothane binary mixture. (a) isothermal VLE at 308.15 K, (b) activity coefficients at 308.15 K, and (c) excess enthalpy at 298.15 K. Symbols represent experimental data [129, 130], solid curves represent Polar PC-SAFT, dashed curves represent UNIQUAC, and dash-dotted curves represent Redlich-Kister

Figure 3.6. 6 and Figure 3.6. 7 demonstrate the phase behavior of halothane containing binary mixtures that form a 1:1 complex. Figure 3.6. 6 (a) and Figure 3.6. 7 (a) depict that both models correlate well the azeotropic vapor pressure of MTBE and THF binary mixtures. In reference to Figure 3.6. 6 (b) and Figure 3.6. 7(b), Polar PC-SAFT shows the expected S-shape for the activity coefficient curves while UNIQUAC retains its nearly linear composition dependence for activity

coefficients at moderate to low concentrations. However, some disagreement exists in Figure 3.6. 7 (b) between Polar PC-SAFT and the activity coefficients obtained from the consistency analysis using the Redlich-Kister expansion. In reference to Figure 3.6. 6 (c) and Figure 3.6. 6 (c), Polar PC-SAFT and UNIQUAC exhibit quite well the symmetric behavior in excess enthalpy that is expected for mixtures that form 1:1 complex. Still, better agreement with experimental data is obtained using Polar PC-SAFT in comparison to UNIQUAC.

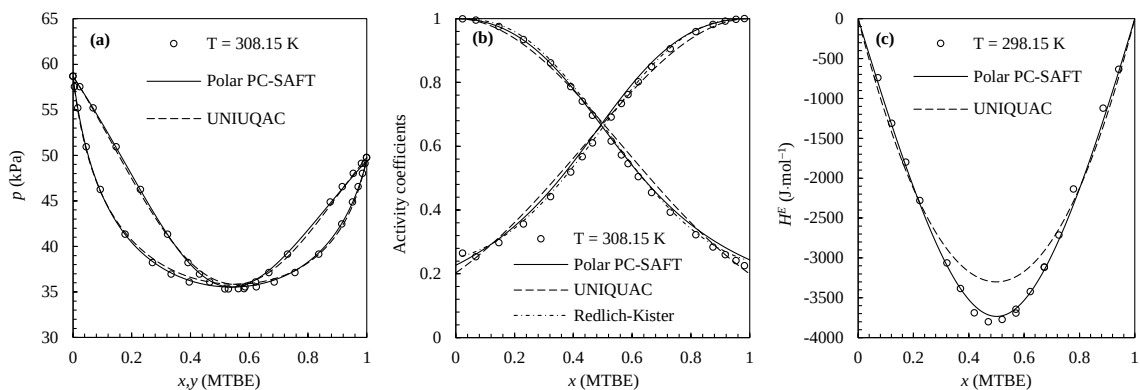


Figure 3.6. 8 Phase behavior of MTBE + halothane binary mixture. (a) isothermal VLE at 308.15 K, (b) activity coefficients at 308.15 K, and (c) excess enthalpy at 298.15 K. Symbols represent experimental data [129, 130], solid curves represent Polar PC-SAFT, dashed curves represent UNIQUAC, and dash-dotted curves represent Redlich-Kister

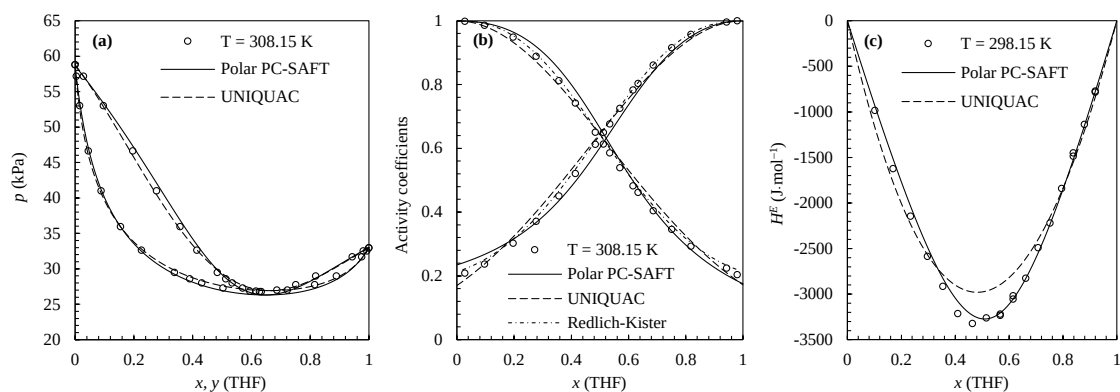


Figure 3.6. 9 Phase behavior of tetrahydrofuran + halothane binary mixture. (a) isothermal VLE at 308.15 K, (b) activity coefficients at 308.15 K, and (c) excess enthalpy at 298.15 K. Symbols represent experimental data [129, 130], solid curves represent Polar PC-SAFT, dashed curves represent UNIQUAC, and dash-dotted curves represent Redlich-Kister

