Solubilities of Triethanolamine Hydrochloride Ionic Liquid in Aqueous Hydrochloric Acid Solutions with Concentrations from (0 to 8.37) $\text{mol}\cdot\text{kg}^{-1}$[†]

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The (solid + liquid) phase equilibria of triethanolamine hydrochloride ([HTEA]Cl) ionic liquid and aqueous hydrochloric acid solutions with concentrations from (0 to 8.37) $\text{mol}\cdot\text{kg}^{-1}$ were determined by a dynamic method within the temperature range of (285.70 to 344.65) K. Solubilities of [HTEA]Cl were found to increase with increasing temperature for all the investigated solutions. However, solubilities of [HTEA]Cl in aqueous hydrochloric acid decrease with the increment of the concentration of the acid due to the common ion effect. K_{SP} values of [HTEA]Cl were obtained by use of the solubility data of [HTEA]Cl in water. The modified Apelblat equation was used successfully to correlate experimental data of solubilities in hydrochloric acid. Molar dissolution enthalpy ΔH_{Sol} of [HTEA]Cl in hydrochloric acid solutions was determined with the newly obtained Apelblat equation parameters.

Introduction

The chemical and physical properties of ionic liquids have been vigorously investigated in the past decade. Because ionic liquids are organic salts, they exhibit many specific characteristics, including high heat capacities, high densities, extremely low volatilities, nonflammability, high thermal stability, and a wide temperature range for the liquid state.[1] Hence, ionic liquids can be applied for catalysis, synthesis, and separation. Ionic liquids have a large number of possible variations in cation and anion combinations. With an increasing awareness of how the structure of an ionic liquid affects its physical properties, the advantages of ionic liquids as compared to volatile organic solvents become evident.[2] To be able to use ionic liquids efficiently, it is important to characterize their fundamental thermodynamic properties and phase behavior in water and other solvents.[3]

Solubility is an important property for ionic liquid and has attracted increased attention. Solubility behavior determines the method of supersaturation generation as well as the yield of crystallization and plays an important role in industrial processes and in theoretical research.[4,5] The use of solid + liquid equilibria (SLE) phase diagrams rather than a trial-and-error approach would greatly reduce the process development time and cost.[6] However, because ionic liquids are relatively new, experimental measurements of phase behavior are relatively limited. The deficiency of solubility data could hinder the development of ionic liquid as solvent and catalyst.

Triethanolamine hydrochloride ([HTEA]Cl) ($C_6H_{15}NO_3\cdot HCl$, CAS No. 637-39-8) is a kind of ammonium ionic liquid and can be used for detecting elements of tin and antimony or as the catalyst in the production of resin. This ionic liquid can be produced by the reaction of triethanolamine and aqueous hydrochloric acid. Its solubilities in water and hydrochloric acid solutions are important for the production process. However, to the best of our knowledge, the solubility data of [HTEA]Cl have not been measured yet.

In this work, triethanolamine hydrochloric with the mass fraction purity of more than 0.98 was synthesized. Then the solid−liquid equilibrium (SLE) temperatures of triethanolamine hydrochloride in water and hydrochloric acid with various concentrations were determined using a dynamic method. Effects of temperature and concentration of hydrochloric acid solution were investigated. The SLE phase diagram was presented. Then the molar dissolution enthalpy ΔH_{Sol} was calculated for these systems.

Experimental Section

Materials. Analytical reagent (AR) grade triethanolamine was obtained from Guangdong Xilong Chemical Co., Ltd., China. Hydrochloric acid with mass fraction of (0.36 to 0.38) and AR grade ethanol were from Beijing Chemical Works, China. All chemicals were used as received, and water used was deionized water.

Synthesis of Triethanolamine Hydrochloride. The synthesis of [HTEA]Cl was performed in a 1 L double-jacket glass reactor, and the temperature was controlled by a water circulator as shown in Figure 1.[7] A standard volume (250 mL) of triethanolamine of 5 $\text{mol}\cdot\text{L}^{-1}$ located in the reactor (a) was kept at temperature 293.15 K with circulating water (b). Solution temperature was monitored with a thermometer (c). Agitation was provided by an agitator (d) with the stirring speed of 200 rpm. Hydrochloric acid (114.6 mL) was added by titration with a pump (e) over 60 min. The slurry was filtered, washed with ethanol, and finally dried in an oven at 323.15 K to remove all volatile components, water, and excessive acid. The mass fraction purity of [HTEA]Cl, determined by titration with silver nitrate solution as the titrant and potassium chromate as the indicator, was above 0.98. Its purity was also verified by ^1H NRM and ^{13}C NRM analyses. The X-ray powder diffraction (XRD) pattern of the synthesized sample is shown in Figure 2.

