SOLUBILITY OF CARBON DIOXIDE IN FIVE PROMISING IONIC LIQUIDS

Thanawat Nonthanasin

A Thesis Submitted in Partial Fulfilment of the Requirements for the Degree of Master of Science The Petroleum and Petrochemical College, Chulalongkorn University in Academic Partnership with The University of Michigan, The University of Oklahoma, Case Western Reserve University, and Institut Français du Pétrole 2013

I28372232

561600

Thesis Title:	Solubility of Carbon Dioxide in Five Promising Ionic Liquids
By:	Thanawat Nonthanasin
Program:	Petrochemical Technology
Thesis Advisors:	Prof. Amr Henni
	Assoc. Prof. Chintana Saiwan

Accepted by The Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.

College Dean

(Asst. Prof. Pomthong Malakul)

Thesis Committee:

em

(Prof. Amr Henni)

Quitan Samin

(Assoc. Prof. Chintana Saiwan)

Kitipart Siemana

(Asst. Prof. Kitipat Siemanond)

Terruhet Surgap

(Dr. Teeradet Supap)

บทคัดย่อ

ธนวัฒน์ นนท์ธนสิน: ความสามารถในการละลายของคาร์บอนไดออกไซด์ในไอออนิก ลิควิด 5 ชนิด (Solubility of Carbon Dioxide in Five Promising Ionic Liquids) อ. ที่ปรึกษา: ศ. คร. อามาร์ เฮนนี และ รศ. คร. จินตนา สายวรรณ์ 204 หน้า

ในปัจจบัน ไอออนิกลิควิคเป็นตัวทำละลายสำหรับกระบวนการจับคาร์บอนไดออกไซด์ ที่ประหยัดพลังงานและเป็นมิตรต่อสิ่งแวคล้อมมากที่สุด งานวิจัยนี้มุ่งเน้นที่การวัดความสามารถ ในการละลายของคาร์บอนไดออกไซด์ในไอออนิกลิกวิคที่อุณหภูมิห้องทั้ง 5 ชนิด ได้แก่ ไตรเอทิล ซัลโฟนิล บิส(ไตรฟลูออโรเมทิลซัลโฟนิล)อิไมด์ ([S₂₂₂][Tf₂N]), ไดเอทิลเมทิล(ทู-เมทอกซีเอทิล) แอมโมเนียม บิส(ไตรฟลูออโรเมทิลซัลโฟนิล)อิไมด์ ([deme][Tf,N]), วัน-โพรพิล-ทรี-เมทิลอิมมิ คาโซเลียม บิส(ไตรฟลูออโรเมทิลซัลโฟนิล)อิไมด์ ([pmim][Tf,N]), วัน-แอลลีล-ทรี-เมทิลอิมมิคา โซเลียม บิส(ไตรฟลูออโรเมทิลซัลโฟนิล)อิไมด์ ([amim][Tf2N]) และ วัน-บิลทิล-โฟร์-เมทิลไพริดิ เนียม เตตระฟลูออโร โบเรต ([4mbp][BF₄]) ที่อุณหภูมิ 313.15, 323.15 และ 333.15 K ภายใต้ความ ดัน 20 บาร์ โดยใช้เครื่องไมโครบาลานซ์ ชนิดกราวิเมตริก ค่าความสามารถในการละลายของ คาร์บอนไดออกไซด์ในตัวทำละลายเหล่านี้ที่ได้จากการทดลองสัมพันธ์กับสมการสถานะเปง-โรบินสันมาตรฐาน, สมการสถานะซอฟว์-เรคลิก-ควองมาตรฐาน, สมการสถานะซอฟว์-เรคลิก-้ควองที่ใช้กฎการผสมแบบควอคราติก, และแบบจำลองสัมประสิทธิ์แอกทิวิตีของ NRTL ด้วยค่า ้ความคลาดเคลื่อนสัมบูรณ์เฉลี่ย (AADs) ที่น่าพึงพอใจ งานวิจัยนี้ได้หาค่าพารามิเตอร์อันตรกิริยาคู่ ้สำหรับสมการสถานะและแบบจำลองสัมประสิทธิ์แอกทิวิคีอีกด้วย จากการทดลองพบว่าการดูด ซึมของคาร์บอนไดออกไซด์มีแนวโน้มลดลงตามลำดับตั้งนี้ [deme][Tf,N] > [pmim][Tf,N] > [amim][Tf2N] > [S222][Tf2N] > [4mbp][BF4] ใอออนิกลิควิด 4 ชนิด [deme][Tf2N], [pmim][Tf2N], [amim][Tf2N], and [S222][Tf2N] ถือว่าเป็นตัวทำละลายที่เป็นทางเลือกสำหรับกระบวนการจับ คาร์บอนไคออกไซค์เนื่องจากมีการคูคซึมคาร์บอนไคออกไซค์ที่สูง ซึ่งสามารถเปรียบเทียบได้กับ ้ไอออนิกลิควิดอื่นๆที่แสดงการดูดซึมทางกายภาพในลักษณะเดียวกัน ที่น่าสนใจกว่านั้นคือ [deme][Tf,N] แสดงความสามารถในการละลายของการ์บอน ใดออกไซด์ที่สูงที่สุดอย่างเห็นได้ชัด ในกลุ่มไอออนิกลิกวิคชนิดแอมโมเนียม นอกจากนี้ วิทยานิพนธ์ฉบับนี้ยังได้นำเสนอค่าคงที่ของ เฮนรี่ เอนทาลปีและเอนโทรปีของการดูดซึมการ์บอนใดออกไซด์ในไอออนิกลิกวิดที่ศึกษาอีก ด้วย

