

CORRELATION OF (LIQUID + LIQUID) EQUILIBRIUM OF SYSTEMS INCLUDING IONIC LIQUIDS

M. Aznar

School of Chemical Engineering, State University of Campinas,
Phone: +(55) (19) 3788-3962, Fax: +(55) (19) 3788-396,
P.O. Box 6066, 13081-970, Campinas - SP, Brazil.
E-mail: maznar@feq.unicamp.br

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Abstract - Ionic liquids are neoteric, environmentally friendly solvents (since they do not produce emissions) composed of large organic cations and relatively small inorganic anions. They have favorable physical properties, such as negligible volatility and wide range of liquid existence. Moreover, many different cations and anions can be used to synthesize ionic liquid, so the properties can be designed by the use of selected combinations of anions and cations. (Liquid + liquid) equilibrium (LLE) data for systems including ionic liquids, although essential for the design and operation of separation processes, are still scarce. However, some recent studies have presented ternary LLE data involving several ionic liquids and such organic compounds as alkanes, alkenes, alkanols, water, ethers and aromatics. In this work, LLE data for 24 ternary systems including ionic liquids from the literature are correlated by using the NRTL model for the activity coefficient. The results are very satisfactory, with *rms* deviations of about 1.4%.

Keywords: (Liquid + liquid) equilibrium; Ionic liquids; Correlation; NRTL.

INTRODUCTION

Ionic liquids are ionic compounds made of bulky, asymmetric organic cations and relatively small inorganic anions, whose melting point is below $T = 273.15$ K. This is an arbitrary limit defined in order to organize the dramatically increasing number of possible applications in chemical processes. Over the past few years, research about ionic liquids has increased greatly, mainly in two directions: as reaction media, specially in homogeneous catalysis, and as solvents for separation processes (Seddon, 1997; Welton, 1999). Particularly for this latter purpose, their physical and chemical properties make them specially suitable as solvents, potentially substituting the most common volatile organic solvents in the chemical industry:

- 1) they have negligible vapor pressures, so atmospheric contamination is avoided;
- 2) they have high thermal/chemical stability and low viscosity, and they are not flammable, explosive or corrosive;
- 3) they have a wide liquid range of over 300 K (as a comparison, water and ammonia have liquid ranges of 100 K and 44 K, respectively);
- 4) their properties can be fine-tuned by selecting the cations and anions, thus making a class of "designer solvents".

Nowadays, most of the ionic liquids studied are based on the imidazolium cation, whose structure is shown in Figure 1. The names and abbreviations for the ionic liquids used in this work are presented in Table 1.

(Liquid + liquid) equilibrium (LLE) data for

*To whom correspondence should be addressed

multicomponent systems including ionic liquids, although essential for the design and operation of separation processes, are still scarce. However, some recent studies (Selvan et al., 2000; Letcher et al., 2003; Letcher and Deenadayalu, 2003; Letcher and Reddy, 2004, 2005; Arce et al., 2004a, 2004b; Jork et al., 2004) have presented ternary LLE data involving several ionic liquids and such organic compounds as alkanes, alkenes, alkanols, water, ethers and aromatics.

In this work, LLE data for ternary systems including ionic liquids from the references above have been correlated by the NRTL model (Renon and Prausnitz, 1968) for the activity coefficient. The ternary systems, together with the *rms* deviations between calculated and experimental compositions in both equilibrium liquid phases, are shown in Table 3. The results are very satisfactory, with *rms* deviations of about 1.4%.