Solubility Measurement. Solid solubility was determined using a dynamic method.[8,9] A jacketed glass vessel with a

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[†] Part of the “Sir John S. Rowlinson Festschrift”.

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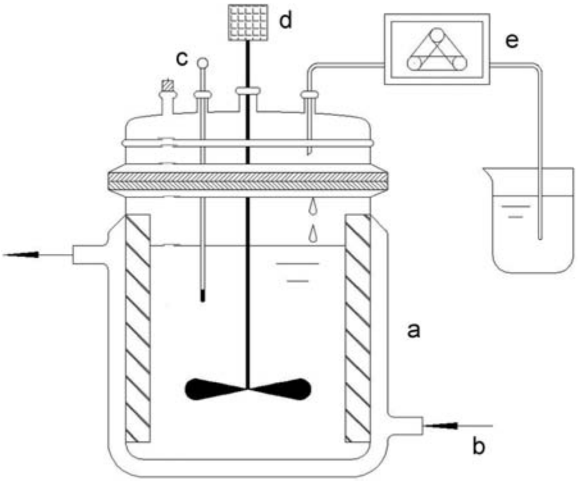


Figure 1. Experimental setup used in the synthesis of [HTEA]Cl.

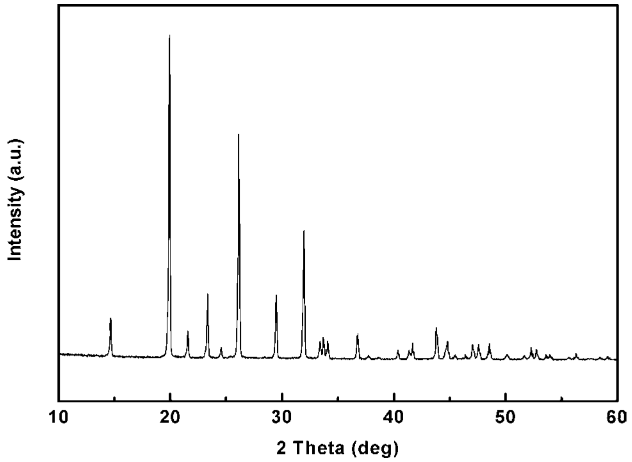


Figure 2. XRD pattern of synthesized [HTEA]Cl.

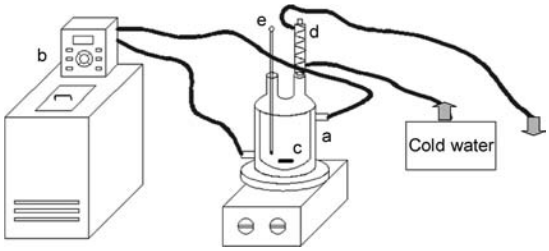


Figure 3. Experimental setup for the solubility measurement of [HTEA]Cl with a dynamic method.

volume of 250 mL was used in this system as can be seen in Figure 3. The solvent of known composition was put into the vessel (a), and the system was maintained at a certain temperature T using a thermostat (b). A known mass of [HTEA]Cl was added into the solvent. A magnetic stirrer was used to provide vigorous agitation to the sample (c). Some time later, more weighted [HTEA]Cl was added if the last trace of salts was observed to disappear. The mixture of solute and solvent was heated very slowly ($<1\ \mathrm{K \cdot h^{-1}}$ near the equilibrium temperature) with continuous stirring. A condenser (d) was used in the system. The temperatures at which crystals disappeared, detected visually, were measured with a thermometer (e). The temperature precision was ± 0.1 K. All the chemical regents were prepared by weighting the pure components with an uncertainty of ± 0.001 g.

