Fluid Phase Equilibria 278 (2009) 54–61

Contents lists available at ScienceDirect

Fluid Phase Equilibria

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

UNIQUAC correlation of liquid–liquid equilibrium in systems involving ionic liquids: The DFT–PCM approach

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ARTICLE INFO

Article history:
Received 3 October 2008
Received in revised form 12 December 2008
Accepted 3 January 2009
Available online 8 January 2009

Keywords:
Ionic liquids
Liquid–liquid equilibrium
UNIQUAC
Quantum calculations
Volume and area parameters

ABSTRACT

In this work, the liquid–liquid equilibrium (LLE) of fifty ternary systems involving twelve different ionic liquids, comprising 408 experimental tie-lines, was correlated by the UNIQUAC model for the activity coefficient. New UNIQUAC structural parameters *r* and *q* for the ionic liquids were determined by quantum chemistry calculations performed with the Gaussian 03 and GAMESS 7.1 packages, including the Density Functional Theory (DFT) for the optimization of the structures and the Polarizable Continuum Method (PCM) for the calculation of molecular areas and volumes. The results, expressed by deviations between experimental and calculated compositions, are very satisfactory, with deviation values about 1.75%.

1. Introduction

Ionic liquids are asymmetrical organic salts composed by large organic cations and relatively small inorganic anions; they are liquid at room temperature, showing a melting point below 100 °C. They are environmentally friendly solvents because they are noninflammable, thermally and chemically stable, most of them can be indefinitely recycled and have extremely low vapor pressures.

Among several possible applications, ionic liquids are potential solvents for liquid extraction processes; however, thermodynamic liquid–liquid equilibrium (LLE) data, essential for the design, optimization and operation of these processes, are still scarce.

The substitution of traditional organic solvent, toxic and highly volatile, by ionic liquids is justified, mainly, for the reduction of volatile organic compounds (VOC) in the atmosphere. Solvents comprise 2/3 of all industrial emissions and 1/3 of all VOC emissions in the United States [1]. Ionic liquids can offer a partial solution of this problem.

Some recent papers [2–19] have studied liquid–liquid equilibrium data for ternary systems containing ionic liquids. The NRTL model [20] has been invariably used for the correlation of these experimental data. Aznar [21] correlated, in a systematic way, the LLE data for 24 ternary systems involving ionic liquids using the NRTL model, with deviations between experimental and calculated compositions about 1.4%. Due to lack of pure component volume and area parameters for ionic liquids, the UNIQUAC model [22] could not be widely used for correlating the experimental data. At the present time, only a few works [23–31] have tried to correlate LLE data for ternary systems including ionic liquids by the UNIQUAC model. Sahandzhieva et al. [23] studied systems involving the ionic liquid [bmim][PF_6]; Banerjee et al. [24] modeled ternary systems including the ionic liquids [bmim][PF_6], [omim][Cl], [emim][BF_4], [bmim][BF_4], [hmim][BF_4], [omim][BF_4], [bmim][PF_6], [hmim][PF_6] and [bmim][TfO]; Naydenov and Bart [25] correlated LLE data for systems involving the ionic liquids [mim][HSO_4], [emim][HSO_4] and [bmim][HSO_4]; Sahoo et al. [26] presented a systematic study correlating LLE data for 29 ternary systems involving eleven ionic liquids; Simoni et al. [27] correlated six ternary systems involving the ionic liquids [emim]BF_4], [emim][$EtSO_4$], [emim][Tf_2N], [dmim][Tf_2N], [bmim][PF_6] and [bmim][Tf_2N]; Pereiro and Rodríguez [28,29] correlated ternary systems involving the ionic liquids [hmim][PF_6] and [omim][PF_6]; finally, Alonso et al. [30,31] modeled LLE data for ternary systems involving the ionic liquids [emim][$EtSO_4$] and [omim][Tf_2].

In this work, LLE data for fifty ternary systems involving twelve different ionic liquids are correlated by the UNIQUAC model. New structural parameters *r* and *q* for the ionic liquids are determined by

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doi:10.1016/j.fluid.2009.01.002

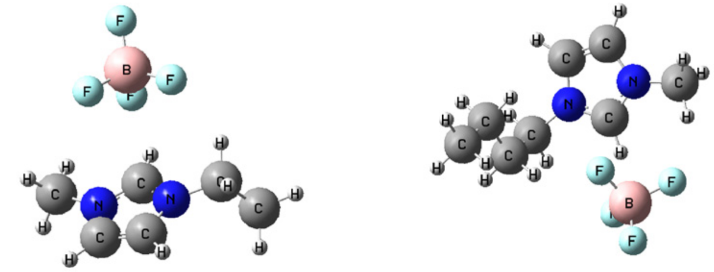
quantum chemistry calculations, including the Density Functional Theory (DFT) for the optimization of the molecular structures and the Polarizable Continuum Model (PCM) for the volume and area calculations.