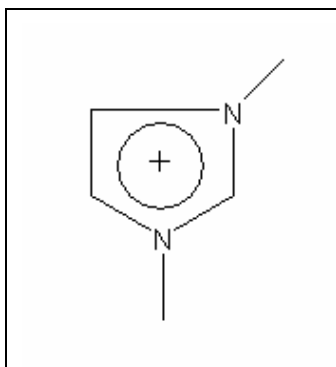


Figure 1: The imidazolium cation

Table 1: Ionic liquids

| Compound | Abbreviation |
|---|--|
| 1-butyl-3-methylimidazolium trifluoromethanesulfonate | [bmim][TfO] |
| 1-octyl-3-methylimidazolium chloride | [omim][Cl] |
| 1-ethyl-3-methylimidazolium triiodide | [emim][I ₃] |
| 1-butyl-3-methylimidazolium triiodide | [bmim][I ₃] |
| 1-hexyl-3-methylimidazolium tetrafluoroborate | [C ₆ mim][BF ₄] |
| 1-hexyl-3-methylimidazolium hexafluorophosphate | [C ₆ mim][PF ₆] |
| 1-ethyl-3-methylimidazolium tetrafluoroborate | [emim][BF ₄] |
| 1-butyl-3-methylimidazolium tetrafluoroborate | [bmim][BF ₄] |

Table 2: Estimated NRTL parameters

| <i>i/j</i> | A_{ij}/K | A_{ji}/K | B_{ij} | B_{ji} | α_{ji} |
|--|------------|------------|----------|----------|---------------|
| water / tetrahydrofuran | 422.70 | 338.49 | - | - | 0.226 |
| water / [emim][BF ₄] | 433.36 | -468.32 | - | - | 0.238 |
| water / [bmim][BF ₄] | 341.16 | -236.81 | - | - | 0.241 |
| ethanol / heptane | 424.50 | 3731.6 | - | - | 0.205 |
| ethanol / 1-hexene | 3.1664 | -13.133 | - | - | 0.464 |
| ethanol / 1-heptene | 44.751 | -7.5333 | - | - | 0.448 |
| ethanol / dodecane | 474.55 | 970.15 | - | - | 0.212 |
| ethanol / hexadecane | 732.50 | 1171.4 | - | - | 0.216 |
| ethanol / <i>tert</i> -amyl ethyl ether | 90.400 | 416.86 | - | - | 0.307 |
| ethanol / [omim][Cl] | -904.52 | -498.92 | - | - | 0.200 |
| ethanol / [C ₆ mim][BF ₄] | 1330.7 | -1239.7 | - | - | 0.200 |
| ethanol / [C ₆ mim][PF ₆] | 5685.7 | -42.149 | - | - | 0.201 |
| ethanol / [bmim][TfO] | 783.84 | -428.12 | - | - | 0.233 |
| methanol / heptane | 5003.3 | 111.35 | - | - | 0.440 |
| methanol / hexadecane | 5023.1 | 2588.1 | - | - | 0.239 |
| methanol / [omim][Cl] | 1172.9 | -2303.3 | - | - | 0.273 |
| heptane / benzene | -553.26 | 1084.4 | - | - | 0.215 |