ABSTRACT

5471025063: Petrochemical Technology Program Thanawat Nonthanasin: Solubility of Carbon Dioxide in Five Promising Ionic Liquids Thesis Advisor: Prof. Amr Henni and Assoc. Prof. Chintana Saiwan 204 pp.
Keywords: Ionic liquids/ CO₂ capture/ CO₂ solubility/ PR/ SRK/ NRTL/ Henry's law constant/ Enthalpy and entropy of absorption

Ionic liquids are presently considered the most energy-efficient and environmentally benign solvents for CO₂ capture. This research aimed at measuring the solubility of CO₂ in five room temperature ionic liquids, triethylsulfonium bis(trifluoromethylsulfonyl)imide ($[S_{222}][Tf_2N]$), diethylmethyl(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide ([deme][Tf₂N]),1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([pmim][Tf₂N]), 1-allyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([amim][Tf₂N]), and 1-butyl-4methylpyridinium tetrafluoroborate ([4mbp][BF₄]) at (313.15, 323.15 and 333.15 K) and at pressure up to 20 bar using a gravimetric microbalance. The experimental solubility data of CO₂ in these solvents were well correlated using the standard Peng-Robinson (PR-EoS), the standard Redlich-Kwong-Soave (SRK-EoS), the SRK-EoS with quadratic mixing rules, and the Non-Random Two-Liquid (NRTL) with satisfactory average absolute deviations (AADs). Binary interaction parameters for these correlations were obtained. The absorption of CO₂ was prone to diminish in this sequence: $[deme][Tf_2N] > [pmim][Tf_2N] > [amim][Tf_2N] > [S_{222}][Tf_2N] >$ [4mbp][BF₄]. Four ionic liquids, [deme][Tf₂N], [pmim][Tf₂N], [amim][Tf₂N], and [S₂₂₂][Tf₂N], are deemed promising due to comparably high CO₂ absorption with physical absorption to other prevalent CO₂-absorbing ionic liquids. More interestingly, $[deme][Tf_2N]$ evidently had the highest CO₂ solubility among all ammonium-based ionic liquids reported in the literature. In addition, Henry's law constants and enthalpies and entropies of absorption for CO₂ in the investigated ionic liquid are also reported.

ACKNOWLEDGEMENTS

I would like to express my wholehearted gratitude to Prof. Amr Henni, my advisor, for giving me an unforgettable opportunity to conduct this research and providing financial supports to me during my stay at the University of Regina. His willingness to devote his time so generously to give me his valuable suggestions and to correct my works has been very much appreciated. Special thanks are also given to Assoc. Prof. Chintana Saiwan, my co-advisor, for her professional guidance, and enthusiastic encouragement. My grateful thanks are extended to Asst. Prof. Kitipat Siemanond and Dr. Teeradet Supap as my thesis committees.

For my research group members, I would really like to extend my appreciation to Kazi Zamshad Sumon and Tursun John Uygur as my trainers for the experimental set-up and procedures. Also, I wish to thank Mohamed Zoubeik and Vasantha Raja Ramamoorthy as my sincere friends as well as their useful advices and discussion. I would also like to acknowledge and thank the University of Regina staffs who buttressed me from beginning through completion: Christine Barlow, Jill Docking, Robyn Fahlman and Melissa Dyck.

I wish to express my acknowledgement to International Test Centre for CO₂ Capture, Petroleum Technology Research Centre, University of Regina, also The Petroleum and Petrochemical College, and the National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, Thailand for the grant and funding support.

For a good life of living in Canada, I would like to give my thanks to my nice friends coming together with me, Wirit Cuptasanti and Wantanee Teerasukakul, for their helps in many things. Moreover, I am indeed thankful to the members of Student Association of Thais at the University of Regina (SATUR), namely, Chitsutha Soomlek, Yanee Lertnimoolchai, Wayuta Srisang, Jarotwan Koiwanit, Suriya Jirasatitsin, Kriengkamol Setameteekul, Wisan Sila, Wasin Sananphanichkul, Wichitpan Rongwong, and all of my friends in Regina who gave me assistance and unforgettably memorable experiences.

Finally, I feel overwhelmingly grateful to my parents for their support and encouragement throughout my study. Thank you very much.

TABLE OF CONTENTS

	Title F	Page		i
	Abstra	act (i	n English)	iii
	Abstra	act (i	n Thai)	iv
	Ackno	owled	lgements	v
	Table	of C	ontents	vi
	List of	f Tab	les	х
	List of	f Fig	ures	xv
СНА	PTFD			
CIIA	I	IN	FRODUCTION	1
	II	LII	TERATURE REVIEW	4
		2.1	Ionic Liquids	4
2.2 Physical Properties	Physical Properties	7		
			2.2.1 Melting Point	8
			2.2.2 Density	10
			2.2.3 Viscosity	12
			2.2.4 Vapor Pressure	16
			2.2.5 Thermal Stability	18
			2.2.6 Surface Tension	20
			2.2.7 Miscibility with Water	23
		2.3	Uses and Applications	24
		2.4	Methods for Measuring Gas Solubilities	25
			2.4.1 Stoichiometric Technique	26
			2.4.2 Pressure Drop Technique	27
			2.4.3 Gravimetric Methods	28
		2.5	Classification of Ionic Liquids for CO ₂ Capture	31
		2.6	CO ₂ Solubility in Conventional Ionic Liquids	32
			2.6.1 Effect of Pressure and Temperature on CO ₂ Solubility	48

