

PREDICTION OF LIQUID-LIQUID EQUILIBRIUM FOR MULTICOMPONENT SYSTEMS INCLUDING IONIC LIQUIDS BY THE ASOG METHOD

D.D. GALLARDO RAMIREZ* and M. AZNAR

University of Campinas, School of Chemical Engineering, Campinas, Brazil.

*Corresponding author: daliagallardo@feq.unicamp.br, +55 (19) 999-225469

I. INTRODUCTION

Ionic liquids (IL) are ionic compounds made of bulky, asymmetric organic cations and relatively small anions, which are liquid at room temperature. The most striking property of ILs is their non detectable vapor pressure; this suggests their utilization as excellent solvents, replacing conventional organic solvents in the context of "green chemistry" [HEINTZ, 2005]. Liquid extraction is a major industrial process in the chemical industry that depends on the physical and chemical properties of a solvent to achieve the separation of complex liquids mixtures. Liquid-liquid equilibrium (LLE) data for multicomponent system including ionic liquids are essential for the design and operation of separation processes, admitting that are still relatively scarce [ROBLES et al., 2010]. Group contribution methods are more effective in the prediction of activity coefficients compared to others methods. The effectiveness of these methods depends on the division of the solution into interacting groups. As the mutual behavior of interacting groups cannot be determined experimentally, thermodynamic models can be used, where the interaction parameters are determined from the behavior of the real system. [PERUMALSAMY & MURUGESAN, 2008]. The main objective in the present work is to predict liquid-liquid equilibrium data from existing data of multicomponent systems containing ionic liquids, using the Analytical Solution of Groups (ASOG) method to get the parameters and activity coefficients of other systems, for which no experimental information is available.

II. METHODOLOGY

1. Liquid-liquid equilibrium. Bibliographic data of experimental liquid-liquid equilibrium of multicomponent systems including ionic liquids, data on molar fraction of its components. In which it appears be such that the equilibrium criterion $f_i^I(T, P, x^I) = f_i^{II}(T, P, x^{II}) \dots (1)$. Introducing the coefficient definition into equation (1) yields $x_i^I \gamma_i^I = x_i^{II} \gamma_i^{II} \dots (2)$

$$\sum_{i=1}^C x_i^I = 1 \quad e \quad \sum_{i=1}^C x_i^{II} = 1 \dots (3)$$

2. Analytical Solution of groups. The ASOG method is based on the assumption that the contribution to the activity coefficient of component i can be separated into two parts, namely, combinatorial part and residual part. [KOJIMA and TOCHIGI, 1979]

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \dots (4)$$

The activity coefficient of component, γ_i , can be calculated by the following equations, where the superscripts FH and G stand for "Flory-Huggins", combinatorial part and "groups" (residual part), respectively:

$$\ln \gamma_i = \ln \gamma_i^{FH} + \ln \gamma_i^G \dots (5)$$

$$\ln \gamma_i^{FH} = 1 + \ln \left(\frac{v_i^{FH}}{\sum_{j=1}^{NC} x_j v_j^{FH}} \right) - \frac{v_i^{FH}}{\sum_{j=1}^{NC} x_j v_j^{FH}} \dots (6)$$

$$\ln \gamma_i^G = \sum_k v_{k,i} (\ln \Gamma_k - \ln \Gamma_k^i) \dots (7)$$

- In these equations, v_i^{FH} is the measure of the size of molecule i , defined as the number of atoms in the molecule (except for hydrogen atoms), while Γ_k is the residual activity coefficient of group k in the mixture, Γ_k^i is the residual activity coefficient of group k in pure compound i and $v_{k,i}$ is the number of atoms (other than hydrogen atoms) in group k in molecule i . Both the residual activity coefficients can be calculated by the Wilson equation.

Wilson's equation :

$$\ln \Gamma_k = 1 - \ln \left(\sum_{l=1}^{NG} X_l a_{k/l} \right) - \sum_{l=1}^{NG} \left(\frac{X_l a_{l/k}}{\sum_{m=1}^{NG} X_m a_{l/m}} \right) \dots (8)$$

$$X_l = \frac{\sum_{i=1}^{NC} x_i v_{l,i}}{\sum_{i=1}^{NC} x_i \sum_{k=1}^{NG} v_{k,i}} \dots (9)$$

$$a_{k/l} = \exp \left(m_{k/l} + \frac{n_{k/l}}{T} \right), a_{k/l} \neq a_{l/k} \dots (10)$$

III. PARAMETER ESTIMATION.

The group interaction parameters can be estimated by using the Fortran code TML-LLE 2.0 [STRAGEVITCH & D'AVILA, 1997]; the procedure is based on the Simplex method [NELDER & MEAD, 1965], and consists in the minimization of a concentration-based objective function, S [SØRENSEN et al., 1979].

$$S = \sum_K^D \sum_J^M \sum_I^{N-1} \left[\left(x_{ijk}^{I,exp} - x_{ijk}^{I,calc} \right)^2 + \left(x_{ijk}^{II,exp} - x_{ijk}^{II,calc} \right)^2 \right] \dots (11)$$

