Solubilities of 1,1′-(Propane-1,3-diyl)-bis(3-methyl-1*H*-imidazolium-1-yl) Dihexafluorophosphate in Different Solvents

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The solubilities of 1,1′-(propane-1,3-diyl)-bis(3-methyl-1*H*-imidazolium-1-yl) dihexafluorophosphate in acetone, 2-butanone, acetophenone, cyclohexanone, acetylacetone, and water were measured at temperatures from (288.55 to 335.25) 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′-(propane-1,3-diyl)-bis(3-methyl-1*H*-imidazolium-1-yl) dihexafluorophosphate.

Introduction

Ionic liquids (ILs) are generally formed by an organic cation and a weakly coordinating anion. They have received vast research interest in recent years because of their unique properties such as high thermal stability, high ionic conductivity, high solvating capacity, negligible vapor pressure, and nonflammability.[1−3] Dicationic ionic liquids have been shown to possess superior physical properties in terms of thermal stability and volatility compared to monocationic ionic liquids.[4,5] 1,1′-(Propane-1,3-diyl)-bis(3-methyl-1*H*-imidazolium-1-yl) dihexafluorophosphate ($[C_3(MIM)_2][PF_6]_2$) is a dicationic ionic liquid and can be proposed as lubricants, especially the high-performance lubricant where high thermal stability and nonvolatility are the prerequisites.[6]

To design any process involving ionic liquids on an industrial scale, it is necessary to know a range of physical properties such 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.[7−9] 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. In this study, the solubilities of $[C_3(MIM)_2][PF_6]_2$ in acetone, 2-butanone, acetophenone, cyclohexanone, acetylacetone, and water have been measured from (288.55 to 335.25) K by a laser monitoring observation technique at atmospheric pressure. The experimental data were correlated by the modified Apelblat equation.[10−12] To our knowledge, this is the first time the solubilities of $[C_3(MIM)_2][PF_6]_2$ have been reported.

Experimental Section

Materials. High-grade $[C_3(MIM)_2][PF_6]_2$ was from our Key Laboratory, and its purity was determined by high-performance liquid chromatography (type Waters 600E, Waters Co.) to be greater than 0.99 in mass fraction and was stored under nitrogen. The molecular structure of $[C_3(MIM)_2][PF_6]_2$ is illustrated in Figure 1. The melting point temperature (T_m) of $[C_3(MIM)_2][PF_6]_2$ is (414.65 to 416.15) K measured by a digital melting point apparatus (type RY-51, Shanghai Precision & Scientific Instrument Co. Ltd.). The solvents used including acetone, 2-butanone, acetophenone, cyclohexanone, and acetylacetone (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 0.995. The water used in the experiments was doubly distilled.

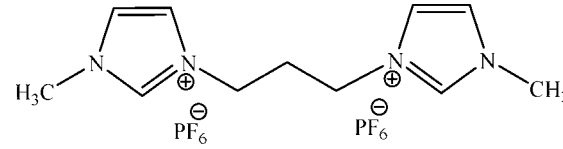

Figure 1. Molecular structure of $[C_3(MIM)_2][PF_6]_2$.

Apparatus and Procedure. The solubility of $[C_3(MIM)_2][PF_6]_2$ was measured by the last crystal disappearance method. 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 superthermostatic 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. 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 $[C_3(MIM)_2][PF_6]_2$ in acetone, 2-butanone, acetophenone, cyclohexanone,

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Table 1. Mole Fraction Solubilities (x) of $[C_3(MIM)_2][PF_6]_2$ in Acetone, 2-Butanone, Acetophenone, Cyclohexanone, Acetylacetone, and Water