	2.6.2 Effect of Structural Variation on CO ₂ Solubility	51
	2.6.2.1 Anion Effect	51
	2.6.2.2 Cation Effect	53
	2.7 Thermodynamic Modeling	54
	2.7.1 Group Contribution Methods for Critical Properties	54
	2.7.2 Equations of State (EoS)	57
	2.7.2.1 The Standard Redlich-Kwong-Soave	
	(SRK-EoS)	59
	2.7.2.2 The Standard Peng-Robinson (PR-EoS)	60
	2.7.2.3 The Redlich-Kwong-Aspen	
	(The SRK with Quadratic Mixing Rules)	62
	2.7.3 Activity Coefficient Model	63
	2.7.3.1 The Non-Random Two-Liquid (NRTL)	63
	2.8 Derivation of Henry's law constant	65
	2.9 Derivation of Enthalpies and Entropies of Absorption	67
III	EXPERIMENTAL	69
	3.1 Materials	69
	3.1.1 Ionic Liquids	69
	3.1.2 Gases	72
	3.2 Experimental Procedures	72
	3.2.1 Density Measurement	72
	3.2.2 Gas Solubility Measurement	73
	3.2.2.1 Preparation of Sample, Accessories	
	and Program	76
	3.2.2.2 Sample Loading	77
	3.2.2.3 New Application Set-up	78
	3.2.2.4 Drying and degassing	78
	3.2.2.5 Isotherm	79
	3.2.2.6 Sample Removal	79

	3.2.3 Buoyancy Correction and Data Treatment	80
IV	RESULTS AND DISCUSSION	84
	4.1 Density of Pure Ionic Liquids	84
	4.2 Solubility of Carbon Dioxide	87
	4.2.1 Experimental Solubility Isotherms	87
	4.2.2 Effects of Temperature and Pressure	90
	4.2.3 Effects of Cations and Anions	91
	4.2.4 Comparison with Ionic Liquids in Our Group	102
	4.3 Thermodynamic Modeling	103
	4.3.1 Critical Property Estimation	103
	4.3.2 Equations of State	104
	4.3.2.1 The Standard Peng-Robinson (PR-EoS)	105
	4.3.2.2 The Standard Redlich-Kwong-Soave	
	(SRK-EoS)	110
	4.3.2.3 The Redlich-Kwong-Soave (SRK)	
	with Quadratic Mixing Rules	114
	4.3.3 Activity Coefficient Model	119
	4.3.3.1 The Non-Random Two-Liquid (NRTL)	119
	4.4 Henry's Law Constants and Enthalpies and Entropies	
	of Absorption	124
	4.4.1 Henry's Law Constants	124
	4.4.2 Enthalpies and Entropies of Absorption	126
V	CONCLUSIONS AND RECOMMENDATIONS	128
	REFERENCES	130

CHAPTER

APPENDICES	
Appendix A Raw Data for Gas Solubility Measurements	
Using The Gravimetric Microbalance	143
Appendix B Critical Property Estimation	159
Appendix C Consistency Test of Densities	164
Appendix D Modeling Results with The AADs	169
Appendix E Henry's Law Constants and Enthalpies and	
Entropies of Absorption	184

CURRICULUM VITAE	204

LIST OF TABLES

TABLEPAGE

2.1	Melting points data for several ionic liquids	9
2.2	Densities (25 °C) of several ionic liquids Chromatography	11
2.3	Viscosity data (25 °C) for various ionic liquids	16
2.4	Thermal decomposition temperatures of several ionic liquids	20
2.5	Surface tension data (25 °C) for several ionic liquids	21
2.6	Literature surveys for the solubility of CO ₂ in numerous	
	ionic liquids	35
2.7	Groups considered for the Modified Lydersen-Joback-Reid	
	method and equations describing the model	56
3.1	Studied ionic liquids	71
3.2	Microbalance components for buoyancy correction	82
4.1	Experimental densities of the five ionic liquids measured at	
	1.01325 bar	86
4.2	Temperature-dependent density correlations for the studied	
	ionic liquids	87
4.3	Experimental solubility (P, T, x) data for $[S_{222}][Tf_2N]$ (1) +	
	CO_2 (2), [deme][Tf ₂ N] (1) + CO_2 (2), [pmim][Tf ₂ N] (1) +	
	CO_2 (2), [amim][Tf ₂ N] (1) + CO_2 (2) and [4mbp][BF ₄] (1)	
	+ CO ₂ (2) systems at 313.15, 323.15 and 333.15 K	89
4.4	Molecular weights, normal boiling temperatures, critical	
	properties, and acentric factors of ionic liquids	104
4.5	Binary interaction parameters of the standard PR-EoS for the	
	ionic liquids $(1) + CO_2 (2)$ system	106
4.6	Average absolute deviation (AAD %) between experimental	
	and estimated values of pressure by the standard PR-EoS for	
	the ionic liquids $+ CO_2$ system	109

