Low Pressure Solubilities of Vinyl Chloride in Ionic Liquids

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The mole fraction solubility of vinyl chloride in 1-butyl-3-methyl imidazolium tetrafluoroborate ([BMIM][BF_4]), 1-butyl-3-methyl imidazolium hexafluorophosphate ([BMIM][PF_6]), 2,4-bis(2-hydroxypropyl)-1,1,3,3-tetramethyl guanidinium tetrafluoroborate ([$TMGHPO_2$][BF_4]), and tetramethyl guanidinelactate (TMGL) is reported as a function of temperature at (293.15, 313.15, and 333.15) K at pressures of up to 2 bar on the basis of a saturation method. The Henry's law constants and enthalpy of solution of vinyl chloride were calculated from the solubility data. The enthalpy of solution is negative for all mixtures.

Introduction

Room-temperature ionic liquids (RTILs) are a relatively new class of compounds that are composed of a bulky organic cation and an organic or inorganic anion. They present properties such as high thermal stability, high ionic conductivity, and nonflammability. Another unique property of RTILs is that they have immeasurably low vapor pressure and are therefore considered to be "green" solvents that may potentially replace many conventional volatile organic solvents in organic synthesis[1] and separation processes.[2] Theoretically, with various combinations of anions and cations, numerous RTILs with very different properties can be synthesized. Therefore, RTILs are considered to be designer solvents. The thermodynamic properties of RTILs and their mixtures are essential because further research and application of RTILs will require an understanding of these properties.[3,4] Expanded QSPR and COSMO-RS models have been developed to model the thermodynamic properties of systems including RTILs; however, the quality of the predictions needs to be further tested.[5−7] The gas solubility in RTILs is useful in the calculation of vapor/liquid equilibria for reaction systems or separation processes.

The solubility data for various gases in different RTILs were determined by the use of different techniques, and Henry's law constants could be derived both from data obtained at pressures close to atmospheric[8,9] or by extrapolation of values obtained at higher pressures.[10,11]

Vinyl chloride is a highly reactive and toxic substance that is widely used in industrial processes. It is the parent compound of one of the most important industrial polymers including polyvinyl chloride. A knowledge of the solubility of vinyl chloride in RTILs is necessary for the further research of both vinyl chloride reaction and gas separation processes in RTILs.

In the present work, the solubility of vinyl chloride in 1-butyl-3-methyl imidazolium tetrafluoroborate ([BMIM][BF_4]), 1-butyl-3-methyl imidazolium hexafluorophosphate ([BMIM][PF_6]), tetramethyl guanidinelactate (TMGL), and 2,4-bis(2-hydroxypropyl)-1,1,3,3-tetramethyl guanidinium tetrafluoroborate ([$TMGHPO_2$][BF_4]) at pressures of up to 2 bar is reported.

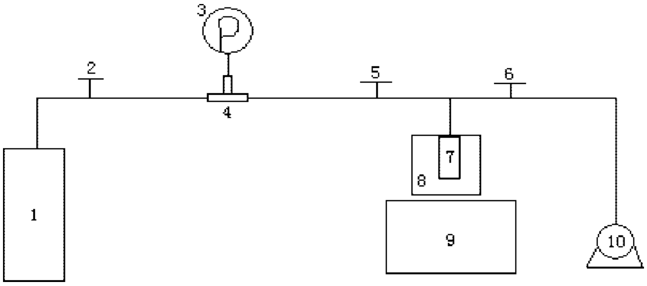

Figure 1. Experimental apparatus: 1, VC reservoir; 2, control valve; 3, pressure gauge; 4, trifurcate valve; 5, control valve; 6, control valve; 7, isochoric cell; 8, thermostat; 9, magnetic stirrer; 10, vacuum pump.