Continuation Table 2

| i/j | A_{ij}/K | A_{ji}/K | B_{ij} | B_{ji} | α_{ij} |
|---|------------|------------|----------|----------|---------------|
| heptane / toluene | 396.63 | 437.94 | 0.5275 | 0.0089 | 0.470 |
| heptane / [omim][Cl] | 2807.9 | 422.51 | - | - | 0.205 |
| heptane / [emim][I ₃] | 3844.0 | 1231.8 | -1.5313 | 0.0626 | 0.245 |
| heptane / [bmim][I ₃] | 1525.8 | 323.55 | -1.4558 | 0.0362 | 0.203 |
| heptane / [C ₆ mim][BF ₄] | 1710.8 | 241.31 | - | - | 0.200 |
| heptane / [C ₆ mim][PF ₆] | 3139.0 | 465.51 | - | - | 0.202 |
| 1-hexene / [C ₆ mim][BF ₄] | 2600.4 | 5796.9 | - | - | 0.200 |
| 1-hexene / [C ₆ mim][PF ₆] | 935.17 | 626.82 | - | - | 0.308 |
| 1-heptene / [C ₆ mim][BF ₄] | 2649.2 | 425.14 | - | - | 0.202 |
| 1-heptene / [C ₆ mim][PF ₆] | 1988.5 | 567.54 | - | - | 0.272 |
| dodecane / benzene | -237.34 | 119.70 | - | - | 0.200 |
| dodecane / [omim][Cl] | 1355.1 | 1861.1 | - | - | 0.326 |
| dodecane / [C ₆ mim][BF ₄] | 5158.0 | 1640.0 | - | - | 0.200 |
| dodecane / [C ₆ mim][PF ₆] | 2104.7 | 766.88 | - | - | 0.200 |
| hexadecane / benzene | -331.67 | -47.676 | - | - | 0.444 |
| hexadecane / [omim][Cl] | 1766.2 | 1015.3 | - | - | 0.269 |
| hexadecane / [C ₆ mim][BF ₄] | 2175.7 | 1207.4 | - | - | 0.200 |
| hexadecane / [C ₆ mim][PF ₆] | 4454.1 | 1476.3 | - | - | 0.200 |
| benzene / [omim][Cl] | 2318.2 | -229.88 | - | - | 0.250 |
| benzene / [C ₆ mim][BF ₄] | 1674.3 | -508.04 | - | - | 0.216 |
| benzene / [C ₆ mim][PF ₆] | 1736.2 | -571.37 | - | - | 0.217 |
| toluene / [emim][I ₃] | 2321.6 | 788.03 | 1.2354 | -0.1449 | 0.382 |
| toluene / [bmim][I ₃] | 2183.1 | 138.32 | -0.5153 | 0.7525 | 0.470 |
| tetrahydrofuran / [emim][BF ₄] | 2293.5 | -225.37 | - | - | 0.200 |
| tetrahydrofuran / [bmim][BF ₄] | 2519.3 | -724.19 | - | - | 0.202 |
| <i>tert</i> -amyl ethyl ether / [omim][Cl] | 2778.7 | 406.84 | - | - | 0.204 |
| <i>tert</i> -amyl ethyl ether / [bmim][TfO] | 1980.4 | 388.19 | - | - | 0.200 |

Table 3: Root mean square deviations in (liquid + liquid) equilibrium data

| System | T/K | ref. | tie lines | rms |
|---|--------|------|------------|-------------|
| [emim][BF ₄] + tetrahydrofuran + water | 337.15 | [9] | 6 | 0.66 |
| [bmim][BF ₄] + tetrahydrofuran + water | 337.15 | [9] | 2 | 0.06 |
| [omim][Cl] + <i>tert</i> -amyl ethyl ether + ethanol | 298.15 | [7] | 11 | 0.86 |
| [bmim][TfO] + <i>tert</i> -amyl ethyl ether + ethanol | 298.15 | [8] | 9 | 0.44 |
| [emim][I ₃] + toluene + heptane | 318.15 | [3] | 14 | 0.90 |
| [bmim][I ₃] + toluene + heptane | 308.15 | [3] | 11 | 1.69 |
| [C ₆ mim][BF ₄] + ethanol + 1-hexene | 298.15 | [6] | 13 | 1.42 |
| [C ₆ mim][BF ₄] + ethanol + 1-heptene | 298.15 | [6] | 8 | 1.71 |
| [C ₆ mim][PF ₆] + ethanol + 1-hexene | 298.15 | [6] | 13 | 1.66 |
| [C ₆ mim][PF ₆] + ethanol + 1-heptene | 298.15 | [6] | 13 | 1.66 |
| [omim][Cl] + benzene + heptane | 298.15 | [5] | 5 | 3.25 |
| [omim][Cl] + benzene + dodecane | 298.15 | [5] | 4 | 2.72 |
| [omim][Cl] + benzene + hexadecane | 298.15 | [5] | 4 | 1.87 |
| [omim][Cl] + methanol + heptane | 298.15 | [4] | 3 | 0.05 |
| [omim][Cl] + ethanol + heptane | 298.15 | [4] | 3 | 0.71 |
| [omim][Cl] + ethanol + dodecane | 298.15 | [4] | 4 | 0.34 |
| [omim][Cl] + methanol + hexadecane | 298.15 | [4] | 5 | 0.12 |
| [omim][Cl] + ethanol + hexadecane | 298.15 | [4] | 5 | 0.41 |
| [C ₆ mim][PF ₆] + benzene + heptane | 298.15 | [10] | 12 | 0.68 |
| [C ₆ mim][PF ₆] + benzene + dodecane | 298.15 | [10] | 7 | 1.92 |
| [C ₆ mim][PF ₆] + benzene + hexadecane | 298.15 | [10] | 5 | 0.98 |
| [C ₆ mim][BF ₄] + benzene + heptane | 298.15 | [10] | 12 | 1.32 |
| [C ₆ mim][BF ₄] + benzene + dodecane | 298.15 | [10] | 7 | 1.06 |
| [C ₆ mim][BF ₄] + benzene + hexadecane | 298.15 | [10] | 9 | 1.48 |
| global | | | 184 | 1.40 |