TABLE

4.7	Binary interaction parameters of the standard SRK-EoS for	
	the ionic liquids $(1) + CO_2(2)$ system	110
4.8	Average absolute deviation (AAD %) between experimental	
	and estimated values of pressure by the standard SRK-EoS	
	for the ionic liquids + CO ₂ system	114
4.9	Binary interaction parameters of the SRK with quadratic	
	mixing rules for the ionic liquids (1) + CO_2 (2) system	115
4.10	Average absolute deviation (AAD %) between experimental	
	and estimated values of pressure by the SRK with quadratic	
	mixing rules for the ionic liquids + CO ₂ system	119
4.11	Binary interaction parameters of the NRTL for the ionic	
	liquids (1) + CO ₂ (2) system ($\alpha = 0.3$)	120
4.12	Average absolute deviation (AAD %) between experimental	
	and estimated values of pressure by the NRTL for the ionic	
	liquids + CO ₂ system	124
4.13	Henry's law constants, enthalpies, and entropies of	
	absorption for CO ₂ in the studied ionic liquids	125
Al	Carbon dioxide in [bmim][PF ₆] at 323.15 K	143
A2	Carbon dioxide in [S ₂₂₂][Tf ₂ N] at 313.15 K	144
A3	Carbon dioxide in [S ₂₂₂][Tf ₂ N] at 323.15 K	145
A4	Carbon dioxide in [S ₂₂₂][Tf ₂ N] at 333.15 K	146
A5	Carbon dioxide in [deme][Tf ₂ N] at 313.15 K	147
A6	Carbon dioxide in [deme][Tf ₂ N] at 323.15 K	148
A7	Carbon dioxide in [deme][Tf ₂ N] at 333.15 K	149
A8	Carbon dioxide in [pmim][Tf ₂ N] at 313.15 K	150
A9	Carbon dioxide in [pmim][Tf ₂ N] at 323.15 K	151
A10	Carbon dioxide in [pmim][Tf ₂ N] at 333.15 K	152
A11	Carbon dioxide in [amim][Tf ₂ N] at 313.15 K	153
A12	Carbon dioxide in [amim][Tf ₂ N] at 323.15 K	154

TABLE

A13

A14

A15

A16

B1

B2

B3

B4

B5

C1

	PAGE
Carbon dioxide in [amim][Tf ₂ N] at 333.15 K	155
Carbon dioxide in [4mbp][BF ₄] at 313.15 K	156
Carbon dioxide in [4mbp][BF ₄] at 323.15 K	157
Carbon dioxide in [4mbp][BF ₄] at 333.15 K	158
The normal boiling temperature, critical properties, and	
acentric factor of [S ₂₂₂][Tf ₂ N]	159
The normal boiling temperature, critical properties, and	
acentric factor of [deme][Tf ₂ N]	160
The normal boiling temperature, critical properties, and	
acentric factor of [pmim][Tf ₂ N]	161
The normal boiling temperature, critical properties, and	
acentric factor of [amim][Tf ₂ N]	162
The normal boiling temperature, critical properties, and	
acentric factor of [4mbp][BF4]	163
The calculated density of $[S_{222}][Tf_2N]$ and comparison with	
the experimental values at a range of temperatures from	
278.15 K to 353.15 K	164

C2	The calculated density of $[deme][Tf_2N]$ and comparison	
	with the experimental values at a range of temperatures from	
	278.15 K to 353.15 K	165
C3	The calculated density of $[pmim][Tf_2N]$ and comparison	
	with the experimental values at a range of temperatures from	
	278.15 K to 353.15 K	166
C4	The calculated density of $[amim][Tf_2N]$ and comparison	
	with the experimental values at a range of temperatures from	
	278.15 K to 353.15 K	167
C5	The calculated density of [4mbp][BF4] and comparison with	

the experimental values at a range of temperatures from 278.15 K to 353.15 K 168

D1	Modeling solubility (P, T, x) data for $[S_{222}][Tf_2N]$ (1) +	
	CO ₂ (2) system at 313.15 K	169
D2	Modeling solubility (P, T, x) data for $[S_{222}][Tf_2N]$ (1) +	
	CO ₂ (2) system at 323.15 K	170
D3	Modeling solubility (P, T, x) data for $[S_{222}][Tf_2N]$ (1) +	
	CO ₂ (2) system at 333.15 K	171
D4	Modeling solubility (P, T, x) data for $[deme][Tf_2N]$ (1) +	
	CO ₂ (2) system at 313.15 K	172
D5	Modeling solubility (P, T, x) data for $[deme][Tf_2N]$ (1) +	
	CO ₂ (2) system at 323.15 K	173
D6	Modeling solubility (P, T, x) data for $[deme][Tf_2N]$ (1) +	
	CO ₂ (2) system at 333.15 K	174
D7	Modeling solubility (P, T, x) data for $[pmim][Tf_2N]$ (1) +	
	CO ₂ (2) system at 313.15 K	175
D8	Modeling solubility (P, T, x) data for $[pmim][Tf_2N]$ (1) +	
	CO ₂ (2) system at 323.15 K	176
D9	Modeling solubility (P, T, x) data for $[pmim][Tf_2N]$ (1) +	
	CO ₂ (2) system at 333.15 K	177
D10	Modeling solubility (P, T, x) data for $[amim][Tf_2N]$ (1) +	
	CO ₂ (2) system at 313.15 K	178
D11	Modeling solubility (P, T, x) data for $[amim][Tf_2N]$ (1) +	
	CO ₂ (2) system at 323.15 K	179
D12	Modeling solubility (P, T, x) data for $[amim][Tf_2N]$ (1) +	
	CO ₂ (2) system at 333.15 K	180
D13	Modeling solubility (P, T, x) data for $[4mbp][BF_4]$ (1) +	
	CO ₂ (2) system at 313.15 K	181
D14	Modeling solubility (P, T, x) data for $[4mbp][BF_4]$ (1) +	
	CO ₂ (2) system at 323.15 K	182

