Correlation of VLE Data for the Thiophene + [bmim][BF₄], +[bmim][PF₆] Binaries Utilized for the Regeneration of Ionic Liquids

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P, *x* data for the thiophene + [bmim][BF₄], + [bmim][PF₆] binaries are correlated using the NRTL equation. It is shown that infinite dilution activity coefficients, γ_i^∞ , determined from the VLE data are different from experimental γ_i^∞ values in the thiophene + [bmim][BF₄] binary; high-performance regeneration of ionic liquids requires VLE data at infinite dilution.

1. Introduction

Phase equilibrium data for ionic liquids (IL) are of importance not only for the theoretical elucidation of solution structures, but also for the practical development of extraction processes using IL solvents. Applications such as replacing high-temperature and high-pressure heterogeneous catalytic liquid-fuel desulfurization processes by extraction with IL solvents have been extensively studied [1, 2]. One particular application of interest is thiophene removal from liquid fuels; hence ternary liquid-liquid equilibria (LLE) data for thiophene + hydrocarbon + IL systems have been extensively reported [2-9]. In addition, binary LLE data [10] and solid-liquid equilibrium (SLE) data [11, 12] have been also reported. However, only Huo et al. [13] have reported vapor-liquid equilibrium (VLE) data for thiophene + IL binaries. In their investigations, the LLE, SLE and VLE data have been successfully correlated using the NRTL equation. However, it is known that different activity coefficient models provide different infinite dilution activity

coefficient values at high solute concentration regions being remote from infinite-dilution conditions [14]. Therefore, model deficiencies may cause significant discrepancies between the predicted and experimental phase equilibria at infinite dilution, which impedes high-performance regeneration of IL.

The purpose of the present investigation is to identify the discrepancies in infinite dilution activity coefficients between the experimental and predicted values using the VLE and LLE data for the thiophene + [bmim][BF₄] and +[bmim][PF₆] binaries. A high-precision correlation for infinite dilution activity coefficients [15] is used for the comparison.

2. Model

Assuming that the vapor pressure of IL is zero, the system pressure, P , at the temperature, T , is formulated as follows:

$$P = \gamma_1 x_1 p_{1s} \quad (1)$$

where γ_1 is the activity coefficient of thiophene in the mixture consisted of thiophene and an IL, and where x_1 is the liquid phase mole fraction of thiophene, while p_{1s} denotes the vapor pressure of thiophene. Huo et al. [13] reported binary VLE data, that is, P and T values at $x_1 = 0.1997, 0.3997$ and 0.5998 for the thiophene + 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF₄] binary and at $x_1 = 0.1997, 0.4001, 0.5997$ and 0.7501 for the 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF₆] binary. Huo et al's P and T data at constant x_1 can be fitted to Eq. 2 using the constants, a and b :

$$\log P = a + \frac{b}{T} \quad (2)$$

The correlation is excellent ($R^2 = 0.99$) for both binaries; therefore, constant-temperature P, x data can be produced using Eq. (2) at five different temperatures, $T = 300$ K, 310 K, 320 K, 330 K and 340 K. In the next step, the P, x data at a constant temperature are correlated using the NRTL equation for calculating γ_1 in Eq. (1). In the correlation procedures, three NRTL parameters, α_{12} , τ_{12} and τ_{21} are determined for optimizing the following objective function:

$$ARD = \frac{1}{n} \sum_{k=1}^n \left| \frac{P_{k,\text{exp}} - P_{k,\text{cal}}}{P_{k,\text{exp}}} \right| \quad (3)$$

where n is the number of data points at a constant temperature. Finally, infinite dilution activity coefficients are determined by applying the NRTL equation at $x_1 = 0$ and 1 as follows:

$$\ln \gamma_1^\infty = \tau_{21} + \tau_{12} e^{-\alpha_{12} \tau_{12}} \quad (4)$$

$$\ln \gamma_2^\infty = \tau_{12} + \tau_{21} e^{-\alpha_{12} \tau_{21}} \quad (5)$$

This analysis shows that $\alpha_{12} = 0.31$ provides the best correlation for the P, x data and this value is used in the subsequent analysis.

3. Results and Discussion

In Figure 1, P is plotted versus x_1 at $T = 300$ K, 310 K, 320 K, 330 K and 340 K for the thiophene (1) + [bmim][BF₄] (2) binary. Figure 1 includes the correlation results as shown using the solid lines. The optimized ARD values were 0.52% , 0.12% , 0.12% , 0.22% , 0.36% at $T = 300$ K, 310 K, 320 K, 330 K and 340 K, respectively, and their average is 0.27% , although P, x data are insufficient at $0.7 < x_1 < 1$. Similar analysis for the thiophene (1) + [bmim][PF₆] (2) binary provides an average ARD of 0.75% . Therefore, it is concluded that the P, x data can be satisfactorily correlated using the NRTL equation. At $T = 340$ K, partial molar excess enthalpy at infinitely dilution for thiophene in

[bmim][BF4] is 1.4 times greater than that in [bmim][PF6], as calculated from the temperature dependency of the infinite dilution activity coefficients [15] determined from the NRTL parameters. This implies that the strength of the molecular interactions between a molecule of thiophene and surrounding [bmim][BF4] ion pairs are 1.4 times greater than that in [bmim][PF6] ion pairs.

Figure 1. P vs. x_1 for the thiophene (1) + [bmim][BF4] (2) binary, ($\circ$) 300 K, (Δ) 310 K, ($\square$) 320 K, ($\bullet$) 330 K, ($\blacktriangle$) 340 K calculated using the data by Huo et al. [13], (—) correlated using the NRTL equation with $\alpha_{12}=0.31$.

