**Phase behavior of novel functional tropine ionic liquids in binary
solvent mixture (water + ethanol): a synergistic effect promoting
solubility**

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Phase diagrams for the binary systems ethanol or water + tropine-type ionic liquids including N-benzyl-tropine hexafluorophosphate, N-(3-methoxybenzyl)-tropine hexafluorophosphate, N-(4-nitrobenzyl)-tropine hexafluorophosphate and related ternary systems (ethanol + water + ionic liquid) were measured with equilibrium method at atmospheric pressure in the temperature range of 278.15 K to 333.15 K. With the increase of temperature, the solubility of these ionic liquids increased obviously and the temperature-sensitive property in binary solvent mixture (water + ethanol) was also proven. On the other side, cosolvency phenomenon was also found in binary system. And it was found that the cosolvency related to the ratio of water and ethanol, as well as the strength of hydrogen bonding between solvent and cationic groups of ILs. The solubility of ionic liquids in the single solvent and certain concentration of binary solvent mixture was correlated by two empirical equations (Apelblat and λh) and two theoretical models (Wilson and NRTL) with good results. This study provides useful information for further research and application of these ionic liquids.

Keywords: Ionic liquids, Solubility models, Cosolvency, Phase diagrams, Binary solvents

1. Introduction

Ionic liquids (ILs) with their special properties are driving new researches and applications in many fields, such as good multi-function solvents applied in extractive distillation process[1], new kind of catalyst[2, 3] and application in the extraction of natural products[4, 5]. Thus various new types of ILs were synthesized in the past decades, such as isoquinoline-based[6], benzothiazolium-based[7], pyridine-based[8] and so on. A large amount of applications in various of fields have been investigated and developed, while the physicochemical property of IL is always essential and can lay the foundation for the application of ILs. Any detailed knowledge of important binary and ternary mixtures behaviour, which is paramount for the design of any technological processes, is of course even significance. For example, some researches focused on the solubility of imidazolium and benzothiazolium ILs in aqueous and alcohol solutions[9-11], and it has been found that benzothiazolium-based ILs have temperature-sensitive property in alcohols[7].

Recently a novel class of ILs derived from tropine were developed by our research group[12] and the data of X-ray powder diffraction of $[C_6Tr][PF_6]$ was discussed[13]. Among of these tropine-type ILs, the hexafluorophosphate which are attached benzene ring with various functional groups were considered to have potential application in the field of separation and extraction for the strong intermolecular interaction including π - π bond and hydrogen bond[12, 14]. However, due to its hydrophobicity, the solubility of ILs in many polar solvent including water and ethanol were so low that limits its application in many fields. As one of the most

popular solvent for extraction, the binary solvent mixture (ethanol and water) is not only a “green” solvent, but also can greatly improve the solubility of hydrophobic ILs[15]. In addition, many distinct strategies for obtaining the desired situations of total miscibility, partial miscibility, or almost complete phase separation can be envisaged based on the solubility of ILs in binary solvent mixture[16]. Moreover, ILs can be recycled by changing the solvent composition. The solubility of tropine-type ILs in water, ethanol and binary solvent mixture are very important for application of these ionic liquids in extraction and separation.

For these reasons, phase diagrams for the binary systems ethanol or water + ILs including N-benzyl-tropine hexafluorophosphate ([Bntr][PF₆]), N-(3-methoxybenzyl)-tropine hexafluorophos ([*m*-MBntr][PF₆]), N-(4-nitrobenzyl)-tropine hexafluorophosphate ([*p*-NBntr][PF₆]) and related ternary systems (ethanol + water + IL) were studied in the temperature range of 278.15 K to 333.15 K. The solubility, temperature-sensitive and cosolvency properties of the ILs were discussed. The experimental solubility was correlated with modified Apelblat equation, λh equation, Willson model and NRTL model. It is hoped that the results could provide important information for further research of ILs in the separation and extraction fields.