TABLE

D15 Modeling solubility (P, T, x) data for $[4mbp][BF_4]$ (1) + CO₂ (2) system at 333.15 K 183 El Experimental fugacity of CO₂ in [S₂₂₂][Tf₂N] at 313.15 K 184 E2 Experimental fugacity of CO₂ in [S₂₂₂][Tf₂N] at 323.15 K 185 Experimental fugacity of CO₂ in [S₂₂₂][Tf₂N] at 333.15 K E3 186 E4 Experimental fugacity of CO₂ in [deme][Tf₂N] at 313.15 K 188 E5 Experimental fugacity of CO₂ in [deme][Tf₂N] at 323.15 K 189 Experimental fugacity of CO₂ in [deme][Tf₂N] at 333.15 K E6 190 E7 Experimental fugacity of CO₂ in [pmim][Tf₂N] at 313.15 K 192 E8 Experimental fugacity of CO₂ in [pmim][Tf₂N] at 323.15 K 193 E9 Experimental fugacity of CO₂ in [pmim][Tf₂N] at 333.15 K 194 Experimental fugacity of CO₂ in [amim][Tf₂N] at 313.15 K E10 196 E11 Experimental fugacity of CO₂ in [amim][Tf₂N] at 323.15 K 197 E12 Experimental fugacity of CO₂ in [amim][Tf₂N] at 333.15 K 198 E13 Experimental fugacity of CO₂ in [4mbp][BF₄] at 313.15 K 200 Experimental fugacity of CO₂ in [4mbp][BF₄] at 323.15 K E14 201 E15 Experimental fugacity of CO₂ in [4mbp][BF₄] at 333.15 K 202

LIST OF FIGURES

FIGURE		PAGE
2.1	Ionic configuration of inorganic salts (left) and ionic liquids	
	(right)	5
2.2	Some cations and anions present in ionic liquids	7
2.3	Plots showing the melting and clearing temperatures	
	observed on heating of (a) $[C_n-mim][PF_6]$, (b) $[C_n-py][PF_6]$,	
	(c) $[C_n-3-Mepy][PF_6]$, and (d) $[C_n-4-Mepy][PF_6]$	9
2.4	Comparison of experimental densities of ionic liquids with	
	calculated values	11
2.5	Viscosities of imidazolium- and pyridinium-based ionic	
	liquids with butyl chain length and different anions at 298.15	
	and 323.15 K (25 and 50 °C)	13
2.6	Viscosities of ionic liquids as a function of temperature: (•),	
	$[bmim][PF_6]; (o), [bmim][Tf_2N]; (\bullet), [bmim][BF_4]; (\Box),$	
	$[N_{4111}][Tf_2N]; (\blacktriangle), [emim][Tf_2N]; (\Delta), [emim][EtSO_4]$	13
2.7	Viscosity of ionic liquids as a function of pressure at 323.15	
	K (50 °C)	14
2.8	The Kugelrohr oven and distillation apparatus	17
2.9	Surface tensions (mJ/m ²) of several ionic liquids as a	
	function of temperature	19
2.10	Some commonly used ionic liquids and the level of water	
	miscibility	24
2.11	Applications of ionic liquids	25
2.12	The schematic of the stoichiometric apparatus	26
2.13	The schematic of the pressure drop apparatus	27
2.14	The IGA003 gravimetric analyzer	29
2.15	The schematic of the intelligent gravimetric analyzer	29

2.16	The schematic of Rubotherm magnetically coupled	
	microbalance	30
2.17	The schematic of quartz crystal microbalance apparatus	31
2.18	CO ₂ solubility in [bmim][PF6] at 25 °C	33
2.19	Proposed mechanism for enhanced CO ₂ solubility in	
	imidazolium acetate	47
2.20	CO ₂ solubility in [bmim][PF ₆] at 283.15, 298.15, and 273.15	
	K (10, 25 and 50 °C)	49
2.21	The CO_2 solubility as a function of pressure up to 28.98 bar	
	in \blacksquare [C ₄ py][Tf ₂ N], and ×[C ₁₂ py][Tf ₂ N] at 298.15 K	50
2.22	The CO ₂ solubility in $[C_4py][Tf_2N]$ at: \blacksquare 298.15 K (25 °C),	
	▲ 313.15 K (40 °C) and × 333.15 K (60 °C)	50
2.23	Henry's law constants for CO2 in various ionic liquids at	
	333.15 K (60 °C)	52
2.24	The effect of alkyl chain length of cations on the $\rm CO_2$	
	solubility in $[C_4py][Tf_2N]$, $[C_8py][Tf_2N]$, $[C_{10}py][Tf_2N]$ and	
	[C ₁₂ py][Tf ₂ N] at 298.15 K (25 °C)	53
2.25	Two types of molecular clusters or cells of binary liquid	
	mixtures	64
3.1	The DMA 4500 density meter	73
3.2	Schematic diagram of Hiden Isochema IGA-003 gravimetric	
	microbalance	74
3.3	IGA-003 configuration set for static gas operation	75
4.1	Liquid density of the studied ionic liquids at temperatures	
	ranging from 278.15 K to 353.15 K: •, $[S_{222}][Tf_2N]; \circ$,	
	$[deme][Tf_2N]; ♥, [pmim][Tf_2N]; △, [amim][Tf_2N]; ■,$	
	$[4mbp][BF_4]$	87

