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Solubility of 1,1′-(Butane-1,4-diyl)-bis(3-methylpyridinium) Dihexafluorophosphate in Different Solvents from (288.15 to 333.15) K

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Using a laser monitoring technique, the solubilities of 1,1′-(butane-1,4-diyl)-bis(3-methylpyridinium) dihexafluorophosphate in water, acetylacetone, acetophenone, cyclohexanone, 2-butanone, and acetone + water were determined at temperatures from (288.15 to 333.15) K at atmospheric pressure. The experimental data were correlated with the modified Apelblat equation and the λh model.

Introduction

Ionic liquids (ILs) have been the object of increasing attention because of their unique physicochemical properties such as high thermal stability, high ionic conductivity, high solvating capacity, negligible vapor pressure, and nonflammability.[1−4] They typically consist of a large organic cation (imidazolium, pyridinium, pyrrolidinium, or quaternary ammonium) and an anion that possesses a highly delocalized charge (PF_6^-, BF_4^-, $CF_3SO_3^-$, or $N(CF_3SO_2)_2^-$); the ions are weakly coordinated to each other. The bulky and asymmetrical configuration of the ions reduces their electrostatic interaction, prevents the ions from neatly packing together in a lattice, and thus results in salts with low melting temperatures. The unique properties of ILs make them suitable candidates as ideal solvents for green chemistry and clean synthesis. ILs have been widely applied to several areas including catalysis, electrochemistry, separation science, biology, and materials for optoelectronic applications.[5−8]

In the literature, most work has focused on monocationic ILs based on different anions, but less attention has been paid to dicationic ILs.[9] Dicationic ILs have been shown to possess superior physical properties in terms of thermal stability and volatility compared to traditional ILs.[10,11] Consequently, they have been proposed as solvents in high-temperature reactions,[12] novel high-temperature lubricants,[13] and ultrastable separation phases[14,15] and have potential in extractions similar to monocationic ILs and mass spectrometry where ordinary ILs fail.[16] An advantage of dicationic ILs over monocationic ILs is that they provide more opportunities to fine-tune their physical and chemical properties. The synthesis and characterization of a wide variety of dicationic ILs was published while our work was in progress.

1,1′-(Butane-1,4-diyl)-bis(3-methylpyridinium) dihexafluorophosphate ($[C_4(MPy)_2][PF_6]_2$) is a kind of dicationic IL which can be proposed as a solvent in high-temperature reactions.

To design any process involving ILs 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.[17−22] In this study, the solubilities of $[C_4(MPy)_2][PF_6]_2$ in water, acetylacetone, acetophenone, cyclohexanone, 2-butanone, and acetone + water have been measured from (288.15 to 333.15) K by a laser monitoring observation technique at atmospheric pressure. The experimental data were correlated by the modified Apelblat equation and the λh model.[22−24] To our knowledge, this is the first time the solubilities of $[C_4(MPy)_2][PF_6]_2$ are reported.

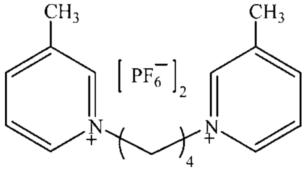

Figure 1. Molecular structure of $[C_4(MPy)_2][PF_6]_2$.

Experimental Section

Materials. The solvents used including acetylacetone, acetophenone, cyclohexanone, 2-butanone, and acetone (purchased from the Tianjin Kemel Chemical Reagent Co., Ltd. of China) were used directly without further purification, and their mass fraction purities were higher than 0.995. High-grade $[C_4(MPy)_2][PF_6]_2$ was from our Key Laboratory, and its purity was determined by high performance liquid chromatography (type Waters 600E, Waters Co.) to be greater than 0.99 in mass fraction and was stored under nitrogen. The molecular structure of $[C_4(MPy)_2][PF_6]_2$ is illustrated in Figure 1. Analysis for water contamination using the Karl Fischer technique (method Titro-Line KF) for the IL showed that the mass fraction was less than 0.0001. The melting point temperature (T_m) of $[C_2(MPy)_2][PF_6]_2$ is (434.55 to 436.25) K measured by a digital melting point apparatus (type RY-51, Shanghai Precision & Scientific Instrument Co. Ltd.). The water used in the experiments was doubly distilled.