2. Experimental

2.1. Materials

The chemical materials and their mass fraction purities were as follows: tropine (CAS Number 120-29-6, standard for chromatography, +98%) was purchased from Aladdin Industrial Corporation (Shanghai, China). Potassium hexafluorophosphate (CAS Number 17084-13-8, +99%) and ethanol (CAS Number 64-17-5, +99.9%) were bought from Kelong Industrial Corporation (Chengdu, China). High-quality ethanol (max. 0.03 % of water content, analytically pure) was further dried with 3 Å molecular sieves. Deionized water was prepared by a UPR-I-5T water purification system from Ulupure Corporation (Chengdu, China). The synthetic routes of [Bntr][PF₆], [*m*-MBntr][PF₆] and [*p*-NBntr][PF₆] were elaborated in the part 2.2. After getting the crude product, ILs were washed several times with water to remove the chloride (coexisting by-product), which was checked that no precipitate (AgCl) would occur by addition of AgNO₃ (0.01mol·kg⁻¹) into the washing liquor. The ILs purity (all above 99.9%) were verified by LC-20AT HPLC spectroscopy (Shimadzu Corporation, Kyoto, Japan) on C18 column and NMR spectroscopy (Bruker, AV II-400 MHz, CD₃OD, Delaware, USA). Vacuum dryness was applied to the ILs samples under moderate temperature (333 K) for 24 hours in order to decrease the water content to a negligible value (less than 0.1 wt. %). The names and structures of tropine-type ILs were listed in [Table 1](#). ILs are defined as the molten salt which their melting point are lower than 373.15 K, but some ILs have high melting points (some above 373.15 K) at atmosphere pressure[12, 17, 18]. ¹H NMR, ¹³C NMR, and MS spectra of [Bntr][PF₆], [*m*-MBntr][PF₆] and [*p*-NBntr][PF₆] are provided as Figures 1S to 9S in the Supporting Information.

2.2. Synthesis of ILs

2.2.1. Synthesis of N-benzyl-tropine hexafluorophosphate [Bntr][PF₆]

Tropine (1.41 g, 0.01 mol) was dissolved in 90 mL toluene, and then benzyl chloride (1.27 g, 0.01 mol) was added into the solution. The reaction solution was refluxed at 373 K for 24 hours. At the end of the reaction, the solvent and the residual benzyl chloride were removed under reduced pressure. The white solids were then dried under vacuum at 323 K after being washed by toluene several times to give N-benzyl-tropine chloride (2.41 g, 0.009 mol). N-benzyl-tropine chloride (2.67 g, 0.01 mol) was dissolved by appropriate amount of deionized water in 150 mL one-neck flask and then potassium hexafluorophosphate (1.84 g, 0.01 mol) was added. The reaction occurred at room temperature with stirring for two hours. Then the residual white solids were washed with plenty of deionized water, and dried under reduced pressure to obtain the product of [Bntr][PF₆] (3.43 g, 0.0091 mol).

2.2.2. Synthesis of N-(*m*-methoxybenzyl)-tropine hexafluorophosphate [*m*-MBntr][PF₆]

Similar procedure as earlier was carried out between tropine and *m*-methoxybenzyl chloride, and the chloride salts underwent metathesis reaction to obtain the product of [*m*-MBntr][PF₆] with the yield of 85%.

2.2.3. Synthesis of N-(*p*-nitrobenzyl)-tropine hexafluorophosphate ([*p*-NBntr][PF₆])

Similar procedure as earlier was carried out between tropine and 4-nitrobenzyl chloride, and the chloride salts underwent metathesis reaction to give [*p*-NBntr][PF₆] with the yield of 82%.

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130 **2.2. Determination of solubility of tropine-type ILs in water and ethanol**

131 The data of solid-liquid phase equilibrium were measured with a static equilibrium
132 method[19]. For every measurement, excessive amounts of ILs were added into
133 solvent in a three-neck flask. The thermometer and condenser pipe were inserted into
134 the flask in the DC-0506 thermostatic bath (± 0.05 K, Gongyi Yuhua Instrument Co.,
135 Ltd., Gongyi, China) at the desired temperature. The equilibrium cell was slowly
136 heated and reached to a constant temperature with continuous stirring for 2 h to 6 h in
137 which the variation of ILs concentration in liquid phase was observed less than 1%.
138 Then the stirring was stopped and the solution was kept still until the upper layer was
139 clear. About 0.5 ml of upper saturated solution was sampled to a previously
140 weight-calibrated tube (± 0.0001 g, ESJ200-4A electronic balance, Shenyang
141 Longteng Electronic Instrument Co., Ltd., Shenyang, China). The sampling tube was
142 closed quickly and tightly, and weighed to determine the mass of the sample. The
143 concentration of the samples was determined by 2800S UV-Vis spectrophotometer
144 (Shunyuhengping Instrument Co., Ltd., Shanghai, China). The maximum wavelength
145 of [Bntr][PF₆], [*m*-MBntr][PF₆] and [*p*-NBntr][PF₆] at the UV-Vis spectrophotometric
146 calibration curves are 254, 278 and 258 nm, respectively. For each temperature, three
147 sampling and measurement were repeated. If the deviation of three values was less
148 than 2%, these data would be considered valid. The average of the three values was
149 considered as solubility in certain temperature. The mole fraction solubility of ILs in
150 solution ($x_{\text{IL},i}$) was calculated as follows:

$$x_{IL,i} = \frac{m_3 / M_2}{(m_1 - m_2 - m_3) / M_1 + m_3 / M_2} \quad (1)$$

where m_1 , m_2 and m_3 (g) represent the mass of the pipe (after sampling), the mass of pipe (before sampling) and the mass of the solute respectively; M_1 is the molar mass of solvent and M_2 is the molar mass of solute. During the process the FTIR of ILs which has been measured is obtained to make sure that anion PF_6 is not broken and form hydrofluoric acid during measurement process. Compared with the IR spectrum of ILs before and after measurement, the peaks at 840 cm^{-1} and 559 cm^{-1} assigned the stretching and bending vibration of hexafluorophosphate[12] are not changed which indicated the anion is not broken during the process of measurement, as shown in figure 1.

In order to verify the accuracy of the measurement, a solubility comparison between the experimental and the literature[20] for benzoic acid in binary solvent mixture of ethanol + heptane was made. As shown in Figure 2, the average relative deviation of the experimental data in this work was 0.56%, which demonstrated that the above experimental facility and technique were reliable for solubility measurement in binary solvent mixture.

2.3. Differential scanning calorimetry (DSC) measurement

A series of thermodynamic properties of the ILs used in this work are listed in Table 2 which was measured with Q2000 DSC (TA Instrument Co., New Castle, USA). Applied scan rate was $10\text{ K}\cdot\text{min}^{-1}$ with a recorder sensitivity of $0.2\text{ }\mu\text{W}$. The apparatus was calibrated with a 0.999999 mole fraction purity indium sample. The DSC diagrams of five ILs are shown in Figure 3. In addition, the sapphire method was used

to measure the change of heat capacity at melting temperature[21], and molar volume of ILs was calculated by the group contribution method[22].

3. Results and Discussion

3.1. The solubility of tropine-type ILs

3.1.1. Temperature-sensitive property of ILs in binary solvent mixture

Experimental solid-liquid phase equilibrium temperatures and related mole fraction solubility of tropine-type ILs in water, ethanol and their mixture are listed in Table 3 and Table 4. It can be seen that the solubility of ILs in water or ethanol and binary solvent mixture increase as the temperature rising. In the binary solvent mixture, the increase of solubility appears more obvious. Considering the solubility variation over a narrow temperature range in binary solvent mixture, for example, the solubility of [Bntr][PF₆] in binary solvent mixture ($\varphi_I=0.700$ or $x_I=0.416$) varies from 0.0154 to 0.0324 between 323.15 K and 333.15 K, it can be clearly known that the solubility varies sharply (almost doubled) with the very small temperature change. This is so called “temperature-sensitive” property[7, 23], which has the vital practical significance to the separation and re-usage of tropine-type ILs from its solution. Moreover, when the temperature is higher, the temperature-sensitive property of tropine-type ILs in binary solvent mixture appears more obvious.

3.1.2. The solubility of three ILs in the same solvent

From the Table 1, it can be clearly seen that the difference of three tropine-type ILs is the structure of cation which is substituted by benzyl, 3-methoxybenzyl and

4-nitrobenzyl respectively. However, their solubility in the same solvent is apparently different. Figure 4 shows that the solubility of [Bntr][PF₆] in water, ethanol and binary solvent mixture are higher than those of [*m*-MBntr][PF₆] and [*p*-NBntr][PF₆], which may be corresponded to the order of hydrogen bonding strength. The intermolecular hydrogen bond is formed in tropine-type ILs due to the introduction of different substituent on the benzene ring, which hinders the formation of hydrogen bonds between IL and solvent. It directly leads to the decrease of the solubility of the ILs. In this study, the formation of hydrogen bonds between the molecules can be proved by IR spectrogram (Perkin Elmer Corporation, L1600300, USA). As the strength of hydrogen bond increased, the assigned peaks of hydroxyl near 3600 cm⁻¹ greatly moved towards short wavenumber and the transmittance increased respectively [24] which is shown in figure 5. Besides, intermolecular hydrogen bonding can also be proved by the melting point. For example, the highest melting point can be observed in [*p*-NBntr][PF₆], mainly caused by the strong intermolecular hydrogen bonding between the IL molecules[18]. Here the reason why [*p*-NBntr][PF₆] forms hydrogen bonds between the molecules more easily is that the electronegativity of nitro group is stronger than substituent group in [*m*-MBntr][PF₆] and [Bntr][PF₆]. Above all, it can be clearly seen that the order of hydrogen bonding strength is [*p*-NBntr][PF₆] > [*m*-MBntr][PF₆] > [Bntr][PF₆]. Thus, the order of solubility of three tropine-type ILs in same solvent is [Bntr][PF₆] > [*m*-MBntr][PF₆] > [*p*-NBntr][PF₆], which is accord with the results of our experiments.

