Fluid Phase Equilibria 303 (2011) 111–114

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Fluid Phase Equilibria

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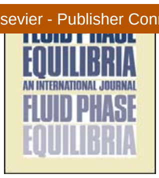

Liquid–liquid equilibrium in ternary ionic liquid systems by UNIFAC: New volume, surface area and interaction parameters. Part II

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ARTICLE INFO

Article history:
Received 16 August 2010
Received in revised form 2 December 2010
Accepted 11 December 2010
Available online 21 December 2010

Keywords:
Ionic liquids
Liquid–liquid equilibria
UNIFAC
Quantum mechanics calculation
Volume and surface parameters

ABSTRACT

Ionic liquids are potential solvents for liquid extraction processes; thermodynamic modeling of liquid–liquid equilibrium (LLE) data is essential for the optimization and operation of these processes. Therefore, ternary LLE data in systems involving ionic liquids have been investigated by several years. In most of the cases, the thermodynamic modeling of these systems has been made using the NRTL model; in some cases, the UNIQUAC model has also been used. The structural parameters of UNIQUAC for ionic liquids have been determined either by empirical correlations or, more recently, through quantum mechanics calculation. This work is a continuation of a recent paper, in which the structural group volume and area parameters for the group-contribution UNIFAC method have been calculated for five ionic liquids following the quantum mechanics approach. In order to optimize the molecular geometry and to calculate the area and volume, the Density Functional Theory (DFT) and the Polarizable Continuum Method (PCM) were used, respectively. The obtained parameters were used to correlate LLE data for fifteen ternary systems, totalizing 155 tie-lines. New interaction parameters were also estimated between the solvent and the ionic liquid functional groups. The results are very satisfactory, with root mean square deviations 0.0037 between experimental and calculated equilibrium mole fractions.

1. Introduction

Ionic liquids have been widely studied due to their unique thermophysical properties, mainly their nonexistent vapor pressure, which allows them to be called green solvents. Ionic liquids are based on large organic cations (e.g. imidazolium, pyridinium, ammonium, phosphonium and triazolium derivatives) and small anions, whose choice allows the physicochemical properties of the ionic liquids to be tuned. In this way, ionic liquids can be made task-specific for a certain application. Applications include the usage of ionic liquids as potential solvents for liquid extraction processes [1].

The study of the liquid–liquid equilibrium data for ternary systems containing ionic liquids have seen made by several papers [2–41]. The NRTL model [42] has been usually used for the correlation of these experimental data. Due to lack of pure component volume and area parameters for ionic liquids, the UNIQUAC model [43] was not widely used; however, some recent works [17,24,33–37,44–49] have correlated LLE data for ternary systems including ionic liquids using this model. Banerjee et al. [44] and Santiago et al. [46,47] used a quantum chemistry approach. The parameters found were considered adequate for the representation of the liquid–liquid equilibrium of ternary systems with ionic liquids. The differences between these two sets seem to be in some details in the energy minimization procedure. The thermodynamic modeling of ternary systems containing ionic liquids using group contribution methods, like UNIFAC [50] and ASOG models [51], is still very scarce, with just a few studies [52–55].

This work is a continuation of our recent paper in correlating LLE of ternary systems with ionic liquids by UNIFAC [55], where 24 ternary systems involving six different ionic liquids were studied, with the determination of the structural volume and area parameters for newly defined UNIFAC functional groups. The determination of the structural parameters was made through quantum mechanics calculations. This method was already described in detail in our previous paper [55]. In this work, LLE data for fifteen ternary systems, totalizing 155 tie-lines, involving five different ionic liquids, are correlated by UNIFAC. Again, new structural parameters *r* and *q* for the ionic liquids are determined by the same methodology [55].

The five ionic liquids studied in this work are 1-hexyl-3-methylimidazolium tetrafluoroborate, [hmim][BF_4]; 1-(2-hydroxyethyl)-3-methylimidozolium tetrafluoroborate, [C_2OHmim][BF_4]; 1-(2-hydroxyethyl)-2,3-dimethylimidazolium tetrafluoroborate,

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0378-3812
doi:10.1016/j.fluid.2010.12.006

Table 1

Volume and surface area structural parameters of ionic liquids cations and anions.

