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Solubilities of 1-Ethylpyridinium Hexafluorophosphate in Ethanol + Water from (278.15 to 345.15) K

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Using a laser monitoring observation technique, the solubilities of 1-ethylpyridinium hexafluorophosphate in ethanol + water binary solvent mixtures have been measured from (278.15 to 345.15) K. The experimental data were well correlated with the modified Apelblat equation. The solubility of 1-ethylpyridinium hexafluorophosphate in ethanol + water is higher than that in water and ethanol, respectively, and reaches the maximum value when the mass fraction (*w*) of water in the ethanol + water binary solvent mixtures is equal to 0.40.

Introduction

Ionic liquids (ILs) have been the object of increasing attention due to their unique physicochemical properties such as high thermal stability, high ionic conductivity, high solvating capacity, negligible vapor pressure, and nonflammability that make them ideal solvents for green chemistry and clean synthesis.[1−7] They are generally salts based on a substituted imidazolium or pyridinium cation and an inorganic anion such as a halide, $[BF_4]^-$, or $[PF_6]^-$ and are very often liquids at room temperature. The use of ionic liquids as solvents for a broad range of chemical processes is potentially one of the most significant developments of the past decade.[1,8]

To design any process involving ILs on an industrial scale, it is necessary not only to know a range of physical properties including viscosity, density, melting point temperature, electrochemical window, heat capacity, and interfacial tension but also to know other thermodynamic properties including phase equilibria such as vapor−liquid equilibria, liquid−liquid equilibria (LLE), and solid−liquid equilibria (SLE). The solubilities of ILS in different solvents have been investigated extensively.[9−14] In this study, the solubilities of solid 1-ethylpyridinium hexafluorophosphate ([EPy][PF_6]) in the ethanol + water binary solvent mixture have been measured from (278.15 to 345.15) K by a laser monitoring observation technique at atmospheric pressure. The experimental data were correlated with the modified Apelblat equation.[15,16]

Experimental Section

Materials. High-grade 1-ethylpyridinium hexafluorophosphate ([EPy][PF_6]) from IoLiTec Ionic Liquids Technologies GmbH & Co. KG was used directly without further purification, and its purity was determined by high-performance liquid chromatography (type Waters 600E, Waters Co.) to be greater than 0.99 in mass fraction. The melting point temperature (T_m) is 376.35 K measured by differential scanning calorimetry (type Q20, TA Instruments). The molecular structure of [EPy][PF_6] is illustrated in Figure 1. High-grade ethanol from Tianjin Kemel Chemical Reagent Co., Ltd. was used directly without further purification, and its mass fraction purity was greater than 99 %. The water content in ionic liquid is less than 10 ppm measured by the Karl Fischer method. The water used in the experiments was double distilled water.

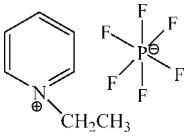

Figure 1. Molecular structure of [EPy][PF_6].

Apparatus and Procedure. The solubilities were measured by a dynamic method at atmospheric pressure.[15,16] The laser monitoring observation technique[17,18] was used to determine the dissolution temperature of a solid−liquid mixture of known composition. The experiments were carried out in a magnetically stirred, jacketed glass vessel (80 cm^3). A constant temperature (± 0.02 K) was maintained by circulating water through the outer jacket from a thermostatically controlled super constant temperature water-bathing (type HWC-52, Shanghai Cany Precision Instrument Co., Ltd.) at the required temperature. A condenser was connected with the vessel to prevent the solvent from evaporating. A mercury-in-glass thermometer was inserted into the inner chamber of the vessels for the measurement of the temperature. The uncertainty of temperature was ± 0.05 K. A laser beam was used to observe the dissolution of the solid−liquid mixture. The light signal transmitted through the vessel was collected by a detector (type FGF-III), which decided the rate of temperature rise and estimated the equilibrium point of the EtOH + H_2O on the basis of the signal change.[19]

Solvents for the solubility measurement were prepared by mass using an analytical balance (type XS104, Mettler-Toledo Co.). The balance has a range of measurement up to 120 g, with an uncertainty of ± 0.0001 g. Before the solubility measurement, through the condenser, high-purity nitrogen (99.9995 % by mass, 30 $mL \cdot min^{-1}$) was fed into the solvent for 1 h to remove the dissolved oxygen. Predetermined amounts of [EPy][PF_6] were weighed and transferred into the vessel. The contents of the vessel were heated very slowly at rates less than 3 $K \cdot h^{-1}$ with continuous stirring. In the processes of solubility measurement, some of the solubility experiments were conducted two or three times to check the reproducibility. The