4.2

4.3

E	PAGE
Absorption of CO ₂ in [bmim][PF ₆] at 323.15 K compared to	
the solubility data obtained in literature: \bullet , this work; \circ ,	
Shiflett and Yokozeki (2005); ▼. Anthony et al. (2002)	88
Comparison of measured isothermal solubility data of $\rm CO_2$	
in different ionic liquids: •, [S ₂₂₂][Tf ₂ N]; •, [deme][Tf ₂ N];	
▼, [pmim][Tf ₂ N]; Δ , [amim][Tf ₂ N]; ■, [4mbp][BF ₄]; red, at	
313.15 K; blue, at 323.15 K; green, at 333.15 K	91

4.4 Comparison of measured isothermal solubility data of CO₂ in different ionic liquids at 313.15 K: •, $[S_{222}][Tf_2N]; \circ$, $[deme][Tf_2N];$ ▼, $[pmim][Tf_2N];$ △, $[amim][Tf_2N];$ ■. $[4mbp][BF_4]$

- 4.5 Comparison of measured isothermal solubility data of CO₂ in different ionic liquids at 323.15 K: •, $[S_{222}][Tf_2N]; \circ$, [deme][Tf₂N]; $\mathbf{\nabla}$, [pmim][Tf₂N]; Δ , [amim][Tf₂N]; $\mathbf{\blacksquare}$. $[4mbp][BF_4]$
- 4.6 Comparison of measured isothermal solubility data of CO₂ in different ionic liquids at 333.15 K: •, $[S_{222}][Tf_2N]; \circ$, [deme][Tf₂N]; $\mathbf{\nabla}$, [pmim][Tf₂N]; Δ , [amim][Tf₂N]; $\mathbf{\blacksquare}$, $[4mbp][BF_4]$
- 4.7 Comparison between the solubility of CO_2 in the studied ionic liquids and others published in the literature at 323.15 K: black \bullet , HEAF; red \bullet , HEL; green ∇ , THEAA; yellow ▲, HEF; blue ■, HEAL; pink ■, HEA; cyan ♦, THEAL; gray \blacklozenge , HEAA; dark red \blacktriangle , [4mbp][BF₄]; dark green \triangledown , $[bmim][BF_4]; dark yellow \bullet, [bmim][PF_6]; dark blue \bullet,$ $[S_{222}][Tf_2N];$ dark pink $\mathbf{\nabla}$, $[amim][Tf_2N];$ dark cyan \mathbf{A} , $[pmim][Tf_2N]; dark gray \blacksquare, [bmim][Tf_2N]; black \blacksquare,$ [deme][Tf₂N]; red \blacklozenge , [hmim][Tf₂N]; green \blacklozenge , [bmpyrr][eFAP]; yellow •, [hmim][eFAP]; blue •, [bmim][Ac]

93

93

94

xviii

PAGE

FIGURE

4	.8	Comparison between the solubility of CO_2 in [deme][Tf ₂ N]	
		and other ammonium-based ionic liquids in the literature at	
		313.15 K: black \bullet , HHEMEA; red \bullet , HHEMEL; green \triangledown ,	
		BHEAL; yellow \blacktriangle , HEL; blue \blacksquare , BHEAA; pink \blacksquare , HEA;	
		cyan \blacklozenge , [deme][Tf ₂ N]	100
4	.9	Comparison of the solubility of CO_2 in [deme][Tf ₂ N] with	
		the existing ionic liquids containing ammonium and	
		phosphonium cations in the literature at 333.15 K: black \bullet ,	
		[choline][Tf ₂ N]; red ●, [N ₄₁₁₁][Tf ₂ N]; green $▼$,	
		$[deme][Tf_2N]; yellow \blacktriangle, [P_{(14)666}][Tf_2N]$	102
4.	10	Comparison of the solubility of CO ₂ in ionic liquids studied	
		in our group at 323.15 K: black \bullet , [4mbp][BF ₄]; red \bullet ,	
		[bmim][TfO]; green $\mathbf{\nabla}$, [bmim][DPH]; yellow \mathbf{A} ,	
		$[(OMe)_2Im][Tf_2N];$ blue \blacksquare , $[S_{222}][Tf_2N];$ pink \blacksquare ,	
		$[amim][Tf_2N]; cyan \blacklozenge, [1b1mp][Tf_2N]; gray \diamondsuit,$	
		$[pmim][Tf_2N]; dark red \blacktriangle, [(OEt)_2Im][Tf_2N]; dark green$	
		$\mathbf{\nabla}$, [deme][Tf ₂ N]	103
4.	11	P-x diagram of the system $[S_{222}][Tf_2N]$ and CO_2 for different	
		temperatures. Symbols represent the experimental data: •, at	
		313.15 K; ○, at 323.15 K; and ▼, at 333.15 K. Lines	
		represent the estimations by the standard PR-EoS: solid line,	
		at 313.15 K; dotted line, at 323.15 K; and dashed line, at	
		333.15 K	106
4.	12	P-x diagram of the system [deme][Tf_2N] and CO_2 for	
		different temperatures. Symbols represent the experimental	
		data: ●, at 313.15 K; ○, at 323.15 K; and ▼, at 333.15 K.	
		Lines represent the estimations by the standard PR-EoS:	
		solid line, at 313.15 K; dotted line, at 323.15 K; and dashed	
		line, at 333.15 K	107