Cation/anion	Volume (Å^3)	Area (Å^2)	R_k	Q_k
[hmim]	186.50	239.99	7.4045	5.782
[omim]	225.69	291.59	8.9605	7.025
[C_2OHmim]	126.99	158.77	5.0419	3.825
[C_2OHdmim]	143.22	175.57	5.6863	4.230
[BF_4]	44.97	62.01	1.7856	1.494
[PF_6]	61.13	83.73	2.4272	2.017

Table 2

UNIFAC energy interaction parameters.

i	j	a_{ij} (K)	a_{ji} (K)
[hmim]	[BF_4]	−3183.1	−1671.4
[hmim]	[CH_3]	43.856	−1158.0
[hmim]	[CH_2]	43.856	−1158.0
[hmim]	[ACH]	611.49	−1318.5
[hmim]	[CH_2=CH]	170.06	−923.05
[hmim]	[OH]	−26.752	−544.83
[omim]	[BF_4]	−335.23	2320.2
[omim]	[PF_6]	473.22	−1497.7
[omim]	[CH_3]	−21.791	325.60
[omim]	[CH_2]	−21.791	325.60
[omim]	[ACH]	9847.9	285.98
[omim]	[$ACCH_3$]	−193.16	592.67
[omim]	[CH_3CO]	3138.9	−1459.3
[omim]	[CH_3COO]	9083.7	68.362
[omim]	[C_4H_4S]	13030.0	78.641
[C_2OHmim]	[BF_4]	−791.87	−796.89
[C_2OHmim]	[CH_3]	−2.4432	2486.0
[C_2OHmim]	[CH_2]	−2.4432	2486.0
[C_2OHmim]	[OH]	−226.89	2562.4
[C_2OHmim]	[H_2O]	−603.59	28.242
[C_2OHdmim]	[BF_4]	−731.53	−7.2107
[C_2OHdmim]	[CH_3]	98.401	3182.5
[C_2OHdmim]	[CH_2]	98.401	3182.5
[C_2OHdmim]	[OH]	−200.33	3241.7
[C_2OHdmim]	[H_2O]	−540.87	448.37
[BF_4]	[CH_3]	2724.4	1925.0
[BF_4]	[CH_2]	2724.4	1925.0
[BF_4]	[ACH]	−224.56	−959.23
[BF_4]	[CH_2=CH]	7216.3	−1325.6
[BF_4]	[OH]	2.7958	2207.6
[BF_4]	[H_2O]	2937.8	−201.12
[BF_4]	[$ACCH_3$]	−134.63	−289.88
[BF_4]	[C_4H_4S]	146.24	−1209.9
[PF_6]	[CH_3]	−161.29	639.62
[PF_6]	[CH_2]	−161.29	639.62
[PF_6]	[CH_3CO]	988.91	3314.8
[PF_6]	[CH_3COO]	−738.21	−39.913
[CH_3]	[C_4H_4S]	109.10	−12.258
[CH_2]	[C_4H_4S]	109.10	−12.258
[ACH]	[C_4H_4S]	−82.667	444.51
[$ACCH_3$]	[C_4H_4S]	−42.370	720.62

[C_2OHdmim][BF_4]; 1-octyl-3-methylimidazolium tetrafluoroborate, [omim][BF4] and 1-octyl-3-methylimidazolium hexafluorophosphate, [omim][PF_6].

2. Molecular geometry

The optimized molecular structures of the ionic liquids through energy minimization using quantum chemical calculations have already been shown in two previous works [46,47]. Density Functional Theory (DFT) calculations were performed according to Becke's three parameter hybrid method [56] with Lee–Yang–Parr (LYP) correlation [57] (B3LYP) using the 6-31++G(d) basis set implemented in Gaussian 03 package [58]. A more detailed description of the method is given in Santiago et al. [46].

3. Choice of UNIFAC groups and the determination of volume and surface area

In this work, the ionic liquids were divided in two groups, cation and anion, for the choice of UNIFAC functional groups, such as described elsewhere [46]. The approach is different from that of Lei et al. [52] and Alevizou et al. [53], who used the imidazolium ring as a functional group. The Polarizable Continuum Method (PCM) of Tomasi et al. [59–61] has been used for the determination of volume and surface area. PCM methods usually utilize the GEnerating POLyhedra (GEPOL) [62] procedure to define the surface and its tessellation. The PCM-GEPOL procedure for the calculation was performed with the PC GAMESS 7.1 package [63]. Again, the details of the methodology are given in Santiago et al. [46].

