Solubilities of Petroleum Ether, Heptane, Phosphorus Trichloride, and Benzene with the [Triethylamine Hydrochloride]−x[$AlCl_3$] Ionic Liquid

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The solubilities of heptane, petroleum ether, phosphorus trichloride and benzene in the [triethylamine hydrochloride]−x[$AlCl_3$] (x = 0.67) ionic liquid in the temperature range from (293.16 to 332.60) K and the solubilities of the ionic liquid in benzene and phosphorus trichloride in the temperature range from (293.16 to 324.95) K have been measured using a cloud-point method. The uncertainty in the solubility was about 3%. The density of [triethylamine hydrochloride]−x[$AlCl_3$] (x = 0.67) has also been measured with an uncertainty of 1%.

Introduction

Ionic liquids (ILs) have received much attention in the past decade because of their attractive features as green solvents and catalysts.[1−4] Acid ionic liquids have been used as catalyst in Friedel−Crafts reactions. Recently, the [triethylamine hydrochloride]−x[$AlCl_3$] (where x = 0.67 is the mole ratio of aluminum trichloride in the ionic liquid) ionic liquid has been used as a catalyst for the preparation of dichlorophenylphosphine (DCPP) by the phosphylation of benzene.[1] At the beginning of the reaction, there are three components in the reactants: benzene, phosphorus trichloride (PCl_3), and the ionic liquid. To model the reaction kinetics and for the separation for the reaction mixture and the solubility data of petroleum ether in the ionic liquid, it is also necessary to model the extraction of the product from the reaction mixtures. It was found that petroleum ether dissolved in the ionic liquid. Hence, the solubility data of PCl_3, benzene, petroleum ether, and heptane in the ionic liquid and the solubility data of the ionic liquid in petroleum ether, heptane, benzene, and PCl_3 are required. There is little literature data for phase equilibrium data involving ionic liquids.[5−8]

Experimental Section

Materials. Triethylhydrogenammonium chloride (AR 99+%), aluminum trichloride (AR 98.5%), petroleum ether (boiling point 60 °C−90 °C), benzene (AR 99.95%; density: measured 0.8758,[20] reported 0.8765;[20] refractive index: measured 1.5025,[20] reported 1.5011[20]), heptane (AR 98.5%; density: measured 0.6840,[20] reported 0.6837;[20] refractive index: measured refraction 1.3880,[20] reported 1.3878[20]), and PCl_3 (AR 95.5%; density: measured 1.5761,[21] reported 1.574;[21] refractive index: measured 1.5171,[14] reported 1.5160[14]) were all purchased from VAS Chemical Reagent Corporation Ltd., Beijing. The petroleum ether was distilled over anhydrous calcium hydride under nitrogen, and the fraction from (63 to 90) °C was used. The heptane and the PCl_3 were distilled over anhydrous calcium hydride under nitrogen before use. The [triethylamine hydrochloride]−x[$AlCl_3$] (x = 0.67) ionic liquid used in this work was prepared according to a procedure described in our previous paper.[1]

In a round-bottomed flask equipped with a magnetic stirrer and a gas inlet valve, under nitrogen, 266.7 g (2 mol) of anhydrous $AlCl_3$ was slowly added to 138 g (1 mol) of triethylhydrogenammonium chloride. The mixture was stirred at 70 °C for 6 h to ensure a complete reaction and kept at this temperature at reduced pressure (about 13.3 kPa) for 3 h. The ionic liquid was kept under dry conditions for the measurement of solubility.

Apparatus and Procedure for Solubility Measurement of Binary Systems. The solubility determination was carried out in a glass cell of 100-cm^3 volume. The glass cell was provided with an external jacket in which water at constant temperature was circulated using a thermostat. A calibrated thermometer monitored the temperature of the water bath with an accuracy of ±0.01 K. For a measurement, the cell was charged with a known mass of ionic liquid with a volume of about 50 cm^3. The composition of the mixture was determined from the mass of the pure component determined using a digital balance prior to mixing. An electronic balance with precision of 0.1 mg was used to determine the mass of the material.

For the measurement of the solubility of heptane, petroleum ether, PCl_3, and benzene in the ionic liquid at each selected temperature, the amount of solute was determined by titration with a known amount of ionic liquid at a constant temperature with continuous stirring until the solution became turbid. The charging inlet was sealed with a rubber plug to prevent the solvent from evaporating. The method of the measurement of the ionic liquid in benzene and PCl_3 is similar to that described above. All of the measurements reported in this paper were repeated three times at each temperature, and the average value was taken. The solubility of heptane, petroleum ether, PCl_3, and benzene in the ionic liquid and the solubility of the ionic liquid in benzene and PCl_3 in the temperature range from (293.16 to 332.60) K are listed in Tables 1 and 2. Figure 1 is the plot of the solubility (in mass fraction) of petroleum ether, heptane, phosphorus trichloride, and benzene in the ionic liquid and the solubil-

