Solubilities of 1,1′-(Propane-1,3-diyl)-bis(pyridinium) Dihexafluorophosphate in Dimethyl Sulfoxide + Water

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The solubilities of 1,1′-(propane-1,3-diyl)-bis(pyridinium) dihexafluorophosphate in dimethyl sulfoxide + water were measured at temperatures from (290.45 to 337.05) K by a laser monitoring observation technique at atmospheric pressure. The experimental data were 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 nonflammability.[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] Consequently, they have been proposed as solvents in high-temperature reactions,[7] novel high-temperature lubricants,[8] ultrastable separation phases,[9] and mass spectrometry where ordinary ILs fail.[10] The synthesis and characterization of a wide variety of dicationic ionic liquids were published while our work was in progress.

An understanding of solid−liquid equilibria (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.[11−16] In this study, the solubilities of 1,1′-(propane-1,3-diyl)-bis(pyridinium) dihexafluorophosphate ($[C_3(Py)_2][PF_6]_2$) in a dimethyl sulfoxide (DMSO) + water binary solvent mixture have been measured from (290.45 to 337.05) K by a laser monitoring observation technique at atmospheric pressure, which could be used for the recrystallization process of the $[C_3(Py)_2][PF_6]_2$. The experimental data were correlated with the modified Apelblat equation.[15,16] To our knowledge, this is the first time the solubilities of $[C_3(Py)_2][PF_6]_2$ have been reported.

Experimental Section

Materials. $[C_3(Py)_2][PF_6]_2$ was from our key laboratory, and its purity was determined by high performance liquid chromatography (type Waters 600E, Waters Co.) to be greater than 99 % in mass fraction and was stored under nitrogen. The molecular structure of $[C_3(Py)_2][PF_6]_2$ is illustrated in Figure 1. Analysis for water contamination using the Karl Fischer technique (method TitroLine KF) for the IL showed that the mass fraction was less than 0.005 %. The melting point temperature (T_m) of $[C_3(Py)_2][PF_6]_2$ is (555.85 to 556.55) K measured by a digital melting point apparatus (type RY-51, Shanghai Precision & Scientific Instrument Co. Ltd.). High-grade DMSO from Tianjin Kemel Chemical Reagent Co., Ltd. was used directly without further purification, and its mass fraction purity was greater than 99 %. The water used in the experiments was double distilled.

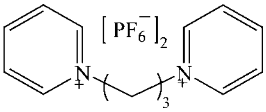

Figure 1. Molecular structure of $[C_3(Py)_2][PF_6]_2$.

Apparatus and Procedure. The solubilities were measured by a dynamic method at atmospheric pressure.[17]

The experiments were carried out in a magnetically stirred, jacketed glass vessel (20 cm^3). A constant temperature (± 0.05 K) 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. 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. At the beginning of the experiment, 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, 10 mL·min^{-1}) was fed into the solvent for 2 h to remove the dissolved oxygen. In the processes of solubility measurement, some of the solubility experiments were conducted at least three times to check the reproducibility, and the mean values were considered as the measured results. The reproducibility of the temperatures was 0.1 K. The deviations of the solubility are less than 2 %. 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 $[C_3(Py)_2][PF_6]_2$ in DMSO + water at different temperatures (T) are presented in Table 1. The mass fraction (w) of water in the solvents was 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70,

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Table 1. Mole Fraction Solubilities (x) of $[C_3(Py)_2][PF_6]_2$ in (w) Water + (1 − w) DMSO, Where w is the Mass Fraction

T/K	10^2x	$10^2\Delta x^a$	T/K	10^2x	$10^2\Delta x^a$
$w = 0.10$					
290.85	4.3220	0.55	311.65	5.8280	0.93
296.35	4.6920	2.06	316.65	6.3190	0.46
301.55	4.8710	0.84	320.95	7.1350	2.86
306.85	5.1980	2.28	326.35	7.6960	1.60
$w = 0.20$					
293.25	2.7010	1.27	318.65	3.7570	0.32
299.75	2.9760	2.10	322.75	4.0980	1.56
305.35	3.1420	0.96	329.55	4.5450	0.28
313.45	3.3810	2.77	333.75	4.9430	0.10
$w = 0.30$					
293.15	0.8770	1.73	314.55	1.4910	0.59
298.35	1.0420	2.10	318.65	1.6330	0.52
303.65	1.1940	2.60	321.55	1.7750	1.61
309.65	1.2980	3.25	327.65	1.9810	0.08
$w = 0.40$					
290.45	0.2490	1.10	316.15	0.6910	0.82
300.95	0.4040	1.77	320.95	0.8000	1.80
306.45	0.5020	1.90	325.65	0.9420	0.09
310.55	0.5670	1.10	332.15	1.1460	1.14
$w = 0.50$					
293.65	0.0404	0.36	317.25	0.2110	1.24
302.15	0.0768	1.05	322.45	0.2810	1.96
307.15	0.1070	0.65	326.95	0.3770	0.93
312.15	0.1500	0.26	332.95	0.5240	0.06
$w = 0.60$					
291.55	0.0320	0.51	314.65	0.1170	0.75
297.55	0.0450	0.19	323.35	0.1850	0.81
305.25	0.0690	0.85	328.15	0.2360	0.55
311.25	0.0960	0.73	334.55	0.3210	0.83
$w = 0.70$					
292.45	0.0207	0.21	314.25	0.0811	0.39
298.35	0.0320	0.67	320.95	0.1130	1.35
303.55	0.0442	1.01	327.45	0.1430	1.48
307.85	0.0581	0.66	337.05	0.2010	0.44
$w = 0.80$					
292.25	0.0125	0.30	315.15	0.0463	0.53
296.65	0.0165	0.12	320.05	0.0584	0.12
299.45	0.0194	0.73	330.95	0.0936	0.52
306.45	0.0292	0.04	337.05	0.1200	0.22
$w = 0.90$					
294.15	0.0106	0.78	318.15	0.0299	1.75
300.15	0.0141	1.12	323.15	0.0379	0.76
307.25	0.0191	0.34	328.35	0.0467	0.17
312.65	0.0241	0.22	333.25	0.0575	0.28