3.1.3. The synergistic effect of solvent

Normally, the solubility of a substance in the binary solvent mixture is between those in single solvents. Solubility of tropine-type ILs in the binary solvent mixture behaves a maximum value which apparently higher than the solubility of tropine-type ILs in any single solvent. And the solubility varied sharply in certain range of solvent mixture. Considering the solubility of tropine-type ILs in different solvents, for example, the solid-liquid phase equilibrium data of [Bntr][PF₆] at 333.15 K (from 9.96×10^{-4} to 3.73×10^{-2}), it can be observed that the solubility varies sharply with the mole fraction change of ethanol in binary solvent mixture. But the content of ethanol is not positive or negative correlation with solubility. The maximum of miscibility is observed for the mole (volume) fraction of ethanol in binary solvent from $x_I=0.461$ to $x_I=0.552$ ($\varphi_I=0.700$ to $\varphi_I=0.800$). As can be seen from the solid-liquid equilibrium for (water + ethanol) mixture, positive synergistic effect can reach a maximum level in this range. It also can be thought that synergistic effect reaches a maximum. Figure 6 shows the solubility of three tropine-type ILs under different systems at the same temperature. The phase equilibrium of [Bntr][PF₆] are shown in Figure 7. From these Figures, it can be clearly found that there is a maximum synergies effect in binary solvent mixture. It was thought that solutes with stable intramolecular hydrogen bonds, forming stable associates in the solution showed the synergistic effects in binary solvents exhibiting $G_E > 0$ [25]. It should be also the main reason why tropine-type ILs occur cosolvency in water + ethanol binary system.

All the three tropine-type ILs have synergistic effects in binary solvent mixture, but the difference of cationic structure could have an impact on it. From the Figure 6 and

Figure 7, it can be clearly found that the maximum of dissolution property of [Bntr][PF₆] is the mole (volume) fraction of ethanol in binary solvent at $x_I=0.552$ ($\varphi_I=0.800$). But the solubility of [m-MBntr][PF₆] and [p-NBntr][PF₆] reach the maximum at $x_I=0.416$ ($\varphi_I=0.700$). It was thought the concentration range of maximum synergistic effect was similar to the azeotropic point. But from the data of solubility in this study, they have a certain difference (the concentration of azeotropic point is $x_I=0.044$)[25]. So it is possible that cosolvency should be more relative to the structure of solute. For these ILs discussed above, the structure of cation could play an important role on its cosolvency behavior.

3.2 Solid–liquid phase equilibrium correlation

3.2.1. Modified Apelblat equation

The dependence of solubility with temperature can be correlated by the modified Apelblat equation,[26, 27] the modified equation is described as:

$$\ln x_{IL} = A + \frac{B}{T} + C \ln T \quad (2)$$

where x_{IL} is the mole fraction solubility of ILs, T is the absolute temperature of the system, and A , B and C are all empirical constants. The values of A and B represent the variation in the solution activity coefficient, and the C value reflects the effect of temperature on the fusion enthalpy.[28]

3.2.2. λh (Buchowski) equation

Another way to describe the relationship between solubility and temperature with only two parameters λ and h is Buchowski–Ksiazaczak λh equation:[29-31]

$$\ln \left[1 + \lambda \left(\frac{1}{x_{IL}} - 1 \right) \right] = \lambda h \left(\frac{1}{T} - \frac{1}{T_m} \right) \quad (3)$$

where T_m is the melting temperature of ILs, λ and h stand for model parameters determined by the experimental data in the system, respectively. The value of λ is identified as the approximate mean association number of solute molecules, which reflects the nonideality of the solution system, and h is the excess mixing enthalpy of solution.[32]

3.2.3. Local Composition models

The equation frequently used for the correlation of the solid-liquid equilibrium data is:

$$\begin{aligned} -\ln x_{IL} = & \frac{\Delta_{fus}H_{IL}}{R} \left(\frac{1}{T} - \frac{1}{T_{fus,IL}} \right) + \frac{\Delta_{tr}H_{IL}}{R} \left(\frac{1}{T} - \frac{1}{T_{IL}} \right) \\ & - \frac{\Delta_{fus}C_{p,IL}}{R} \left(\ln \left(\frac{T}{T_{fus,IL}} \right) + \frac{T_{fus,IL}}{T} - 1 \right) + \ln \gamma_{IL} \end{aligned} \quad (4)$$

where γ_{IL} , x_{IL} , $\Delta_{fus}H_{IL}$, $\Delta_{fus}C_{p,IL}$, $T_{fus,IL}$, T , $T_{tr,IL}$ and $\Delta_{tr}H_{IL}$ are activity coefficient, mole fraction, enthalpy of fusion, difference in solute heat capacity between the liquid and solid phase at melting temperature, equilibrium temperature, transition temperature and enthalpy of the solid-solid phase transition, respectively. If a solid-solid phase transition occurs before fusion, the solubility equation for temperatures below that of the phase transition must include the effect of the transition. However, the ILs in our work would not occur solid-solid phase transition at the temperature below their melting point.