THERMODYNAMIC MODEL

The concept of local composition, introduced by Wilson (1964), basically establishes that the composition of the system in the neighborhood of a given molecule is not the same as the “bulk” composition, because of intermolecular forces. The NRTL – *non-random, two-liquid* – model by Renon and Prausnitz (1968) for the activity coefficient is based on the local composition concept, and it is applicable to partially miscible systems. In order to take into account the effect of temperature on (liquid + liquid) equilibrium, the original NRTL model has been empirically extended (Stragevitch, 1997). Santos et al. (2000) and Santos et al. (2001) used this approach to represent the salt effect on the (liquid + liquid) equilibrium of the {water + ethanol + 1-pentanol} and {water + 1-butanol + acetone} systems. The extended NRTL model is given by

$$\ln \gamma_i = \frac{\sum_j \tau_{ji} G_{ji} x_j}{\sum_k G_{ki} x_k} + \sum_j \frac{x_j G_{ij}}{\sum_k G_{kj} x_k} \left(\tau_{ij} - \frac{\sum_k \tau_{kj} G_{kj} x_k}{\sum_k G_{kj} x_k} \right), \quad (1)$$

where

$$\tau_{ij} = \frac{\Delta g_{ij}}{RT} \quad (2)$$

$$\frac{\Delta g_{ij}}{R} = A_{ij} + B_{ij} T \quad (3)$$

$$G_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (\alpha_{ij} = \alpha_{ji}) \quad (4)$$

Here, Δg_{ij} represents the energy interactions between compounds i and j , while α_{ij} is the non randomness parameter, derived from the local composition assumption. Thus, there are five adjustable parameters for each pair of substances: A_{ij} , A_{ji} , B_{ij} , B_{ji} and α_{ij} . These parameters can be estimated with experimental data, by using the procedure below. When the data are at the same temperature, the extended NRTL model reduces to the original NRTL model, and hence the B_{ij} terms of eq. (3) vanish.

Despite the fact that it is intended for nonelectrolyte solutions, the NRTL method has been used for ionic liquids by some authors (Arce et al., 2004a, 2004b), since an appropriate model for ionic liquids has not yet been developed, either for correlation or prediction.

PARAMETER ESTIMATION

Parameters were estimated using the Fortran code TML-LLE 2.0 (Stragevitch, 1997); the procedure is based on the Simplex method proposed by Nelder and Mead (1965), and consists in the minimization of a concentration-based objective function, S (Sørensen et al., 1979).

$$S = \sum_k^D \sum_j^M \sum_i^{N-1} \left\{ \left(x_{ijk}^{I, \text{exp}} - x_{ijk}^{I, \text{calc}} \right)^2 + \left(x_{ijk}^{II, \text{exp}} - x_{ijk}^{II, \text{calc}} \right)^2 \right\} \quad (5)$$

