Solubilities of 1,1-(Hexane-1,6-diyl)-bis(pyridinium) Dihexafluorophosphate in (Water + Acetone)

Xu-Zhao Yang,* Jun Wang, and Zhen-Zhen Zhang

Henan Provincial Key Labortory of Surface and Interface Science, Zhengzhou University of Light Industry,
Henan 450002, People's Republic of China

The solubilities of 1,1-(hexane-1,6-diyl)-bis(pyridinium) dihexafluorophosphate in a solvent of (acetone + water) were determined at temperatures from (288.15 to 328.35) K by a synthetic method at atmospheric pressure of 0.1 MPa. The experimental data were well correlated with the modified Apelblat equation.

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 inflammability.[1−4] Dicationic ionic liquids have been shown to possess superior physical properties in terms of thermal stability and volatility compared to traditional ionic liquids.[5,6]

To design any process involving ionic liquids on an industrial scale, it is necessary to know a range of physical properties, including viscosity, density, interfacial tension, and heat capacity, as well as solid−liquid equilibrium (SLE) data. An understanding of SLE is of paramount importance for the design of separation processes, especially antisolvent crystallization. There is a pressing need to develop better solvents for separation. The solubilities of ILs in different solvents have been investigated extensively.[7−12] In this study, the solubilities of solid 1,1-(hexane-1,6-diyl)-bis(pyridinium) dihexafluorophosphate ($[C_6(Py)_2][PF_6]_2$) in a solvent of (acetone + water) have been measured at temperatures from (288.15 to 328.35) K by a laser monitoring observation technique at atmospheric pressure. The experimental data were correlated by the modified Apelblat equation.[13]

Experimental Section

Materials. High-grade acetone was obtained from Tianjin Kemel Chemical Reagent Co., Ltd., with a a mass fraction purity greater than 0.99 and was used directly without further purification. $[C_6(Py)_2][PF_6]_2$, of structure shown in Figure 1, was obtained from our Key Laboratory with a mass fraction purity as determined by high-performance liquid chromatography (type Waters 600E, Waters Co.) of greater than 0.99 and was stored under nitrogen. Analysis for water contamination using the Karl Fischer technique (method TitroLine KF) for the IL showed the water mass fraction was less than 0.0001. The melting point temperature (T_m) of $[C_6(Py)_2][PF_6]_2$ was determined, with a digital melting point apparatus (type RY-51, Shanghai Precision & Scientific Instrument Co. Ltd.) between (507.25 and 508.05) K. The water used in the experiments was doubly distilled.

Apparatus and Procedure. The solubilities were measured by a dynamic method at atmospheric pressure of about 0.1 MPa.[14] The laser monitoring observation technique 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 of volume about 20 cm^3. A temperature was maintained by circulating water through the outer jacket from a super thermostatic water-circulator bath (type HWC-52, Shanghai Cany Precision Instrument Co., Ltd.) at the required temperature with a variation of ± 0.05 K. A condenser was connected with the vessel to prevent the solvent from evaporating. A calibrated mercury-in-glass thermometer was inserted into the inner chamber of the vessels for the measurement of the temperature. The laser monitoring system consists of a laser generator, a photoelectric transformer, and a light intensity display. 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). From this measurement, the rate of temperature increase was estimated. The equilibrium with (acetone + water) was determined based on the signal change. At commencement of the experiment, the laser beam path was scattered by unsolved $[C_6(Py)_2][PF_6]_2$ particles suspended in solution resulting in a decrease of intensity of the laser beam that had traversed the

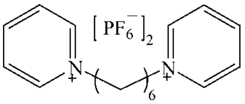

Figure 1. Molecular structure of $[C_6(Py)_2][PF_6]_2$.

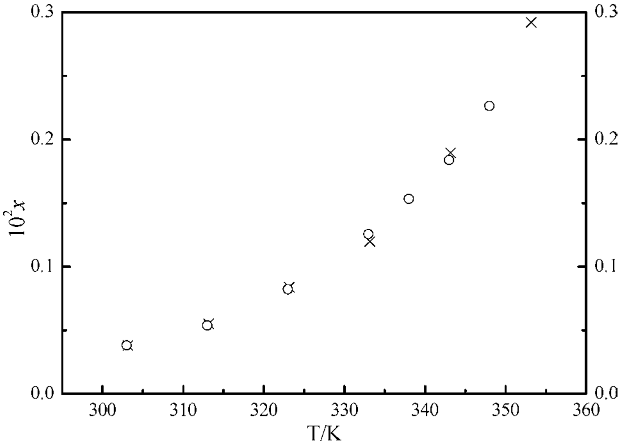

Figure 2. Solubility of 2-hydroxybenzoic acid in water: ×, this work; ○, literature.[13]

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* Corresponding author. E-mail: xuzhao5378@sina.com.