In this study, two local composition methods (the Wilson[33], NRTL[34] equations) which describe the Gibbs excess free energy of mixing (G^E) were used to represent

the solute activity coefficients (γ_1). The exact mathematical forms of those equations were presented in literature[35].

3.2.4 Correlation of the solubility data.

The methods to correlate the data of solubility can be evaluated with the *ARD*, (average relative deviation), *AAD* (average absolute deviation) and R^2 (coefficient of determination) as follow:

$$ARD = \frac{1}{N} \sum_{i=1}^N \frac{|x_{IL,i} - x_{IL,i}^{cal}|}{x_{IL,i}} \quad (5)$$

$$AAD = \frac{1}{N} \sum_{i=1}^N |x_{IL,i} - x_{IL,i}^{cal}| \quad (6)$$

$$R^2 = 1 - \frac{\sum_{i=1}^N (x_{IL,i} - x_{IL,i}^{cal})^2}{\sum_{i=1}^N (x_{IL,i} - \bar{x}_{IL,i})^2} \quad (7)$$

where $x_{IL,i}$ and $x_{IL,i}^{cal}$ represent the experimental and calculated solubility values respectively, $\bar{x}_{IL,i}$ is the average experimental solubility values, and N is the number of experimental point.

The correlation results of both equations are presented in [Table 5](#) and [Table 6](#). These indicate that both equations are suitable for correlation of the solubility of ILs in binary solvent mixture with temperature variation. The *ARD*, *AAD* and R^2 of four equations are list in [Table 7](#). For all models used in this work, the modified Apelblat equation shows best correlation with the overall ARD are 4.89% (NRTL), 3.04% (Wilson), 1.33% (modified Apelblat), and 5.26% (λh), respectively. These results can be interpreted to predict that there is a very complex interaction between the molecules in the solution: the self-association of the solvent; the self-association of

the IL and opposing these two associations is a solvent-IL interaction[36]. In addition, the result of fitting in binary solvent mixture is better than those in ternary systems using NRTL model, while the conditions of Wilson are completely opposite. Modified Apelblat equation is suitable for all systems. From a general view, the correlation goodness of the selected models ranks is as following order: modified Apelblat equation > Wilson model > NRTL model > λh equation.

4. Conclusion

Solubility of the three tropine-type ILs in water, ethanol and their binary solvent mixture at a series of temperatures was determined and further correlated by two empirical equations and two theoretical models with good agreement. The cosolvency phenomenon exists in binary solvent mixture (water + ethanol) and can prompt much higher ILs solubility in binary solvent than in single solvent. The cosolvency varies largely with composition of binary mixture and appears more obvious at higher temperature. The difference of solubility of tropine-type ILs in water, ethanol and binary solvent mixture could suggest that the competition between hydrogen bonded ILs molecules, hydrogen bonded solvent molecules and the interaction of unlike molecules is an important factor for determining the phase behaviour. A positive synergistic effect can promote the dissolution of ILs in binary solvents which has been noted in all binary solvent mixture in this study. The solubility of ILs in single solvent is low while the solubility in binary solvent is high. Therefore, the IL can be dissolved at binary solvent system and be recovered by adding water or ethanol. On the other

side, IL and solvents can be perfectly separated by cooling since the solubility of IL in single solvent (water, ethanol) at low temperature is small. The solubility and cosolvency would provide a new way to dissolve and recover ILs, especially in hydrophilic system.

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Figure 1. The FTIR of [Bntr][PF₆] before and after measurement: —, [Bntr][PF₆] before measurement; —, [Bntr][PF₆] after measurement.

Figure 2. Solubility of benzoic acid in binary solvent mixture of ethanol + heptane as a function of temperature: ○, the experimental values; □, the literature values.

Figure 3. DSC at the scan rate 10 K·min⁻¹. (a) [Bntr][PF₆]; (b) [*m*-MBntr][PF₆]; (c) [*p*-NBntr][PF₆];

Figure 4. The solubility of three tropine-type ILs in water(a), 40% ethanol(b), 70% ethanol(c) and ethanol(d), respectively. ▲, [Bntr][PF₆]; ■, [*m*-MBntr][PF₆]; ●, [*p*-NBntr][PF₆]; —, calculated values by the modified Apelblat equation.