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

The molecular energy interaction and the non randomness parameters estimated by the procedure above are shown in Table 2. With these parameters, (liquid + liquid) equilibrium calculations can be made. Comparisons between experimental and calculated data can be made through root mean square (*rms*) absolute deviations between the experimental and the calculated composition of each component in both phases. These *rms* deviations are given by

$$rms = 100 \sqrt{\frac{\sum_n^M \sum_i^{N-1} \left(x_{\text{exp}}^I - x_{\text{calc}}^I \right)^2 + \left(x_{\text{exp}}^{II} - x_{\text{calc}}^{II} \right)^2}{2MN}} \quad (6)$$

RESULTS AND DISCUSSION

The results of the correlation, shown in Table 3 and Figures 2-4, are very satisfactory. In Table 3, the *rms* deviations for each one of the calculations are shown, with the values always below 3.3% and generally below 1%. The global value for *rms* was about 1.4%. Arce et al. (2004a, 2004b) used NRTL to correlate the LLE for the {[bmim][TfO]} + tert-

amyl ethyl ether + ethanol} and {[omim][Cl] + tert-amyl ethyl ether + ethanol} systems at $T = 298.15$ K. They obtained *rms* deviations of 0.31% and 0.71%, respectively. These values are of the same order as those obtained in this work for the same systems, 0.44% and 0.86%, respectively.

In Figures 2-4, comparisons between experimental and calculated tie lines are shown for the {[bmim][TfO] + tert-amyl ethyl ether + ethanol} system at $T = 298.15$ K (Arce et al., 2004b), the {[C₆mim][PF₆] + ethanol + 1-hexene} system at $T =$

298.15 K (Letcher and Reddy, 2004) and the {[bmim][I₃] + toluene + heptane} system at $T = 308.15$ K (Selvan et al., 2000). Similar figures could be plotted for all the systems in this work. It is easy to see that there is very good agreement between experimental and calculated liquid phase compositions. From the *rms* deviations and the visual analysis of the figures, it can be concluded that the NRTL model is able to correlate the (liquid + liquid) equilibrium of ternary systems including ionic liquids with good precision.

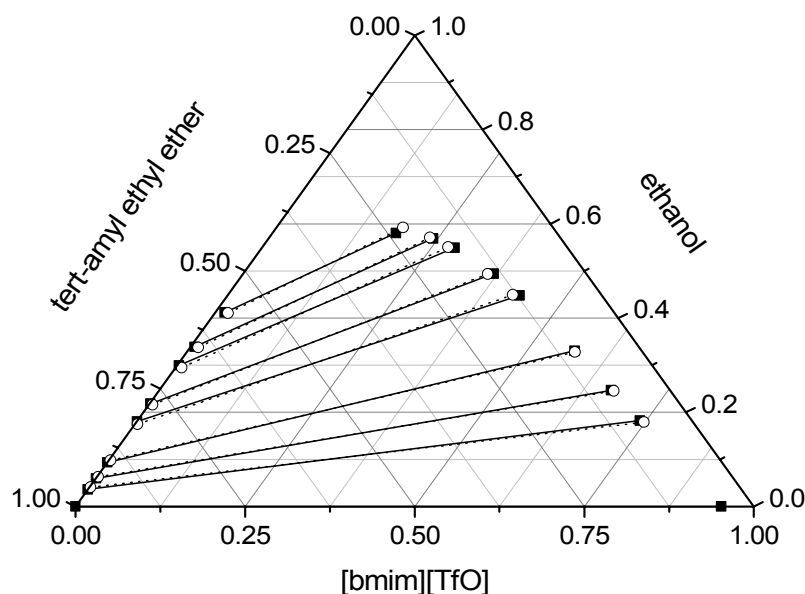


Figure 2: Experimental and calculated LLE for the {[bmim][TfO] + tert-amyl ethyl ether + ethanol} system at $T = 298.15$ K. ■, experimental [8]; ○, calculated.