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Table 1. Mole Fraction Solubilities (x) of $[C_6(Py)_2][PF_6]_2$ in (w) Water + (1 − w) Acetone, Where w is the Mass Fraction

T/K	10^2x	$10^2\Delta x^a$	T/K	10^2x	$10^2\Delta x^a$
$w = 0.00$					
288.15	0.3987	0.71	308.15	0.4583	0.79
293.15	0.4015	0.75	313.15	0.5094	0.23
298.15	0.4088	0.34	317.15	0.5588	0.62
303.15	0.4307	0.57	322.35	0.6552	0.71
$w = 0.10$					
289.25	0.7731	0.36	312.85	1.4710	0.57
295.15	0.9183	1.67	317.95	1.7101	1.14
299.65	1.0044	1.28	322.35	1.9272	0.39
303.65	1.1346	0.10	326.55	2.1529	0.80
308.45	1.2755	1.38			
$w = 0.20$					
288.15	0.7128	0.65	312.95	1.4018	1.02
294.15	0.8293	0.19	318.25	1.6204	0.79
298.45	0.9285	0.47	322.25	1.8096	0.67
303.15	1.0490	1.03	328.15	2.0982	1.07
308.65	1.2280	0.35			
$w = 0.30$					
288.15	0.4925	0.60	312.75	1.0542	0.64
294.15	0.5770	0.69	318.25	1.258	0.56
298.15	0.6501	0.72	322.45	1.4657	0.08
303.15	0.7675	0.34	327.15	1.7376	0.02
308.85	0.9239	0.46			
$w = 0.40$					
288.75	0.2788	0.05	312.15	0.7318	0.24
293.75	0.3534	0.43	317.65	0.8794	0.32
298.65	0.4312	1.01	323.15	1.0400	0.25
304.15	0.5498	1.03	328.15	1.1909	0.33
307.65	0.6154	0.97			
$w = 0.50$					
288.85	0.1226	0.15	312.15	0.4287	0.74
293.95	0.1715	0.62	317.65	0.5207	0.49
298.95	0.2255	0.96	322.35	0.6101	0.02
304.15	0.3005	0.81	327.85	0.7131	0.10
307.85	0.3522	0.63			
$w = 0.60$					
291.35	0.0257	0.76	313.35	0.2588	0.20
294.35	0.0413	0.17	317.95	0.3111	0.72
299.15	0.0786	0.67	322.95	0.3435	1.36
303.85	0.1304	0.63	328.05	0.3552	1.34
308.45	0.1917	0.27			
$w = 0.70$					
291.15	0.0080	0.04	313.25	0.1119	0.18
294.15	0.0148	0.09	317.75	0.1392	0.29
298.95	0.0293	0.05	322.85	0.1611	0.60
303.65	0.0511	0.32	327.85	0.1705	0.49
308.25	0.0784	0.09			
$w = 0.80$					
288.85	0.0066	0.44	313.15	0.0376	0.14
292.85	0.0096	0.96	317.15	0.0456	0.15
298.35	0.0146	0.88	323.15	0.0589	0.06
303.65	0.0216	0.70	328.15	0.0703	0.02
308.15	0.0283	0.40			
$w = 0.90$					
288.95	0.0030	0.88	313.35	0.0144	0.42
292.95	0.0040	0.93	317.35	0.0178	0.26
298.45	0.0058	0.60	323.35	0.0244	0.60
303.85	0.0081	0.21	328.35	0.0318	0.57
308.35	0.0106	0.55			
$w = 1.00$					
288.25	0.0027	0.18	312.65	0.0111	0.48
294.85	0.0042	0.16	318.15	0.0140	0.44
299.15	0.0054	0.35	322.45	0.0167	0.03
303.55	0.0070	0.08	327.35	0.0200	0.06
308.25	0.0090	0.19			

[a] $\Delta x = x - x_c/x$, where x_c is the solubility value calculated from eq 1.