Apparatus and Procedure. The solubilities were measured by a dynamic method at atmospheric pressure. The laser monitoring observation technique[25,26] 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 (20 cm^3). A constant temperature (± 0.05 K) was maintained by circulating water through the

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Table 1. Mole Fraction Solubility of $[C_4(MPy)_2][PF_6]_2$ in Pure Solvents

T	$10^3\ x$				
K	water	acetylacetone	acetophenone	cyclohexanone	2-butanone
288.15	0.002	1.194		0.205	2.887
293.15	0.003	1.574		0.333	3.279
298.15	0.005	2.139	0.748	0.510	3.793
303.15	0.008	2.818	1.025	0.746	4.390
308.15	0.014	3.683	1.380	0.967	4.960
313.15	0.024	4.624	1.827	1.209	5.565
318.15	0.039	5.985	2.398	1.463	6.232
323.15	0.063	8.071	3.108	1.640	7.059
328.15	0.098	10.094	4.283	1.800	7.709
333.15	0.157	13.556	5.557	1.855	8.564

Table 2. Mole Fraction Solubilities (x) of $[C_4(MPy)_2][PF_6]_2$ in (w) Water + (1 − w) Acetone, Where w is the Mass Fraction

T/K	$10^2\ x$	T/K	$10^2\ x$	T/K	$10^2\ x$	T/K	$10^2\ x$
			$w = 0.10$				
290.35	3.337	299.85	4.388	308.45	5.397	317.15	6.382
294.95	3.821	303.65	4.870	312.15	5.868	323.15	6.926
			$w = 0.20$				
288.65	2.059	300.15	3.239	308.15	3.949	317.15	4.484
292.15	2.398	303.35	3.560	314.15	4.323	322.15	4.670
			$w = 0.30$				
288.55	1.326	299.95	2.144	307.15	2.660	318.15	3.429
294.15	1.723	304.15	2.463	312.65	3.046	324.15	3.804
			$w = 0.40$				
293.95	1.067	303.55	1.566	312.35	2.227	320.45	3.079
299.15	1.325	307.65	1.853	316.65	2.659	325.25	3.637
			$w = 0.50$				
292.15	0.553	303.15	0.809	312.15	1.162	320.35	1.664
298.55	0.679	307.85	0.966	316.65	1.425	323.15	1.913
			$w = 0.60$				
288.35	0.177	298.95	0.322	307.65	0.499	317.35	0.794
294.85	0.260	303.35	0.407	313.15	0.649	323.15	1.037
			$w = 0.70$				
290.15	0.065	299.15	0.116	307.65	0.196	318.15	0.337
295.15	0.090	303.35	0.153	312.55	0.254	323.65	0.444
			$w = 0.80$				
289.15	0.010	298.85	0.032	308.15	0.070	319.15	0.128
293.15	0.017	303.35	0.048	312.15	0.092	323.15	0.149
			$w = 0.90$				
289.15	0.004	299.05	0.022	308.35	0.066	319.15	0.121
293.15	0.008	303.45	0.040	313.45	0.095	323.15	0.131

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 (0.999995 by mass, 20 $\text{cm}^3\cdot\text{min}^{-1}$) was fed into the solvent for 2 h to remove the dissolved oxygen. Predetermined amounts of $[C_4(MPy)_2][PF_6]_2$ were weighed and transferred into the vessel. 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 0.02. In this work, the uncertainty for solubility measurement is estimated on the basis of the principle of the error propagation to be 0.02 at the 0.95 confidence level.

Table 3. Parameters of Equations 1 and 3 for $[C_4(MPy)_2][PF_6]_2$ in Pure Solvents

	λh equation			Apelblat equation			
solvent	λ	h	10^4 (rmsd)	A	B	C	10^4 (rmsd)
water	0.1601	61606	0.01	19.11	−9721	0.23	0.01
acetylacetone	0.5677	9425	1.88	−123.69	1069	20.00	1.33
acetophenone	0.3182	18151	0.58	−129.82	951	20.96	0.41
cyclohexanone	0.0333	115775	1.26	1290.69	−63630	−190.41	0.11
2-butanone	0.0261	74591	0.87	52.96	−4667	−7.53	0.35

Table 4. Parameters of Equations 1 and 3 for the $[C_4(MPy)_2][PF_6]_2$ + Water + Acetone System at Various Contents of Water (w) in the Mixed Solvent

	λh equation			Apelblat equation			
w	λ	h	10^3 (rmsd)	A	B	C	10^4 (rmsd)
0.10	0.2270	7589	1.67	299.33	−15563	−43.93	2.20
0.20	0.3314	7096	1.80	734.78	−35403	−108.74	1.84
0.30	0.2065	11046	1.30	487.19	−24647	−71.69	1.63
0.40	0.6626	5672	0.17	−76.91	139	12.65	1.53
0.50	0.4439	9024	0.38	−506.97	19712	76.50	0.58
0.60	0.4101	11306	0.04	63.39	−7123	−7.95	0.34
0.70	0.2710	19197	0.04	222.80	−15033	−31.45	0.14
0.80	0.1571	36932	0.08	1682.19	−83109	−247.75	0.04
0.90	0.5863	12511	0.09	3483.44	−167093	−514.53	0.04

Results and Discussion

The measured mole fraction solubilities (x) of $[C_4(MPy)_2][PF_6]_2$ in pure water, acetylacetone, acetophenone, cyclohexanone, and 2-butanone at different temperatures (T) are presented in Table 1, and those in acetone + water binary mixtures are presented in Table 2. The mass fractions (w) of water in the solvents were 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, and 0.90.

