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Global Phase Behaviors of Trifluoromethane in Ionic Liquid [bmim][PF_6]

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In a recent article, Shariati et al. have reported that the global phase behavior of trifluoromethane and room-temperature ionic liquid [bmim][PF_6] mixtures belongs to the type III fluid according to the classification of van Konynenburg and Scott. However, their assessment on the fluid classification was based on their very limited experimental data without any thermodynamic modeling. On the other hand, we have recently reported experimental solubility behaviors of trifluoromethane and [bmim][PF_6] mixtures, together with those for other hydrofluorocarbon + ionic liquid mixtures and stated that the phase behavior of these mixtures belongs to the type V fluid mixture based on our equation-of-state model predictions. In order to confirm our predictions, important vapor-liquid-liquid equilibrium data have been obtained experimentally, and we show that the present mixture is definitely not the type III fluid but belongs to type V. Also, we demonstrate that our EOS model based on our vapor-liquid equilibrium (VLE) data alone has correctly predicted the global phase behavior of the present binary system, as well as unusually large negative excess molar volumes. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 3952–3957, 2006

Keywords: phase equilibria, solubility, ionic liquid, trifluoromethane, equation of state, type V mixture, excess molar volume

Introduction

Room temperature ionic liquids (RTILs) belong to a new class of compounds, which are molten salts with low melting points (<100°C). Their thermodynamic and transport properties as well as electrochemical properties are intensively being studied.[1] It is quite natural to wonder whether ordinary chemicals interacting with this new class of compounds behave very differently in their mixture properties. So far, most of the thermodynamic and transport properties of mixtures are reported to be not much different from those of ordinary chemical compounds. In fact, we have shown that thermodynamic phase behaviors of mixtures with RTILs can be well modeled with ordinary equation-of-state (EOS) or activity models for non-electrolyte solutions without taking into account the speciation effect of electrolytes.[2-5]

Recently, Shariati et al. reported experimental (high pressure) solubility data of trifluoromethane (R-23) + RTIL, 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF6]),[6] and claimed that this binary mixture belongs to the Type III fluid behavior according to the classification of van Konynenburg and Scott.[7,8] However, their conclusion was based neither on extensive experimental data nor a proper thermodynamic model; it was rather based on purely guesswork. On the other hand, we have recently studied low pressure (< 2 MPa) solubilities of various hydrofluorocarbons (HFCs) including R-23

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in [bmim][PF_6],[4] and predicted that these mixtures belong to Type V instead of Type III based on our EOS models.[2,3,9,10]

Our solubility data were limited within the vapor liquid equilibrium (VLE) regions, but our EOS correlation based on these data has shown the liquid-liquid phase separation (LLE) in the HFC rich-side solutions with lower critical solution temperatures (LCSTs). Although EOS models are generally more reliable in extrapolating properties beyond experimental data, compared with the case of activity models, vapor-liquid-liquid equilibrium (VLLE) behaviors must be confirmed by experimental data, since VLLE or LLE behaviors are not always predicted well with thermodynamic models based on VLE data alone. Particularly, the global phase behavior for Types III, IV, or V depends critically on the three phase (VLLE) behavior, as illustrated in Figure 1. More detailed descriptions of these fluid types can be found in Refs. 7, 8, 11, 12.

In order to prove our EOS model predictions, VLLE experiments have been performed with the volumetric method, which has been used successfully for R-125 (pentafluoroethane) + [bmim][PF_6] mixtures.[13] In addition, in order to show the existence of an LCST, some cloud-point measurements have also been made. First, we describe our EOS model for the R-23 + [bmim][PF6] system based on only VLE data.[4] Phase behavior predictions by this EOS model are then compared with the present experimental VLLE data as well as high pressure solubility data in the literature.[6] Our statement on the type of fluid behavior (Type V) is confirmed by the present study. In addition to the phase behavior, we discuss unusually large negative excess molar volumes discovered in the present VLLE experiments, and show that such large excess molar volumes are also explained by the present EOS model.