Acetone		2-Butanone		Acetophenone		Cyclohexanone		Acetylacetone		Water	
T/K	10^2x	T/K	10^2x	T/K	10^2x	T/K	10^2x	T/K	10^2x	T/K	10^2x
289.15	3.6470	290.15	0.2918	289.15	0.0417	289.65	0.0151	288.55	0.0598	289.15	0.0077
293.15	4.0120	294.15	0.3386	293.15	0.0461	294.15	0.0222	293.15	0.0876	293.15	0.0102
296.65	4.3330	299.35	0.4042	296.65	0.0500	299.15	0.0331	297.45	0.1198	297.65	0.0137
301.15	4.8540	303.15	0.4576	302.15	0.0560	303.15	0.0443	302.65	0.1718	304.75	0.0216
306.15	5.5060	308.15	0.5237	307.15	0.0619	308.15	0.0622	307.85	0.2406	309.35	0.0289
310.15	6.0500	313.25	0.5981	312.15	0.0683	313.25	0.0852	313.15	0.3246	313.25	0.0366
315.15	6.8140	318.15	0.6713	317.35	0.0743	318.15	0.1116	317.65	0.4112	317.15	0.0454
321.15	7.7190	323.15	0.7377	321.65	0.0807	323.15	0.1431	323.15	0.5315	322.65	0.0611
		328.15	0.8110	328.15	0.0899	328.15	0.1812	327.35	0.6394	327.15	0.0780
		335.25	0.9126	333.15	0.0996	333.15	0.2240	334.65	0.8404	332.65	0.1040

acetylacetone, and water are listed in Table 1 and graphically plotted in Figure 2. The relationship between the mole fraction solubility and temperature is described by the modified Apelblat equation.[12]

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

where x is the mole fraction solubility of $[C_3(MIM)_2][PF_6]_2$, 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

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

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.

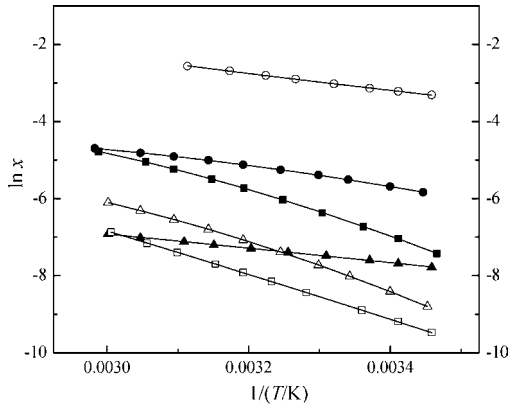

Figure 2. Mole fraction solubilities of $[C_3(MIM)_2][PF_6]_2$ in different solvents. ○, acetone; ●, 2-butanone; ▲, acetophenone; Δ, cyclohexanone; ■, acetylacetone; □, water; —, calculated from eq 1.

Table 2. Parameters of Equation 1 for the $[C_3(MIM)_2][PF_6]_2$ in Acetone, 2-Butanone, Acetophenone, Cyclohexanone, Acetylacetone, and Water

solvent	A	B	C	10^4 (rmsd)
acetone	−45.16	37	7.36	2.81
2-butanone	246.65	−13723	−36.19	0.23
acetophenone	17.12	−2713	−2.74	0.05
cyclohexanone	503.93	−28634	−73.01	0.05
acetylacetone	469.03	−26594	−67.84	0.08
water	72.65	−8622	−9.23	0.02

Conclusions

From Tables 1 and 2 and Figure 2, we can draw the following conclusions: (a) The solubility of $[C_3(MIM)_2][PF_6]_2$ acetone, 2-butanone, acetophenone, cyclohexanone, acetylacetone, and water is a function of temperature and increases with an increase in temperature. (b) The best solubility of $[C_3(MIM)_2][PF_6]_2$ was shown in acetone in this study. The solubility of $[C_3(MIM)_2][PF_6]_2$ in different solvents is in the following order: acetone > 2-butanone > acetylacetone > water. This may be caused by polarity and will be studied further. (c) The calculated solubilities of $[C_3(MIM)_2]$-$[PF_6]_2$ are in good agreement with the experimental data, which indicates that the modified Apelblat equation can be used to correlate the solubility data of $[C_3(MIM)_2][PF_6]_2$. The experimental solubilities and correlation equation in this work can be used for solvent selection and model research in the process of crystallization of $[C_3(MIM)_2][PF_6]_2$.

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