The relationship between mole fraction of the solubility and temperature is described by the λh model and the modified Apelblat equation. The λh model which is a semiempirical equation is shown as follows

$$\ln\left[1 + \frac{\lambda(1 - x)}{x}\right] = \lambda h\left[\frac{1}{(T/\text{K})} - \frac{1}{(T_m/\text{K})}\right] \qquad (1)$$

where x is the mole fraction of the solubility of $[C_4(MPy)_2][PF_6]_2$ at the system temperature T, T_m is the normal melting temperature of $[C_4(MPy)_2][PF_6]_2$, and λ and h are the model parameters

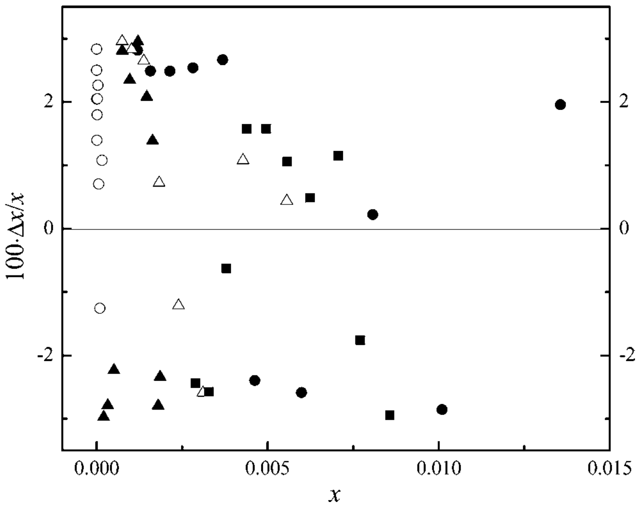

Figure 2. Residual deviations $\Delta x = x(\text{expt.}) - x(\text{calc.})$ of the solubility of $[C_4(MPy)_2][PF_6]_2$ in pure solvents for eq 1 as a function of experimental solubility x. ○, water; ●, acetylacetone; △, acetophenone; ▲, cyclohexanone; ■, 2-butanone.

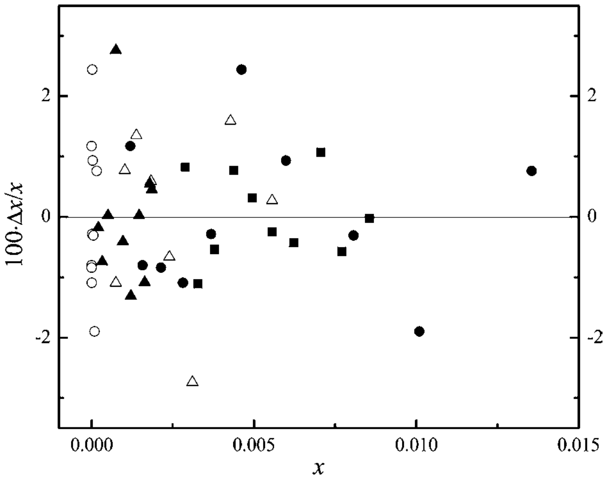

Figure 3. Residual deviations $\Delta x = x(\text{expt.}) - x(\text{calc.})$ of the solubility of $[C_4(MPy)_2][PF_6]_2$ in pure solvents for eq 3 as a function of experimental solubility x. ○, water; ●, acetylacetone; △, acetophenone; ▲, cyclohexanone; ■, 2-butanone.

