Physical Properties and Models of Ionic Liquid-Supercritical CO_2 Systems for Developing Biomass Reaction and Separation Processes

(Summary version)

by

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March 2015

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Chapter 1

Introduction

1.1 Proposal for processing biomass with ionic liquid and CO_2 systems

In summary, there are several desirable characteristics of a sustainable biomass process:

i) versatile reaction solvent (ionic liquid)

ii) efficient hydrogenation or oxidation reaction environment

iii) environmentally-friendly separation system

In this work, ionic liquid-CO_2 biphasic system is proposed to efficiently process biomass according to the graphical image shown in Figure 1-1.

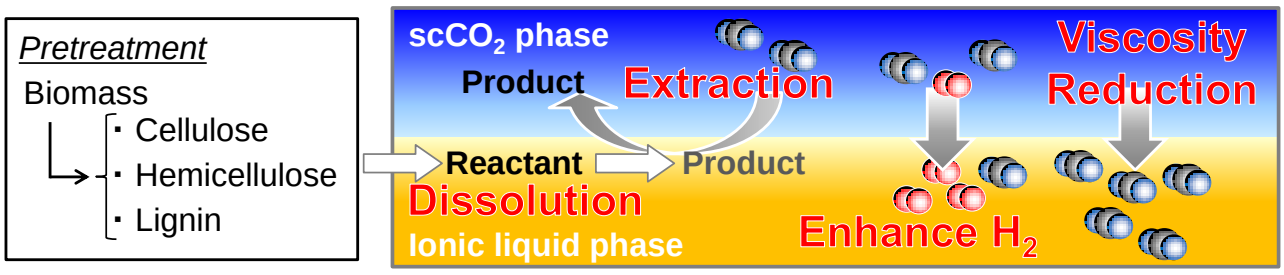


Figure 1-1 Graphical image of ionic liquid-CO_2 system for biomass reaction and separation.

Supercritical carbon dioxide ($scCO_2$), that has a critical temperature of 304 K and a critical pressure of 7.38 MPa, is often used as an environmentally-friendly solvent due to its non-toxic properties, its low cost and the moderate conditions required for reactions and separations.

The ionic liquid-CO_2 biphasic system as shown in Figure 1-1 has some desirable characteristics. First of all, an ionic liquid with high hydrogen bond basicity is expected to dissolve both cellulose and lignocellulose, and is suitable as a solvent for biomass processing. For example, ball-milling pretreatment for the cellulose was chosen by Liu et al.[1, 2] to transform microcrystalline cellulose into an amorphous state, however, it has been confirmed that a decrease in cellulose crystallinity occurs by pretreatment with biomass-soluble ionic liquids that lead to an improvement in reaction efficiency for enzymatic hydrolysis.[3] Thus, the use of an ionic liquid solvent can eliminate mechanical pretreatment steps.

Carbon dioxide can act as extractant that dissolves various organic solvents in its supercritical state over a wide range of temperatures and pressures and product separation can be by simple depressurization, adsorption, absorption or other chemical operations. Therefore, simple procedures can be used for product recovery and solvent recycle. For hydrogenolysis of cellulose with H_2 gas in ionic liquids, carbon dioxide can also act as an auxiliary solvent for H_2 solubilities. CO_2 has been reported to increase the solubility of light gases such as O_2 and CH_4 in ionic liquids.[4] Although transport properties are not the main target of this thesis, carbon dioxide can be used as a viscosity reducing agent for cellulose-ionic liquid solutions.[5, 6] Therefore, it is expected that the ionic liquid-CO_2 biphasic system is suitable for the biomass reactions and separations described above, synthesis of 5-HMF, decomposition of lignin and hydrogenolysis of cellulose.

For developing a system (Fig. 1-1), physical properties are needed to be measured and assessed quantitatively. The partition coefficient, which is a key property for biphasic systems, is

needed and so this thesis reports partition coefficients for many different solutes in ionic liquid-CO_2 biphasic systems. Enhancement effect for H_2 solubility in ionic liquids using CO_2 should be studied so that engineering relationships can be developed. Fundamental physical properties such as densities and viscosities are required to develop theoretical relationships. Despite the expected advantages for ionic liquid-CO_2 systems, data required for assessing the proposal presented in this chapter are presently unavailable.

