Solubility of 1,1′-(Butane-1,4-diyl)-bis(3-methyl-1*H*-imidazolium-1-yl) Dihexafluorophosphate in Water, Acetophenone, Cyclohexanone, Acetylacetone, and 2-Butanone

Xu-Zhao Yang* and Jun Wang

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

The solubility of 1,1′-(butane-1,4-diyl)-bis(3-methyl-1*H*-imidazolium-1-yl) dihexafluorophosphate in water, acetophenone, cyclohexanone, acetylacetone, and 2-butanone was measured at temperatures from (283.15 to 333.15) K by a laser monitoring observation technique at atmospheric pressure. The experimental data were correlated with the modified Apelblat equation, which can be used as a useful model in the purification process of 1,1′-(butane-1,4-diyl)-bis(3-methyl-1*H*-imidazolium-1-yl) dihexafluorophosphate.

Introduction

Dicationic ionic liquids have been shown to possess superior physical properties in terms of thermal stability and volatility compared to monocationic ionic liquids.[1,2] 1,1′-(Butane-1,4-diyl)-bis(3-methyl-1*H*-imidazolium-1-yl) dihexafluorophosphate ($[C_4(MIM)_2][PF_6]_2$) is a dicationic ionic liquid and could be used as a lubricant, especially a high-performance lubricant where high thermal stability and nonvolatility are the prerequisites.[3] An understanding of solid−liquid equilibria (SLE) is of paramount importance for the design of separation processes, especially antisolvent crystallization. The solubility of solid compounds in solvents plays a crucial role in the determination of proper solvents and the development and operation of crystallization processes. Therefore, knowing the solubility of the product is necessary. The solubilities of ionic liquids in different solvents have been investigated extensively.[4−6] In this study, the solubilities of $[C_4(MIM)_2][PF_6]_2$ in water, acetophenone, cyclohexanone, acetylacetone, and 2-butanone have been measured from (283.15 to 333.15) K by a laser monitoring observation technique at atmospheric pressure. The experimental data were correlated by the modified Apelblat equation.[7,8] To our knowledge, this is the first time the solubilities of $[C_4(MIM)_2][PF_6]_2$ are reported.

Experimental Section

Materials. The solvents used including acetophenone, cyclohexanone, acetylacetone, and 2-butanone (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 %. High-grade $[C_4(MIM)_2][PF_6]_2$ 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 $[C_4(MIM)_2][PF_6]_2$ is illustrated in Figure 1. The melting point temperature (T_m) of $[C_4(MIM)_2][PF_6]_2$ is (390.65 to 392.65) 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.

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

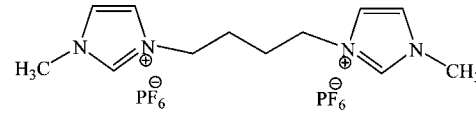

Figure 1. Molecular structure of $[C_4(MIM)_2][PF_6]_2$.

Apparatus and Procedure. The solubility of $[C_4(MIM)_2][PF_6]_2$ was measured by a dynamic method at atmospheric pressure. 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 (15 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. The masses of the solvent and solute were weighed using an analytical balance (type XS104, Mettler-Toledo Co.) with an accuracy 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 2 h to remove the dissolved oxygen. The uncertainty 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 $[C_4(MIM)_2][PF_6]_2$ in water, acetophenone, cyclohexanone, acetylacetone and 2-butanone are listed in Table 1. The relationship between the mole fraction solubility and the temperature is described by the modified Apelblat equation.[7]

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

where x is the mole fraction solubility of $[C_4(MIM)_2][PF_6]_2$ and A, B, and C are empirical constants. The values of A, B, and C

10.1021/je900826p
Published on Web 12/14/2009

Table 1. Mole Fraction Solubility (x) of $[C_4(MIM)_2][PF_6]_2$ in Water, Acetophenone, Cyclohexanone, Acetylacetone, and 2-Butanone

