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Thermodynamic modeling of refrigerants solubility in ionic liquids using original and ε^* -Modified Sanchez–Lacombe equations of state



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ABSTRACT

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1. Introduction

Ionic liquid (IL), also known as liquid electrolyte or liquid salt, is a term customarily used to refer to organic salts that form a stable and wide liquid range of over 300 K. Ionic liquids have a melting temperature below T=373.15 K and consist of a small organic or inorganic anion and a large asymmetric organic cation; the suitable choice of which could be used to adjust and tune the specific properties of the ionic liquids on demand. Due to their nonflammability, high thermal stability, recyclability and almost negligible vapor pressure, which essentially eliminates hazardous emissions to the atmosphere, these compounds are considered as environmentally benign solvents. Detailed reviews regarding ionic liquids synthesis and their various novel applications ranging from being used as alternatives to conventional organic solvents to their use as catalysts and catalytic supports are available in the literature [1–3]. In particular, Ionic liquids have found increasing application, alongside various refrigerant gases, both in separation and engineering applications; in which detailed phase equilibria and thermodynamics modeling are needed for their further development [4]. More specifically, Ionic liquids have been used to facilitate the separation of refrigerants and intermediates that often have very similar physico-chemical properties; for instance, the case of an azeotropic hydrofluorocarbon mixture containing

Ionic liquids can dramatically improve the efficiency of absorption refrigeration processes due to their negligibly small vapor pressure; where the IL absorbs the refrigerant gas in one stage and subsequently releases the high-pressure gas upon addition of heat. In the current study, phase equilibrium data (P-T-x) of a diverse set of refrigerants in different types of ionic liquids are modeled with the aid of two equations of state based on lattice fluid theory, i.e. Sanchez–Lacombe and ε^* -Modified Sanchez–Lacombe EOSs. The characteristic parameters of the pure components were determined from a database of 3086 experimental liquid density datapoints for 11 refrigerants and 12 ILs. According to the results obtained by considering the experimental data of 25 binary IL/refrigerant mixtures comprised of 88 isotherms with a total of 658 datapoints, both EOSs can successfully correlate the solubility data with AARDs of %5.773 and %5.771 for SL and ε^* -Modified SL EOSs, respectively.

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difluoromethane and pentafluoroethane could be of note [5]. Also, ionic liquids can dramatically improve the efficiency of absorption refrigeration processes where the IL absorbs the refrigerant gas in one stage and subsequently releases the high-pressure gas upon addition of heat. Moreover, the major drawback of the current liquid solvents, with even low volatility, used in refrigeration processes is the necessity for costly and bulky equipment to remove their contamination from the high-pressure gas. In this regard, ionic liquids with their very low vapor pressure, help in preventing contamination of the refrigerant gas with solvent and hence maintaining the refrigeration capacity of the refrigerant. Furthermore, one of the major challenges imposed upon the prospective use of ILs as alternatives to conventional solvents is their relatively higher viscosity which in turn translates into slower mass transport rates and hence larger capital costs and process equipment, e.g. heat exchangers and contactors. In addressing this issue, dramatic improvements have been reported for the mass transport properties, i.e. viscosity and diffusivity, of ILs when used alongside refrigerants [6]. Proper designing, as well as optimization of these and other IL/refrigerant applications requires reliable quantitative modeling of the high-pressure phase behavior and equilibria data of the systems of interest. Especially, correlating and predicting the phase equilibria data, which essentially quantify the solubility of each component in all the contacting phases, could be very valuable in the design stage of the aforementioned processes. For instance, identification of the regions over which the IL/refrigerant systems are miscible, and hence not conducive to separation or absorption refrigeration,







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Table 1

Data sources used for evaluating the pure component characteristic parameters of the EOSs. In the table the pressure and temperature values have been rounded to the closest integer.

Substance	Fitting range			
	P (MPa)	T (K)	N.D.	Reference
Refrigerants				
R-14	0-57	0-224	86	[19]
R-23	0-4	121-295	94	[20]
R-41	7–70	130-315	220	[21]
R-50	0-35	91-191	267	[22]
R-124	1-36	104-400	149	[23]
R-125	1-68	180-350	178	[24]
R-E125	5-35	243-326	161	[21]
R-134	1-5	274-367	59	[25]
R-161	0-3	231-343	45	[26]
R-290	1-51	207-353	79	[27]
R-134a	1-80	283-363	32	[28]
Ionic liquids				
[Hmim][Tf2N]	0-65	293-338	162	[29]
[Emim][PF6]	10-200	353-472	129	[30]
[Emim][TFSI]	1-100	283-373	84	[31]
[Bmim][PF6]	0-200	313-472	181	[32]
[Bmim][Tf2N]	0-60	293-473	237	[33]
[Bmim][CH3SO4]	0-35	283-353	261	[34]
[Emim][EtSO4]	0-140	283-413	151	[35]
[Bmim][NO3]	0.1	283-363	15	[36,37]
[Hmim][BF4]	10-200	313-473	180	[30]
[Omim][BF4]	0-60	283-323	117	[38]
[Emim][BF4]	10-200	313-472	180	[30]
[Hmim][PF6]	10-200	313-472	180	[30]

Cation: [Hmim], 1-Hexyl-3-Methylimidazolium; [Emim], 1-Ethyl-3-methylimidazolium; [Bmim], 1-Butyl-3-methylimidazolium; [Omim], 3-Methyl-1-Octylimidazolium. Anion: [Tf2N], Bis(TrifluoroMethylSulfonyl); [PF6], Hexafluorophosphate; [TFSI], Bis(TrifluoroMethylSulfonyl); [CH3SO4], Methyl Sulfate; [EtSO4], Ethyl Sulfate; [NO3], Nitrate; [BF4], Tetrafluoroborate.