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Table 1. Measured Mass Fraction Solubilities (*S*) of Petroleum Ether, Benzene, Heptane, and Phosphorus Trichloride in the [Triethylamine Hydrochloride]−*x*[AlCl$_3$] (*x* = 0.67) Ionic Liquid

		S	
compounds	*T*/K	experimental	RD%
petroleum ether	294.66	0.0440	0.6818
	298.16	0.0450	0.2222
	303.17	0.0472	0.4237
	308.20	0.0503	1.3917
	313.16	0.0563	0.8881
	317.95	0.0601	2.4958
	323.17	0.0696	0.4310
heptane	293.16	0.0305	0.3279
	298.22	0.0326	2.1472
	303.90	0.0345	1.7391
	313.13	0.0381	0.5249
	317.50	0.0402	0.2488
	323.17	0.0439	1.5945
	332.60	0.0497	1.0060
phosphorus trichloride	293.20	0.2716	0.1105
	298.04	0.2763	0.0724
	302.64	0.2795	0.2147
	308.16	0.2864	0.5019
	313.66	0.2897	0.0345
	319.07	0.2935	0.3407
	324.16	0.2994	0.1336
benzene	293.65	0.5715	0.0175
	297.65	0.5702	0.0351
	303.75	0.5679	0.0088
	308.85	0.5665	0.0094
	314.15	0.5656	0.0177
	318.95	0.5651	0.0354
	324.05	0.5646	0.0012

Table 2. Measured Mass Fraction Solubilities (*S*) of the [Triethylamine Hydrochloride]−*x*[AlCl$_3$] (*x* = 0.67) Ionic Liquid in Benzene and Phosphorus Trichloride

		S	
compounds	*T*/K	experimental	RD%
benzene	294.05	0.0103	0.2339
	298.15	0.0098	0.4781
	302.95	0.0091	1.0989
	308.65	0.0084	1.1905
	313.75	0.0080	1.2500
	319.25	0.0072	0.3740
	324.95	0.0065	0.1077
phosphorus trichloride	293.16	0.0009	0.3226
	298.15	0.0010	4.2647
	303.65	0.0012	0.3253
	309.15	0.0016	3.8221
	313.65	0.0022	1.5996
	318.05	0.0026	4.1538
	324.15	0.0038	0.2634

ity of the ionic liquid in phosphorus trichloride and benzene. The estimated accuracy of the solubility value based on the uncertainty analysis was about 3%.

Density Measurement of the [Triethylamine Hydrochloride]−x[AlCl$_3$] Ionic Liquid. The density of the ionic liquid was measured using a 50-cm^3 pycnometer calibrated with distilled water. The mass was determined on an electronic balance with a precision of ±0.1 mg. The filled pycnometer was then immersed in a thermostated bath with temperature control precision of ±0.01 K. A stirrer was applied to the bath to speed up the establishment of temperature equilibrium. A description of the apparatus and measurement procedure is given in our previous paper.[9] The densities of the ionic liquid are listed in Table 3. The estimated accuracy of the density value, based on uncertainty analysis, was within 1%.

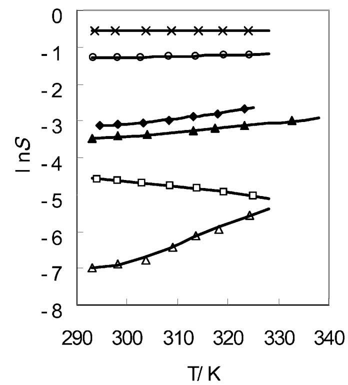

Figure 1. Solubility (in mass fraction) of petroleum ether, heptane, phosphorus trichloride, and benzene in the ionic liquid and the solubility of the ionic liquid in phosphorus trichloride and benzene. Measured solubility of ◆, petroleum ether; ▲, heptane; ○, phosphorus trichloride; and ×, benzene in the ionic liquid and the measured solubilities of the ionic liquid in △, phosphorus trichloride and □, benzene. −, Calculated values according to eq 1.