Figure 5. The main infrared absorption peak of hydroxy at tropine ring above 3000 cm⁻¹.

Figure 6. The solubility of [Bntr][PF₆](a), [*m*-MBntr][PF₆](b) and [*p*-NBntr][PF₆](c) in binary solvent mixture from 313.15 K to 333.15 K, respectively. ■, 313.15 K; ●, 318.15 K, ▲, 323.15 K; ▼, 328.15 K; ✱, 333.15 K; —calculated values by the modified Apelblat equation.

Figure 7. The solubility of [Bntr][PF₆] in different binary solvent mixture from 278.15 K to 333.15 K, respectively. ■, water; □, 20% ethanol; ●, 40% ethanol; ○, 50% ethanol; ▲, 60% ethanol; △, 70% ethanol; ◆, 80% ethanol; ◇, 90% ethanol; ✱, ethanol; —, calculated values by the modified Apelblat equation.

Table 1

Names and structures of three kinds of tropine-type ionic liquids

Name	abbreviation	Structure
N-benzyl-tropine hexafluorophosphate	[Bntr][PF ₆]
N-(3-methoxybenzyl)-tropine hexafluorophosphate	[<i>m</i> -MBntr][PF ₆]
N-(4-nitrobenzyl)-tropine hexafluorophosphate	[<i>p</i> -NBntr][PF ₆]

406 **Table 2**
 407 Physical constants of the pure tropine-type ILs.

Ionic liquid	$V_m^{298.15K}$	$T_{fus,IL}$ (K)	$\Delta_{fus}H_{IL}$ (kJ·mol ⁻¹)	$\Delta_{fus}C_{p,IL}$ (J·mol ⁻¹ ·K ⁻¹)
[Bntr][PF ₆]	307.4	420.97	19.17	8.05
[<i>m</i> -MBntr][PF ₆]	344.7	439.31	29.79	26.59
[<i>p</i> -NBntr][PF ₆]	337.1	519.78	25.87	11.22

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Table 3

Mole fraction solubility of the three ILs in water, ethanol and their binary solvent mixture from 278.15 K to 303.15 K

φ_I	x_I	$10^4 x_{IL}$					
		278.15 K	283.15 K	288.15 K	293.15 K	298.15 K	303.15 K
[Bntr][PF ₆]							
0.000	0.000	1.61	1.85	2.23	2.55	2.92	3.73
0.200	0.071	1.69	2.24	2.84	3.89	4.99	6.41
0.400	0.170	4.01	5.29	6.86	9.18	11.7	15.2
0.500	0.234	9.12	10.7	12.9	15.6	20.0	24.9
0.600	0.315	13.2	15.5	19.4	25.5	32.4	40.0
0.700	0.416	16.4	19.3	23.2	29.5	37.7	47.8
0.800	0.552	18.5	21.4	26.4	33.1	40.5	50.9
0.900	0.733	10.6	14.0	17.2	21.2	25.9	34.0
1.000	1.000	5.68	6.67	7.49	8.61	10.3	12.6
[<i>m</i> -MBntr][PF ₆]							
0.000	0.000	0.96	1.11	1.31	1.53	1.78	2.13
0.200	0.071	0.96	1.26	1.65	2.16	2.78	3.62
0.400	0.170	2.31	3.00	4.05	4.05	7.05	9.14
0.500	0.234	4.27	5.46	7.08	9.35	12.6	16.2
0.600	0.315	6.05	7.77	9.83	12.6	16.6	21.2
0.700	0.416	7.39	9.13	11.5	15.1	18.8	24.2
0.800	0.552	7.55	9.78	12.1	15.4	19.3	24.6
0.900	0.733	5.68	6.94	8.78	10.8	13.8	17.4
1.000	1.000	2.76	3.37	4.21	5.03	6.11	7.37
[<i>p</i> -NBntr][PF ₆]							
0.000	0.000	0.32	0.39	0.47	0.55	0.66	0.77
0.200	0.071	0.35	0.46	0.59	0.75	0.95	1.20
0.400	0.170	0.75	0.94	1.19	1.52	1.90	2.42
0.500	0.234	1.15	1.47	1.82	2.57	2.86	3.51
0.600	0.315	1.57	2.00	2.45	3.01	3.75	4.52
0.700	0.416	2.19	2.47	2.90	3.55	4.19	5.15
0.800	0.552	1.97	2.34	2.73	3.24	3.89	4.76
0.900	0.733	1.41	1.65	1.89	2.27	2.65	3.15
1.000	1.000	0.38	0.44	0.50	0.60	0.69	0.81

The relative standard uncertainty is: $10^4 u(x_{IL}) = \pm 0.01$, $u(T) = \pm 0.05$, $u(p) = \pm 0.05$. The experiment is conducted under atmosphere pressure.