Experimental Section

Materials. The vinyl chloride gas with a minimum purity of 99.99 % was purchased from Dalian Airichem Specialty Gases & Chemicals and was used as received. The RTILs [BMIM][PF_6] (CAS no.174501-64-5) and [BMIM][BF_4] (CAS no. 174501-65-6) were purchased from Henan Lihua Pharmaceutical with a minimum mole fraction purity of 99 %; the chloride and water mass fractions were $< 8 \cdot 10^{-4}$ and $< 1 \cdot 10^{-3}$ (g/g), respectively. The RTILs TMGL and [$TMGHPO_2$][BF_4] were synthesized in our laboratory. The TMGL[12,13] and [$TMGHPO_2$][BF_4][14] were synthesized and purified according to references, respectively. To remove traces of volatile compounds from the RTILs, the RTILs were kept in vacuum (about 10^{-6} bar) at 343 K for 24 h prior to use. The as-prepared TMGL and [$TMGHPO_2$][BF_4] were characterized by NMR, and no impurity peak was found. The estimated minimum mole fraction purity of the TMGL and [$TMGHPO_2$][BF_4] was 99 %. Some of the physical properties of these RTILs were presented in the literature.[12−14]

Apparatus and Measurements. The experimental method used for the gas solubility measurement was based on an isochoric saturation technique. The experimental apparatus used for vinyl chloride solubility measurements is schematically represented in Figure 1. The apparatus was composed of a gas reservoir, a thermostat, a pressure gauge, an isochoric cell, a vacuum pump, and a magnetic stirrer. The temperature was determined by two calibrated platinum resistance thermometers placed in the heating jacket of the cell with an uncertainty below

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Table 1. Solubility of Vinyl Chloride in [BMIM][BF_4], [BMIM][PF_6], TMGL, and [$TMGHPO_2$][BF_4][a]

	[BMIM][BF_4]		[BMIM][PF_6]		TMGL		[$TMGHPO_2$][BF_4]	
T/K	*P*/bar	*x*	*P*/bar	*x*	*P*/bar	*x*	*P*/bar	*x*
293.15	0.30	0.037	0.28	0.052	0.25	0.032	0.50	0.109
	0.72	0.088	0.69	0.136	0.67	0.085	0.88	0.190
	1.10	0.139	1.14	0.224	1.05	0.132	1.19	0.282
	1.22	0.152	1.26	0.255	1.21	0.164	1.37	0.371
	1.34	0.176	1.46	0.283	1.34	0.196	1.50	0.474
	1.51	0.203	1.59	0.317	1.48	0.219	1.62	0.534
	1.67	0.244	1.73	0.331	1.59	0.238	1.70	0.578
	1.74	0.262	1.88	0.359	1.75	0.279	1.83	0.637
	1.91	0.298	1.98	0.386	1.93	0.330	1.95	0.741
	2.00	0.339					2.00	0.796
313.15	0.24	0.016	0.30	0.017	1.04	0.077	0.48	0.041
	0.68	0.049	0.76	0.047	1.16	0.085	1.03	0.086
	1.11	0.081	1.15	0.076	1.38	0.118	1.32	0.127
	1.32	0.098	1.36	0.089	1.60	0.151	1.68	0.174
	1.54	0.114	1.53	0.106	1.83	0.181	1.94	0.224
	1.83	0.134	1.72	0.123	2.00	0.212		
	2.00	0.159	1.92	0.149				
			2.00	0.157				
333.15	0.49	0.010	0.43	0.003	0.58	0.007	0.55	0.020
	0.92	0.026	0.85	0.009	0.93	0.017	0.93	0.043
	1.19	0.037	1.10	0.016	1.43	0.043	1.41	0.089
	1.43	0.051	1.50	0.037	1.80	0.064	1.80	0.129
	1.67	0.071	1.85	0.064				

[a] *x* denotes mole fraction of vinyl chloride in the RTILs.

± 0.1 K. The low-pressure pressure gauge had an uncertainty of approximately ± 0.001 bar in the experimental pressure range.

In a typical experiment, the desired amount of RTIL was loaded in the isochoric cell, the volume of the cell was fixed, and the air in the system was eliminated by the vacuum pump; then, vinyl chloride was charged into the cell from the gas reservoir, and the liquid phase was stirred. The system was considered to have reached equilibrium if the pressure of the system had been unchanged over time for 2 h. Then the pressure of the system was recorded, and the cell was weighed. The mass of the cell was determined with an electronic balance (Sartorius BS224S) with an uncertainty of ± 0.0001 g. The solubility of gas in a given RTIL was determined by the shifted quality of the isochoric cell. To verify the validation of the apparatus, we determined the solubility of CO_2 in a choline chloride + urea mixture[15] with this apparatus, and the results were consistent with ref 15.