CHAPTER 4

CONCLUSION

The application of SAFT-AC as an accurate model to determine the VLE, SLE and interfacial properties of refrigerant systems was evaluated in this work. Overall, results were found to be in good agreement with experimental data. For VLE, SAFT-AC was employed to fully predict the solubility of HFO- and HC-based refrigerants in commercial POE lubricants. The solubility of HFOs in VG lubricants showed positive deviation from Raoult's law which increased with increasing the refrigerant dipole moment. On the other hand, the solubility of hydrocarbons in VG lubricants showed negative deviation from Raoult's law which increased with decreasing the POE molecular weight. VLE calculations were extended to predict the interfacial properties of refrigerant blends through the successful integration of SAFT-AC with Butler's classical equation. The surface tension of R-125 + R-143a and R-134a + R-152a binary mixtures exhibited weak dependence on composition over a wide range of temperatures. This can be attributed to the azeotropic phase behaviour exhibited in the bulk by both systems. On the other hand, mixtures of R-32 with R-152a, R-143a and R-134a exhibited near ideal solution behaviour in the bulk and in the interface. An azeotropic phase behaviour was shown in the bulk for R-32 + R-125 binary mixtures. This was reflected at the interface with a non-linear dependence for surface tension on mixture composition. For SLE, binary mixtures of R-744 + HFC showed a eutectic behaviour that was weakly dependent on the refrigerant's carbon and fluorine number. The eutectic composition was found to be at around 14 mol. % R-744 for all systems considered in this work, suggesting that the phase behaviour is dominated by simple van der Waals interactions.

The thermodynamics of solvation of chloroform and halothane in oxygenated solvents was studied in this work using the Polar PC-SAFT equation of state, UNIQUAC and Redlich-Kister activity coefficient models. The vapor phase was modeled using Polar PC-SAFT and all binary interactions were set to zero. Within the SAFT framework, ethers under consideration were modeled with one association site that can cross-associate with chloroform or halothane while acetone and methyl acetate were modeled with two association sites that can cross-associate with chloroform or halothane. The SAFT cross-association parameters, UNIQUAC and Redlich-Kister binary interaction parameters were fitted to experimental isothermal VLE data. Results show that traditional excess Gibbs free energy models are unable to capture properly the composition dependence of the activity coefficients. The activity coefficient of oxygenated solvents in haloalkanes exhibits a S-shape that is attributed to strong solvation interactions. However, excess Gibbs free energy models exhibit a nearly linear dependence for these activity coefficients on composition at moderate to low concentrations. Through explicitly accounting for such interactions, Polar PC-SAFT was able to accurately predict activity coefficients near and at infinite dilution. Infinite dilution activity coefficients are of great importance to the industry because most of the separation stages are needed at low concentrations. Unlike UNIQUAC and Redlich-Kister, the proper prediction of the hydrogen bonding distribution in these systems has also allowed Polar PC-SAFT to simultaneously fit the excess enthalpy. The thermodynamics of solvation of chloroform and halothane in oxygenated solvents was studied in this work using the Polar PC-SAFT equation of state, UNIQUAC and Redlich-Kister activity coefficient models. The vapor phase was modeled using Polar PC-SAFT and all binary interactions were set to zero.

Within the SAFT framework, ethers under consideration were modeled with one association site that can cross-associate with chloroform or halothane while acetone and methyl acetate were

modeled with two association sites that can cross-associate with chloroform or halothane. The SAFT cross-association parameters, UNIQUAC and Redlich-Kister binary interaction parameters were fitted to experimental isothermal VLE data. Results show that traditional excess Gibbs free energy models are unable to capture properly the composition dependence of the activity coefficients. The activity coefficient of oxygenated solvents in haloalkanes exhibits a S-shape that is attributed to strong solvation interactions. However, excess Gibbs free energy models exhibit a nearly linear dependence for these activity coefficients on composition at moderate to low concentrations. Through explicitly accounting for such interactions, Polar PC-SAFT was able to accurately predict activity coefficients near and at infinite dilution. Infinite dilution activity coefficients are of great importance to the industry because most of the separation stages are needed at low concentrations. Unlike UNIQUAC and Redlich-Kister, the proper prediction of the hydrogen bonding distribution in these systems has also allowed Polar PC-SAFT to simultaneously fit the excess enthalpy.