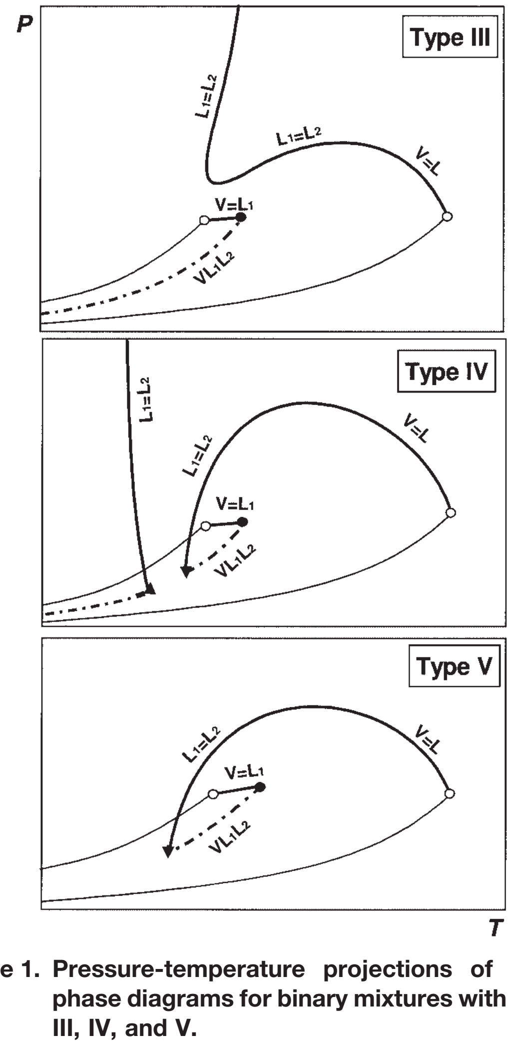

Figure 1. Pressure-temperature projections of global phase diagrams for binary mixtures with Types III, IV, and V.

Thick solid lines: VLE (or LLE) critical locus. Thin solid lines: vapor pressure curves of pure compounds. Open circles: VLE critical points of pure compounds. Closed circles: VLLE end point at the VLE critical locus. Triangles: VLLE endpoint in the three phase. Broken/dot lines: VLLE three-phase line.

Thermodynamic Model

Equation of state

In order to understand the global phase behavior of the present system, we have employed a generic Redlich-Kwong (RK) type of cubic equation of state (EOS),[9,10] which is written in the following form:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \tag{1}$$

$$a(T) = 0.427480\,\frac{R^2T_c^2}{P_c}\,\alpha(T) \tag{2}$$

$$b = 0.08664\,\frac{RT_c}{P_c}, \quad (R\text{: universal gas constant}). \tag{3}$$

The temperature-dependent part of the a parameter in the EOS for pure compounds is modeled by the following empirical form[9]:

$$\alpha(T) = \sum_{k=0}^{\leq 3} \beta_k (1/T_r - T_r)^k, \quad \text{for } T_r \equiv T/T_c \leq 1, \tag{4a}$$

$$\alpha(T) = \beta_0 + \beta_1[\exp\{2(1-T_r)\} - 1], \quad \text{for } T_r \geq 1. \tag{4b}$$

The coefficients β_k, are determined so as to reproduce the vapor pressure of each pure compound. It should be noted that Eq. 4b is implemented for $T_r \geq 1$ in the present study, in order for $\alpha(T)$ to be physically meaningful for refrigerant gases at even very high temperatures: always $\alpha(T) > 0$ and a decreasing function with T. At $T_r = 1$, Eqs. 4a and 4b are set to be analytically continuous.

For ionic liquids, however, usually no vapor pressure data are available (or practically non-volatile); and, furthermore, no data for the critical parameters (T_c and P_c) exist. The critical parameters can be estimated in various ways. As discussed in Ref. 10, rough estimates for the critical parameters of non-volatile compounds are sufficient for the present purpose. On the other hand, the temperature-dependent part of the a parameter of ionic liquids (Eq. 4) is significantly important when we try to correlate the solubility (pressure-temperature-composition: PTx) data, although the vapor pressure of ionic liquid is essentially zero at the temperature of interest. Therefore, the coefficient β_1 for ionic liquids in Eq. 4 are usually treated as an