4.13	P-x diagram of the system $[pmim][Tf_2N]$ and CO_2 for	
	different temperatures. Symbols represent the experimental	
	data: ●, at 313.15 K; ○, at 323.15 K; and ▼, at 333.15 K.	
	Lines represent the estimations by the standard PR-EoS:	
	solid line, at 313.15 K; dotted line, at 323.15 K; and dashed	
	line, at 333.15 K	107
4.14	P-x diagram of the system $[amim][Tf_2N]$ and CO_2 for	
	different temperatures. Symbols represent the experimental	
	data: ●, at 313.15 K; ○, at 323.15 K; and ▼, at 333.15 K.	
	Lines represent the estimations by the standard PR-EoS:	
	solid line, at 313.15 K; dotted line, at 323.15 K; and dashed	
	line, at 333.15 K	108
4.15	P-x diagram of the system $[4mbp][BF_4]$ and CO_2 for	
	different temperatures. Symbols represent the experimental	
	data: ●, at 313.15 K; ○, at 323.15 K; and ▼, at 333.15 K.	
	Lines represent the estimations by the standard PR-EoS:	
	solid line, at 313.15 K; dotted line, at 323.15 K; and dashed	
	line, at 333.15 K	108
4.16	Comparison of isothermal solubility data of CO_2 in different	
	ionic liquids: •, $[S_{222}][Tf_2N]; \circ, [deme][Tf_2N]; \mathbf{V},$	
	$[pmim][Tf_2N]; \Delta, [amim][Tf_2N]; and \blacksquare, [4mbp][BF_4]; red, at$	
	313.15 K; blue, at 323.15 K; and green, at 333.15 K. Lines	
	represent the estimations by the standard PR-EoS	109
4.17	P-x diagram of the system $[S_{222}][Tf_2N]$ and CO_2 for different	
	temperatures. Symbols represent the experimental data: \bullet , at	
	313.15 K; ○, at 323.15 K; and ▼, at 333.15 K. Lines	
	represent the estimations by the standard SRK-EoS: solid	
	line, at 313.15 K; dotted line, at 323.15 K; and dashed line,	
	at 333.15 K	111

4.18	P-x diagram of the system [deme][Tf ₂ N] and CO_2 for	
	different temperatures. Symbols represent the experimental	
	data: ●, at 313.15 K; ○, at 323.15 K; and ▼, at 333.15 K.	
	Lines represent the estimations by the standard SRK-EoS:	
	solid line, at 313.15 K; dotted line, at 323.15 K; and dashed	
	line, at 333.15 K	111
4.19	P-x diagram of the system $[pmim][Tf_2N]$ and CO_2 for	
	different temperatures. Symbols represent the experimental	
	data: ●, at 313.15 K; ○, at 323.15 K; and ▼, at 333.15 K.	
	Lines represent the estimations by the standard SRK-EoS:	
	solid line, at 313.15 K; dotted line, at 323.15 K; and dashed	
	line, at 333.15 K	112
4.20	P-x diagram of the system [amim][Tf ₂ N] and CO_2 for	
	different temperatures. Symbols represent the experimental	
	data: ●, at 313.15 K; ○, at 323.15 K; and ▼, at 333.15 K.	
	Lines represent the estimations by the standard SRK-EoS:	
	solid line, at 313.15 K; dotted line, at 323.15 K; and dashed	
	line, at 333.15 K	112
4.21	P-x diagram of the system $[4mbp][BF_4]$ and CO_2 for	
	different temperatures. Symbols represent the experimental	
	data: ●, at 313.15 K; ○, at 323.15 K; and ▼, at 333.15 K.	
	Lines represent the estimations by the standard SRK-EoS:	
	solid line, at 313.15 K; dotted line, at 323.15 K; and dashed	
	line, at 333.15 K	113
4.22	Comparison of isothermal solubility data of CO_2 in different	
	ionic liquids: •, $[S_{222}][Tf_2N]$: \circ , $[deme][Tf_2N]$; \triangledown ,	
	$[pmim][Tf_2N]; \Delta, [amim][Tf_2N]; and \blacksquare, [4mbp][BF_4]; red, at$	
	313.15 K; blue, at 323.15 K; and green, at 333.15 K. Lines	
	represent the estimations by the standard SRK-EoS	113

4.23	P-x diagram of the system $[S_{222}][Tf_2N]$ and CO_2 for different	
	temperatures. Symbols represent the experimental data: \bullet , at	
	313.15 K; ○, at 323.15 K; and ▼, at 333.15 K. Lines	
	represent the estimations by the SRK with quadratic mixing	
	rules: solid line, at 313.15 K; dotted line, at 323.15 K; and	
	dashed line, at 333.15 K	116
4.24	P-x diagram of the system [deme][Tf ₂ N] and CO_2 for	
	different temperatures. Symbols represent the experimental	
	data: •, at 313.15 K; \circ , at 323.15 K; and \triangledown , at 333.15 K.	
	Lines represent the estimations by the SRK with quadratic	
	mixing rules: solid line, at 313.15 K; dotted line, at 323.15	
	K; and dashed line, at 333.15 K	116
4.25	P-x diagram of the system $[pmim][Tf_2N]$ and CO_2 for	
	different temperatures. Symbols represent the experimental	
	data: •, at 313.15 K; ○, at 323.15 K; and ▼, at 333.15 K.	
	Lines represent the estimations by the SRK with quadratic	
	mixing rules: solid line, at 313.15 K; dotted line, at 323.15	
	K; and dashed line, at 333.15 K	117
4.26	P-x diagram of the system $[amim][Tf_2N]$ and CO_2 for	
	different temperatures. Symbols represent the experimental	
	data: ●, at 313.15 K; ○, at 323.15 K; and ▼, at 333.15 K.	
	Lines represent the estimations by the SRK with quadratic	
	mixing rules: solid line, at 313.15 K; dotted line, at 323.15	
	K; and dashed line, at 333.15 K	117
4.27	P-x diagram of the system $[4mbp][BF_4]$ and CO_2 for	
	different temperatures. Symbols represent the experimental	
	data: •, at 313.15 K; ○, at 323.15 K; and ▼, at 333.15 K.	
	Lines represent the estimations by the SRK with quadratic	
	mixing rules: solid line, at 313.15 K; dotted line, at 323.15	
	K; and dashed line, at 333.15 K	118