To compare the experimental γ_1^∞ values with those predicted using the NRTL equation applied to the P , x data, a high-precision correlation method for the infinite dilution activity coefficients is used [15]; which shows that the relationship between the following X and Z calculated from VLE data converges to a line [15]:

$$X = \frac{p_{1s} + p_{2s}}{P_{c1} + p_{2s}} \quad (6)$$

$$Z = \frac{\gamma_1^\infty p_{1s} - p_{2s}}{P_{c1} - p_{2s}} \quad (7)$$

X denotes an index of proximity ratio to the critical point, while Z reflects non-dimensional infinite dilution pressure slope at $x_1 = 0$. P_{c1} denotes the critical pressure of the lighter component. Eq. (6) shows that this correlation is applied to the thiophene + [bmim][BF4] binary data, however, to demonstrate that LLE and VLE data converge to the same XZ line, Z is plotted versus X for the 1-butanol (1) + water (2) binary (Figure 2). Mutual solubility data are cited from the literature [16], and the γ_1^∞ values are determined from the mutual solubility data using the UNIQUAC equation. It is well known that activity coefficient equations such as the NRTL and UNIQUAC equations can successfully correlate not only VLE but also LLE data for binary and ternary systems [16, 17]. Figure 2 includes VLE data cited from the literature [17]. For the constant-pressure VLE data, the Z value is calculated at an average temperature, $(T_1 + T_2)/2$, using the boiling points, T_1 and T_2 , of components 1 and 2, respectively. The LLE data form a converged XZ line as denoted by the ($\circ$)

Figure 2. Z vs. X for the 1-butanol (1) + water (2) binary, ($\circ$) mutual solubility data [16], ($\bullet$) constant-temperature VLE data [17], ($\times$) constant-pressure VLE data [17], (-) representing the LLE data.

Figure 3. Z vs. X determined from infinite dilution activity coefficient data [18] for the ($\bullet$) 1-butanol (1) + water (2) and ($\circ$) methanol (1) + water (2) binaries, (- - -) representing the VLE and LLE data for the 1-butanol + water, (-) representing the VLE data for the methanol + water binary.

symbols and the solid line. Figure 2 also shows that the constant-temperature and constant-pressure data converge to the same line determined from the LLE data. Furthermore, to show that VLE data and infinite dilution activity coefficient data converge to the same line, in Figure 3, Z is plotted versus X for the 1-butanol (1) + water (2) binary, where γ_1^∞ data are cited from the literature [18] as shown using the ($\bullet$) symbols. Figure 3 includes the XZ dashed line determined from the LLE data shown in Figure 2. Figure 3 also includes the XZ relationships for the methanol (1) + water (2) binary, where γ_1^∞ data were cited from the same ref. [18], as denoted using the ($\circ$) symbols. In Figure 3, the solid line represents the methanol + water VLE data. For the methanol + water binary, the Margules

equation is used, because it successfully correlates the P , x data. Figure 3 shows that the γ_1^∞ value determined from the VLE and LLE data is identical with the experimental γ_1^∞ value. Moreover, Figures 2 and 3 show that each binary has its own thermodynamic consistency line, because experimental errors disappear from the high-precision correlation, as determined from the phase equilibrium data reported by different authors using different equipment for different phase equilibria: i.e., VLE and LLE, at different solute concentration regions including infinite dilution and nearly pure liquid state.

Finally, in Figure 4, Z is plotted versus X for the thiophene (1) + [bmim][BF4] (2) binary. The solid line represents the binary VLE data, as calculated using the NRTL equation. As denoted using the ($\circ$) symbols, Figure 4 includes the XZ relationship calculated from the NRTL binary parameters representing the thiophene + [bmim][BF4] + heptane ternary LLE data [3]. Therefore, even if an IL is involved, the VLE and LLE data converge to the same XZ line, as is the case for the aqueous binary (Figure 2). Figure 4 also includes the XZ relationships calculated from the experimental γ_1^∞ values measured by gas-liquid chromatography [19, 20] as shown by the ($\bullet$) and ($\times$) symbols, respectively. Figure 4 clearly demonstrates that the infinite dilution activity coefficients determined from the VLE and LLE data using the NRTL equation show significant deviations from the experimental data. The trend might be intrinsic to the solute infinitely diluted in an IL. A similar comparison for the thiophene + [bmim][PF6] binary is not possible, because the γ_1^∞ data cannot be found in the literature.

Figure 4. Z vs. X for the thiophene (1) + [bmim][BF4] (2) binary, (solid line) determined from the binary VLE data, ($\circ$) calculated from the NRTL binary parameters cited from the thiophene (1) + [bmim][BF4] (2) + heptanes (3) ternary LLE data [3], ($\bullet$) γ_1^∞ data by Zhang et al. [19], ($\times$) γ_1^∞ data by Revelli et al. [20].

In conclusion, the VLE data for the thiophene (1) + [bmim][BF4] (2) and thiophene (1) + [bmim][PF6] (2) binaries can be successfully correlated using the NRTL equation. However, the high-performance regeneration of IL should use infinite dilution activity coefficient data derived from the low solute concentration regions, because the infinite dilution activity coefficients predicted from the VLE and LLE data significantly deviate from the experimental data for the thiophene (1) + [bmim][BF4] (2) binary (readers can use the VLE calculation at <http://www.sskato.jp>).

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