Table 1. Pure Components' EOS Constants Used in the Present Study

	$M/g \cdot mol^{-1}$	T_c/K	P_c/MPa	β_0 —	β_1 —	β_2 —	β_3 —
R-23	70.013	299.07	4.836	1.0019	0.47672	−0.09216	0.02386
[bmin][PF$_6$]	284.18	860.5	2.645	1.0	0.62627	0	0

adjustable fitting parameter using $\beta_0 = 1$ and $\beta_2 = \beta_3 = 0$ in the solubility data analysis, together with the binary interaction parameters discussed below. However, once it is determined for a particular ionic liquid using a certain binary system, it will be used as a fixed constant for any other binary systems containing that ionic liquid.

Then, the a and b parameters for a general N-component mixture are modeled in terms of binary interaction parameters[10]:

$$a = \sum_{i,j=1}^{N} \sqrt{a_i a_j} f_{ij}(T)(1 - k_{ij}) x_i x_j, \quad a_i = 0.427480 \frac{R^2 T_{ci}^2}{P_{ci}} \alpha_i(T) \tag{5}$$

$$f_{ij}(T) = 1 + \tau_{ij}/T, \quad \text{where } \tau_{ij} = \tau_{ji}, \quad \text{and } \tau_{ii} = 0. \tag{6}$$

$$k_{ij} = \frac{l_{ij} l_{ji}(x_i + x_j)}{l_{ji} x_i + l_{ij} x_j}, \quad \text{where } k_{ii} = 0. \tag{7}$$

$$b = \frac{1}{2} \sum_{i,j=1}^{N} (b_i + b_j)(1 - k_{ij})(1 - m_{ij}) x_i x_j, \qquad b_i = 0.08664 \frac{RT_{ci}}{P_{ci}}, \tag{8}$$

where $m_{ij} = m_{ji}$, and $m_{ii} = 0$.

T_{ci}: critical temperature of i-th species.

P_{ci}: critical pressure of i-th species.

x_i: mole fraction of i-th species.

In the above model, there are maximum four binary interaction parameters: l_{ij}, l_{ji}, m_{ij}, and τ_{ij} for each binary pair. It should be noted that when $l_{ij} = l_{ji}$ in Eq. 7 and $f_{ij} = 1$ in Eq. 6, Eq. 5 becomes the ordinary quadratic-mixing rule for the a parameter. The present EOS model has been successfully applied for highly non-symmetric (with respect to the polarity and size) mixtures, such as various refrigerant/oil mixtures.[9,10] The fugacity coefficient ϕ_i of i-th species for the present EOS model, which is needed for the phase equilibrium calculation, is given by:

$$\ln \phi_i = \ln \frac{RT}{P(V-b)} + b_i'\left(\frac{1}{V-b} - \frac{a}{RTb(V+b)}\right) + \frac{a}{RTb}\left(\frac{a_i'}{a} - \frac{b_i'}{b} + 1\right) \ln \frac{V}{V+b} \tag{9}$$

where $a_i' \equiv (\partial na/\partial n_i)_{n_{j \neq i}}$ and $b_i' \equiv (\partial nb/\partial n_i)_{n_{j \neq i}}$; n = total mole number and n_i = mole number of i-th species (or $x_i = n_i/n$). The explicit forms of a_i' and b_i' may be useful for readers and given by:

$$a_i' = 2 \sum_{j=1}^{N} \sqrt{a_i a_j} f_{ij} x_j \left\{1 - k_{ij} - \frac{l_{ij} l_{ji}(l_{ij} - l_{ji}) x_i x_j}{(l_{ji} x_i + l_{ij} x_j)^2}\right\} - a \tag{10}$$

$$b_i' = \sum_{j=1}^{N} (b_i + b_j)(1 - m_{ij}) x_j \left\{1 - k_{ij} - \frac{l_{ij} l_{ji}(l_{ij} - l_{ji}) x_i x_j}{(l_{ji} x_i + l_{ij} x_j)^2}\right\} - b \tag{11}$$

Phase equilibria (α, β, γ, . . . , coexisting phases) for an N-component system can be obtained by solving the following equilibrium conditions:

$$x_i^{\alpha} \phi_i^{\alpha} = x_i^{\beta} \phi_i^{\beta} = x_i^{\gamma} \phi_i^{\gamma} = \ldots, \quad (i = 1, \ldots, N) \tag{12}$$

where x_i^{α}, x_i^{β}, x_i^{γ}, ... : mole fractions of α, β, γ, . . . phases for the *i-th* species ϕ_i^{α}, ϕ_i^{β}, ϕ_i^{γ}, . . . : fugacity coefficients of α, β, γ, . . . phases for the *i-th* species.