References

1. Du, K., et al., *A study on the cycle characteristics of an auto-cascade refrigeration system*. Experimental Thermal and Fluid Science, 2009. **33**(2): p. 240-245.
2. Qin, Y., et al., *Energy and exergy performance evaluation of a three-stage auto-cascade refrigeration system using low-GWP alternative refrigerants*. International Journal of Refrigeration, 2021. **126**: p. 66-75.
3. Clark, E. and S.J.O.A.U.E. Wagner, *The Kigali Amendment to the Montreal Protocol: HFC Phase-Down*. 2016: p. 1-7.
4. Missimer, D.J., *Refrigerant conversion of auto-refrigerating cascade (ARC) systems*. International Journal of Refrigeration, 1997. **20**(3): p. 201-207.
5. He, Y., et al., *Theoretical performance comparison for a regenerator-enhanced three-stage auto-cascade refrigeration system using different zeotropic mixed refrigerants*. Energy Build., 2023. **283**: p. 112815.
6. Ruhemann, M., *The separation of gases*. 1950, J. Chem. Educ. p. 530-531.
7. Andrija, F., *Compression process for refrigeration*, in U.S. Patent No. 3,203,194. 1965.
8. Protocol, M.J.W., DC: US Government Printing Office, *Montreal protocol on substances that deplete the ozone layer*. 1987. **26**: p. 128-136.
9. Wang, Q., et al., *Numerical investigations on the performance of a single-stage auto-cascade refrigerator operating with two vapor–liquid separators and environmentally benign binary refrigerants*. Applied energy, 2013. **112**: p. 949-955.
10. Calm, J.M.J.i.J.o.R., *The next generation of refrigerants—Historical review, considerations, and outlook*. 2008. **31**(7): p. 1123-1133.
11. Cheng, Z., et al., *Performance evaluation of novel double internal auto-cascade two-stage compression system using refrigerant mixtures*. Applied Thermal Engineering, 2020. **168**: p. 114898.
12. Sivakumar, M. and P. Somasundaram, *Exergy and energy analysis of three stage auto refrigerating cascade system using Zeotropic mixture for sustainable development*. Energy conversion and management, 2014. **84**: p. 589-596.
13. Di Nicola, G., et al., *Blends of carbon dioxide and HFCs as working fluids for the low-temperature circuit in cascade refrigerating systems*. International Journal of Refrigeration, 2005. **28**(2): p. 130-140.
14. Madani, H., et al., *(Vapor+liquid) equilibrium data for (carbon dioxide+1,1-difluoroethane) system at temperatures from (258 to 343)K and pressures up to about 8MPa*. Journal of Chemical Thermodynamics, 2008. **40**(10): p. 1490-1494.
15. Abrams, D.S. and J.M. Prausnitz, *Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems*. AIChE Journal, 1975. **21**(1): p. 116-128.
16. Maurer, G. and J. Prausnitz, *On the derivation and extension of the UNIQUAC equation*. Fluid Phase Equilibria, 1978. **2**(2): p. 91-99.
17. Renon, H. and J.M. Prausnitz, *Local compositions in thermodynamic excess functions for liquid mixtures*. AIChE journal, 1968. **14**(1): p. 135-144.

18. Chapman, W.G. and W.A. Fouad, *Activity Coefficients from an Equation of State: Novel Approach for Fast Phase Equilibrium Calculations*. Industrial & Engineering Chemistry Research, 2021. **60**(48): p. 17733-17744.
19. Chapman, W.G. and W.A. Fouad, *Beyond Flory–Huggins: Activity Coefficients from Perturbation Theory for Polar, Polarizable, and Associating Solvents to Polymers*. Industrial & Engineering Chemistry Research, 2022. **61**(48): p. 17644-17664.
20. Fouad, W.A. and L.F. Vega, *The phase and interfacial properties of azeotropic refrigerants: the prediction of azeotropes from molecular theory*. Physical Chemistry Chemical Physics, 2017. **19**(13): p. 8977-8988.
21. Fouad, W.A. and L.F. Vega, *Next generation of low global warming potential refrigerants: Thermodynamic properties molecular modeling*. AIChE Journal, 2018. **64**(1): p. 250-262.
22. Fouad, W.A. and L.F. Vega, *Transport properties of HFC and HFO based refrigerants using an excess entropy scaling approach*. The Journal of Supercritical Fluids, 2018. **131**: p. 106-116.
23. Fouad, W.A. and L.F. Vega, *On the anomalous composition dependence of viscosity and surface tension in refrigerant blends*. Journal of Molecular Liquids, 2018. **268**: p. 190-200.
24. Li, Y., W.A. Fouad, and L.F. Vega, *Interfacial anomaly in low global warming potential refrigerant blends as predicted by molecular dynamics simulations*. Physical Chemistry Chemical Physics, 2019. **21**(39): p. 22092-22102.
25. Fouad, W.A. and L.F. Vega, *Molecular modeling of the solubility of low global warming potential refrigerants in polyol ester lubricants*. International Journal of Refrigeration, 2019. **103**: p. 145-154.
26. Fouad, W.A., *Thermal Conductivity of Pure Fluids and Multicomponent Mixtures Using Residual Entropy Scaling with PC-SAFT—Application to Refrigerant Blends*. Journal of Chemical & Engineering Data, 2020. **65**(12): p. 5688-5697.
27. Fouad, W.A. and H. Alasiri, *Molecular dynamic simulation and SAFT modeling of the viscosity and self-diffusion coefficient of low global warming potential refrigerants*. Journal of Molecular Liquids, 2020. **317**: p. 113998.
28. Fouad, W.A., et al., *Predicting the phase equilibria of refrigerant gas hydrate systems in the presence of electrolytes using molecular theory*. Journal of Molecular Liquids, 2023. **391**: p. 123211.
29. Butler, J.A.V., *The thermodynamics of the surfaces of solutions*. Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character, 1932. **135**(827): p. 348-375.
30. Palmer, D.A., *CRC Handbook of Applied Thermodynamics*. 2019: CRC press.
31. Asprion, N., H. Hasse, and G. Maurer, *Application of IR-spectroscopy in thermodynamic investigations of associating solutions*. Fluid phase equilibria, 2003. **205**(2): p. 195-214.
32. Fouad, W.A., et al., *Understanding the Thermodynamics of Hydrogen Bonding in Alcohol-Containing Mixtures: Self Association*. Journal of Physical Chemistry B, 2015. **119**(44): p. 14086–14101.
33. Wertheim, M.S., *Fluids with highly directional attractive forces. I. Statistical thermodynamics*. Journal of statistical physics, 1984. **35**(1-2): p. 19-34.