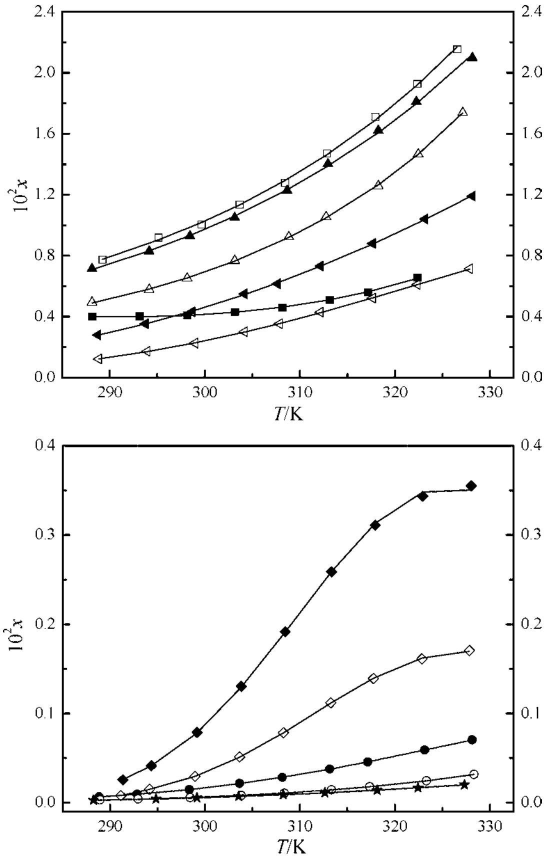

Figure 3. Solubilities of $[C_6(Py)_2][PF_6]_2$ in (w) Water + (1 − w) Acetone, where w is the mass fraction. ■, $w = 0.00$; □, $w = 0.10$; ▲, $w = 0.20$; △, $w = 0.30$; solid triangle pointing left, $w = 0.40$; open triangle pointing left, $w = 0.50$; ◆, $w = 0.60$; ◇, $w = 0.70$;K; ○, $w = 0.80$; ●, $w = 0.90$; ★, $w = 1.00$; —, calculated from eq 1.

solution and exited the vessel. The intensity of the laser observed increased as the scatters decreased owing to $[C_6(Py)_2][PF_6]_2$ dissolving in the solution. When the $[C_6(Py)_2][PF_6]_2$ had completely dissolved, the laser beam intensity returned to the value obtained prior to addition of the IL, and the solubility temperature was determined.

Solvents mixtures were prepared gravimetrically with an analytical balance (type XS104, Mettler-Toledo Co.) of maximum mass 120 g, with an uncertainty of ± 0.0001 g. To remove oxygen from the solvent and apparatus, high-purity nitrogen (mass fraction 0.999995) was flowed through the condenser at a rate of 0.3 $cm^3 \cdot s^{-1}$ for a time of 2 h. Predetermined masses of $[C_6(Py)_2][PF_6]_2$ were weighed and transferred into the vessel. The contents of the vessel were heated at rates less than 1 $K \cdot h^{-1}$ with continuous stirring to approach the solid−liquid equilibrium. Some of the solubility experiments were performed thrice to determine the reproducibility, and the mean values were used for the results. The reproducibility of the equilibrium temperature was 0.1 K, which corresponds to a relative error in composition < ± 1 %. To verify the performance of both the apparatus and procedures, solubility measurements were performed with 2-hydroxybenzoic acid and water, and the results were compared with the literature and found to differ by < 2 % as Figure 2 shows.[15] 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

The measured mole fraction solubilities (x) of $[C_6(Py)_2][PF_6]_2$ in (acetone + water) as a function of temperature (T) are presented in Table 1. The mass fraction (w) of water in the

Table 2. Parameters of Equation 1 for the $[C_6(Py)_2][PF_6]_2$ + Water + Acetone System at Various Contents of Water (*w*) in the Mixed Solvent

w	*A*	*B*	*C*	10^4 (rmsd)
0.00	−692.76	30044	102.94	0.30
0.10	−178.17	5717	27.09	1.30
0.20	−136.02	3802	20.81	1.16
0.30	−270.33	9508	40.97	0.43
0.40	194.48	−12104	−27.97	0.37
0.50	504.82	−26966	−73.80	0.19
0.60	2726.02	−131151	−402.52	0.24
0.70	2725.15	−131806	−402.15	0.05
0.80	736.91	−38908	−107.98	0.01
0.90	138.95	−11610	−19.27	0.01
1.00	360.39	−20968	−52.64	0.01

solvents was 0.00, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, and 1.00. The experimental values and calculated values are shown in Figure 3. The relationship between the mole fraction solubility and temperature is described by the modified Apelblat equation.[13]

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

where x is the mole fraction solubility of $[C_6(Py)_2][PF_6]_2$ 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

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

where N is the number of experimental points; x_{ci} is the solubility calculated by eq 1; and x_i represents the experimental solubility value.

From Table 1 and Table 2, 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 $[C_6(Py)_2][PF_6]_2$ in (acetone + water). The experimental solubility and correlation equation in this work can be used as essential data and models to assist with the purification process for $[C_6(Py)_2][PF_6]_2$.

The results listed in Table 1 are shown in Figure 3 for ($[C_6(Py)_2][PF_6]_2$ + acetone + water). They describe the temperature dependence of the solubility at various compositions of the mixed solvent. From the results shown in Table 1 and Figure 3, it can be seen that the solubility of $[C_6(Py)_2][PF_6]_2$ in (acetone + water) has a maximum value. According to Scatchard−Hildebrand's theory,[16] the solubility of a solid is a maximum in that solvent whose solubility parameter is the same as that of the solute. So the solubility of $[C_6(Py)_2][PF_6]_2$ may be a maximum in (acetone and water), which could be used for the recrystallization process of $[C_6(Py)_2][PF_6]_2$.

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