Fluid Phase Equilibria 409 (2016) 408–416

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Modeling gas solubilities in imidazolium based ionic liquids with the $[Tf_2N]$ anion using the GC-EoS

Selva Pereda [a], [*], Sona Raeissi [b], Alfonsina E. Andreatta [c], Susana B. Bottini [a], Maaike Kroon [e], Cor J. Peters [d], [e]

[a] *Planta Piloto de Ingeniería Química, Universidad Nacional del Sur-CONICET, Camino La Carrindanga Km 7, CC 717, 8000 Bahía Blanca, Buenos Aires, Argentina*
[b] *School of Chemical and Petroleum Engineering, Shiraz University, Mollasadra Ave., Shiraz, 71345, Iran*
[c] *IDTQ Grupo vinculado PLAPIQUI-CONICET, Universidad Nacional de Cordoba X5016GCA, Av. Vélez Sarsfield, 1611 Córdoba, Argentina*
[d] *The Petroleum Institute, Chemical Engineering Department, P.O. Box 2533, Abu Dhabi, United Arab Emirates*
[e] *Eindhoven University of Technology, Department of Chemical Engineering and Chemistry, Separation Technology Group, Den Dolech 2, 5612 AZ Eindhoven, The Netherlands*

ARTICLE INFO

Article history:
Received 31 August 2015
Received in revised form
9 October 2015
Accepted 21 October 2015
Available online 24 October 2015

Keywords:
GC-EoS
Group contribution
Equation of state
1-Alkyl-3-methylimidazolium
bis(trifluoromethyl-sulfonyl)imide
1-Alkyl-3-methylimidazolium
bis(trifluoromethyl-sulfonyl)amide
CO_2
CO
H_2
Alkane

ABSTRACT

The group contribution equation of state (GC-EoS) is extended to model gas solubilities in the homologous 1-alkyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl) imide family. The gases considered in this work are CO_2, CO, H_2, CH_4, and C_2H_6. The model parameters were estimated on the basis of 1400 experimental data points in the temperature range of 278–460 K and pressures up to 160 bars. A correlation is also presented to calculate the critical diameter, a characteristic parameter of the GC-EoS repulsive term, as a function of the ionic liquid molar volume. Density data is most often available for ionic liquids; hence, the correlation provides a predictive method for ionic liquids not included in the parameterization process. The new parameters were then used to predict the phase behavior of binary mixtures containing different solutes (including C_3H_8, C_4H_{10}, and C_6H_{14}) and ionic liquids with different chain lengths than those used in the parameterization process.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

There are a number of industrial processes that call for an efficient technology for CO_2 recovery from gas streams: for example, the removal of acid gases from natural gas or biogas, the purification of the products of steam reforming, the water gas shift reaction and the integrated gasification cycle. Additionally, the growing concern about global warming and environmental pollution, are making governmental regulations on CO_2 emissions more stringent every day.

Currently, the available commercial CO_2 capture technologies include chemical and physical absorption, physical adsorption, membrane separation and cryogenic distillation. A number of authors have proposed, as an alternative method, the use of ionic liquid supported membranes for CO_2 separation [1,2]. Room temperature ionic liquids (RTILs or simply ILs) are liquid organic salts, having negligible vapor pressure and high solvation power. These characteristics make them good candidates to replace conventional organic solvents. Moreover, many ILs have high thermal stability. This property, together with the fact that they have almost no vapor pressure, minimize solvent losses in the gas stream and help to reduce the solvent make-up required in separation processes.

A thermodynamic model able to predict gas solubility in ionic liquids is required for the proper design and optimization of such processes. A literature review on the thermodynamic models

---

[*] Corresponding author.
E-mail addresses: spereda@plapiqui.edu.ar (S. Pereda), raeissi@shirazu.ac.ir (S. Raeissi), aandreatta@plapiqui.edu.ar (A.E. Andreatta), cpeters@pi.ac.ae (C.J. Peters).

http://dx.doi.org/10.1016/j.fluid.2015.10.037
0378-3812/© 2015 Elsevier B.V. All rights reserved.

applied to ionic liquid mixtures, shows that various approaches have been investigated, mainly consisting of equations of state [3–9] and excess Gibbs energy models such as NRTL [10–12], UNIQUAC [12–14], and UNIFAC [15–17]. However, each method has its own advantages and shortcomings over the others. For example, the excess Gibbs energy models are not suitable for high-pressure conditions typical in gas processing, while the classic cubic equations of state face the limitation of the lack of experimental information on the critical properties of ionic liquids. Considering such shortcomings and the large variety of ionic liquids that may be available, group contribution methods appear to be an interesting alternative. The group contribution equation of state (GC-EoS) is an attractive model, taking into account that the information on the critical properties of pure compounds may not be required. Another advantage of using the GC-EoS is its ability to model phase equilibria in size-asymmetric mixtures [18–20]. GC-EoS uses the Carnahan-Starling [21] equation for hard spheres, which is a more realistic model for the repulsive contribution than the simple van der Waals repulsive term used by the majority of cubic equations of state. The combination of this repulsive term with a group contribution NRTL attractive term, makes the GC-EOS a promising tool to model the phase behavior of mixtures of gases and ionic liquids. Breure et al. [22] were the first to use the GC-EoS to model CO_2 solubility in ionic liquids. Bubble points were predicted for mixtures of CO_2 with the homologous families of 1-alkyl-3-methylimidazolium hexafluorophosphate and tetrafluoroborate. The agreement between experimental and predicted bubble points were excellent for pressures up to 20 MPa, even for pressures up to about 100 MPa. The results showed the capability of the GC-EOS to describe phase equilibria of such systems. Later, Bermejo et al. [23] used the GC-EoS to describe the phase behavior of different gases with ionic liquids of the methylimidazolium bis[(trifluoromethyl) sulfonyl]imide family. For most of the systems, the average deviations between experimental data and model predictions were below 10%. However, since at the time that the article was published, experimental data on the other members of the homologous family were yet unavailable, the authors concluded that further studies with the GC-EoS would be required to verify the applicability of the model to other members of the family.