34. Wertheim, M.S., *Fluids with highly directional attractive forces. II. Thermodynamic perturbation theory and integral equations*. Journal of statistical physics, 1984. **35**(1-2): p. 35-47.
35. Wertheim, M.S., *Fluids with highly directional attractive forces. III. Multiple attraction sites*. Journal of statistical physics, 1986. **42**(3-4): p. 459-476.
36. Wertheim, M.S., *Fluids with highly directional attractive forces. IV. Equilibrium polymerization*. Journal of statistical physics, 1986. **42**(3-4): p. 477-492.
37. Chapman, W.G., G. Jackson, and K.E. Gubbins, *Phase equilibria of associating fluids: chain molecules with multiple bonding sites*. Molecular Physics, 1988. **65**(5): p. 1057-1079.
38. Chapman, W.G., et al., *SAFT: Equation-of-state solution model for associating fluids*. Fluid Phase Equilibria, 1989. **52**: p. 31-38.
39. Chapman, W.G., et al., *New reference equation of state for associating liquids*. Industrial & Engineering Chemistry Research, 1990. **29**(8): p. 1709-1721.
40. Passarello, J.-P. and P. Tobaly, *Modeling some alcohol/alkane binary systems using the SAFT equation of state with a semipredictive approach*. Industrial & engineering chemistry research, 2003. **42**(21): p. 5383-5391.
41. Jog, P.K., A. Garcia-Cuellar, and W.G. Chapman, *Extensions and applications of the SAFT equation of state to solvents, monomers, and polymers*. Fluid phase equilibria, 1999. **158**: p. 321-326.
42. Chapman, W.G., et al., *Phase behavior applications of SAFT based equations of state—from associating fluids to polydisperse, polar copolymers*. Fluid phase equilibria, 2004. **217**(2): p. 137-143.
43. Fu, Y.-H. and S.I. Sandler, *A simplified SAFT equation of state for associating compounds and mixtures*. Industrial & engineering chemistry research, 1995. **34**(5): p. 1897-1909.
44. Gross, J. and G. Sadowski, *Application of perturbation theory to a hard-chain reference fluid: an equation of state for square-well chains*. Fluid Phase Equilibria, 2000. **168**(2): p. 183-199.
45. Gross, J. and G. Sadowski, *Perturbed-chain SAFT: An equation of state based on a perturbation theory for chain molecules*. Industrial & engineering chemistry research, 2001. **40**(4): p. 1244-1260.
46. Gross, J. and G. Sadowski, *Application of the perturbed-chain SAFT equation of state to associating systems*. Industrial & engineering chemistry research, 2002. **41**(22): p. 5510-5515.
47. Courtial, X., et al., *Vapor–liquid equilibrium in the n-butane+ methanol system, measurement and modeling from 323.2 to 443.2 K*. Fluid Phase Equilibria, 2009. **277**(2): p. 152-161.
48. Jog, P.K. and W. Chapman, *Application of Wertheim's thermodynamic perturbation theory to dipolar hard sphere chains*. Molecular Physics, 1999. **97**(3): p. 307-319.
49. Jog, P.K., et al., *Application of dipolar chain theory to the phase behavior of polar fluids and mixtures*. Industrial & engineering chemistry research, 2001. **40**(21): p. 4641-4648.
50. Al-Saifi, N.M., E.Z. Hamad, and P. Englezos, *Prediction of vapor–liquid equilibrium in water–alcohol–hydrocarbon systems with the dipolar perturbed-chain SAFT equation of state*. Fluid Phase Equilibria, 2008. **271**(1): p. 82-93.
51. Soo, C.-B., et al., *Vapor–liquid equilibrium measurements and modeling of the n-butane+ ethanol system from 323 to 423K*. Fluid Phase Equilibria, 2009. **286**(1): p. 79-87.