EOS parameters

The pure component EOS parameters in this study are listed in Table 1; for R-23, Ref. 14 was used to set up the parameters, and for [bmim][PF6], those in our previous works[2,3] were employed. The mixture EOS in the present model is constructed with maximum four binary interaction parameters as discussed in the previous section: l_{ij}, l_{ji}, m_{ij}, and τ_{ij} ($i, j = 1, 2$). These adjustable parameters have been determined by non-linear least-squares analyses with the object function of a sum of all PTx data points for $(1 - P_{obs}/P_{calc})^2$: P_{obs} = observed pressure and P_{calc} = pressure of model calculation. Only our experimental VLE (low pressure solubility) data[4] have been used to develop the EOS model of the present binary mixture. Other available experimental data, such as high pressure solubility data[6] and the VLLE data in the present study, will be used for the validation of the present EOS model prediction. An optimal fit of the analysis was obtained using three parameters ($l_{12} = l_{21}$, m_{12}, and τ_{12}) with a standard deviation in pressure of 16.5 kPa, and the determined parameters are given in Table 2.

Experimental Verification of Model

As has been mentioned in our previous work,[3] the present EOS model predicts liquid-liquid phase separations with an LCST in the R-23 rich-side solutions. However, the EOS parameters were developed with limited VLE data[4] alone. The

Table 2. Optimal Binary Interaction Parameters

System (1)/(2)	l_{12}	l_{21}	m_{12}	τ_{12}/K
R-23/[bmim][PF$_6$]	0.07687	l_{12}	−0.08739	37.88

Table 3. Experimental VLLE results for R-23 (1) + [bmim][PF$_6$] (2) System

T/K	x_1/mol %	x'_1/mol %	$\bar{V}$/cm^3 · mol^{-1}	$\bar{V}'$/cm^3 · mol^{-1}	$\bar{V}^{ex}$/cm^3 · mol^{-1}	$\bar{V}^{ex'}$/cm^3 · mol^{-1}
293.6	77.3 ± 2.0	100.1 ± 0.3	87.8 ± 3.0	86.2 ± 3.0	−26.2 ± 3.0	−0.2 ± 3.0
285.6	81.2 ± 2.0	99.7 ± 3.0	86.5 ± 3.0	73.6 ± 3.0	−14.0 ± 3.0	−2.8 ± 3.0
280.2	85.3 ± 2.0	99.6 ± 0.3	79.4 ± 3.0	70.6 ± 3.0	−12.0 ± 3.0	−1.7 ± 3.0

x_1: R-23 composition in one liquid, x'_1: R-23 composition in another equilibrium liquid; $\bar{V}$: molar volume of one liquid, $\bar{V}'$: molar volume of another equilibrium liquid; $\bar{V}^{ex}$: excess molar volume of one liquid, $\bar{V}^{ex'}$: excess molar volume of another equilibrium liquid.

extrapolated phase behavior with such EOS must be supported by experimental data. In order to verify the present EOS predictions, we have conducted VLLE experiments described in the next subsection for R-23 + [bmim][PF6] binary mixtures with the volumetric method, which has been successfully applied to the VLLE behavior of the R-125 (pentafluoroethane) + [bmim][PF$_6$] system.[13]

VLLE experiments and EOS predictions

A sample of [bmim][PF6] (Fluka Chemika, Lot and Filling no. 1152141 and 31505335, assay ≥ 96.0%, CAS No. 174501–64-5) was heated and stirred in a Pyrex® glass tube to 343.15 K (PolyScience constant temperature bath, model 1157) while under a vacuum of 5 × 10−10 MPa (Pfeiffer turbo vacuum pump, model TSH 071) for 10 days to remove any trace amounts of water or other impurities. R-23 (CAS No. 75–46-7) was obtained from DuPont Fluoroproducts (Wilmington, DE) with a purity of 99.9% determined by GCMS and used without further purification. VLLE experiments have been made with these samples at constant temperatures of 293.6, 285.6, and 280.2 K using the volumetric method.[13] Experimental apparatus and procedure as well as detail error analyses are given in Ref. 13. Observed liquid phase compositions and molar volumes are shown in Table 3.