1.2 Goal and objectives

The goal of this thesis is to develop theory for separation and reaction with the ionic liquid-supercritical CO_2 biphasic system described in Figure 1-1 through the use of physical property measurements and by assessing property correlations with fundamental models. To make progress towards the goal, the following objectives were formulated.

Objective 1: Literature survey on ionic liquid-CO_2 biphasic systems

The first objective is to survey the literature to understand knowledge gaps in both experimental data and theoretical methods for density, viscosity, partitioning, CO_2 solubility and H_2 solubility in the presence of CO_2 (Chapter 2).

Objective 2: Partitioning of furan derivatives produced by synthesis of 5-HMF

The second objective is to measure infinite dilution partition coefficients of furan derivatives in [bmim]Cl (1-butyl-3-methylimidazolium chloride)-CO_2 system and to develop a semi-empirical model for their correlation (Chapter 3).

Objective 3: Partitioning of benzene derivatives produced by depolymerization of lignin

The third objective is to measure infinite dilution partition coefficients of benzene derivatives in [amim]Cl (1-allyl-3-methylimidazolium chloride)-CO_2 system and to develop a theoretical model based on equation of state theory for their correlation (Chapter 4).

Objective 4: Fundamental physical properties for development of equations of state

The fourth objective is to measure physical properties (atmospheric density and viscosity, and high pressure density) of ionic liquids that are able to dissolve biomass and to determine parameters for equations of state (Chapter 5).

Objective 5: Enhancement of H_2 solubility by CO_2 for hydrogenolysis of cellulose

The fifth objective is to propose a method to assess the enhancement effect of H_2 solubility by CO_2 in ionic liquids and to study conditions theoretically favorable for hydrogenolysis of cellulose in biomass-soluble ionic liquids (Chapter 6).

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Chapter 2

Literature review

2.1 Introduction

Fundamental physical properties of ionic liquid and ionic liquid-CO_2 biphasic systems are important for the development of biomass reaction and separation processes. In this chapter, literature surveys are made to understand knowledge gaps in both experimental data and theoretical methods related to the physical properties of density, viscosity, partitioning, CO_2 solubility and H_2 solubility in the presence of CO_2.

2.2 Conclusions

For developing biomass reaction and separation processes with ionic liquid-CO_2 biphasic system, fundamental physical properties of ionic liquid (e.g. density) and ionic liquid-CO_2 biphasic system (e.g. CO_2 solubility) are important and have been summarized in this chapter.

Partition coefficients of benzene or furan derivatives as solutes in ionic liquid-CO_2 biphasic

systems are scarce and a predictive model is still not developed from both approaches of semi-empirical models or equation of state models. Chapter 3 aims at measuring partition coefficients of furan derivatives in [bmim]Cl-CO_2 biphasic systems and developing a semi-empirical model. Chapter 4 aims to measure partition coefficients of benzene derivatives in [amim]Cl-CO_2 biphasic systems and to apply equations of state, ePC-SAFT model for developing a predictive theoretical model.

High pressure densities are mostly unavailable for biomass-soluble ionic liquids and most literature measurements are limited to 100 MPa. Chapter 5 aims at measuring high pressure densities of ionic liquids that dissolve biomass at conditions of pressure of up to 200 MPa. In Chapter 5, the derivative properties calculated from experimental densities using several models are evaluated for understanding detailed physical properties of ionic liquids, and the reliability of equations of state are compared and evaluated by extrapolation.

Solubility of H_2 in the presence of CO_2 in an ionic liquid are limited and the enhancement effect by CO_2 has not been evaluated quantitatively especially at high pressures. Chapter 6 aims at assessing the effect of CO_2 by developing a simple predictive model for determining conditions for hydrogenolysis of biomass in ionic liquid-CO_2 biphasic systems.

Chapter 3

Measurement of infinite dilution partition coefficients of furan derivatives in [bmim]Cl-CO_2 biphasic system and application of the LSER-δ model

3.1 Introduction

Partition coefficients are important for assessing ionic liquid-supercritical CO_2 biphasic systems in reaction and separation processes. As discussed in the previous chapter, partition coefficients of benzene and furan derivatives in biomass soluble ionic liquids are scarce and models are needed to reduce the experimental effort required for their determination.

