Solubility of 1,1′-(Ethane-1,2-diyl)-bis(3-methylpyridinium) Dihexafluorophosphate in Different Solvents

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Using a laser monitoring technique, the solubilities of 1,1′-(ethane-1,2-diyl)-bis(3-methylpyridinium) dihexafluorophosphate in acetone, 2-butanone, acetylacetone, cyclohexanone, water, 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] Dicationic ILs have been shown to possess superior physical properties in terms of thermal stability and volatility compared to monocationic ILs.[5,6] 1,1′-(Ethane-1,2-diyl)-bis(3-methylpyridinium) dihexafluorophosphate ($[C_2(MPy)_2][PF_6]_2$) is a dicationic IL, which can be proposed as solvents 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.[7−12] In this study, the solubilities of $[C_2(MPy)_2][PF_6]_2$ in acetone, 2-butanone, acetylacetone, cyclohexanone, water, 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.[12−14] To our knowledge, this is the first time the solubilities of $[C_2(MPy)_2][PF_6]_2$ are reported.

Experimental Section

Materials. High-grade $[C_2(MPy)_2][PF_6]_2$ was from our Key Laboratory, and its purity was determined by high performance liquid chromatography (type Waters 600E, Waters Co.) to be greater than 99 % in mass fraction; it was stored under nitrogen. The molecular structure of $[C_2(MPy)_2][PF_6]_2$ 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 0.01 %. The melting point temperature (T_m) of $[C_2(MPy)_2][PF_6]_2$ is (546.85 to 548.05) K measured by a digital melting point apparatus (type RY-51, Shanghai Precision & Scientific Instrument Co. Ltd.). The solvents used including acetone, 2-butanone, acetylacetone, and cyclohexanone (purchased from the Tianjin Kemel Chemical Reagent Co., Ltd. of China) were used directly without further purification, and their mass fraction purity was higher than 99.5 %. The water used in the experiments was doubly distilled.

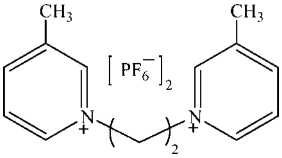

Figure 1. Molecular structure of $[C_2(MPy)_2][PF_6]_2$.

Table 1. Mole Fraction Solubilities (x) of $[C_2(MPy)_2][PF_6]_2$ in Acetone, 2-Butanone, Acetylacetone, Cyclohexanone, and Water

T/K	10^2x	T/K	10^2x	T/K	10^2x	T/K	10^2x
			Acetone				
288.15	0.2693	296.95	0.3071	312.15	0.3614	323.15	0.4051
291.15	0.2825	301.35	0.3234	316.15	0.3832		
295.15	0.3008	307.15	0.3458	320.65	0.3927		
			2-Butanone				
288.15	0.0439	299.15	0.0505	312.65	0.0599	328.15	0.073
292.15	0.0464	304.15	0.0544	317.65	0.0643	333.15	0.0779
295.65	0.0486	308.15	0.0574	323.15	0.0686		
			Acetylacetone				
288.15	0.0225	301.65	0.0323	313.65	0.0476	329.15	0.083
293.15	0.0253	303.15	0.0336	319.15	0.058	333.15	0.0966
297.15	0.0286	308.25	0.0398	323.15	0.0661		
			Cyclohexanone				
288.15	0.0104	303.15	0.016	318.15	0.0224	333.15	0.0298
293.15	0.0121	308.15	0.018	323.15	0.0247		
298.15	0.0141	313.65	0.0206	328.15	0.0274		
			Water				
288.15	0.0016	300.15	0.0037	313.15	0.0077	327.65	0.0145
292.15	0.0022	304.15	0.0047	318.15	0.0098	333.15	0.0176
296.15	0.0029	308.65	0.0061	323.15	0.0121		

Apparatus and Procedure. The solubilities were measured by a dynamic method at atmospheric pressure.[11,12] The laser monitoring observation technique[15,16] 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 outer jacket from a super thermostatic