Table 1. Experimental Mole Fraction Solubilities of [HTEA]Cl in Water and K_{SP} Values Calculated by Equation 3 with Solubility Data

T/K	x_1	m_1	K_{SP}
285.70	0.0335	1.926	3.71
292.47	0.0399	2.309	5.33
298.37	0.0462	2.691	7.24
303.45	0.0525	3.078	9.48
308.65	0.0587	3.464	12.00
311.05	0.063	3.735	13.95
316.05	0.0699	4.175	17.43
318.35	0.0747	4.485	20.12
322.00	0.0815	4.930	24.30
326.65	0.0884	5.387	29.02
333.05	0.0998	6.159	37.93
339.25	0.1108	6.923	47.92
344.65	0.1215	7.684	59.04

Results and Discussion

Solubility of [HTEA]Cl in Water. The solubilities of [HTEA]Cl in water were measured with the procedure mentioned above at the temperature range of (285.70 to 344.65) K. The results are listed in Table 1 and presented in Figure 4. It was found that the solubility of [HTEA]Cl in water increases sharply with increasing temperature over the investigated temperatures. As can be seen in Figure 4, the solubility increases to more than 3.7 times when the temperature increases from (285.7 to 344.65) K.

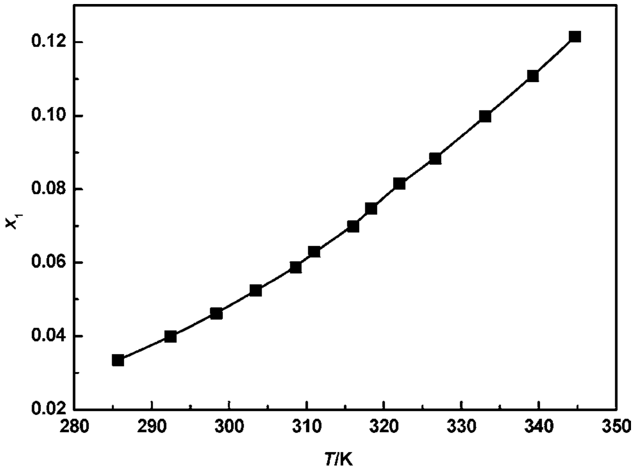


Figure 4. Mole fraction solubility (x_1) of [HTEA]Cl in water.

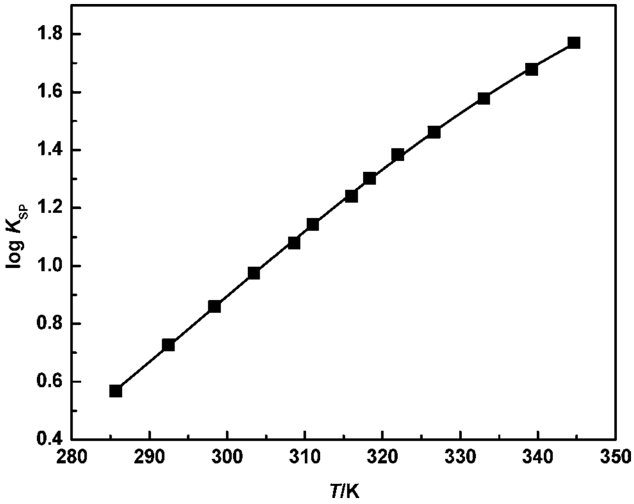


Figure 5. Values of log K_{SP} of [HTEA]Cl in water. ■, log K_{SP} obtained by experimental solubility data of [HTEA]Cl in pure water with eq 3; solid line, log K_{SP} values correlated with eq 4.

Table 2. Experimental Mole Fraction Solubilities of [HTEA]Cl (1) in Aqueous Hydrochloric Acid Solutions with Different Concentrations of HCl (2)