In order to prove the existence of an LCST of the VLLE curve, cloud-point measurements[13] have also been performed with four samples (R-23 of 76.9, 88.8, 93.5, and 94.7 mol %). Starting at a low temperature of 263.15 K, where only one liquid phase existed, we have observed cloud points at 292.7, 277.2, 273.2, and 272.2 ± 1 K, respectively, for the above four mixtures of R-23. Based on these measurements, the LCST is estimated to be about 272 K at about 94 mol % of R-23.

Then, the EOS model predictions have been compared with observed VLE and VLLE data in Figure 2 using *PTx* phase diagrams, and they are in excellent agreement with the experimental data, showing VLLE in the R-23 rich-side solutions with an LCST. Figure 2 suggests the Type V mixture behavior for this binary system, according to the classification of van Konynenburg and Scott.[7,8] Figure 3 presents *Tx* (temperature-composition) phase diagrams of the present binary system. In addition to the VLLE with the LCST, the EOS model predicts another separated VLLE curve with a UCST (upper critical solution temperature) of about 190 K at very low temperatures. If this is real, the system will belong to the Type IV mixture instead of V; see Figure 1. However, this separated VLLE curve likely interferes with solid phases and will be well inside the solid phase, as shown in Figure 3. The SLE (solid-liquid equilibrium) curve in Figure 3 was calculated with the Schröder equation (as an ideal mixture)[15] using the melting points (283.51 and 118.02 K) and the latent heats of melting (19.60 and 4.058 kJ·mol^{-1}) for [bmim][PF$_6$][16] and R-23,[14] respectively.

High pressure data and EOS predictions

It is interesting and important to see whether the present EOS model based on our low pressure (less than 2 MPa) VLE

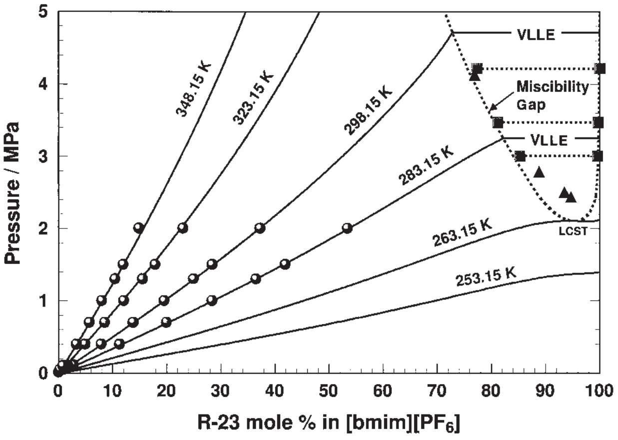

Figure 2. Isothermal *PTx* phase diagrams for R-23 + [bmim][PF$_6$] mixtures.

Solid lines and broken lines: the present EOS predictions. Circles: VLE experimental data,[4] which were used to construct the present EOS model. Squares: experimental VLLE data of this study. Triangles: experimental cloud-point data of this study.

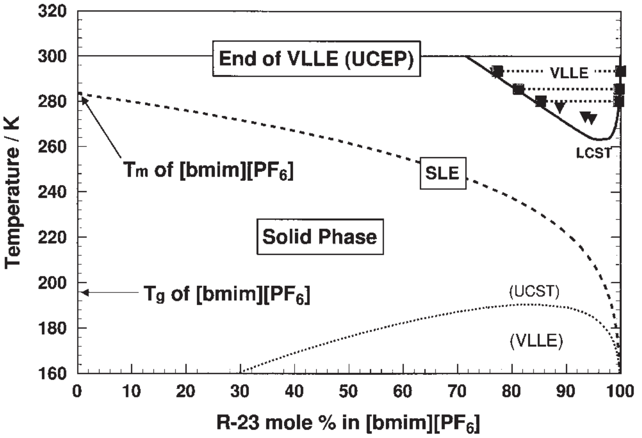

Figure 3. *Tx* phase diagrams for R-23 + [bmim][PF$_6$] mixtures.