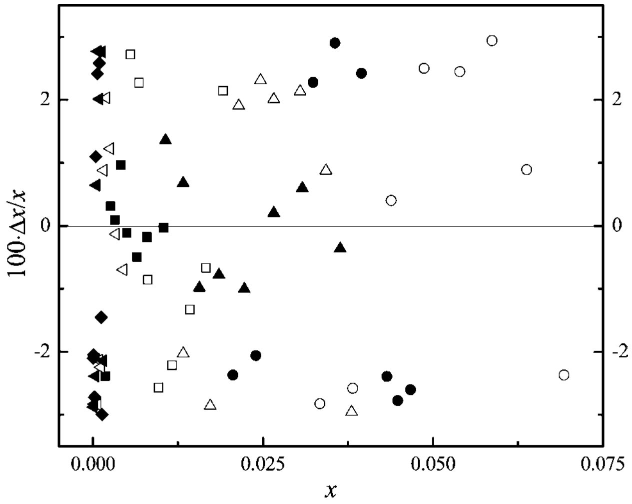

Figure 4. Residual deviations $\Delta x = x(\text{expt.}) - x(\text{calc.})$ of the solubility of $[C_4(MPy)_2][PF_6]_2$ in (w) water + (1 − w) acetone for eq 1 as a function of experimental solubility x, where w is the mass fraction. ○, $w = 0.10$; ●, $w = 0.20$; △, $w = 0.30$; ▲, $w = 0.40$; □, $w = 0.50$; ■, $w = 0.60$; open left-pointing triangle, $w = 0.70$; solid left-pointing triangle, $w = 0.80$; ◆, $w = 0.90$.

determined by the experimental data in the systems together with the root-mean-square deviations (rmsd's) which are listed in Tables 3 and 4, respectively. The scatter plot of residual deviations of the solubility of $[C_4(MPy)_2][PF_6]_2$ in pure solvents and water + acetone mixtures for eq 1 were plotted in Figures 2 and 4. The rmsd is defined as

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

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.

The modified Apelblat equation is shown as follows

$$\ln x = A + \frac{B}{T/\text{K}} + C\ln(T/\text{K}) \tag{3}$$

where x is the mole fraction solubility of $[C_4(MPy)_2][PF_6]_2$, T is the absolute temperature, and A, B, and C are empirical constants. The values of A, B, C, and rsmd values obtained from the experimental solubility data in the systems are listed in Tables 3 and 4. The scatter plot of residual deviations of the solubility of $[C_4(MPy)_2][PF_6]_2$ in pure solvents and water + acetone mixtures for eq 3 were plotted in Figures 3 and 5.

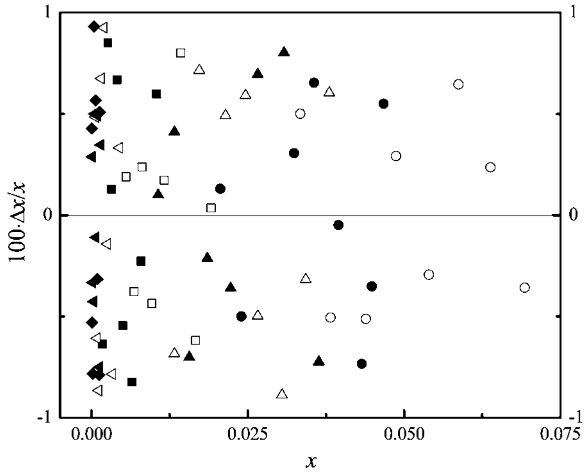

Figure 5. Residual deviations $\Delta x = x(\text{expt.}) - x(\text{calc.})$ of the solubility of $[C_4(MPy)_2][PF_6]_2$ in (w) water + (1 − w) acetone for eq 3 as a function of experimental solubility x, where w is the mass fraction. ○, $w = 0.10$; ●, $w = 0.20$; △, $w = 0.30$; ▲, $w = 0.40$; □, $w = 0.50$; ■, $w = 0.60$; open left-pointing triangle, $w = 0.70$; solid left-pointing triangle, $w = 0.80$; ◆, $w = 0.90$.

From Tables 1 and 3 and Figures 2 and 3, we can draw the following conclusions: (a) The solubility of $[C_4(MPy)_2][PF_6]_2$ in water, acetylacetone, acetophenone, cyclohexanone, and 2-butanone is a function of temperature and increases with the increase in temperature. (b) The calculated solubilities of $[C_4(MPy)_2][PF_6]_2$ are in good agreement with the experimental data, which indicate that the equations can be used to correlate the solubility data of $[C_4(MPy)_2][PF_6]_2$. (c) The Apelblat equation was more accurate than the λh equation for this system.

From Tables 2 and 4 and Figures 4 and 5, it can be seen that the calculated solubilities are in good agreement with the experimental data, which indicate that the equations can be used to correlate the solubility data of $[C_4(MPy)_2][PF_6]_2$ in acetone + water. The Apelblat equation was more accurate than the λh equation for this system. The solubility of $[C_4(MPy)_2][PF_6]_2$ increases at constant temperature with the increase of the amount of acetone in the mixed solvent. The solubilities of $[C_4(MPy)_2][PF_6]_2$ in the mixed solvent are small at low temperatures but quickly increase at high temperatures. Accordingly, the experimental solubility data and the correlation equations in this work can be used as fundamental data and models in the purification process of $[C_4(MPy)_2][PF_6]_2$.

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