4.28	Comparison of isothermal solubility data of CO ₂ in different	
	ionic liquids: •, $[S_{222}][Tf_2N]; \circ, [deme][Tf_2N]; \lor$,	
	$[pmim][Tf_2N]; \Delta, [amim][Tf_2N]; and \blacksquare, [4mbp][BF_4]; red, at$	
	313.15 K; blue, at 323.15 K; and green, at 333.15 K. Lines	
	represent the estimations by the SRK with quadratic mixing	
	rules	118
4.29	P-x diagram of the system $[S_{222}][Tf_2N]$ and CO_2 for different	
	temperatures. Symbols represent the experimental data: \bullet , at	
	313.15 K; ○, at 323.15 K; and ▼, at 333.15 K. Lines	
	represent the estimations by the NRTL: solid line, at 313.15	
	K; dotted line, at 323.15 K; and dashed line, at 333.15 K	121
4.30	P-x diagram of the system [deme][Tf ₂ N] and CO_2 for	
	different temperatures. Symbols represent the experimental	
	data: •, at 313.15 K; ○, at 323.15 K; and ▼, at 333.15 K.	
	Lines represent the estimations by the NRTL: solid line, at	
	313.15 K; dotted line, at 323.15 K; and dashed line, at	
	333.15 K	121
4.31	P-x diagram of the system $[pmim][Tf_2N]$ and CO_2 for	
	different temperatures. Symbols represent the experimental	
	data: •, at 313.15 K; ○, at 323.15 K; and ▼, at 333.15 K.	
	Lines represent the estimations by the NRTL: solid line, at	
	313.15 K; dotted line, at 323.15 K; and dashed line, at	
	333.15 K	122
4.32	P-x diagram of the system $[amim][Tf_2N]$ and CO_2 for	
	different temperatures. Symbols represent the experimental	
	data: ●, at 313.15 K; ○, at 323.15 K; and ▼, at 333.15 K.	
	Lines represent the estimations by the NRTL: solid line, at	
	313.15 K; dotted line, at 323.15 K; and dashed line, at	
	333.15 K	122

4.33	P-x diagram of the system $[4mbp][BF_4]$ and CO_2 for	
	different temperatures. Symbols represent the experimental	
	data: ●, at 313.15 K; ○, at 323.15 K; and ▼, at 333.15 K.	
	Lines represent the estimations by the NRTL: solid line, at	
	313.15 K; dotted line, at 323.15 K; and dashed line, at	
	333.15 K	123
4.34	Comparison of isothermal solubility data of CO ₂ in different	
	ionic liquids: •, $[S_{222}][Tf_2N]; \circ, [deme][Tf_2N]; \vee,$	
	[pmim][Tf ₂ N]; △, $[amim]$ [Tf ₂ N]; and ■, $[4mbp]$ [BF ₄]; red, at	
	313.15 K; blue, at 323.15 K; and green, at 333.15 K. Lines	
	represent the estimations by the NRTL	123
4.35	Henry's law constants for CO_2 in $[S_{222}][Tf_2N]$,	
	[deme][Tf ₂ N], [pmim][Tf ₂ N], [amim][Tf ₂ N] and	
	[4mbp][BF ₄] at 313.15, 323.15 and 333.15 K	126
E1	Determining the Henry's law constant for CO ₂ in	
	$[S_{222}][Tf_2N]$	186
E2	Determining the enthalpy of absorption for CO_2 in	
	$[S_{222}][Tf_2N]$	187
E3	Determining the entropy of absorption for CO ₂ in	
	$[S_{222}][Tf_2N]$	187
E4	Determining the Henry's law constant for CO_2 in	
	$[deme][Tf_2N]$	190
E5	Determining the enthalpy of absorption for CO ₂ in	
	$[deme][Tf_2N]$	191
E6	Determining the entropy of absorption for CO ₂ in	
	[deme][Tf ₂ N]	191
E 7	Determining the Henry's law constant for CO ₂ in	
	[pmim][Tf ₂ N]	194

E8	Determining the enthalpy of absorption for CO_2 in	
	[pmim][Tf ₂ N]	195
E9	Determining the entropy of absorption for CO_2 in	
	[pmim][Tf ₂ N]	195
E10	Determining the Henry's law constant for CO ₂ in	
	[amim][Tf ₂ N]	198
E11	Determining the enthalpy of absorption for CO_2 in	
	[amim][Tf ₂ N]	199
E12	Determining the entropy of absorption for CO_2 in	
	[amim][Tf ₂ N]	199
E13	Determining the Henry's law constant for CO ₂ in	
	[4mbp][BF ₄]	202
E14	Determining the enthalpy of absorption for CO ₂ in	
	[4mbp][BF ₄]	203
E15	Determining the entropy of absorption for CO_2 in	
	[4mbp][BF ₄]	203