The method used to determine the volume and surface area for all cation and anion groups for the five ionic liquids in this work was described in our previous work [55]. From the values obtained for [BF_4] anion group, the values for cation groups [hmim], [omim], [C_2OHmim] and [C_2OHdmim] can be easily found by difference, since the values for [bmim][BF_4] are already known [46] by the same DFT calculations explained in the previous section; the volume and surface area were calculated by the PCM method. The volume and surface of the cation and anion groups in this work are presented in Table 1. Volume and surface area for functional groups in traditional solvents are taken from Magnussen et al. [64].

4. The UNIFAC method

In order to determine the activity coefficient, the UNIFAC method has two parts: one combinatorial part that represents the contribution due to differences in size and shape of the molecules in the mixture, and one residual part that represents the effects of interaction between group pairs in the molecule. The equations for UNIFAC-LLE are well known and will not be shown here. The structural parameters for volume and surface area, R and Q, for the cation and anion groups in this work are also shown in Table 1. These values are calculated by

$$R = \frac{V \times N_A}{V_{VW}}, \qquad Q = \frac{A \times N_A}{A_{VW}} \tag{1}$$

where N_A is the Avogadro's number (6023×10^{23} mol^{-1}). For the standard segment volume V_{VW} and area A_{VW}, there were used the values suggested by Bondi [65], 15.17 cm^3/mol and 2.5×10^9 cm^2/mol, respectively.

5. Parameter estimation

The estimation of the interaction group parameters was performed using a flash liquid–liquid calculation implemented in the Fortran code TML-LLE 2.0 [66,67]; the procedure is based on the Simplex method proposed by Nelder and Mead [68], and consists in the minimization of a concentration-based objective function, S [69] defined by:

$$S = \sum_{k}^{D} \sum_{j}^{M} \sum_{i}^{N-1} \{ (x_{ijk}^{\mathrm{I,exp}} - x_{ijk}^{\mathrm{I,calc}})^2 + (x_{ijk}^{\mathrm{II,exp}} - x_{ijk}^{\mathrm{II,calc}})^2 \} \tag{2}$$

Here, D is the number of data sets, N and M are the number of components and tie-lines in each data set, respectively; the superscripts I and II refer to the two liquid phases in equilibrium, while the superscripts 'exp' and 'calc' refer to the experimental and calculated values of the liquid phase concentration.

With the interaction parameters estimated by the procedure above, comparisons between the experimental and the calculated composition of each component in each of the two phases were

Table 3
UNIFAC correlation results for LLE.

Systems	Tie lines	T (°C)	Reference	δx (%)
1-Hexene + ethanol + [hmim][BF_4]	12	25	[7]	2.59
1-Heptene + ethanol + [hmim][BF_4]	8	25	[8]	2.66
Heptane + benzene + [hmim][BF_4]	12	25	[11]	2.65
Dodecane + benzene + [hmim][BF_4]	7	25	[11]	2.94
Hexadecane + benzene + [hmim][BF_4]	9	25	[12]	2.57
1-Butanol + water + [C_2OHmim][BF_4]	10	20	[12]	2.72
1-Butanol + water + [C_2OHdmim][BF_4]	9	20	[12]	4.13
Heptane + thiophene + [omim][BF_4]	10	25	[12]	3.68
Dodecane + thiophene + [omim][BF_4]	12	25	[12]	3.50
Hexadecane + thiophene + [omim][BF_4]	11	25	[13]	4.24
Octane + thiophene + [omim][BF_4]	11	25	[13]	5.41
Toluene + thiophene + [omim][BF_4]	11	25	[13]	6.12
Hexane + cyclohexane + [omim][BF_4]	10	25	[14]	4.87
Cyclohexane + 2-butanone + [omim][PF_6]	10	25	[14]	2.70
Hexane + ethyl acetate + [omim][PF_6]	13	25	[16]	2.05
Global	155			3.72

made through root mean square (*rms*) deviation, given by:

$$\delta x = 100\sqrt{\frac{\sum_i^M \sum_j^N (x_{ij}^{\mathrm{I,exp}} - x_{ij}^{\mathrm{I,calc}})^2 + (x_{ij}^{\mathrm{II,exp}} - x_{ij}^{\mathrm{II,calc}})^2}{2MN}} \quad (3)$$

6. Results and discussion

The determination of the structural parameters is made through a quantum mechanics calculation, in two parts: first, an optimization of the molecular geometry is made through the Density Functional Theory; second, the volume and area are determined by the Polarizable Continuum Method. A consistent partition of the molecule in newly defined functional groups is made. At last, the structural volume and area parameters and experimental data from the literature are used to estimate new interaction energy parameters between the functional groups in ionic liquids and in traditional solvents.