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Table 1. Mole Fraction Solubilities (x) of [EPy][PF_6] in (w) Water + (1 − w) Ethanol, Where w is the Mass Fraction

T/K	10^2x	$10^2\Delta x^a$	T/K	10^2x	$10^2\Delta x^a$
$w = 0.00$					
278.15	0.0084	0.00	313.15	0.0718	−13.79
283.15	0.0121	0.00	318.15	0.0976	−11.07
288.15	0.0171	0.00	323.15	0.1497	4.74
293.15	0.0224	−6.69	328.15	0.1891	1.64
298.15	0.0324	−1.85	333.15	0.2519	4.45
303.15	0.0561	19.61	338.15	0.3076	−0.49
308.15	0.0610	0.00	343.15	0.3894	−1.16
$w = 0.10$					
278.15	0.1645	0.00	313.15	0.5109	−0.61
283.15	0.2001	0.00	318.15	0.5830	0.15
288.15	0.2404	0.00	323.15	0.6673	1.99
293.15	0.2883	0.94	328.15	0.7351	0.82
298.15	0.3348	0.24	333.15	0.8011	−0.75
303.15	0.3891	0.36	338.15	0.8891	0.19
308.15	0.4430	1.58	343.15	0.9633	−0.62
$w = 0.20$					
278.15	0.2540	0.00	313.15	0.6811	−1.31
283.15	0.3025	0.00	318.15	0.7639	−0.38
288.15	0.3562	0.03	323.15	0.8488	0.39
293.15	0.4134	0.27	328.15	0.9343	0.94
298.15	0.4808	0.69	333.15	1.0020	−0.41
303.15	0.5409	0.72	338.15	1.0862	−0.03
308.15	0.6230	1.16	343.15	1.1647	−0.10
$w = 0.30$					
278.15	0.2414	0.04	313.15	0.7085	−0.49
283.15	0.2932	0.03	318.15	0.7946	0.08
288.15	0.3507	0.03	323.15	0.8831	0.67
293.15	0.4162	0.58	328.15	0.9705	1.03
298.15	0.4843	0.43	333.15	1.0473	0.43
303.15	0.5510	0.76	338.15	1.1210	−0.20
308.15	0.6252	1.09	343.15	1.1923	−0.70
$w = 0.40$					
278.15	0.2352	0.00	313.15	0.7387	0.46
283.15	0.2901	0.03	318.15	0.8211	0.16
288.15	0.3516	0.03	323.15	0.8986	−0.58
293.15	0.4213	0.47	328.15	0.9846	−0.13
298.15	0.4913	0.24	333.15	1.0498	−1.42
303.15	0.5553	2.70	338.15	1.1523	1.15
308.15	0.6698	2.70	343.15	1.2077	−0.01
$w = 0.50$					
278.15	0.2139	0.00	313.15	0.6007	−0.05
283.15	0.2568	0.00	318.15	0.6702	0.19
288.15	0.3043	0.03	323.15	0.7381	−0.01
293.15	0.3523	1.08	328.15	0.8032	−0.61
298.15	0.4152	0.72	333.15	0.8728	−0.61
303.15	0.4742	0.44	338.15	0.9374	−1.06
308.15	0.5381	0.54	343.15	1.0299	1.45
$w = 0.60$					
278.15	0.1628	0.00	313.15	0.4673	−0.68
283.15	0.1964	0.00	318.15	0.5224	−0.54
288.15	0.2338	0.00	323.15	0.5804	−0.12
293.15	0.2736	0.48	328.15	0.6427	0.79
298.15	0.3211	0.50	333.15	0.6959	0.24
303.15	0.3705	0.89	338.15	0.7511	0.11
308.15	0.4162	0.36	343.15	0.8024	−0.36
$w = 0.70$					
278.15	0.1204	0.00	313.15	0.3942	0.66
283.15	0.1477	0.00	318.15	0.4436	−0.18
288.15	0.1789	0.00	323.15	0.4947	−1.05
293.15	0.2109	1.42	328.15	0.5506	−1.31
298.15	0.2544	0.63	333.15	0.6141	−0.54
303.15	0.2991	1.20	338.15	0.6866	1.19
308.15	0.3435	0.49	343.15	0.7420	0.26
$w = 0.80$					
278.15	0.0981	0.51	313.15	0.3245	1.05
283.15	0.1208	1.44	318.15	0.3741	1.60
288.15	0.1439	0.13	323.15	0.4298	2.50
293.15	0.1741	1.33	328.15	0.4857	2.44
298.15	0.1932	5.30	333.15	0.5345	0.39
303.15	0.2340	2.05	338.15	0.5916	−0.52
308.15	0.2747	1.20	343.15	0.6434	−2.64
$w = 0.90$					
278.15	0.0862	0.00	313.15	0.2737	−0.11
283.15	0.1035	0.00	318.15	0.3168	0.16
288.15	0.1235	0.08	323.15	0.3646	0.30
293.15	0.1453	0.83	328.15	0.4157	−0.02
298.15	0.1752	1.37	333.15	0.4735	−0.04
303.15	0.2036	0.54	338.15	0.5370	−0.09
308.15	0.2330	1.37	343.15	0.6079	0.07
$w = 1.00$					
278.15	0.0474	0.00	313.15	0.1861	0.11
283.15	0.0581	0.00	318.15	0.2162	−3.33
288.15	0.0711	0.00	323.15	0.2603	−2.80
293.15	0.0857	1.17	328.15	0.3247	1.54
298.15	0.1051	0.29	333.15	0.3866	1.42
303.15	0.1301	1.84	338.15	0.4541	0.24
308.15	0.1588	2.83	343.15	0.5352	−0.39