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

Table 2. Parameters of Equation 1 for the $[C_3(Py)_2][PF_6]_2$ + Water + DMSO System at Various Contents of Water (w) in the Mixed Solvent

w	A	B	C	10^4 (rmsd)
0.10	−321.86	13255	48.15	10.29
0.20	−237.12	9619	35.33	4.93
0.30	19.26	−2976	−2.43	2.36
0.40	148.13	−10025	−21.09	0.87
0.50	103.39	−10512	−13.27	0.25
0.60	−78.62	−1161	13.14	0.13
0.70	489.11	−27335	−71.17	0.10
0.80	195.34	−13676	−27.75	0.02
0.90	−120.03	1593	18.56	0.02

0.80, and 0.90. The experimental values and calculated values are shown in Figure 2. The relationship between the mole fraction solubility and temperature is described by the modified Apelblat equation.[15−17]

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

where x is the mole fraction solubility of $[C_3(Py)_2][PF_6]_2$, 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 $[C_3(Py)_2][PF_6]_2$ in DMSO + water. The overall rmsd of 72 data points for the DMSO + water system at various contents of water in the mixed solvent is 0.0237 %. The experimental solubility and correlation equation in this work can be used as essential data and models to serve the purification process of $[C_3(Py)_2][PF_6]_2$.

From the data shown in Table 1, the T, x curves for the $[C_3(Py)_2][PF_6]_2$ + DMSO + water system are shown in Figure 2. It described the temperature dependence of the solubility at various compositions of the mixed solvent. From the results shown in Table 1 and Figure 2, it can be seen that the solubility of $[C_3(Py)_2][PF_6]_2$ increases at constant temperature with the increase of the amount of DMSO in the mixed solvent, which

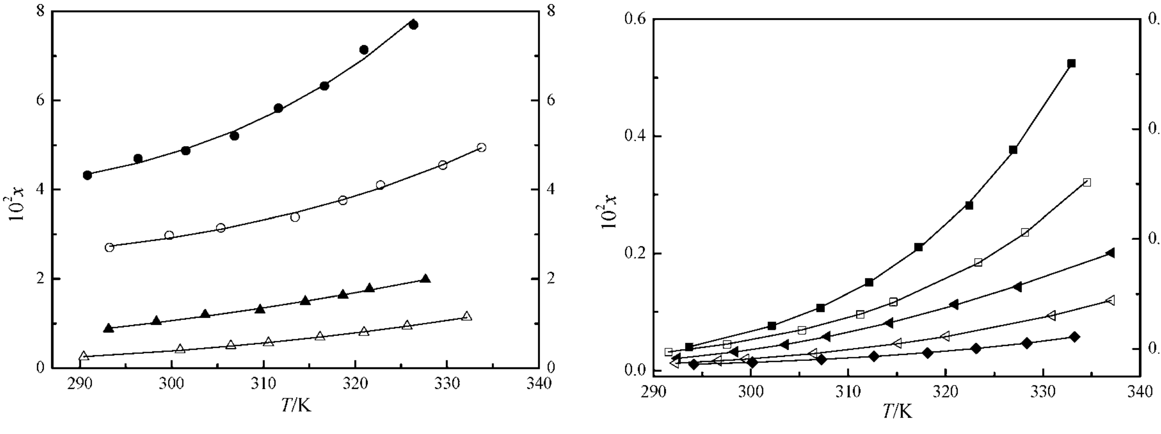

Figure 2. Solubilities of $[C_3(Py)_2][PF_6]_2$ in (w) Water + (1 − w) DMSO, where w is the mass fraction: ●, w = 0.10; ○, w = 0.20; ▲, w = 0.30; Δ, w = 0.40; ■, w = 0.50; □, w = 0.60; solid triangle pointing left, w = 0.70; open triangle pointing left, w = 0.80; ◆, w = 0.90; —, calculated from eq 1.

could be used for the recrystallization process of the $[C_3(Py)_2][PF_6]_2$.

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