Table 3. Densities of the [Triethylamine Hydrochloride]−*x*[AlCl$_3$] (*x* = 0.67) Ionic Liquid

	ρ/g·cm^{-3}	
T/K	experimental	RD%
273.17	1.3135	0.0533
285.16	1.3028	0.0691
293.42	1.2960	0.0463
302.96	1.2885	0.0155
313.16	1.2808	0.1093
323.67	1.2723	0.1572
332.65	1.2646	0.1661
342.93	1.2521	0.1118
352.78	1.2418	0.2577
363.17	1.2371	0.0970
370.94	1.2289	0.0244

Table 4. Parameters in Equation 1 Pertaining to the Correlations of the Solubilities of Petroleum Ether, Heptane, Benzene, and Phosphorus Trichloride in the [Triethylamine Hydrochloride]−*x*[AlCl$_3$] (*x* = 0.67) Ionic Liquid Ionic Liquid (IL) and the Solubilities of the IL in Benzene and Phosphorus Trichloride

systems	*a*	*b*	*c*
petroleum ether + IL	2.2158	−0.0149	2.5522×10^{-5}
heptane + IL	0.4089	−0.0029	5.3178×10^{-6}
PCl_3 + IL	0.0149	8.7655×10^{-4}	0
benzene + IL	1.2821	−0.0044	6.7505×10^{-6}
IL + PCl_3	0.2752	−0.0019	3.1633×10^{-6}
IL + benzene	0.0464	-1.2275×10^{-4}	0

Correlation. The solubility (in mass fraction *S*) of petroleum ether, heptane, benzene, and PCl_3 in the ionic liquid and the solubility of the ionic liquid in benzene and PCl_3 were all correlated as a function of temperature (*T*/K) by following general form of second-order polynomial:

$$S = a + b(T/K) + c(T/K)^2 \tag{1}$$

Parameters *a*, *b*, and *c* correlated for the different systems are listed in Table 4. The relative deviation (RD%) of the experimental data from the smoothed results based on eq 1 are listed in Tables 1−3.

$$\mathrm{RD\%} = \frac{|S_{\mathrm{exptl}} - S_{\mathrm{calcd}}|}{S_{\mathrm{exptl}}} \times 100 \tag{2}$$

The experimental data and the smoothed results are shown in Figure 1. The absolute average deviation (AAD%)

of the measured data from the smoothed data is defined as

$$\mathrm{AAD\%} = \frac{1}{N}\sum_i \frac{|S_i^{\mathrm{exptl}} - S_i^{\mathrm{calcd}}|}{S_i^{\mathrm{exptl}}} \times 100 \qquad (3)$$

where the superscript exptl stands for experimental values and calcd stands for the calculated values. The AAD% values of the measured solubility of heptane, petroleum ether, PCl_3, and benzene are 1.1%, 0.9%, 0.2%, and 0.02%, respectively. The AAD% values of the measured solubility of the ionic liquid in benzene and PCl_3 are 0.5% and 3.0%, respectively.

The density of the [triethylamine hydrochloride]−x[$AlCl_3$] ($x = 0.67$) ionic liquid was correlated as a function of temperature (T/K) by adopting a linear equation:

$$\rho/\mathrm{g{\cdot}cm^{-3}} = 1.5516 - 8.6925 \times 10^{-4}(T/\mathrm{K}) \qquad (4)$$

According to eq 3, the AAD% of the measured density of the ionic liquid is 0.09%.

Discussion

Within the temperature range, the solubility of heptane, petroleum ether, and PCl_3 in the [triethylamine hydrochloride]−x[$AlCl_3$] ($x = 0.67$) ionic liquid and the solubility of the ionic liquid in PCl_3 increased with increasing temperature. At the same temperature, the solubility of heptane is slightly lower than that of petroleum ether. Thus, the solubility of heptane in the ionic liquid increased from 0.0304/S at 293.16 K to 0.0492/S at 332.60 K, whereas that of petroleum ether increased from 0.0443/S at 294.66 K to 0.0693/S at 323.17 K. The solubility of PCl_3 in the ionic liquid increased from 0.2716/S at 293.20 K to 0.2994/S at 324.16 K, which was much higher than that of heptane and petroleum ether, whereas that of benzene at a similar temperature decreased from 0.5715/S to 0.5640/S. However, the ionic liquid had only slight solubility in PCl_3 or benzene. Therefore, the two phases are formed when mixing benzene, PCl_3, and the ionic liquid. One phase is an ionic liquid-rich phase with some benzene and PCl_3 dissolved in it; another phase belongs to the excess amount of the benzene and PCl_3 mixture and only a very small amount of the ionic liquid dissolved in it. After reaction, the mixture separated into two phases. From the point of view of reactant recovery, this advantage is obvious. For the catalysis reaction of benzene and PCl_3 using another ionic liquid[10] ([BuPy]Cl−x[$AlCl_3$], where [BuPy]Cl = N-butylpyridium chloride and $x = 0.67$ is an optimized mole ratio of aluminum trichloride, $AlCl_3$, in the ionic liquid), the reaction mixture was in a one-phase state after the reaction. The DCPP in the reaction mixture was extracted with petroleum ether directly. However, the unreacted PCl_3, benzene, and petroleum ether remained in the ionic liquid, so the thus-obtained ionic liquid was not reusable. The solubility data determined in this paper will provide a basis for designing a much more successful isolating process.

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