The twelve ionic liquids studied in this work are 1-ethyl-3-methylimidazolium tetrafluoroborate, [emim][BF$_4$]; 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF$_4$]; 1-hexyl-3-methylimidazolium tetrafluoroborate, [hmim][BF$_4$]; 1-octyl-3-methylimidazolium tetrafluoroborate, [omim][BF$_4$]; 1-(2-hydroxylethyl)-3-methylimidazolium tetrafluoroborate, [C$_2$OHmim][BF$_4$]; 1-(2-hydroxylethyl)-2,3-dimethylimidazolium tetrafluoroborate, [C$_2$OHdmim][BF$_4$]; 4-methyl-N-butylpyridinium tetrafluoroborate, [mebupy][BF$_4$]; 1-octyl-3-methylimidazolium chloride, [omim][Cl]; 1-ethyl-3-methylimidazolium trifluoromethanesulfonate, [emim][TfO]; 1-butyl-3-methylimidazolium trifluoromethanesulfonate, [bmim][TfO]; 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF$_6$]; and 1-hexyl-3-methylimidazolium hexafluorophosphate, [hmim][PF$_6$].

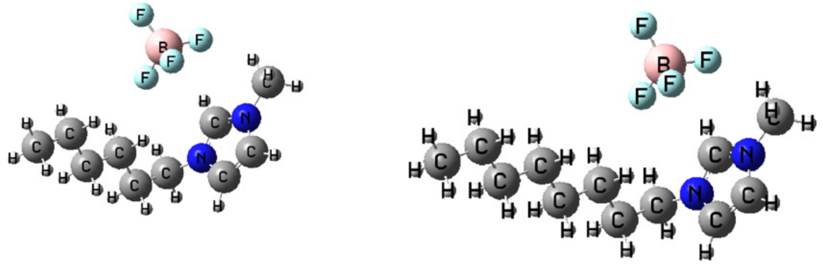
2. Equilibrium geometry

Before the determination of the volume and surface area it is necessary to obtain the equilibrium geometry of the molecule in the ideal phase from molecular energy minimization. In this work, quantum chemical calculations are used as a tool to predict the equilibrium geometry stability for ionic liquids; the highest accurate chemical structures of the ionic liquids using the most advanced quantum chemical theory are beyond the scope of this paper.

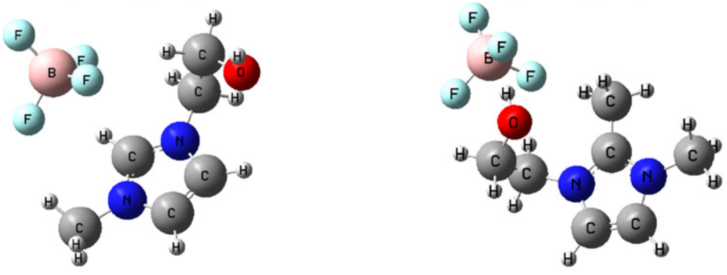
The Restricted Hartree Fock (RHF) method with the 3-21G* basis set was used for a first estimative of the equilibrium geometry. Thereafter, the Hartree–Fock structures were used as input for full optimization with the Density Functional Theory (DFT). The DFT calculations were performed according to Becke's three parameter hybrid method [32] with Lee–Yang–Parr (LYP) correlation [33] (B3LYP) using the 6-31++G(d) basis set implemented in Gaussian 03 package [34]. This basis set produces reliable results with an accept-



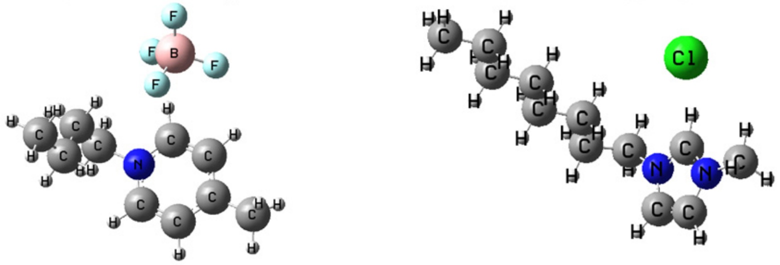
[emim][BF$_4$] [bmim][BF$_4$]



[hmim][BF$_4$] [omim][BF$_4$]



[C$_2$OHmim][BF$_4$] [C$_2$OHdmim][BF$_4$]



[mebupy][BF$_4$] [omim][Cl]

Fig. 1. 3D structures of ionic liquids optimized by Gaussian 03.