x_1	T/K	x_1	T/K
$x_2 = 0.0179$ (1.01 $\text{mol}\cdot\text{kg}^{-1}$)		$x_2 = 0.0367$ (2.12 $\text{mol}\cdot\text{kg}^{-1}$)	
0.0375	296.55	0.0305	296.35
0.0435	301.30	0.0366	301.85
0.0494	305.95	0.0427	306.85
0.0552	310.65	0.0486	311.85
0.0610	315.00	0.0545	316.05
0.0667	318.00	0.0603	319.70
0.0723	321.30	0.0661	324.55
0.0779	325.95	0.0718	327.80
0.0834	329.05	0.0774	331.35
0.0888	332.10	0.0840	335.15
0.0941	335.35	0.0895	338.55
0.0994	338.65		
$x_2 = 0.0550$ (3.23 $\text{mol}\cdot\text{kg}^{-1}$)		$x_2 = 0.0748$ (4.49 $\text{mol}\cdot\text{kg}^{-1}$)	
0.0192	289.15	0.0194	292.85
0.0255	296.55	0.0257	300.25
0.0317	302.65	0.0320	306.85
0.0377	308.25	0.0381	312.75
0.0438	313.15	0.0442	317.60
0.0497	317.25	0.0502	321.95
0.0556	321.30	0.0561	326.35
0.0614	325.95	0.0619	330.55
0.0671	329.65	0.0677	334.35
0.0727	333.55	0.0734	337.75
0.0783	336.65		
$x_2 = 0.0925$ (5.85 $\text{mol}\cdot\text{kg}^{-1}$)		$x_2 = 0.1163$ (7.31 $\text{mol}\cdot\text{kg}^{-1}$)	
0.0212	295.75	0.0195	294.85
0.0281	304.85	0.0258	303.57
0.0349	311.10	0.0320	310.95
0.0416	316.55	0.0382	315.85
0.0482	321.95	0.0443	320.95
0.0547	326.95	0.0503	326.25
0.0611	331.35	0.0562	330.35
0.0675	335.45	0.0620	334.55
0.0737	339.05	0.0678	338.55
0.0799	342.45	0.0735	341.75
		0.0792	345.25
$x_2 = 0.1309$ (8.37 $\text{mol}\cdot\text{kg}^{-1}$)			
0.0196	296.35		
0.0260	304.90		
0.0323	311.55		
0.0385	317.35		
0.0447	322.90		
0.0507	328.15		
0.0567	332.55		
0.0626	336.65		
0.0684	340.45		
0.0742	344.30		

The solubility data of [HTEA]Cl in water were used to calculate a fundamental thermodynamic parameter, K_{SP}, the solubility product of the salt. Solubility equilibrium of [HTEA]Cl in water can be described by the following dissolution reaction

$$[\text{HTEA}]\text{Cl} \leftrightarrow [\text{HTEA}]^{+} + \text{Cl}^{-} \tag{1}$$

The solubility product of [HTEA]Cl, $K_{\text{SP,[HTEA]Cl}}$, is expressed as the following equation

$$K_{\text{SP,[HTEA]Cl}} = a_{[\text{HTEA}]^{+}} a_{\text{Cl}^{-}} \tag{2}$$

where $a_{[\text{HTEA}]^{+}}$ and $a_{\text{Cl}^{-}}$ are the activity of cation $[\text{HTEA}]^{+}$ and anion Cl^{-} in solution. To make it simple, the activities can be replaced by concentrations of ions as follows

$$K_{\text{SP,[HTEA]Cl}} = m_{[\text{HTEA}]^{+}} m_{\text{Cl}^{-}} \tag{3}$$

where $m_{[\text{HTEA}]^{+}}$ and $m_{\text{Cl}^{-}}$ are the concentration of cation $[\text{HTEA}]^{+}$ and anion Cl^{-} in molality. The values of $K_{\text{SP,[HTEA]Cl}}$ calculated with the solubility data in water are also listed in Table 1. These K_{SP} values were correlated with an empirical equation as shown below[7,10]

$$\log_{10} K_{\text{SP,[HTEA]Cl}} = -114.625 + \frac{10686.419}{T} + 0.391T - 0.0004162T^{2} \tag{4}$$

where T is the temperature in Kelvin. The results are well fitted as can be seen in Figure 5.

Solubility of [HTEA]Cl in HCl Solutions. The same procedure was used to measure solubilities of [HTEA]Cl in hydrochloric acid solutions with concentrations from (1.01 to 8.37) $\text{mol}\cdot\text{kg}^{-1}$ within the temperature range of (289.15 to 345.25) K. The results are given in Table 2 and presented in Figures 6a and 6b. A 3-D diagram of solubilities of [HTEA]Cl in aqueous hydrochloric acid solutions is shown in Figure 7. It can be seen that the solubility values are dependent on the system temperature and the concentration of HCl. The solubilities of [HTEA]Cl increase with increasing temperature in all solvents over the investigated temperatures. However, the common ion effect makes it decrease with increasing concentration of aqueous hydrochloric acid.[11,12]

Figures 8a and 8b show that the logarithm of the mole fraction solubility x_1 determined in this work plotted against the inverse temperature shows good linearity. Therefore, we decided to correlate the solubility data by the modified Apelblat equation[13,14]