In the present work, the GC-EOS is applied to model gas solubilities (H_2, CO_2, CO, CH_4, C_2H_6) in the various members of the homologous 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide family (abbreviated as [$C_n$mim][Tf_2N]). Furthermore, liquid–liquid equilibria is also considered and modeled. The predictive capability of the equation is of particular significance in this work, since the critical diameter of the ionic liquid is not fitted to experimental data. It is predicted with a general correlation proposed in this work, as a function of the density of the pure ionic liquid, a property which is most often readily known for ionic liquids. In this way, our approach provides a predictive capacity, which widens the applicability of the model to different conditions and multiphase equilibria, as compared to the previous GC models for gas solubility in ionic liquids.

2. Thermodynamic model

The group contribution equation of state was proposed by Skjold-Jørgensen [24,25], for modeling particularly high-pressure equilibria. The model is based on the generalized van der Waals partition function, combined with the local composition principle and a group contribution approach. Based on extensive testing, the GC-EOS has proven to be a reliable method for phase equilibrium calculations for mixtures containing widely differing components.

The GC-EoS can be written as the sum of two different contributions to the residual Helmholtz energy:

$$A^{res} = A^{rep} + A^{att} \quad [1]$$

The Carnahan–Starling repulsive term follows the expression developed by Mansoori and Leland [26] for mixtures of hard spheres. It is a function of the critical hard sphere diameter, characteristic of the pure-compound molecular size, and has no binary or higher-order parameters. This free-volume contribution makes the model especially suited for predicting the effects of large molecular size differences on the excess properties of the mixture, as shown in several publications on the subject of supercritical fluid applications [27–31].

The attractive term is a group contribution version of the NRTL expression, with density-dependent mixing rules. The attractive energy between like groups is calculated from pure group parameters; binary parameters are introduced to quantify interactions between unlike groups. Details of the model are given in the Appendix.

When the GC-EOS model is applied to ILs, it is necessary to determine the functional groups that conform the molecules. Similar to UNIFAC, groups should be defined as neutral as possible. For this reason, the ionic core (cation + anion) is defined as the IL group, while the hydrocarbon chain is divided into the paraffinic groups CH_3 and CH_2 (see Fig. 1). This makes possible to describe the complete members of the [$C_n$mim][Tf_2N] family with only three functional groups, leading to an important reduction in the number of binary interaction parameters.

2.1. Parameterization of the repulsive term

The free volume term of the residual Helmholtz energy contains only one characteristic parameter, which is the critical hard sphere diameter (dc). There are three different ways to calculate dc for each compound: (i) direct calculation from the critical temperature and pressure (see Equation (A6) in the Appendix); (ii) optimization of dc by fitting a given point of the pure-component vapor pressure curve; (iii) computation of dc with a correlation for high molecular weight compounds proposed by Bottini et al. [18], based on the van der Waals molecular volume r_i^{vdW}:

$$\log(dc_i) = 0.4152 + 0.4128 \cdot \log\left(r_i^{vdW}\right) \quad [2]$$

In the case of permanent gases, the first procedure must be used. Ordinary solvents are generally modeled using method (ii), which usually gives dc values within 5% of those given by method (i). However, this difference is important, since pure component vapor pressures are quite sensitive to dc [25]. High molecular weight compounds present extremely low vapor pressures and their critical properties are usually unknown. For this reason, they require the use of method (iii). Ionic liquids also have negligible vapor pressures and unknown critical points. Bottini et al. [18] estimated r_i^{vdW} using the Bondi [32] group contribution method. However, the latter method was developed for non-ionic organic compounds, so its use for ionic liquids would be inappropriate. In addition, several

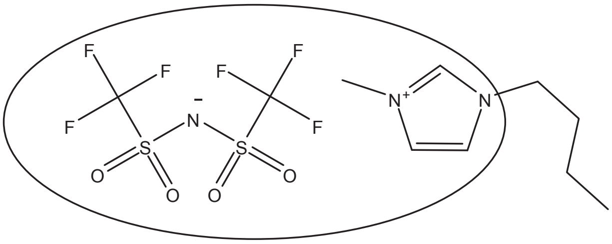

Fig. 1. Group definition for [-mim][Tf_2N].

Download English Version:

https://daneshyari.com/en/article/201372

Download Persian Version:

https://daneshyari.com/article/201372

Daneshyari.com