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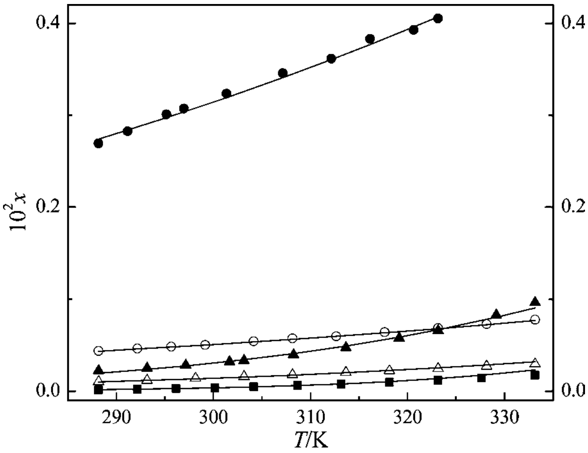

Figure 2. Mole fraction solubilities of $[C_2(MPy)_2][PF_6]_2$ in pure solvents. ●, acetone; ○, 2-butanone; ▲, acetylacetone; Δ, cyclohexanone; ■, water; solid line, calculated from the λh model.

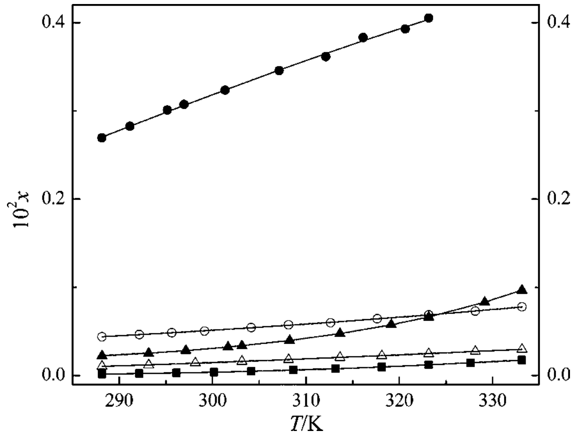

Figure 3. Mole fraction solubilities of $[C_2(MPy)_2][PF_6]_2$ in pure solvents. ●, acetone; ○, 2-butanone; ▲, acetylacetone; Δ, cyclohexanone; ■, water; solid line, calculated from the modified Apelblat equation.

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. 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), which decided the rate of temperature rise and estimated the equilibrium point of the acetone + water on the basis of the signal change. In the early stage of the experiment, the laser beam was blocked by the unsolved particles of $[C_2(MPy)_2][PF_6]_2$ in the solution, so the intensity of the laser beam penetrating the vessel was lower. The intensity increased gradually along with the increase of the amount of $[C_2(MPy)_2][PF_6]_2$ dissolved. When the last portion of $[C_2(MPy)_2][PF_6]_2$ just disappeared, the intensity of the laser beam penetrating the vessel reached the maximum, and the temperature was recorded.

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, 20 mL·min^{-1}) was fed into the solvent for 2 h to remove the dissolved oxygen. Predetermined amounts of $[C_2(MPy)_2][PF_6]_2$ 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 2 %. In this work, the uncertainty for solubility

Table 2. Mole Fraction Solubilities (x) of $[C_2(MPy)_2][PF_6]_2$ in (w) Water + (1 − w) Acetone, Where w is the Mass Fraction