52. Mourah, M., et al., *Modelling LLE and VLE of methanol+ n-alkane series using GC-PC-SAFT with a group contribution k ij*. Fluid Phase Equilibria, 2010. **298**(1): p. 154-168.
53. Dominik, A., et al., *Modeling of polar systems with the perturbed-chain SAFT equation of state. Investigation of the performance of two polar terms*. Industrial & engineering chemistry research, 2005. **44**(17): p. 6928-6938.
54. Sauer, S.G. and W.G. Chapman, *A parametric study of dipolar chain theory with applications to ketone mixtures*. Industrial & engineering chemistry research, 2003. **42**(22): p. 5687-5696.
55. von Solms, N., M.L. Michelsen, and G.M. Kontogeorgis, *Computational and physical performance of a modified PC-SAFT equation of state for highly asymmetric and associating mixtures*. Industrial & engineering chemistry research, 2003. **42**(5): p. 1098-1105.
56. Grenner, A., et al., *Modeling phase equilibria of alkanols with the simplified PC-SAFT equation of state and generalized pure compound parameters*. Fluid phase equilibria, 2007. **258**(1): p. 83-94.
57. Liang, X., et al., *Prediction of the vapor–liquid equilibria and speed of sound in binary systems of 1-alkanols and n-alkanes with the simplified PC-SAFT equation of state*. Fluid Phase Equilibria, 2013. **360**: p. 222-232.
58. Grenner, A., et al., *Evaluation of the Nonrandom Hydrogen Bonding (NRHB) Theory and the Simplified Perturbed-Chain– Statistical Associating Fluid Theory (sPC-SAFT). 1. Vapor– Liquid Equilibria*. Industrial & Engineering Chemistry Research, 2008. **47**(15): p. 5636-5650.
59. de Villiers, A.J., C.E. Schwarz, and A.J. Burger, *New association scheme for 1-alcohols in alcohol/water mixtures with sPC-SAFT: The 2C association scheme*. Industrial & Engineering Chemistry Research, 2011. **50**(14): p. 8711-8725.
60. Tybjerg, P.C., et al., *Phase equilibria modeling of methanol-containing systems with the CPA and sPC-SAFT equations of state*. Fluid Phase Equilibria, 2010. **288**(1): p. 128-138.
61. Huang, S.H. and M. Radosz, *Equation of state for small, large, polydisperse, and associating molecules*. Industrial & Engineering Chemistry Research, 1990. **29**(11): p. 2284-2294.
62. Huang, S.H. and M. Radosz, *Equation of state for small, large, polydisperse, and associating molecules: extension to fluid mixtures*. Industrial & Engineering Chemistry Research, 1991. **30**(8): p. 1994-2005.
63. Yarrison, M. and W.G. Chapman, *A systematic study of methanol + n-alkane vapor–liquid and liquid–liquid equilibria using the CK-SAFT and PC-SAFT equations of state*. Fluid phase equilibria, 2004. **226**: p. 195-205.
64. Tamouza, S., et al., *Group contribution method with SAFT EOS applied to vapor liquid equilibria of various hydrocarbon series*. Fluid phase equilibria, 2004. **222**: p. 67-76.
65. Tamouza, S., et al., *Application to binary mixtures of a group contribution SAFT EOS (GC-SAFT)*. Fluid phase equilibria, 2005. **228**: p. 409-419.
66. dos Ramos, M.C., et al., *Extending the GC-SAFT-VR approach to associating functional groups: Alcohols, aldehydes, amines and carboxylic acids*. Fluid Phase Equilibria, 2011. **306**(1): p. 97-111.
67. Papaioannou, V., et al., *Simultaneous prediction of vapour–liquid and liquid–liquid equilibria (VLE and LLE) of aqueous mixtures with the SAFT- γ group contribution approach*. Fluid Phase Equilibria, 2011. **306**(1): p. 82-96.

68. Kontogeorgis, G.M., et al., *An equation of state for associating fluids*. Industrial & engineering chemistry research, 1996. **35**(11): p. 4310-4318.
69. Yakoumis, I.V., et al., *Vapor-liquid equilibria for alcoholhydrocarbon systems using the CPA Equation of state*. Fluid Phase Equilibria, 1997. **130**(1): p. 31-47.
70. Voutsas, E.C., I.V. Yakoumis, and D.P. Tassios, *Prediction of phase equilibria in water/alcohol/alkane systems*. Fluid Phase Equilibria, 1999. **158**: p. 151-163.
71. Voutsas, E., et al., *An evaluation of the performance of the Cubic-Plus-Association equation of state in mixtures of non-polar, polar and associating compounds: Towards a single model for non-polymeric systems*. Fluid Phase Equilibria, 2007. **261**(1): p. 343-350.
72. Tsivintzelis, I., et al., *The role of monomer fraction data in association theories—Can we improve the performance for phase equilibrium calculations?* Fluid Phase Equilibria, 2014. **365**: p. 112-122.
73. Asprion, N., H. Hasse, and G. Maurer, *FT-IR spectroscopic investigations of hydrogen bonding in alcohol–hydrocarbon solutions*. Fluid phase equilibria, 2001. **186**(1): p. 1-25.
74. Fouad, W.A., et al., *Understanding the thermodynamics of hydrogen bonding in alcohol-containing mixtures: cross-association*. Journal of Physical Chemistry B, 2016. **120**(13): p. 3388-3402.
75. Prausnitz, J.M., R.N. Lichtenthaler, and E.G. De Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*. 1998: Pearson Education.
76. Mathias, P.M., *Sensitivity of Process Design to Phase Equilibrium • A New Perturbation Method Based Upon the Margules Equation*. Journal of Chemical & Engineering Data, 2014. **59**(4): p. 1006-1015.
77. Boublik, T., *Hard-Sphere Equation of State*. Journal of Chemical Physics, 1970. **53**(1): p. 471-472.
78. Mansoori, G., et al., *Equilibrium thermodynamic properties of the mixture of hard spheres*. Journal of Chemical Physics, 1971. **54**(4): p. 1523-1525.
79. Rowley, R., et al., *DIPPR Data Compilation of Pure Chemical Properties*. Design Institute for Physical Properties. <http://dippr.byu.edu>, Brigham Young University Provo Utah, 2006.
80. Barker, J.A. and D. Henderson, *Perturbation theory and equation of state for fluids. II. A successful theory of liquids*. Journal of Chemical Physics, 1967. **47**(11): p. 4714-4721.
81. Gross, J. and G. Sadowski, *Perturbed-chain SAFT: An equation of state based on a perturbation theory for chain molecules*. Industrial and Engineering Chemistry Research, 2001. **40**(4): p. 1244-1260.
82. Razzouk, A., et al., *Vapor pressure measurements in the range 10–5Pa to 1Pa of four pentaerythritol esters: Density and vapor–liquid equilibria modeling of ester lubricants*. Fluid Phase Equilibria, 2007. **260**(2): p. 248-261.
83. Redlich, O. and J.N. Kwong, *On the thermodynamics of solutions. V. An equation of state. Fugacities of gaseous solutions*. Chemical reviews, 1949. **44**(1): p. 233-244.
84. Lohmann, J. and J. Gmehling, *Solid–Liquid Equilibria for Seven Binary Systems*. Journal of Chemical & Engineering Data, 2001. **46**(2): p. 333-336.
85. Enders, S., H. Kahl, and J. Winkelmann, *Surface Tension of the Ternary System Water + Acetone + Toluene*. Journal of Chemical & Engineering Data, 2007. **52**(3): p. 1072-1079.
86. Smith, J.M., et al., *Introduction to Chemical Engineering Thermodynamics*. 1949: McGraw-Hill Singapore.