φ_I and x_I are the volume and mole fractions of ethanol (1) in the solvent mixture free of tropine ILs(3), respectively.

x_{IL} is the mole fraction of the solubility of ILs at the system temperature T .

Table 4

Mole fraction solubility of the three ILs in water, ethanol and their binary solvent mixture from 308.15 K to 333.15K

φ_I	x_I	$10^4 x_{II}$					
		308.15 K	313.15 K	318.15 K	323.15 K	328.15 K	333.15 K
[Bntr][PF ₆]							
0.000	0.000	4.22	4.91	5.67	7.05	8.80	9.96
0.200	0.071	8.02	9.43	11.7	16.1	19.0	24.0
0.400	0.170	21.4	27.6	35.9	49.0	61.5	80.6
0.500	0.234	32.4	42.5	55.9	76.3	103	151
0.600	0.315	53.0	70.4	96.5	135	191	284
0.700	0.416	62.6	81.7	111	154	218	324
0.800	0.552	70.5	92.1	128	172	268	373
0.900	0.733	42.6	54.3	70.4	92.7	124	180
1.000	1.000	14.9	18.0	22.6	27.7	35.6	45.7
[<i>m</i> -MBntr][PF ₆]							
0.000	0.000	2.56	2.99	3.76	4.67	5.44	6.57
0.200	0.071	4.74	6.08	7.70	9.88	12.5	16.0
0.400	0.170	12.5	16.8	21.5	28.2	35.2	48.4
0.500	0.234	21.2	27.1	35.9	46.8	60.2	80.0
0.600	0.315	28.9	36.4	47.8	64.4	85.6	117
0.700	0.416	31.4	41.1	55.3	75.9	100	136
0.800	0.552	31.5	41.0	56.1	75.0	99.8	136
0.900	0.733	24.4	30.7	36.9	49.8	67.2	86.1
1.000	1.000	9.45	11.7	14.5	19.2	23.2	29.3
[<i>p</i> -NBntr][PF ₆]							
0.000	0.000	0.93	1.07	1.28	1.53	1.81	2.27
0.200	0.071	1.48	1.91	2.41	2.98	3.55	4.35
0.400	0.170	3.08	3.90	4.85	6.01	7.26	8.25
0.500	0.234	4.47	5.56	6.79	8.51	10.7	12.4
0.600	0.315	5.67	6.59	8.72	10.8	13.3	16.5
0.700	0.416	6.44	7.95	9.67	12.0	15.0	18.3
0.800	0.552	5.81	6.83	8.40	10.1	12.6	15.5
0.900	0.733	3.68	4.41	5.25	6.46	7.67	9.31
1.000	1.000	0.94	1.11	1.34	1.61	1.93	2.31

The relative standard uncertainty is: $10^4 u(x_{IL}) = \pm 0.01$, $u(T) = \pm 0.05$, $u(p) = \pm 0.05$. The experiment is conducted under atmosphere pressure.

Table 5

Correlation of the solubility data of (ethanol(1) + water(2) + ILs) ternary systems by means of Apelblat and λh equations: values of parameters and measures of deviations.

φ_I	x_I	Apelblat				λh		
		A	B	C	10^2ARD	λ	h	10^2ARD
[Bntr][PF ₆]								
0.000	0.000	-205.21	6316	30.88	1.88	0.0047	603164	3.45
0.200	0.071	1.15	-4179	0.92	2.38	0.0346	126217	2.47
0.400	0.170	-195.34	4248	30.60	1.38	0.1665	30141	3.79
0.500	0.234	-597.80	22831	90.39	0.91	0.2023	23250	10.05
0.600	0.315	-654.71	25044	99.15	1.83	0.3991	12197	10.13
0.700	0.416	-647.81	24873	98.07	1.34	0.4755	10325	10.68
0.800	0.552	-767.23	30180	115.92	1.88	0.5997	8374	12.38
0.900	0.733	-441.33	15915	67.05	2.26	0.1782	23852	7.15
1.000	1.000	-448.39	17044	67.46	1.00	0.0237	134215	6.99
[m -MBntr][PF ₆]								
0.000	0.000	-267.89	8977	40.22	1.09	0.0051	608571	4.66
0.200	0.071	-116.39	871	18.48	0.37	0.0436	107257	2.11
0.400	0.170	-177.70	3352	27.94	1.43	0.1758	28946	3.05
0.500	0.234	-209.46	4964	32.66	0.99	0.2572	19202	3.13
0.600	0.315	-370.63	12297	56.69	0.99	0.3016	15893	5.80
0.700	0.416	-431.26	15075	65.71	0.83	0.3430	13918	7.47
0.800	0.552	-459.33	16457	69.83	1.28	0.3144	14818	7.84
0.900	0.733	-370.58	12581	56.48	1.93	0.1915	23567	6.05
1.000	1.000	-288.81	9379	43.87	1.22	0.0342	107944	5.31
[p -NBntr][PF ₆]								
0.000	0.000	-139.95	3215	20.98	1.20	0.0051	594028	2.43
0.200	0.071	-40.19	-2194	6.72	0.98	0.0418	101681	1.32
0.400	0.170	-86.36	-55	13.69	1.83	0.0863	49350	2.13
0.500	0.234	-121.82	1681	18.96	1.03	0.0907	44304	2.26
0.600	0.315	-183.07	4602	28.04	1.17	0.0969	39962	3.77
0.700	0.416	-296.38	9929	44.81	1.30	0.0888	41839	5.21
0.800	0.552	-269.53	8895	40.69	0.76	0.0525	64850	4.25
0.900	0.733	-235.77	7608	35.46	0.70	0.0218	140868	4.07
1.000	1.000	-239.72	7839	35.78	0.84	0.0050	599989	4.33