Results and Discussion

Solubility of Vinyl Chloride in Room-Temperature Ionic Liquids. The solubility of vinyl chloride in [BMIM][BF_4], [BMIM][PF_6], TMGL, and [$TMGHPO_2$][BF_4] was determined at (293.15, 313.15, and 333.15) K at pressures ranging from 0.2 to 2 bar. The results are presented in Table 1. The solubility results are given in terms of mole fractions of solute (x) in Table 1.

The solubility isotherms at (293.15, 313.15, and 333.15) K for each of the four RTILs are also shown in Figures 2, 3, and 4, respectively. The solubility of vinyl chloride in these RTILs at the given temperature increases with increasing pressure and decreases with temperature at the same pressure. From Table 1 and Figures 2, 3, and 4, the solubility of vinyl chloride in [$TMGHPO_2$][BF_4] is highest at the same temperature and pressure compared to that of other RTILs. The mole fraction of vinyl chloride in [BMIM][PF_6] is slightly higher than that in [BMIM][BF_4] and TMGL at 293.15 K. However, TMGL exhibits a better adsorption ability for vinyl chloride than do [BMIM][BF_4] and [BMIM][PF_6] at 313.15 K. The solubility of vinyl chloride in [BMIM][BF_4], [BMIM][PF_6], and TMGL is similar at the same pressure and temperature on the whole.

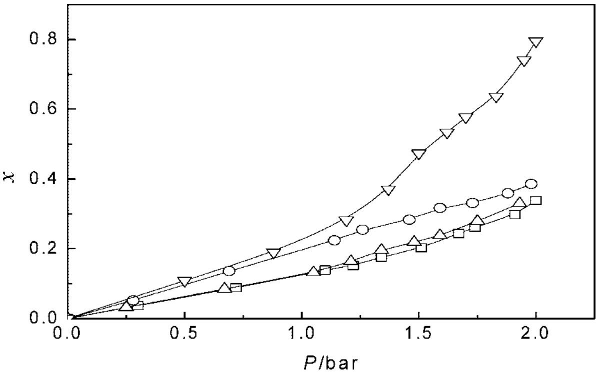

Figure 2. Mole fraction of vinyl chloride (x) at 293.15 K in: □, [BMIM][BF_4]; ○, [BMIM][PF_6]; △, TMGL; ▽, [$TMGHPO_2$][BF_4].

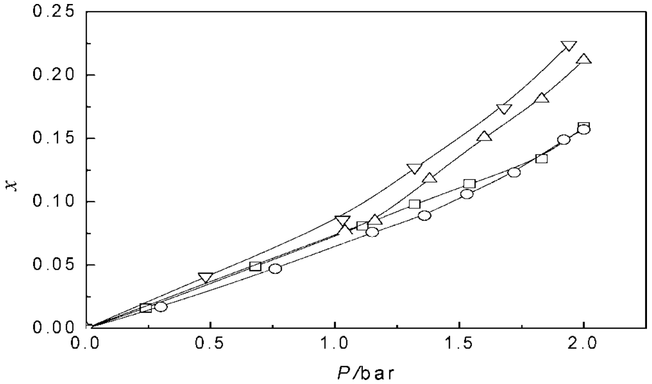

Figure 3. Mole fraction of vinyl chloride (x) at 313.15 K in: □, [BMIM][BF_4]; ○, [BMIM][PF_6]; △, TMGL; ▽, [$TMGHPO_2$][BF_4].

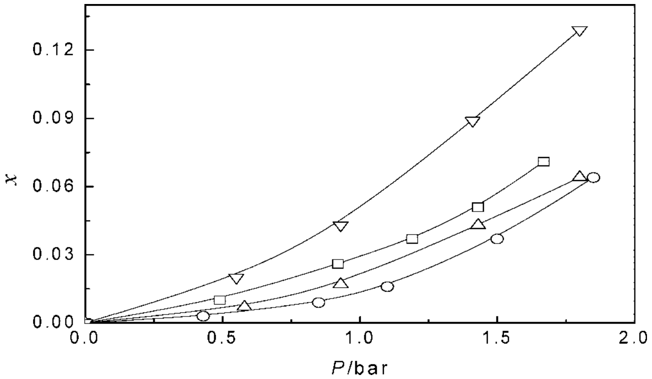

Figure 4. Mole fraction of vinyl chloride (x) at 333.15 K in: □, [BMIM][BF_4]; ○, [BMIM][PF_6]; △, TMGL; and ▽, [$TMGHPO_2$][BF_4].