87. Plank, C.A., et al., *Reduction of total-pressure vapor—liquid equilibrium data. Common pitfalls encountered*. Fluid Phase Equilibria, 1981. **6**(1-2): p. 39-59.
88. Stevenson, J.M., et al., *Solvation of nitrogen compounds in Titan's seas, precipitates, and atmosphere*. Icarus, 2015. **256**: p. 1-12.
89. McGlashan, M. and R. Rastogi, *The thermodynamics of associated mixtures. Part 1.—Dioxan+ chloroform*. Transactions of the Faraday Society, 1958. **54**: p. 496-501.
90. Inglese, A., *Thermodynamics of hydrogen-bonded complex formation in chloroform+ cyclic ether mixtures*. Thermochimica acta, 1992. **199**: p. 173-187.
91. Staverman, A., *The entropy of high polymer solutions. Generalization of formulae*. Recueil des Travaux Chimiques des Pays-Bas, 1950. **69**(2): p. 163-174.
92. Poling, B.E., J.M. Prausnitz, and J.P. O'connell, *Properties of Gases and Liquids*. 2001: McGraw-Hill Education.
93. Redlich, O. and A.T. Kister, *Algebraic Representation of Thermodynamic Properties and the Classification of Solutions*. Industrial & Engineering Chemistry, 1948. **40**(2): p. 345-348.
94. Sun, Y., et al., *Phase behavior of R1234yf and R600a in pentaerythritol tetranonanoate*. International Journal of Refrigeration, 2020. **109**: p. 135-142.
95. Morais, A.R.C., et al., *Solubility and Diffusivity of Hydrofluoroolefin Refrigerants in a Polyol Ester Lubricant*. Industrial & Engineering Chemistry Research, 2020. **59**(13): p. 6279-6287.
96. Luca, F.F.C.a.J.R.B.J.L.G.M.D., *PHASE EQUILIBRIUM DATA FOR R-290 + POE ISO 32 MIXTURES BETWEEN 283.15 AND 343.15 K*. 2022.
97. Czubinski, F.F., et al., *Phase equilibrium and liquid viscosity data for R-290/POE ISO 22 mixtures between 283 and 353 K*. International Journal of Refrigeration, 2020. **114**: p. 79-87.
98. Cui, J., et al., *Surface Tension and Liquid Viscosity of R32+R1234yf and R32+R1234ze*. Journal of Chemical & Engineering Data, 2016. **61**(2): p. 950-957.
99. Kobayashi, M. and H. Nishiumi, *Vapor–liquid equilibria for the pure, binary and ternary systems containing HFC32, HFC125 and HFC134a*. Fluid Phase Equilibria, 1998. **144**(1): p. 191-202.
100. Lee, B.G., et al., *Phase Equilibria of Chlorofluorocarbon Alternative Refrigerant Mixtures*. Journal of Chemical & Engineering Data, 1999. **44**(2): p. 190-192.
101. Li, S., et al., *Measurements and correlation of vapor-liquid equilibrium for difluoromethane (R-32) + 2,3,3,3-tetrafluoroprop-1-ene (R-1234yf) and pentafluoroethane (R-125) + propane (R-290)*. Fluid Phase Equilibria, 2021. **538**: p. 113010.
102. Yang, T., et al., *Vapor–Liquid Equilibria for the Binary and Ternary Systems of Difluoromethane (R32), 1,1-Difluoroethane (R152a), and 2,3,3,3-Tetrafluoroprop-1-ene (R1234yf)*. Journal of Chemical & Engineering Data, 2018. **63**(3): p. 771-780.
103. Heide, R., *The surface tension of HFC refrigerants and mixtures*. International Journal of Refrigeration, 1997. **20**(7): p. 496-503.
104. Bi, S., et al., *Surface tension and liquid viscosity measurement for binary mixtures of R134a with R1234yf and R1234ze(E)*. Fluid Phase Equilibria, 2016. **414**: p. 60-64.
105. Duran-Valencia, C., et al., *Vapor–Liquid Equilibrium (VLE) Data for the Carbon Dioxide (CO₂) + 1,1,1,2-Tetrafluoroethane (R134a) System at Temperatures from 252.95 K to*