T/K	10^2x	T/K	10^2x	T/K	10^2x	T/K	10^2x
$w = 0.10$							
290.25	0.6320	301.95	0.7980	312.05	0.9790	2.05	1.2090
298.05	0.7410	307.65	0.8990	317.85	1.1030	327.25	1.3140
$w = 0.20$							
291.15	0.5020	302.35	0.7320	312.15	0.9410	322.05	1.1660
298.55	0.6620	307.25	0.8190	318.05	1.0650	327.55	1.2780
$w = 0.30$							
291.05	0.3980	303.75	0.5790	313.55	0.7510	322.95	0.9630
297.15	0.4870	308.65	0.6450	317.95	0.8320	327.45	1.0970
$w = 0.40$							
291.75	0.2140	304.35	0.3660	314.35	0.5020	324.25	0.6560
297.95	0.2830	308.15	0.4160	318.65	0.5740	327.95	0.7210
$w = 0.50$							
289.35	0.0603	301.55	0.1650	311.75	0.2820	321.65	0.3840
296.15	0.1110	305.45	0.2110	317.25	0.3380	326.05	0.4210
$w = 0.60$							
289.95	0.0563	300.45	0.0962	311.25	0.1540	320.65	0.2240
295.25	0.0744	304.65	0.1170	316.35	0.1890	325.75	0.2680
$w = 0.70$							
290.85	0.0106	301.35	0.0316	311.05	0.0609	321.05	0.0958
295.55	0.0179	305.95	0.0440	316.25	0.0795	326.25	0.1130
$w = 0.80$							
290.25	0.0047	301.35	0.0140	311.95	0.0280	321.35	0.0417
297.05	0.0097	307.35	0.0211	316.85	0.0351	325.35	0.0481
$w = 0.90$							
293.35	0.0025	302.15	0.0048	312.95	0.0095	322.95	0.0171
297.65	0.0034	307.45	0.0068	316.85	0.0122	326.75	0.0216

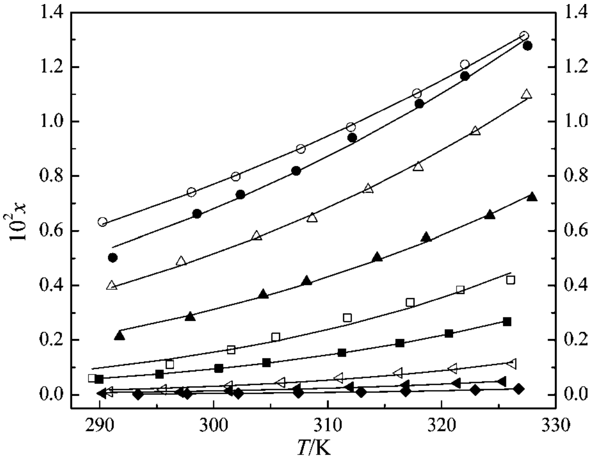

Figure 4. Solubilities of $[C_2(MPy)_2][PF_6]_2$ in (w) water + (1 − w) acetone, where w is the mass fraction. ○, $w = 0.10$; ●, $w = 0.20$; Δ, $w = 0.30$; ▲, $w = 0.40$; □, $w = 0.50$; ■, $w = 0.60$; open left-pointing triangle, $w = 0.70$; solid left-pointing triangle, $w = 0.80$; ◆, $w = 0.90$; solid line, calculated from the λh model.

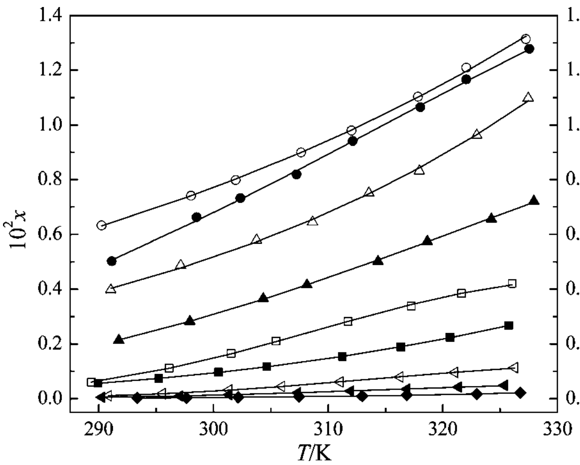

Figure 5. Solubilities of $[C_2(MPy)_2][PF_6]_2$ in (w) water + (1 − w) acetone, where w is the mass fraction. ○, $w = 0.10$; ●, $w = 0.20$; Δ, $w = 0.30$; ▲, $w = 0.40$; □, $w = 0.50$; ■, $w = 0.60$; open left-pointing triangle, $w = 0.70$; solid left-pointing triangle, $w = 0.80$; ◆, $w = 0.90$; solid line, calculated from the modified Apelblat equation.

measurements 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 $[C_2(MPy)_2][PF_6]_2$ in pure acetone, 2-butanone, acetylacetone, cyclohexanone, and water at different temperatures (T) are presented in Table 1 and graphically plotted in Figures 2 and 3. Those in acetone + water are presented in Table 2 and Figures 4 and 5. The mass fraction (w) of water in the solvents was 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, and 0.90.