In this chapter, new partition coefficients for furan and furan derivative compounds (2-methylfuran, 2-ethylfuran, furfural and furfuryl alcohol) in the ionic liquid (1-butyl-3-methylimidazolium chloride, [bmim]Cl)-CO_2 biphasic system are reported. The furan derivative compounds were selected as common intermediates that occur in biotransformations and are regarded as platform chemicals for future sustainable processes.[1-3] Since furan derivatives are presently being synthesized from carbohydrates[4, 5] or from biomass[6, 7] as summarized in Chapters 1 and 2, the data are expected to provide some guidance for downstream separations.

The Sanchez-Lacombe equation of state (SL EoS) is used to correlate the data and to

discuss trends in the data. A new functional relationship based on a linear solvation energy relationship (LSER) and regular solution theory, which called LSER-δ model, is proposed for compressible phases, and the model proposed in this thesis as modified by other researchers is also applied. These models are compared with each other to discuss solute-ionic liquid interactions and to consider development of a prediction model.

3.2 Conclusions

In this chapter, new partition coefficient data of furan derivatives in [bmim]Cl-CO_2 biphasic system were measured at high pressures (9-21 MPa) and over a temperature range of 313-353 K. The partition coefficients of furan derivatives in the [bmim]Cl-CO_2 biphasic system were compared with those of benzene derivatives. The general trend of the partition coefficients of furan derivatives in [bmim]Cl-CO_2 biphasic systems was according to the order of the vapor pressure of each solute, and this trend corresponded to that reported for benzene derivatives in previous works.

The SL EoS (Sanchez-Lacombe equation of state) could correlate the partition coefficient data to within a maximum ARD (average relative deviation) of 8.2 %. For prediction of partition coefficient without fitting parameters, however, correlations for the interaction parameters are needed. As future work on SL EoS development, a prediction method that uses only pure component descriptors could be fruitful provided that there are a sufficient number of data.

The LSER (Linear Solvation Energy Relationship)-δ model, and the entropic LSER-δ model were applied to the partition coefficient data. Both of the LSER-δ model and entropic LSER-δ model could correlate the data for [bmim]Cl-CO_2 biphasic system to within 11.8 % and 11.5 %, respectively.

The partition coefficients of benzene and furan derivatives that have been measured are limited to only one ionic liquid, [bmim]Cl that can dissolve biomass. The ARDs for LSER-δ model and SL EoS model are sufficiently low, however, both models still require consirerable experimental data and neither model can be used to reliably predict the partition coefficients in ionic liquid-CO_2 biphasic systems. Experimental data for other ionic liquids that can dissolve biomass are needed to assess possible ionic liquids for processing biomass, and other theory needs to be examined and compared with methods in this chapter.

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Chapter 4

Measurement of infinite dilution partition coefficients of benzene derivatives in [amim]Cl-CO_2 biphasic system and application of the ePC-SAFT model

4.1 Introduction

The key chemical property of an ionic liquid being able to dissolve, convert or pretreat biomass is thought to be related to its hydrogen bond basicity, which means that the ionic liquid must act as a hydrogen bond acceptor. The ionic liquid [amim]Cl (1-allyl-3-methylimidazolium chloride) has attracted a great deal of attention in the field[1-3] since it has a high hydrogen bond basicity,[4] and its melting temperature is low (290 K[5]) and its viscosity is moderate (ca. 485 mPa·s at 313 K[6]) that can allow efficient reactions and separations to occur at ambient temperatures. As described in Chapter 2, there are few partition coefficient data for biomass-soluble ionic liquids. Partition coefficients for alkylimidazolium halide ionic liquids that dissolve biomass are limited to [bmim]Cl (1-butyl-3-methylimidazolium chloride).[7]

Theoretical approaches are one of the methods to evaluate the partition coefficients in ionic liquid-CO_2 system. The LSER-δ model as shown in Chapter 3 is based on a semi-empirical relationship that allows quantitative correlation of partition coefficient data and study of solute

interactions within an LSER theoretical framework. Equations of state, such as SL EoS (Sanchez-Lacombe equation of state) or SAFT (Statistical Associating Fluid Theory) are able to provide good correlation of many systems, but still require a considerable number of phase equilibria data to determine the EoS parameters. Recently, the ePC-SAFT (electrolytes Perturbed-Chain Statistical Associating Fluid Theory) equation of state was proposed for ionic liquid-CO_2 systems[8] in which those authors found that the ePC-SAFT could provide quantitative prediction of the solubility of CO_2 in ionic liquids without any adjustable fitting parameters. Therefore, in this work, the ePC-SAFT EoS was applied to predict partition coefficients of selected solutes in the [amim]Cl-CO_2 biphasic system.