[a] $\Delta x = (x - x_{cal.})/x$, where $x_{cal.}$ is the solubility value calculated from eq 1.

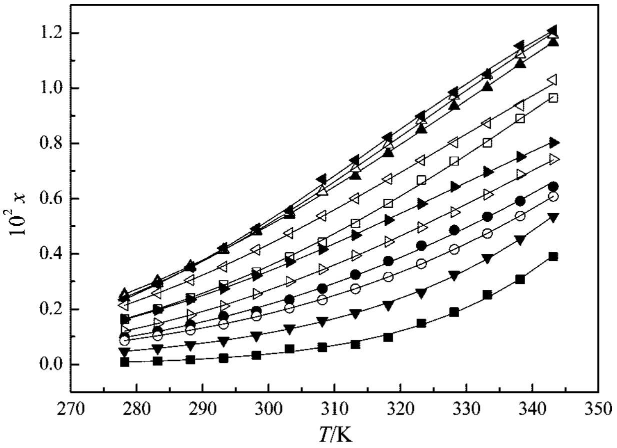

Figure 2. Solubilities of [EPy][PF_6] in (w) water + (1 − w) ethanol, where w is the mass fraction. ■, $w = 0.00$; □, $w = 0.10$; ▲, $w = 0.20$; △, $w = 0.30$; solid triangle pointing left, $w = 0.40$; open triangle pointing left, $w = 0.50$; solid triangle pointing right, $w = 0.60$; open triangle pointing right, $w = 0.70$; ●, $w = 0.80$; ○, $w = 0.90$; ▼, $w = 1.00$; —, calculated from eq 1.

Table 2. Parameters of Equation 1 for the [EPy][PF_6] + Water + Ethanol System at Various Contents of Water (w) in the Mixed Solvent

w	A	B	C	10^4 (rmsd)
0.00	14.12	−5791.71	−0.48	0.63
0.10	118.82	−7908.27	−17.20	0.51
0.20	127.20	−7965.58	−18.57	0.44
0.30	170.88	−10065.10	−25.00	0.48
0.40	220.40	−12373.08	−32.33	0.84
0.50	144.78	−8818.62	−21.18	0.54
0.60	149.53	−9099.71	−21.90	0.23
0.70	137.68	−8837.95	−20.01	0.37
0.80	81.48	−6392.37	−11.62	0.73
0.90	8.60	−3112.69	−0.79	0.12
1.00	−76.62	177.44	12.14	0.37

reproducibility of the measurements was 0.1 K, which corresponds to a relative error in composition smaller than ± 1 %.[20] In this work, the uncertainty for solubility measurement is estimated on the basis of the principle of the error propagation to be 2.0 % at the 95 % confidence level.