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 [ROBLES et al., 2010]. Comparisons between experimental and calculated compositions of each component in both phases can be made through root mean square (rms) absolute deviations, given by:

$$\text{rms} = 100 \sqrt{\frac{\sum_K^D \sum_J^M \sum_I^{N-1} \left(x_{ijk}^{I,exp} - x_{ijk}^{I,calc} \right)^2 + \left(x_{ijk}^{II,exp} - x_{ijk}^{II,calc} \right)^2}{2MN}} \dots (12)$$

IV. RESULTS

In figure 1, represents the results obtained by ROBLES et al. (2010) for the prediction of LLE for the m-xylene + octane + [mebupy][BF₄] system at 348.15 °K are shown. It can be seen that the predictions by ASOG are in a very good agreement with the experimental data determined by MEINSDERMA et al. (2006). Original results from this research are still in progress.

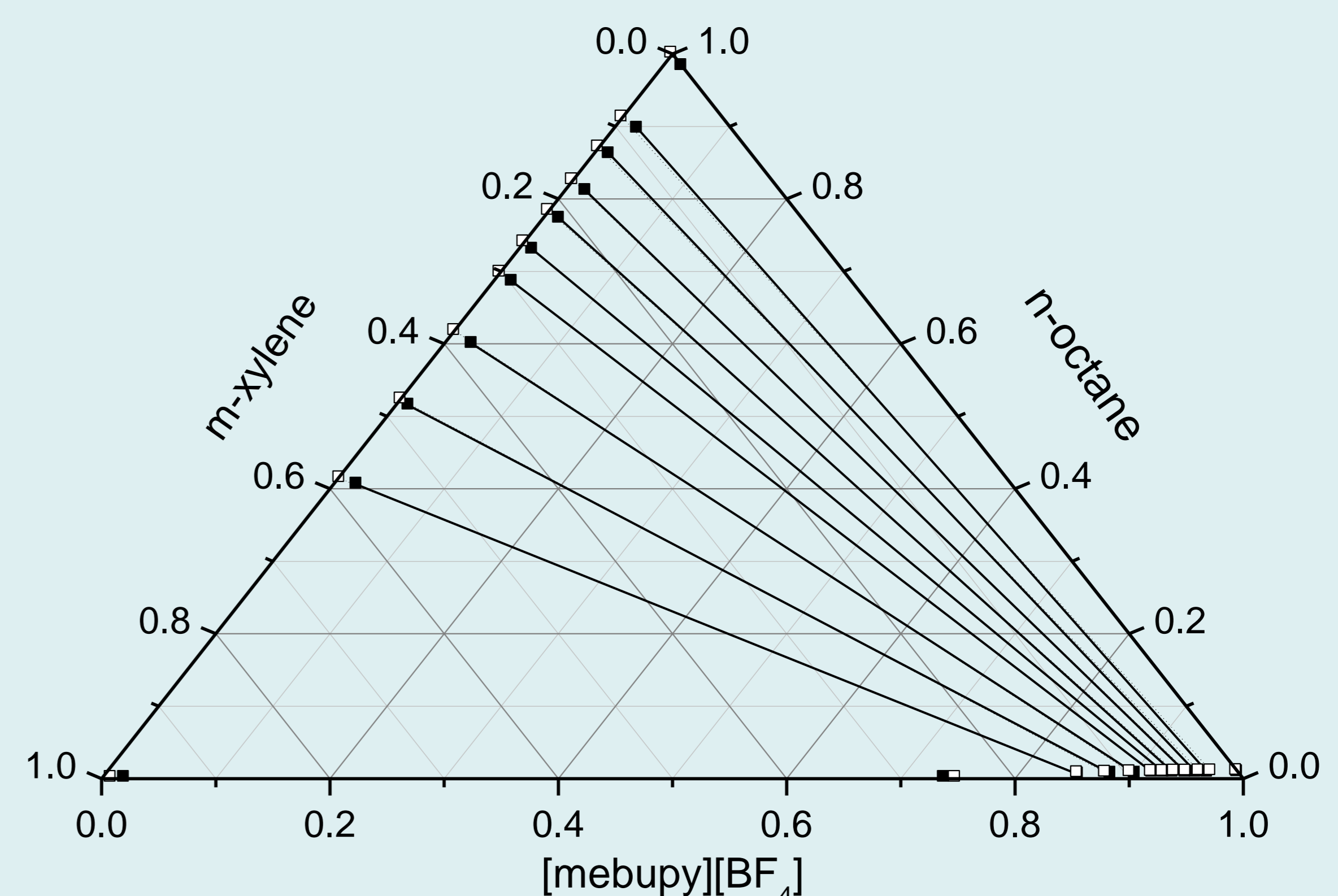


Figure 1. LLE for m-xylene + octane + [mebupy][BF₄] at 348.15 K ; □ experimental [MEINSDERMA et al., 2006]; ■ ASOG [ROBLES et al., 2010].

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VI. FINANCIAL SUPPORT