In this chapter, the first objective was to measure atmospheric densities and viscosities, and high pressure (~200 MPa) densities of [amim]Cl (1-allyl-3-methylimidazolium chloride) because these physical properties are needed to determine parameters in equation of state theories. The second objective was to measure partition coefficients for a fundamental set of benzene derivative solutes (chlorobenzene, bromobenzene, benzaldehyde and benzyl alcohol) in the [amim]Cl-CO_2 biphasic system over a wide range of temperatures (313-353 K) and pressures (6-21 MPa) by applying a supercritical fluid chromatography technique. These solutes were selected to discuss interactions between solute-CO_2 or solute-ionic liquid by comparison with reported data of previous work[7, 9] and Chapter 3. The third objective of this work was to evaluate the ePC-SAFT equation for its prediction of partition coefficients in the [amim]Cl-CO_2 biphasic system. Correlation of the data with the ePC-SAFT EoS is also considered and results are compared with correlation by the LSER-δ model. Finally, the fourth objective of this work was to calculate separation factors of solutes in the system, for the purposes of assessing the separation of non-polar and polar solutes in the ionic liquid-CO_2 biphasic system.

4.2 Conclusions

In this chapter, densities and viscosities of [amim]Cl at atmospheric pressure, and densities at pressures up to 200 MPa were measured. The trend of density with pressure or temperature corresponded to previous ionic liquids reported in the literature. The measured high pressure densities could be correlated by the Tait equation and the ePC-SAFT to within low deviations (<0.06 %).

The infinite dilution partition coefficient of benzene-derivative solutes in [amim]Cl-CO_2 biphasic systems at 313-353 K and 6-21 MPa were measured and correlated with the ePC-SAFT model. The ePC-SAFT model was unable to predict the data but could correlate the data to within an ARD of 20 %. One of the reasons why the ARD for ePC-SAFT model had large deviations for predicting infinite dilution partition coefficients is because the ionic term is insufficient for representing ionic liquid-solute or CO_2-solute interactions although the term was suitable for representing CO_2-ionic liquid interactions in the CO_2-ionic liquid data without any interaction parameters. At a given temperature and pressure, the partition coefficients for the hydrogen-bonding solute, benzyl alcohol, correlated with the ionic liquid hydrogen bond basicity. The basicity of the ionic liquid may be a key parameter for developing a predictive model with the ePC-SAFT in the future. The entropic empirical LSER-δ model was able to correlate the partition coefficient data to within an ARD of 8.9 %.

Separation factors were calculated with the ePC-SAFT over a range of pressures. The separation factors of all solutes relative to the polar solute (benzyl alcohol) were always greater than 100 at all pressures studied. Based on the trends of the separation factors with pressure, the [amim]Cl-CO_2 biphasic system is more favorable for nonpolar-polar separations than the [bmim]Cl-CO_2 biphasic system, which means that [amim]Cl is probably better suited for

downstream processing of biomass in systems that use an ionic liquid with CO_2.

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Chapter 5

Measurement and correlation of high pressure densities, atmospheric pressure densities and viscosities of ionic liquids that dissolve biomass

5.1 Introduction

The density and viscosity of an ionic liquid are important fundamental property, however, for ionic liquids that dissolve cellulose, these data are still scarce as described in Chapter 2. The derivative properties of the density, namely, the isobaric expansivity and the isothermal compressibility, are necessary to evaluate the physical characteristics of an ionic liquid in many mechanical applications. [1-3] In this chapter, high pressure densities and atmospheric pressure densities and viscosities are reported for three ionic liquids that can be used for processing biomass, namely, 1-ethyl-3-methylimidazolium methylphosphate ([emim][MP]), 1-ethyl-3-methylimidazolium diethylphosphate ([emim][DEP]) and 1-butyl-3-methylimidazolium acetate ([bmim][Ac]).

Densities of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf_2N]) at pressures greater than 140 MPa have not been reported yet[4-9] and in this chapter,

measurements of [bmim][Tf_2N] are used to demonstrate the apparatus and to extend the range to 200 MPa. High pressure densities (P<200 MPa) of [emim][MP] and [emim][DEP] have not been reported in the literature. The Tait equation was used to correlate the experimental data and to calculate derivative properties. The trends of the isobaric thermal expansivity and isothermal compressibility of the ionic liquids with temperature are compared with the properties of methanol within the framework of the theory of corresponding states.