Henry's Law Constant. At low pressure, the solubility of a gas in a liquid is frequently described in terms of Henry's law, which is defined as[16]

$$k_H \equiv \lim_{x \to 0} \frac{f^L}{x} \approx \frac{P}{x} \tag{1}$$

where k_H is the Henry's law constant of vinyl chloride in RTILs, x is the mole fraction of vinyl chloride, and f^L and P are the fugacity and pressure of vinyl chloride, respectively. Because the RTILs have negligible vapor pressures, the fugacity of vinyl chloride is deemed to be equal to the pressure of the gas. Henry's law constant depends on temperature but is not sensitive to pressure under 1.1 bar. From eq 1, for a gas that behaves nearly ideally, the solubility is linearly related to the pressure. This is

Table 2. Henry's Law Constants (k_H) at Three Temperatures and Enthalpies of Dissolution ($\Delta_{sol}H$) for Vinyl Chloride Dissolved in the RTILs

RTIL	k_H/bar T = 293.15 K	 T = 313.15 K	 T = 333.15 K	$\Delta_{sol}H$ kJ·mol^{-1}
[BMIM][BF$_4$]	6.01	12.94	22.93	−28.1
[BMIM][PF$_6$]	5.15	12.68	25.43	−39.5
TMGL	5.94	9.08	25.39	−29.4
[TMGHPO$_2$][BF$_4$]	2.94	8.67	13.17	−25.6

verified by the solubility experimental measurements of ethane, methane, and argon in [BMIM][PF$_6$].[16] However, in this experiment, the solubility of vinyl chloride in RTILs was not linear for the measured pressure range; the Henry's law constant was obtained by extrapolation of P/x versus pressure curves to zero pressure. The Henry's law constants of vinyl chloride at different temperatures are listed in Table 2. Because the Henry's law constant is obtained from the extrapolation, the uncertainty is relatively large. The estimated uncertainty of Henry's law constant is 3 %.

Enthalpy of Solution. The enthalpy of solution $\Delta_{sol}H$ is related to the strength of the interaction between the liquid and the gas, and it is another important parameter of the systems. $\Delta_{sol}H$ can be calculated from the dependence of the solubility on temperature by the use of the following equation[17]

$$\Delta_{sol}H = H_1 - H_g = R\left(\frac{\partial \ln P_1}{\partial(1/T)}\right)_{x_1} \tag{2}$$

where H_1 is the partial molar enthalpy of vinyl chloride in solution, H_g is the enthalpy of the pure vinyl chloride in the ideal gas phase, P_1 is the partial pressure of vinyl chloride, T is the temperature, and x is the mole fraction of vinyl chloride dissolved in the system. The values of P_1 at different temperatures with fixed x were obtained from the curves in Figures 2, 3, and 4. The ln P_1 is a linear function of $1/T$ at fixed x. Therefore, $\Delta_{sol}H$ is independent of composition (x) and equal to the infinite dilution values, which coincides with the van't Hoff equations[17,18] and can be calculated from the slopes of the curves. $\Delta_{sol}H$ values of vinyl chloride in different RTILs are presented in Table 2. The estimated uncertainty of the enthalpy of solution is 2.5 %. Under all conditions, the enthalpy of solution is negative, which indicates that the dissolution of the gas is exothermic. Other thermodynamic functions of solvation such as the standard Gibbs energy and the entropy could also be calculated from knowing the value of the enthalpy.[19]

Conclusions

The mole fraction of vinyl chloride in [BMIM][BF$_4$], [BMIM][PF$_6$], [TMGHPO$_2$][BF$_4$], and TMGL at (293.15, 313.15, and 333.15) K increases with increasing pressure and decreases with temperature at the same pressure. The solubility of vinyl chloride in [TMGHPO$_2$][BF$_4$] is highest at the same temperature and pressure compared to that of other RTILs. The Henry's law constants and enthalpy of solution of vinyl chloride derived from the solubility data showed that the dissolution of the gas is exothermic.

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