could be readily accomplished by way of thermodynamics modeling. Still and to the best of the authors' knowledge, use of equations of state in the thermodynamics modeling of IL/ refrigerant mixtures is scarce in the published literature. Recently, Ren and Scurto [4] used a cubic equation of state, i.e. Peng–Robinson EOS [7] alongside the van der Waals 2-parameter mixing rule (PR-vdW2) to correlate the isothermal vapor–liquid equilibrium data for four binary mixtures of the type IL/refrigerant. Furthermore, Faúndez et al. [8] correlated and tested for thermodynamic consistency the data of nineteen binary IL/ refrigerant mixtures with the modified Peng–Robinson EOS proposed by Kwak and Mansoori [9].

The present study considers the data of 25 binary IL/refrigerant mixtures at pressures ranging from 0.01 to 12.05 MPa and temperatures spanning 283–449 K. These data include 88 isotherms with a total of 658 datapoints. An equation of state based on lattice fluid theory and a modified version of it are successfully employed and compared in their ability to correlate these experimental solubility data for the first time. Furthermore, in order to ascertain their relative accuracy, the results obtained here are compared with the available published results of other authors who have employed other equations of state.

2. Thermodynamic modeling

The lattice–fluid model was proposed by Sanchez and Lacombe [10] to describe thermodynamic properties of molecular fluids of arbitrary size. In this and other models based on lattice-hole theory [11,12], which are essentially based on statistical thermodynamics, the molecules are presumed to be consisting of repeating units called segments. This framework is similar to the concept of monomer in polymer sciences; the difference being that while the latter has its roots in physical reality, molecular segments are imaginary or mathematical units. Nonetheless, the common denominator between all such theories is that they consider the movement of each molecule segment to be restricted to the neighborhood of one of the lattice sites; so that, it is usual to consider only the effect of nearest neighbors on the molecule segment within its cell [13]. In the current study two variations of Sanchez–Lacombe (SL) equation of state [10,14,15], which are themselves based on lattice–fluid theory are employed. With three substance dependent characteristic parameters, the original SL EOS is represented by Eqs. ((1) and (2)):

$$\tilde{\rho}^{2} + \tilde{P} + \tilde{T}(\ln(1 - \tilde{\rho}) + (1 - \frac{1}{r})\tilde{\rho}) = 0$$
(1)

$$\tilde{T} = \frac{T}{T^*}, \tilde{P} = \frac{P}{P^*}, \tilde{\rho} = \frac{\rho}{\rho^*}$$

$$\varepsilon^* = RT^*, \upsilon^* = \frac{RT^*}{P^*}, r = \frac{MP^*}{RT^*\rho^*}$$
(2)

where T^* , P^* and ρ^* are the characteristic parameters of the EOS for each pure component that differ from the critical parameters, M is the molecular weight and R is the universal gas constant. The characteristic parameters, ε^* , υ^* and r represent the interaction energy, the characteristic volume and the segment length for pure substances, respectively; which are themselves directly related to T^* , P^* and ρ^* by Eq. (2) and hence both constant sets could be used interchangeably. In this form, the interaction energy, ε^* , is treated as a constant.

Following the original work of Sanchez and Lacombe, Machida et al. [16] proposed a simple modification to take into account the temperature dependence of hydrogen bonding and ionic interactions. In their work, a simple function in the form of the Langmuir equation was used that reduces to the original SL EOS at high temperatures; and introduces temperature dependence into the interaction energy parameter, ε^* , as in Eq. (3):

$$\varepsilon^*(T) = \varepsilon_0 \frac{\alpha T}{1 + \alpha T} \tag{3}$$

where α is a constant that gives temperature dependence to ε^* and ε_0 is the asymptotic value of the interaction energy, which ε^* attains at the high temperature limit. For this formulation, which they dubbed as ε^* -Modified SL EOS, the authors reported large improvements over the original SL EOS in the calculation of liquid densities of polar fluids and ionic liquids, especially in the high-pressure compressed-liquid region.

For application of the original SL EOS, as well as the ε^* -Modified SL EOS to mixtures, the combining rules, as presented in Eq. (4), were applied:

$$P^{*} = \sum_{i} \sum_{j} \phi_{i} \phi_{j} P_{ij}^{*} P_{ij}^{*} = (1 - k_{ij}) (P_{i}^{*} P_{j}^{*})^{1/2}$$

$$T^{*} = P^{*} \sum_{i} (\frac{\phi_{i}^{0} T_{i}^{*}}{P_{i}^{*}}) \quad \nu^{*} = \sum_{i} (\phi_{i}^{0} \nu_{i}^{*})$$

$$\phi = \frac{r_{i} x_{i}}{r} \qquad \phi_{i}^{0} \frac{r_{i}^{0} x_{i}}{r}$$

$$r = \sum_{i} (x_{i} r_{i}^{0}) \quad r_{i} = r_{i}^{0} \frac{\nu_{i}^{*}}{\nu^{*}}$$
(4)

where φ_i° and φ_i represent the closed-packed volume fraction of component *i* in pure state and mixture, respectively, r_i^{0} and r_i represent the segment length of component *i* in pure state and mixture, respectively, and k_{ij} is a binary interaction parameter between component *i* and *j*. In comparing the original Sanchez– Lacombe EOS with its ε^* -Modified formulation in representing the solubility of refrigerants in ILs, comparisons are made between the Download English Version:

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