Methanol is considered to be a representative molecular solvent whose properties are well known and its critical pressure and polarity are comparable with that of the ionic liquids. Four equations of state from two types, that is, SL EoS (Sanchez-Lacombe equation of state) and ε^*-mod SL EoS (ε^*-modified Sanchez-Lacombe equation of state) that belong to lattice fluid theory and PC-SAFT (Perturbed-Chain Statistical Associating Fluid Theory) and ePC-SAFT (electrolytes Perturbed-Chain Statistical Associating Fluid Theory) that belong to statistical associating fluid theory are applied to high pressure densities of the ionic liquids and their applicability is assessed.

Viscosities of the ionic liquids are measured at atmospheric pressures at (293-373) K. two models are examined for viscosity data correlation, namely, the Vogel-Fulcher-Tammann equation and the free volume model of Doolittle.

5.2 Conclusions

In this chapter, densities of four ionic liquids at pressures up to 200 MPa were measured. Among the ionic liquids, densities for two phosphate-containing ionic liquids were newly measured at high pressure and those for acetate and fluorine-containing ionic liquids were newly measured for a range of pressures up to 200 MPa. The trend of density with pressure or temperature of the ionic liquids studied in this work was in accordance with previous reports on high pressure densities in

the literature. The measured densities of this work could be correlated by the Tait equation with low deviation (<0.03 %).

The derivative properties, α_P and β_T, were calculated using Tait equation with parameters determined by correlation to the experimental data. The trends of α_P and β_T of the four studied ionic liquids are the same as those of the molecular solvent methanol in terms of corresponding states using reduced temperature.

Equations of state were applied to correlate the high pressure densities. The ε^*-mod SL EoS and ePC-SAFT showed the best correlation among SL EoS, ε^*-mod SL EoS, PC-SAFT and ePC-SAFT. Good correlation of the data by ε^*-mod SL EoS can be attributed to the temperature dependent interaction energy. The inclusion of Coulombic contribution between cation and anion in the ePC-SAFT is considered to be an important point for theoretical description of high pressure densities of ionic liquids. While both models represented for high pressure densities sufficiently well, the advantages of ePC-SAFT compared with the ε^*-mod SL EoS are that the ePC-SAFT equation requires only three pure component parameters and these parameters can probably be generalized with molecular parameters such as the molecular weight of the ionic liquid.

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Chapter 6

Enhancement ratio (*ER*) for describing H_2 solubility in H_2-CO_2-ionic liquid systems

6.1 Introduction

The enhancement of O_2, CH_4, CO and H_2 gas solubilities by CO_2 in solvents has been highlighted in the literature with the motivation to improve reaction efficiency.[1, 2] Akien and Poliakoff[3] provide an instructive example of using either gas fugacity or total pressure for analysis of gas solubility enhancement in gas expanded liquids for reactive systems and note that many authors do not truly compare solubility enhancement by CO_2.

Kumelan et al.[4] made fundamental solubility measurements of H_2-CO_2-ionic liquid systems. They reported that the solubility of H_2 in the ternary H_2-CO_2-[hmim][Tf_2N] system H_2 solubility could be increased by up to 20% per unit CO_2 molality. As discussed in Chapter 2, however, it is not simple to select effective conditions for a reaction, since the H_2 solubility depends not only on the concentration of CO_2 in the ionic liquid, but also on the temperature range. A correlation method for evaluating the H_2 gas solubility in an ionic liquid in the presence of CO_2 is required.

Furthermore, a predictive method is needed that can estimate the CO_2 enhancement of H_2 solubility in an ionic liquid, since many data do not exist for gas mixture-ionic liquid systems, especially for ionic liquids that dissolve cellulose or biomass. Therefore, in this chapter, the first objective was to propose a definition denoted as the enhancement ratio (*ER*) to help interpret the effect that CO_2 will have on H_2 solubility in an ionic liquid. The second objective in this chapter was to provide a simple correlation and a predictive method for the *ER* using binary gas solubility-ionic liquid data available in the literature. Finally, the third objective of this chapter was to estimate the H_2 solubility enhancement that can be obtained with CO_2 for ionic liquids that are able to dissolve monosaccharides, cellulose and lignocellulose.