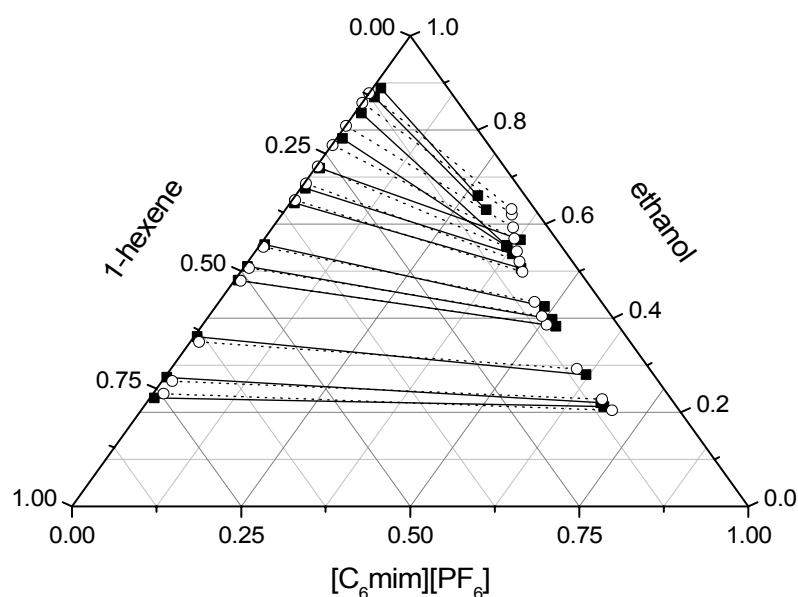


Figure 3: Experimental and calculated LLE for the {[C₆mim][PF₆] + ethanol + 1-hexene} system at $T = 298.15$ K. ■, experimental [6]; ○, calculated.

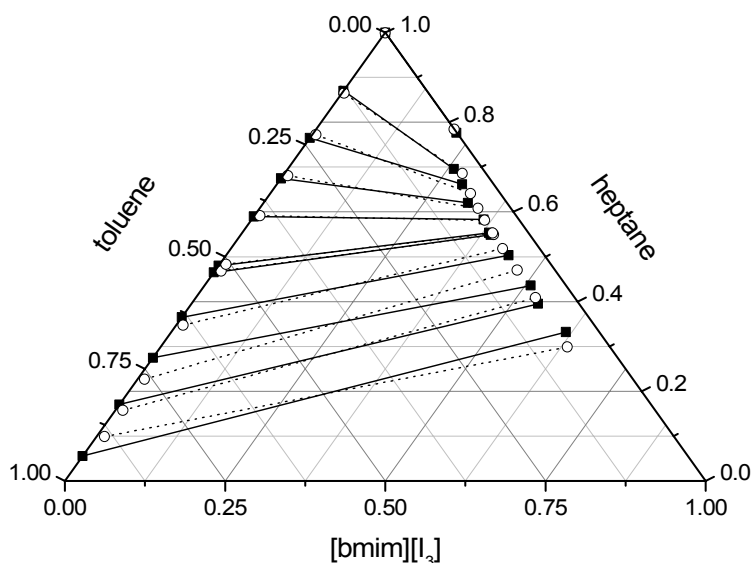


Figure 4: Experimental and calculated LLE for the {[bmim][I₃] + toluene + heptane} system at $T = 308.15$ K. ■, experimental [3]; ○, calculated.

CONCLUSION

Ternary (liquid + liquid) equilibrium data for 24 systems including ionic liquids were correlated by the NRTL model for the activity coefficient. Molecular energy interaction and non randomness parameters were estimated by minimization of a composition-based objective function using the Simplex method. The results of the correlation were very satisfactory, with *rms* deviations between experimental and calculated equilibrium compositions always below 3.3% and, in most cases, below 1%, with a global value of about 1.4%. It can be concluded that the NRTL model is able to correlate the (liquid + liquid) equilibrium of ternary systems including ionic liquids with good precision.

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