T/K	$10^2\ x$	$10^2\ \Delta x^a$	T/K	$10^2\ x$	$10^2\ \Delta x^a$
		Water			
283.15	0.0095	1.05	313.15	0.0456	0.00
288.45	0.0124	0.81	318.35	0.0608	0.33
293.15	0.0156	0.64	323.15	0.0790	0.13
298.15	0.0203	0.49	328.15	0.1051	0.57
303.65	0.0274	0.36	333.15	0.1377	0.51
308.15	0.0348	0.00			
		Acetophenone			
299.65	0.1269	0.08	318.15	0.6771	0.18
303.65	0.1982	0.25	323.15	0.9193	0.23
307.35	0.2855	0.11	328.15	1.1723	0.09
313.15	0.4716	0.08	332.15	1.3681	0.12
		Cyclohexanone			
283.15	0.0563	0.00	313.15	0.5288	0.17
288.15	0.0900	0.00	318.25	0.6883	0.19
293.15	0.1385	0.36	323.15	0.8571	0.05
298.35	0.2059	0.39	328.15	1.0494	0.27
302.15	0.2712	0.18	333.15	1.2428	0.19
308.65	0.4098	0.10			
		Acetylacetone			
283.15	0.2525	0.04	309.15	0.7681	0.10
288.15	0.2602	0.08	314.15	1.2064	0.10
293.15	0.2949	0.00	320.15	2.2718	0.19
297.45	0.3519	0.03	325.15	4.0891	0.21
302.65	0.4728	0.00	330.15	7.8392	0.06
		2-Butanone			
283.15	0.8379	0.12	309.15	2.3484	0.67
288.15	0.9361	0.04	315.15	3.4853	0.38
294.15	1.1357	0.20	320.15	4.9612	0.17
299.15	1.3972	0.27	325.15	7.2793	0.04
304.15	1.7780	0.22			

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

Table 2. Parameters of Equation 1 for the $[C_4(MIM)_2][PF_6]_2$ in Water, Acetophenone, Cyclohexanone, Acetylacetone, and 2-Butanone

solvent	A	B	C	10^4 (rmsd)
water	−293.78	8720.03	44.94	0.03
acetophenone	1394.31	−71550.80	−203.80	0.10
cyclohexanone	589.61	−32122.20	−85.66	0.13
acetylacetone	−2128.15	90655.40	319.17	0.34
2-butanone	−1118.27	46280.60	168.27	0.83

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

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

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 scatterplot of residual deviations of the solubility of $[C_4(MIM)_2][PF_6]_2$ for eq 1 was plotted in Figure 2. From Tables 1 and 2 and Figure 2, we can draw the following conclusions: (a) The solubility of $[C_4(MIM)_2][PF_6]_2$ in water, acetophenone, cyclohexanone, acetylacetone, and 2-butanone is a function of temperature and increases with increasing temperature. (b) The best solubility of $[C_4(MIM)_2][PF_6]_2$ was shown in 2-butanone in this study. (c) The calculated solubilities of $[C_4(MIM)_2][PF_6]_2$ are in good agreement with the experimental data, which indicate that the equation can be used to correlate the solubility data of $[C_4(MIM)_2][PF_6]_2$. The experimental solubilities and correlation equation in this work can be used for solvent selection and model research in the process of crystallization of $[C_4(MIM)_2][PF_6]_2$.

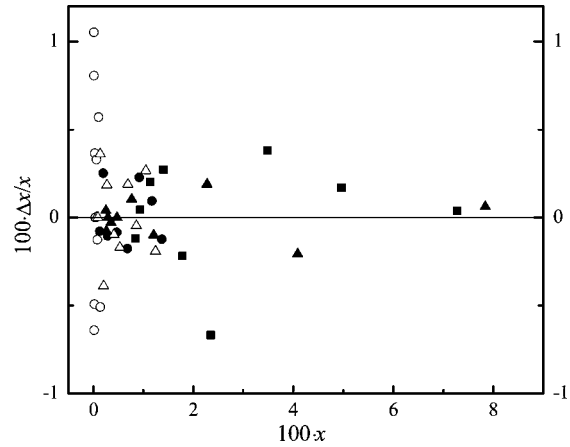

Figure 2. Residual deviations Δx of the solubility of $[C_4(MIM)_2][PF_6]_2$ for eq 1 as a function of experimental solubility x. ○, water; ●, acetophenone; △, cyclohexanone; ▲, acetylacetone; ■, 2-butanone.

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Received for review October 12, 2009. Accepted December 7, 2009.

JE900826P