6.2 Conclusions

In this chapter, a definition for enhancement ratio (*ER*) based on molality was proposed and applied to available H_2-CO_2-ionic liquid systems. It was found that the *ER* was convenient for examining the trends of solubility change of H_2 in an ionic liquid with CO_2 concentration or temperature. The *ER* clearly shows the effect that CO_2 has on hydrogen solubility, for example, it was found that CO_2 could not always enhance H_2 solubility because there were regions where *ER* falls below unity for some ionic liquids such as [hmim][Tf_2N].

A simple correlation for H_2 solubility in ionic liquids in the presence of CO_2 was developed from available binary and ternary data. The correlation could provide reliable estimation of H_2 solubility enhancement by CO_2 for six biomass-insoluble ionic liquids at 313-453 K. Detailed analyses or measurements of the free volume of ionic liquids are needed to improve the model.

Volume expansivity with molar volume of gas and ionic liquid mixture and volume of pure ionic liquid at atmospheric pressure are calculated for H_2-ionic liquid, CO_2-ionic liquid, other

gas-ionic liquid and H_2-CO_2-ionic liquid systems. The volume expansivity was proportional to mole fraction of gas, and the slope was independent on species of gas. The mechanism of the behavior was not discovered perfectly yet but should be related and explained with free volume or other physical properties.

The form of the correlation was modified to allow prediction of H_2 solubility enhancement by CO_2 in ionic liquids from a small number of parameters. H_2 solubility in the presence of CO_2 was predicted for ionic liquids that dissolve biomass using the model developed in this work. The predictive model allows the ranking of ionic liquids being considered for hydrogenolysis or hydrogenation of biomass according to their hydrogen solubility and their enhancement ratio that can be controlled with the CO_2 molality.

In summary, a ratio was defined that describes the enhancement of a target gas solubility (H_2) by a carrier gas (CO_2) in a nonvolatile solvent (ionic liquid). It was found that the enhancement ratio, *ER*, was helpful to examine the trends of H_2 enhancement in an ionic liquid by CO_2. The *ER* was applied to ionic liquids that dissolve biomass and it was suggested that some ionic liquids can be preferable for hydrogenolysis or hydrogenation of biomass according to their gas enhancement characteristics.

6.3 References

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Chapter 7

Conclusions and future work

7.1 Summary and conclusions

In this thesis, the goal was to develop theory for separation and reaction in ionic liquid-supercritical CO_2 biphasic systems described in Figure 1-10 (Chapter 1) through the use of physical property measurements and by assessing property correlations with fundamental models. The conclusions for each chapter are summarized as follows.

Objective 1: Literature survey on ionic liquid-CO_2 biphasic systems (Chapter 2)

For developing biomass reaction and separation processes with ionic liquid-CO_2 biphasic system, fundamental physical properties of ionic liquid (e.g. density) and ionic liquid-CO_2 biphasic system (e.g. CO_2 solubility) are tabulated Chapter 2. According to literature survey performed on partition coefficients of benzene or furan derivatives as solutes in ionic liquid-CO_2 biphasic systems, predictive models have not yet been developed from either semi-empirical models or equation of state models. High pressure densities of biomass soluble ionic liquids are scarce and most

literature measurements are limited to 100 MPa. The derivative properties calculated from experimental densities using thermodynamic models are needed to understand detailed physical properties of ionic liquids, and the reliability of equations of state models. For hydrogenolysis of cellulose with H_2 gas in ionic liquid reaction solvent, solubility of H_2 is low, but can be enhanced with CO_2. Solubility measurements of H_2 in the presence of CO_2 in an ionic liquid are limited and the enhancement effect by CO_2 has not been evaluated quantitatively at high pressures. A predictive model that could calculate hydrogen solubility enhancement effects in biomass-soluble ionic liquids would be useful for assessing the CO_2-ionic liquid biphasic systems for reactions.