Results and Discussion

To our knowledge, this is the first time the solubilities of [EPy][PF_6] IL has been measured. The measured mole fraction solubilities (x) of [EPy][PF_6] in the ethanol + water binary solvent mixture at different temperatures (T) are presented in Table 1. The mass fraction (w) of water in the solvents was 0, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, and 1.00, respectively. The experimental values and calculated values are shown in Figure 2. The relationship between mole fraction of the solubility and temperature is described by the modified Apelblat equation.[20,21]

$$\ln x = A + \frac{B}{T/\mathrm{K}} + C\ln(T/\mathrm{K}) \qquad (1)$$

where x is the mole fraction solubility of [EPy][PF_6]; T is the absolute temperature; and A, B, and C are empirical constants. The values of A, B, and C obtained from the experimental solubility data in the systems together with the root-mean-square deviations (rmsd's) are listed in Table 2, respectively. The rmsd is defined as

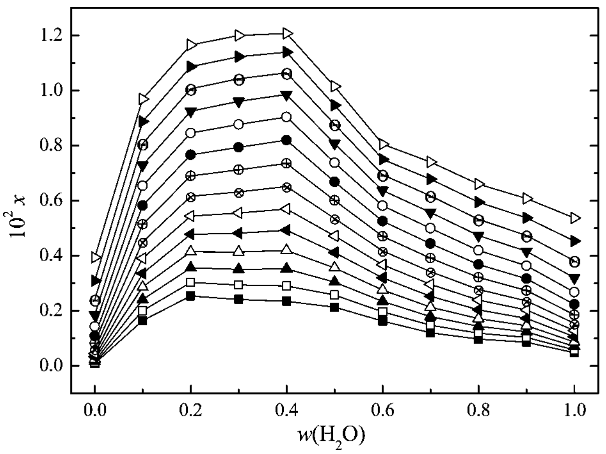

Figure 3. Dependence of the solubilities (x) calculated from eq 1 at (278.15 to 345.15) K on the mass fraction (w) of water in the [EPy][PF_6] + water + ethanol system. ■, $T = 278.15$ K; □, $T = 283.15$ K; ▲, $T = 288.15$ K; △, $T = 293.15$ K; solid triangle pointing left, $T = 298.15$ K; open triangle pointing left, $T = 303.15$ K; ⊗, $T = 308.15$ K; ⊕, $T = 313.15$ K; ●, $T = 318.15$ K; ○, $T = 323.15$ K; ▼, $T = 328.15$ K; Θ, $T = 333.15$ K; solid triangle pointing right, $T = 338.15$ K; open triangle pointing right, $T = 343.15$ K; —, calculated from eq 1.

$$\text{rmsd} = \left[\sum_{i=1}^{N} \frac{(x_{ci} - x_i)^2}{N}\right]^{1/2} \qquad (2)$$

where N is the number of experimental points and x_c is the solubility calculated by eq 1.

Table 1, Table 2, and Figure 2 show that the calculated solubilities are in good agreement with the experimental data, which indicate that the modified Apelblat equation can be used to correlate the solubility data of [EPy][PF_6] in ethanol + water. The overall rmsd of 154 data points for the ethanol + water system at various contents of water in the mixed solvent is 0.0053 %. The experimental solubility and correlation equation in this work can be used as essential data and models to serve the synthesis and purification process of [EPy][PF_6].

By using the data shown in Table 1, the dependence of the solubilities x calculated from eq 1 and values of A, B, and C on the mass fraction w of water in solvent for the [EPy][PF_6] + ethanol + water system were given in Figure 3. It showed the relations between the solubility and the composition of the mixed solvent at fixed temperatures. From the results shown in Table 1 and Figure 3, it can be seen that the solubility of [EPy][PF_6] in the ethanol + water mixture is higher than that in water and ethanol, respectively. It also can be seen from Figure 3 that solubility of [EPy][PF_6] in the ethanol + water system has a maximum value at $w = 0.40$. According to Scatchard−Hildebrand's theory,[22] the solubility of a solid is a maximum in that solvent whose solubility parameter is the same as that of the (liquid) solute; therefore, a plot of solubility versus solvent composition should go through a maximum. Therefore, the solubility of the solute in the solvent is the largest when the solubility parameters (δ) of the solute and the solvent are the same. For the binary solvent system of A and B, it is possible that the solubility got to be the maximum when the solubility parameter met the following relationship: $\delta_A < \delta_1 < \delta_B$. The values of the solubility parameter of [EPy][PF_6], ethanol, and water are 30.25 $J^{1/2} \cdot cm^{-3/2}$ (calculated by the inverse gas chromatography method[23]), 26.39 $J^{1/2} \cdot cm^{-3/2}$, and 47.90 $J^{1/2} \cdot cm^{-3/2}$, respectively, so the solubility of [EPy][PF_6] may get to be the maximum in the binary solvent system of ethanol and water, which may be used to serve the purification process of [EPy][PF_6].

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