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

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

where x is the mole fraction of the solubility of $[C_2(MPy)_2][PF_6]_2$ at the system temperature T, T_m is the normal melting temperature of $[C_2(MPy)_2][PF_6]_2$, and λ and h are the model parameters 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 rmsd is defined as

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

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

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

where x is the mole fraction solubility of $[C_2(MPy)_2][PF_6]_2$, T is the absolute temperature, and A, B, and C are empirical constants. The values of A, B, and C and rsmd values obtained from the experimental solubility data in the systems are listed in Tables 3 and 4.

From Tables 1 and 3 and Figures 2 and 3, we can draw the following conclusions: (a) The solubility of $[C_2(MPy)_2][PF_6]_2$ acetone, 2-butanone, acetylacetone, cyclohexanone, and water is a function of temperature and increases with an increase in temperature. (b) The best solubility of $[C_2(MPy)_2][PF_6]_2$ was shown in acetone in this study. (c) The calculated solubilities of $[C_2(MPy)_2][PF_6]_2$ are in good agreement with the experimental data, which indicate that the equations can be used to correlate the solubility data of $[C_2(MPy)_2][PF_6]_2$. (d) 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 $[C_2(MPy)_2][PF_6]_2$ in acetone + water. The Apelblat equation was more accurate than the λh equation for this system. The solubility of $[C_2(MPy)_2][PF_6]_2$ increases at constant temperature with the increase of the amount of acetone in the mixed solvent. The solubilities of $[C_2(MPy)_2][PF_6]_2$ 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 $[C_2(MPy)_2][PF_6]_2$.

Table 3. Parameters of Equations 1 and 3 for the $[C_2(MPy)_2][PF_6]_2$ in Acetone, 2-Butanone, Acetylacetone, Cyclohexanone, and Water

	λh equation			Apelblat equation			
solvent	λ	h	10^4 (rmsd)	A	B	C	10^4 (rmsd)
acetone	0.0050	126165	0.31	76.17	−4622	−11.66	0.20
2-butanone	0.0013	648285	0.02	−40.38	478	5.47	0.02
acetylacetone	0.0391	82491	0.14	−337.92	12513	50.51	0.02
cyclohexanone	0.0047	498706	0.01	119.08	−7773	−17.88	0.01
water	0.1629	34272	0.005	395.00	−22923	−57.65	0.002

Table 4. Parameters of Equations 1 and 3 for the $[C_2(MPy)_2][PF_6]_2$ + Water + Acetone System at Various Contents of Water (w) in the Mixed Solvent

	λh equation			Apelblat equation			
w	λ	h	10^4 (rmsd)	A	B	C	10^4 (rmsd)
0.10	0.1052	16903	0.56	−60.77	946	9.25	0.60
0.20	0.1902	11726	1.70	242.26	−13385	−35.52	0.78
0.30	0.2531	10260	0.93	−91.44	1749	14.09	0.76
0.40	0.2724	10920	1.01	318.75	−17598	−46.61	0.28
0.50	0.6107	6500	1.84	1271.71	−62525	−187.56	0.33
0.60	0.3840	10397	0.16	75.23	−11803	−25.05	0.05
0.70	0.6100	8265	0.44	1464.61	−72707	−215.73	0.07
0.80	0.2664	18912	0.16	1335.33	−66623	−196.76	0.04
0.90	0.3770	16067	0.01	128.60	−11572	−17.56	0.01

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