Objective 2: Partitioning of furan derivatives produced by synthesis of 5-HMF (Chapter 3)

New partition coefficient data of furan derivatives in [bmim]Cl-CO_2 biphasic system were measured at high pressures (9-21 MPa) and over a temperature range of 313-353 K. The partition coefficients of furan derivatives in the [bmim]Cl-CO_2 biphasic system were compared with those of benzene derivatives. The general trend of the partition coefficients of furan derivatives in [bmim]Cl-CO_2 biphasic systems mainly corresponded to the order of the vapor pressure of each solute. The SL EoS (Sanchez-Lacombe equation of state) could correlate the partition coefficient data to within a maximum ARD (average relative deviation) of 8.2%. For prediction of partition coefficient without fitting parameters, however, correlations for the interaction parameters are needed. The LSER (linear solvation energy relationship)-δ model, and the entropic LSER-δ model were applied to the partition coefficient data. The LSER-δ model and entropic LSER-δ model could correlate the data for the [bmim]Cl-CO_2 biphasic system to within 11.8% and 11.5%, respectively, for all solutes studied.

Objective 3: Partitioning of benzene derivatives produced by depolymerization of lignin (Chapter 4)

New partition coefficient data of benzene derivatives in [amim]Cl-CO_2 biphasic system were measured at high pressures (6-21 MPa) and over a temperature range of 313-353 K and correlated with the ePC-SAFT model. For developing the ePC-SAFT model, densities of [amim]Cl are reported at pressures up to 200 MPa and used to determine pure component parameters of the model. The trend of density with pressure or temperature corresponded to previous ionic liquids reported in the literature. The measured high pressure densities could be correlated by the Tait equation and the ePC-SAFT to within low deviations (<0.06%). The ePC-SAFT model was unable to predict partition coefficient data but could correlate the data to within an ARD of 20%. The entropic LSER-δ model was able to correlate the partition coefficient data to within an ARD of 8.9%. Separation factors were calculated with the ePC-SAFT over a range of pressures. The separation factors of all solutes relative to the polar solute (benzyl alcohol) were always greater than 100 at the conditions studied. Based on the trends of the separation factors with pressure, the [amim]Cl-CO_2 biphasic system is more favorable for nonpolar-polar separations than the [bmim]Cl-CO_2 biphasic system, which means that [amim]Cl is probably better suited for processing biomass in which the reaction product is non-polar (e.g. *n*-hexane).

Objective 4: Fundamental physical properties for development of equations of state (Chapter 5)

Densities of four ionic liquids that dissolves biomass, [emim][MP], [emim][DEP] and [bmim][Ac] at pressures up to 200 MPa were measured. Data for [bmim][Tf_2N] were measured over the same range at pressures (200 MPa) to validate the procedures used. The trend of density with pressure or temperature of the ionic liquids studied in this thesis was in accordance with

previous reports on high pressure densities in the literature. The measured densities of this work could be correlated by the Tait equation with low deviation (<0.03 %). The derivative properties, α_P and β_T, were calculated using the Tait equation with parameters determined by correlation to the experimental data. The trends of α_P and β_T of the four studied ionic liquids are the same as those of the molecular solvent methanol in terms of corresponding states using the reduced temperature. Equations of state were applied to correlate the high pressure densities. The ε^*-mod SL EoS and ePC-SAFT equations showed the best correlation among the equations of state studied. Good correlation of the data by ε^*-mod SL EoS can be attributed to its temperature dependent interaction energy. From the excellent precision of ePC-SAFT, it is considered that an important point for high pressure density correlation of ionic liquids is related to Coulombic contributions between cation and anion that is accounted for in the ionic term of the model While the ε^*-mod SL EoS and the ePC-SAFT models correlated the high pressure densities of ionic liquids well, the advantages of the ePC-SAFT compared with the ε^*-mod SL EoS is that ePC-SAFT requires only three pure component parameters and it can be predictive quantitatively for CO_2-ionic liquid binary systems.

Objective 5: Enhancement of H_2 solubility by CO_2 for hydrogenolysis of cellulose (Chapter 6)

A definition for enhancement ratio (*ER*) based on molality was newly proposed and applied to available H_2-CO_2-ionic liquid systems. It was found that the *ER* was convenient for examining the trends of solubility change of H_2 in an ionic liquid with CO_2 concentration or temperature. The *ER* clearly shows the effect that CO_2 has on hydrogen solubility, for example, it was found that CO_2 could not always enhance H_2 solubility in an ionic liquid because there are regions where *ER* fell below unity for some ionic liquids such as [hmim][Tf_2N]. A simple correlation for H_2