Table 6

Correlation of the solubility data of (ethanol(1) + water(2) + ILs) ternary systems by means of Wilson and NRTL equations: values of parameters and measures of deviations.

φ_I	x_I	NRTL (J mol ⁻¹)			Wilson (J mol ⁻¹)		
		g_{12} - g_{11}	g_{21} - g_{22}	10^2ARD	g_{12} - g_{11}	g_{21} - g_{22}	10^2ARD
[Bntr][PF ₆]							
0.000	0.000	-7033.66	32100.73	1.98	5266.10	25857.78	3.03
0.200	0.071	-1211.70	14890.86	7.13	6649.89	7641.77	4.26
0.400	0.170	-5835.92	24114.25	8.66	5563.11	6369.30	3.67
0.500	0.234	-5128.68	20425.78	6.54	4179.17	6322.82	2.15
0.600	0.315	-4432.85	17159.60	5.47	3807.51	5656.88	1.60
0.700	0.416	-4278.94	16387.94	4.38	3714.14	5338.93	1.68
0.800	0.552	-4461.88	16780.27	9.14	3996.29	4844.67	2.27
0.900	0.733	-4850.17	18976.39	6.39	5027.35	4831.64	0.80
1.000	1.000	-4981.19	21280.34	4.00	5706.87	7753.87	5.41
[<i>m</i> -MBntr][PF ₆]							
0.000	0.000	-7414.18	31128.29	1.40	2702.45	89814.43	5.57
0.200	0.071	-472.29	11899.80	2.96	4143.93	7415.71	0.91
0.400	0.170	-1057.72	10097.43	14.29	3592.89	5849.59	2.04
0.500	0.234	-1441.40	9281.90	12.08	2340.68	5664.43	1.40
0.600	0.315	-6177.54	20764.77	7.07	2224.90	5151.62	1.48
0.700	0.416	-6084.68	20129.73	5.66	2346.41	4721.65	2.77
0.800	0.552	-6044.09	19897.23	4.86	2650.79	4353.40	3.28
0.900	0.733	-6325.25	21775.34	5.20	3159.33	4390.12	3.24
1.000	1.000	-5634.76	20889.29	2.57	3310.72	7041.59	4.31
[<i>p</i> -NBntr][PF ₆]							
0.000	0.000	-6696.07	28832.24	1.26	3755.20	55002.24	3.05
0.200	0.071	-2772.28	16595.98	1.15	5057.73	7650.22	1.20
0.400	0.170	-577.54	11558.99	2.18	4035.83	6856.76	1.76
0.500	0.234	-1369.92	11590.78	1.97	3230.75	6667.97	1.26
0.600	0.315	-2522.50	12732.56	3.32	2700.52	6520.47	2.29
0.700	0.416	-3816.43	15037.10	4.53	2271.30	6677.36	4.31
0.800	0.552	-5015.36	18465.81	3.10	2004.39	8040.14	3.65
0.900	0.733	-6246.86	23646.27	2.45	2677.42	12375.92	4.00
1.000	1.000	-7042.44	30128.18	2.29	6666.11	57730.28	10.69

Table 7

The total average ARD , AAD and R^2 of four equations.

parameter error	fitted equation			
	Apelblat	λh	Wilson	NRTL
$ARD/\%$	1.33	5.26	3.04	4.89
$AAD/10^4$	0.43	2.95	1.45	2.73
R^2	0.999	0.988	0.995	0.991

434 Figure 1

435

436 Figure 2

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438 Figure 3

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440 Figure 4

441
442 Figure 5

443
444 Figure 6

Figure 7

Graphical Abstract