- 292.95 K and Pressures up to 2 MPa. *Journal of Chemical & Engineering Data*, 2002. **47**(1): p. 59-61.
106. Kim, S.A., K.-P. Yoo, and J.S. Lim, *High pressure isothermal vapor-liquid equilibria for the binary system of carbon dioxide (CO₂)+1,1,1-trifluoroethane (R-143a)*. *Korean Journal of Chemical Engineering*, 2010. **27**(6): p. 1887-1891.
 107. Rivollet, F., et al., *Vapor-liquid equilibrium data for the carbon dioxide (CO₂) + difluoromethane (R32) system at temperatures from 283.12 to 343.25 K and pressures up to 7.46 MPa*. *Fluid Phase Equilibria*, 2004. **218**(1): p. 95-101.
 108. Di Nicola, G., et al., *Solid-Liquid Equilibria for the CO₂ + R152a and N₂O + R152a Systems*. *Journal of Chemical & Engineering Data*, 2007. **52**(6): p. 2451-2454.
 109. Di Nicola, G., G. Santori, and R. Stryjek, *Solid-Liquid Equilibria for the Carbon Dioxide + 1,1-Tetrafluoroethane and Nitrous Oxide + 1,1-Tetrafluoroethane Systems*. *Journal of Chemical & Engineering Data*, 2008. **53**(8): p. 1980-1983.
 110. Magee, J.W., *Molar Heat Capacity at Constant Volume of 1,1-Difluoroethane (R152a) and 1,1,1-Trifluoroethane (R143a) from the Triple-Point Temperature to 345 K at Pressures to 35 MPa*. *International Journal of Thermophysics*, 1998. **19**(5): p. 1397-1420.
 111. Wang, X., et al., *Investigation on solid-liquid equilibrium for trifluoromethane (R23) plus difluoromethane (R32) binary system*. *International Journal of Refrigeration*, 2021. **126**: p. 238-245.
 112. Di Nicola, G., et al., *Solid-Liquid Equilibria for the CO₂ + R125 and N₂O + R125 Systems: A New Apparatus*. *Journal of Chemical & Engineering Data*, 2006. **51**(6): p. 2209-2214.
 113. Di Nicola, G., et al., *Solid-liquid equilibria measurements of the carbon dioxide+2,3,3,3-tetrafluoroprop-1-ene and carbon dioxide+trans-1,3,3,3-tetrafluoropropene mixtures*. *Fluid Phase Equilibria*, 2013. **354**: p. 54-58.
 114. Di Nicola, G., et al., *Solid-liquid equilibria for the CO₂+N₂O, CO₂+R32, and N₂O+R32 systems*. *Fluid Phase Equilibria*, 2007. **256**(1): p. 86-92.
 115. Di Nicola, G., et al., *Solid-Liquid Equilibria for the CO₂ + R143a and N₂O + R143a Systems*. *International Journal of Thermophysics*, 2009. **30**(4): p. 1155-1164.
 116. Dohnal, V., et al., *Thermodynamic study of complex formation by hydrogen bonding in halogenoalkane-oxygenated solvent mixtures: halothane with acetone, methyl acetate, tetrahydrofuran and methyl tert-butyl ether*. *Journal of the Chemical Society, Faraday Transactions*, 1993. **89**(7): p. 1025-1033.
 117. Dohnal, V., et al., *Thermodynamic study of complex formation by hydrogen bonding in halogenoalkane-oxygenated solvent mixtures. Halothane with propyl ether, isopropyl ether, 1, 4-dioxane and 2, 5-dioxahexane*. *Journal of the Chemical Society, Faraday Transactions*, 1996. **92**(11): p. 1877-1886.
 118. Dohnal, V. and M. Costas, *Thermodynamics of complex formation in chloroform-oxygenated solvent mixtures*. *Journal of solution chemistry*, 1996. **25**(7): p. 635-656.
 119. Apelblat, A., A. Tamir, and M. Wagner, *Thermodynamics of acetone-chloroform mixtures*. *Fluid Phase Equilibria*, 1980. **4**(3-4): p. 229-255.
 120. Chevalier, J.-L. and D. Bares, *Systèmes binaires chloroforme-éthers aliphatiques-I.—Chaleurs de mélange à 25° C*. *Journal de Chimie Physique*, 1969. **66**: p. 1448-1452.
 121. Martin, M.C., M.J. Cocero, and F. Mato, *Vapor-liquid equilibrium data at 25° C for six binary systems containing methyl acetate or methanol, with dichloromethane, chloroform, or 1, 2-trans-dichloroethylene*. *Journal of solution chemistry*, 1991. **20**(1): p. 87-95.