solubility in ionic liquids in the presence of CO_2 was developed from available binary/ternary data. The correlation could provide estimation of H_2 solubility enhancement by CO_2 for six biomass-insoluble ionic liquids at 313-453 K. Detailed analyses or measurements of the free volume of ionic liquids are needed to improve the model. The form of the *ER* correlation was modified to allow prediction of H_2 solubility enhancement by CO_2 in ionic liquids from a small number of parameters. H_2 solubility in the presence of CO_2 was predicted for ionic liquids that dissolve biomass using the model developed in this work. The predictive model allows the ranking of ionic liquids being considered for hydrogenolysis or hydrogenation of biomass according to their hydrogen solubility and their enhancement ratio that can be controlled with the CO_2 molality. Among the ionic liquids studied in this thesis, [bmim]Cl would seem to be the most favorable to use for hydrogenolysis of cellulose, because [bmim]Cl not only has a high *ER* but it also has a high H_2 solubility in the binary system.

7.2 Future work

There are a number of topics that are listed below for future work.

Future work 1: Measurement of actual product extraction from biomass processing

For all three biomass processing proposed in this thesis, that is, i) synthesis of 5-HMF, ii) depolymerization of lignin and iii) hydrogenolysis of cellulose, infinite dilution partition coefficient of model compounds such as furan and benzene derivatives were measured in this thesis. Since the infinite dilution partition coefficient is at extremely low concentrations of solute, the extraction of actual product (e.g. 5-HMF) by pressurized CO_2 should be confirmed. Jing et al.[1] reported

5-HMF solubility in CO_2 pressures up to 20 MPa with and without ethanol as cosolvent. The authors reported that the polar cosolvent, ethanol enhanced solubility of 5-HMF in non-polar CO_2 and they concluded that the ethanol acts to reduce the energy of the process. Therefore, the synthesis of low-polar chemicals (e.g. DMF) may be probably a better choice than 5-HMF as a product that can be extracted from the ionic liquid with supercritical CO_2 without co-solvent.

Future work 2: Predictive model for partition coefficient in ionic liquid-CO_2 biphasic system

Both theoretical and semi-empirical approaches were unable to predict partition coefficients in CO_2-ionic liquid biphasic systems. The ePC-SAFT model has the potential to be modified by adding or revising the perturbation term because the specific interaction between polar solute and ionic liquid that has high hydrogen bond basicity was confirmed from experimental and calculated results. The LSER-δ model also has possibility to be modified. Parameters are now available for a small group of CO_2-ionic liquid biphasic systems and as further systems are measured, it may be possible to group some ionic liquids that belong to same category (e.g. high hydrogen bond basicity group) to make a generalized model for a specific common cation or common anion ionic liquids.

Future work 3: Predictive model for high pressure densities of ionic liquids with equations of state

The ε^*-mod SL EoS and ePC-SAFT could correlate and extrapolate the high pressure densities of ionic liquids pressures up to 200 MPa. Especially, the ePC-SAFT was reported to predict CO_2 solubility in ionic liquid without any fitting parameters. Therefore, a generalized method to determine pure component parameters for these equations of state could have great impact on theoretical predictive methods.

Future work 4: Detailed analysis of enhancement effect for H_2 solubility with other methods

The enhancement ratio developed in this thesis may be helpful to understand or choose conditions in reactions or separations that use not only ionic liquids, but also polymer solutions and possibly expanded liquids. As a future direction, experimental measurements and simulations are needed for gas mixture solubilities (O_2-CO_2, H_2-CO_2, CH_4-CO_2, H_2S-CH_4, CO-CO_2) with ionic liquids especially those related to biomass or biomass-related reactions. The mechanism of the enhancement, that is, the dominant factor of *ER* is not yet understood. One of the most promising approaches for understanding *ER* is to study the free volume of the ionic liquid. Ramdin et al.[2] summarized Henry's constants of CO_2 at 333 K and free volumes for more than 30 ionic liquids, and confirmed roughly a linear relationship between them. The order of the occupied volume, which is the complement of the free volume, has an inverse order with the *ER*. The determination of free volume or occupied volume with equations of state, is an indirect approach that contains approximations in the equations of state theory. Experimental and theoretical methods (molecular simulation) are needed to study the free volume of ionic liquids especially in the presence of a gas (e.g. CO_2) and other common organic solvents (e.g. *n*-hexane, ethanol). Beichel et al.[3] used positron annihilation lifetime spectroscopy (PALS) to determine the free volume of ionic liquids experimentally. PALS should become a powerful tool for understanding the free volume of ionic liquids and new measurements are needed especially for ionic liquids related to biomass.

7.3 References

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