The volume and surface area for the cation and anion groups in the five ionic liquids in this work are shown in Table 1. In this table also appear the UNIFAC structural parameters R and Q calculated by Eq. (1). Table 2 shows the UNIFAC energy interaction parameters estimated by the minimization of Eq. (2), according to the procedure described above. The results of the correlation for the 15 ternary systems, expressed as deviations between experimental and calculated compositions, according to Eq. (3), are presented in Table 3. Figs. 1 and 2 show the results for two selected systems.

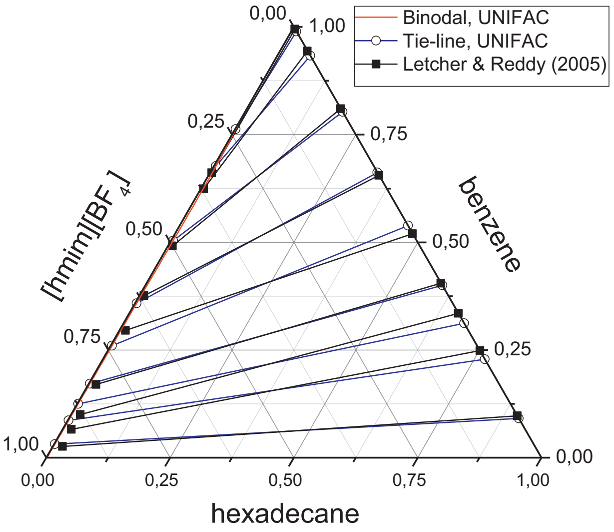

Fig. 1. Liquid–liquid equilibria for the hexadecane + benzene + [hmim][BF_4] system.

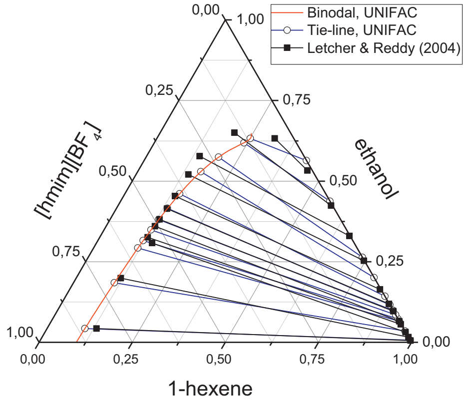

Fig. 2. Liquid–liquid equilibria for the 1-hexene + ethanol + [hmim][BF_4] system.

From the obtained deviations between experimental and calculated compositions, it can be concluded that the UNIFAC method, with energy interaction parameters estimated by the Simplex minimization, and structural parameters for ionic liquids obtained by the PCM model, with the molecular structures optimized by the DFT quantum calculations, was able to successfully correlate the liquid–liquid equilibrium data, showing a global deviation of about 3.7% for all 155 tie-lines. These results are considered satisfactory when compared with those presented by Santiago et al. [48], who obtained a global deviation of 1.6%.

7. Conclusions

Liquid–liquid equilibrium data for fifteen ternary systems including four ionic liquids at different temperatures were correlated by the UNIFAC method. The structural parameters of volume and surface area of the UNIFAC method were determined by quantum chemistry calculations using the Polarizable Continuum Method, with molecular structures optimized by the Density Functional Theory. For the determination of UNIFAC functional groups, the ionic liquids were divided into cation and anion groups. The energy interaction parameters of the UNIFAC method were estimated using the minimization of a composition-based objective function, using the Simplex method. With these parameters, the experimental data were correlated and the results of the calculations compared with the experimental data through deviations in compositions of both phases. The results are very satisfactory, with root mean square deviations 0.0037 between experimental and calculated equilibrium mole fractions.

List of symbols

A	surface area
D	number of data sets
M	number of tie-lines
N	number of components
N_A	Avogadro's number
R, Q	volume and surface area of UNIFAC functional groups
S	objective function
V	volume
x	mole fraction

Greek letters

δ	deviation

Super/subscripts

calc	calculated
exp	experimental
i, j	components
I, II	liquid phases at equilibrium
VW	van der Waals

Acknowledgments

The financial support by CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) and FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) is gratefully acknowledged. M. Aznar is the recipient of a CNPq fellowship.

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