Solid line and dotted line: miscibility gaps (VLLE) predicted by the present EOS model. Broken line: calculated SLE (solid-liquid equilibrium) line; see text for details. Squares: experimental VLLE data of the present study. Triangles: experimental cloud-point data of this study. Tm: melting point temperature. Tg: glass transition temperature.

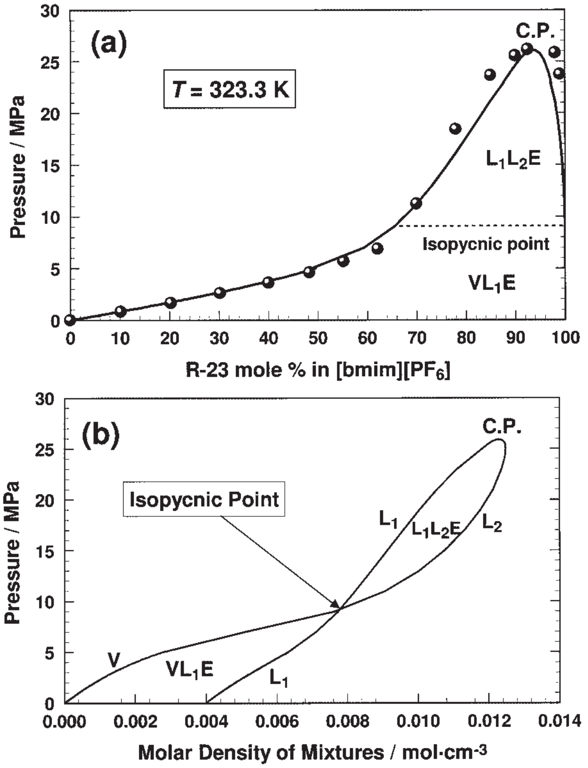

Figure 4. High pressure isothermal *PTx* phase diagram at T = 323.3 K (a), and the corresponding *PD* phase diagram (b) for R-23 + [bmim][PF_6] mixtures.

Lines: calculated by the present EOS model. Circles: experimental data.[6] C.P.: critical point.

data can properly predict high-pressure phase behaviors. The model calculations are compared in Figure 4a with experimental isothermal (323.3 K) *Px* data reported in the literature.[6] The agreement is quite reasonable. A rather sharp rise in pressure around 70 mole % of R-23 is due to the transition from VLE to LLE. It happens at the so-called isopycnic point,[17] which is shown clearly in the *PD* (isothermal pressure-density) diagram of Figure 4b. The isopycnic point occurs above the critical temperature of the more volatile compound, and at this point the vapor *molar* density of VLE becomes equal to that of the corresponding liquid phase. In the higher pressures above this point, the vapor molar density becomes higher than that of the corresponding liquid phase, and then the thermodynamic equilibrium results in LLE. A *PD* diagram like Figure 4b is quite useful for understanding complex high-pressure phase behaviors.[17]

Discussion

Using rather limited VLE data alone, the present mixture EOS has been constructed, and the phase behaviors predicted by this EOS are found to be quite reliable. The EOS predictions have been well confirmed with the present experimental liquid-liquid separations with an LCST as well as high-pressure solubility data in the literature.[6] Thus, it is very encouraging to see the power of the present EOS model, which can be applied to the extrapolated regions of thermodynamic variables (T, P, and compositions) beyond the experimental data used for the model development.