122. Ohta, T., H. Asano, and I. Nagata, *Thermodynamic study of complex formation in four binary liquid mixtures containing chloroform*. Fluid Phase Equilibria, 1980. **4**(1-2): p. 105-114.
123. Clará, R.A., et al., *Density, Viscosity, Vapor– Liquid Equilibrium, and Excess Molar Enthalpy of [Chloroform+ Methyl tert-Butyl Ether]*. Journal of Chemical & Engineering Data, 2010. **55**(12): p. 5862-5867.
124. Sharma, S. and J. Singh, *Excess enthalpies of di-n-butyl ether and methyl-tert-butyl ether with chloroalkanes at 26.9° C*. Journal of solution chemistry, 1995. **24**(2): p. 145-151.
125. Becker, F., et al., *Interpretation von Dampfdruckdiagrammen binärer flüssiger Mischungen mit Hilfe von Gleichgewichtsmodellen*. Zeitschrift für Physikalische Chemie, 1974. **92**(4-6): p. 169-192.
126. Becker, F. and M. Kiefer, *Mischungswärmen und Verbindungsbildung in binären flüssigen Systemen*. Zeitschrift für Naturforschung A, 1971. **26**(6): p. 1040-1046.
127. Sólamo, H.N. and A.C. Gomez Marigliano, *Excess properties and vapor-liquid equilibrium data for the chloroform+ tetrahydrofuran binary system at 30 C*. Journal of solution chemistry, 1993. **22**(10): p. 951-962.
128. Conti, G., et al., *Excess molar enthalpies and excess molar heat capacities of (chloroform+ tetrahydrofuran+ cyclohexane) at the temperature 298.15 K*. Journal of Chemical Thermodynamics, 1997. **29**(8): p. 865-877.
129. Costas, M., et al., *Excess molar enthalpies of binary mixtures of 2-bromo-2-chloro-1, 1, 1-trifluoroethane (halothane) with oxygenated and hydrocarbon solvents*. Thermochimica acta, 1993. **213**: p. 23-34.
130. Fenclová, D. and V.r. Dohnal, *(Vapour+ liquid) equilibria of {1-bromo-1-chloro-2, 2, 2-trifluoroethane (halothane)+ an oxygenated solvent or hexane}*. Journal of Chemical Thermodynamics, 1993. **25**(6): p. 689-697.

Vitae

Name :Engr. Ahsan Kamil

Nationality :Pakistan

Date of Birth :10/30/1997

Email :ahsankamil32@gmail.com

Address :House No. 1074, Block Q, Post office: G-1 Market,
Postal code:5417, Johar Town, Lahore, Punjab, Pakistan

Academic Background :M.S in Chemical Engineering

King Fahd University of Petroleum & Minerals (KFUPM),
Dhahran, 31261, Kingdom of Saudi Arabia.

B.S in Chemical Engineering

University of Engineering & Technology (UET), Lahore,
Pakistan.

Published Papers

1. Wael A. Fouad, and **Ahsan Kamil**, “Predicting the VLE, SLE and surface tension of refrigerant systems using a SAFT-based KF0055activity coefficient model” Fluid Phase Equilibria. (Under-Review)
2. **Ahsan Kamil**, Wael A. Fouad, Sumnesh K. Gupta, and Walter G. Chapman, “Phase Equilibrium of Cross-Associating mixtures using association theory-based equation of State.” Industrial Engineering & Chemistry Research, Vol. no. 61, Issue no. 42, pp. 15639-15648, 2022, American Chemical Society (ACS). DOI: 10.1021/acs.iecr.2c01707

Appendix

The activity coefficient of species “i” in a mixture is calculated using Redlich-Kister expansion through a power series that is a function of the difference in mole fractions found in the mixture:

$$\ln \gamma_i = \sum_j \left[\sum_{i=0}^5 x_j A_{n,ij} (x_i - x_j) \right] \quad (\text{A.1})$$

After power series expansion,

$$\ln \gamma_i = \sum_j \left[\sum_{n=1}^5 x_j A_{n,ij} (x_i - x_j)^{n-2} (nx_i - x_j) - \frac{1}{2} \sum_k \sum_{n=1}^5 x_j x_k A_{n,jk} (x_j - x_k)^{n-2} [(2n-1)x_j - x_k] \right] \quad (\text{A.2})$$

Where the temperature dependent $A_{1,ij}$ and $A_{3,ij}$ coefficients of the series, for unlike species, are defined as following:

$$A_{1,ij} = \frac{A_{ij}}{T} \quad (\text{A.3})$$

$$A_{3,ij} = \frac{B_{ij}}{T} \quad (\text{A.4})$$

The remaining series coefficients were set to zero in this work.

$$A_{2,ij} = A_{4,ij} = A_{5,ij} = 0 \quad (\text{A.5})$$

In the first term of the Redlich-Kister expansion, $A_{n,ji}$ is related to $A_{n,ij}$ through the following relationship:

$$A_{n,ji} = A_{n,ij}(-1)(n-1) \quad (\text{A.6})$$

While in the second term of the Redlich-Kister expansion, $A_{n,kj}$ is related to $A_{n,jk}$ through the following relationship:

$$A_{n,kj} = A_{n,jk}(-1)^{(n-1)} \quad (\text{A.7})$$