With the present EOS model, we have calculated many more *PTx* diagrams, such as Figures 2 and 4, in order to understand the global phase behavior, and it has been confirmed to be Type V; see Figure 1. As discussed earlier, the possibility for Type IV was eliminated due to the solid phase intervention. The type III behavior is clearly rejected from Figure 3. It is worth mentioning here that our prediction of the Type V behavior for R-125 + [bmim][PF6] has also experimentally been confirmed recently.[13]

Observed large negative excess molar volumes in [bmim][PF6] rich-side liquids are noteworthy; see Table 3. The magnitude is nearly more than 10 times larger than that of ordinary liquid mixtures (typically about 0 ± 2 cm3·mol^{-1}).[11] The excess molar volume $\bar{V}^{ex}$ is defined as:

$$\bar{V}^{ex} = \bar{V}_{mix} - \bar{V}_1^0 X_1 - \bar{V}_2^0 X_2, \qquad (13)$$

where $\bar{V}_{mix}$ is a molar volume of a mixture solution, $\bar{V}_i^0$ is a molar volume of the *i-th* pure compound, and X_i is a mole fraction of the *i-th* compound in the mixture solution. Then, it is interesting to check whether the present EOS model can predict such large negative excess molar volumes. Figure 5 presents the EOS calculation, compared with the present experimental values. The observed large negative $\bar{V}^{ex}$ values and their temperature dependence of [bmim][PF6] rich-side liquids are reasonably consistent with the EOS predicted behaviors. Although the numerical agreement is not great, the EOS prediction may be regarded as being surprisingly good, considering the fact that any simple cubic EOS such as the present case is well known about the very poor prediction on the liquid density (or liquid molar volume). The present fair results for $\bar{V}^{ex}$ is partly due to the *difference* calculations, as seen in Eq. 13, instead of absolute liquid molar volumes.

Concerning $\bar{V}^{ex}$, it should be mentioned that similarly large negative excess volumes have been reported for R-125 and CO2 mixtures with ionic liquid [bmim][PF_6].[13] Although such

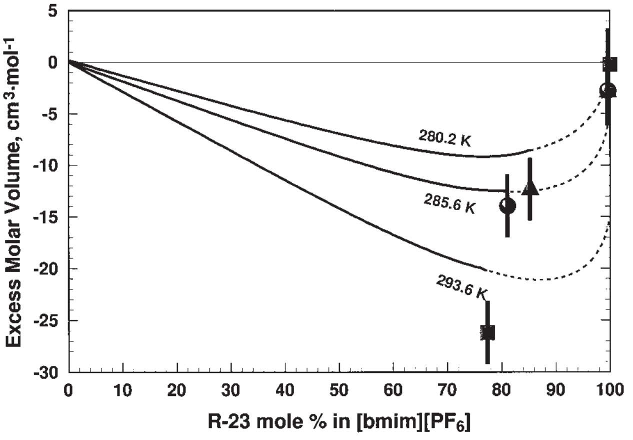

Figure 5. Excess molar volumes as a function of R-23 mol % for R-23 + [bmim][PF_6] mixtures.

Solid lines: calculated by the present EOS model. Dotted lines: hypothetical curves within the liquid-liquid separation regions. Symbols with error bars: the present experimental data, squares: 293.6 K, circles: 285.6 K, and triangles: 280.2 K.

large $\bar{V}^{ex}$ can be predicted with the present EOS model, a real question will be what is the physical meaning for such large negative excess molar volumes. In this respect, Rowlinson and Swinton state in their textbook[11]: "*The excess volume is strongly dependent on the ratio of the molar volumes of the two pure components and thus the experimental values are less directly related to molecular type*." However, very strong intermolecular interactions such as hydrogen bonding and/or compound formation may also be involved in the present large $\bar{V}^{ex}$.

Conclusions

The global phase behavior of R-23 + [bmim][PF_6] binary mixtures has been confirmed as Type V, based on our EOS model, which has been validated by the present VLLE data as well as high pressure solubility data in the literature.[6] Also, the present study shows that our EOS model based on low pressure VLE data alone can be highly reliable when extrapolating thermodynamic properties.

Very large negative excess molar volumes in the present system have been found. Then, it is shown that the present EOS model has been able to predict such behaviors. This may indicate that the molecular size ratio of the two compounds is responsible at least partly for the large excess volumes, since the EOS contains the molecular size effect through the excluded volumes (the *b* parameter in Eq. 8). However, the real physical meaning of this finding is not completely clear, and some molecular dynamics calculations may provide further insight.

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