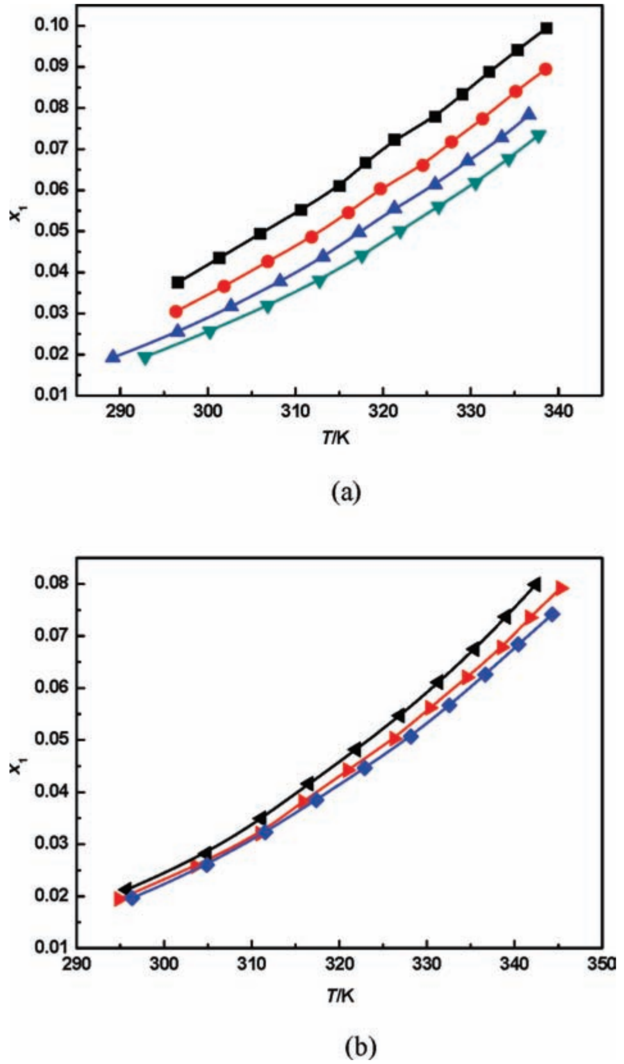
$$\ln x_1 = a + \frac{b}{T/\text{K}} \tag{5}$$

where x_1 and T are mole fraction solubility of solute and absolute temperature, respectively, and a and b are empirical parameters. The values of the two parameters were evaluated by nonlinear least-squares method. The root-mean-square deviation (rmsd) is defined as

$$\text{rmsd} = \left[\frac{1}{n}\sum_{i=1}^{n}(x_{1,i}^{\text{cal}} - x_{1,i}^{\text{exp}})^{2}\right]^{1/2} \tag{6}$$

where n is the number of experimental points; $x_{1,i}^{\text{cal}}$ is the solubility calculated by eq 5; and $x_{1,i}^{\text{exp}}$ is the experimental value of mole fraction solubility. The values of a, b, and rmsd for the solubilities of triethanolamine hydrochloride in hydrochloric acid solutions are given in Table 3. It can be observed that the correlated solubilities agree well with the experimental values. This indicates that the modified Apelblat equation is a successful description of the solubilities of [HTEA]Cl in hydrochloric acid solutions.

The solubilities of [HTEA]Cl in hydrochloric acid solutions were predicted at T = (300, 310, 320, 330, 340, and 350) K using the modified Apleblat equation and parameters from Table 3. Hence, the SLE phase diagram of [HTEA]Cl in aqueous hydrochloric acid solutions was constructed by the calculated solubility data as shown in Figure 9. It can be seen in Figure 9 that each curve indicates one boundary of the crystallization compartments, as an important feature of the phase diagram.[6] The crystallization region can be found by the curves in the



(a)

(b)

Figure 6. Mole fraction solubility of [HTEA]Cl (x_1) in aqueous hydrochloric acid solutions with various concentration (x_2). (a) ■, $x_2 = 0.0179$; ●, $x_2 = 0.0367$; ▲, $x_2 = 0.0550$; ▼, $x_2 = 0.0748$. (b) Solid triangle pointing right, $x_2 = 0.0925$; solid triangle pointing left, $x_2 = 0.1163$; ◆, $x_2 = 0.1309$.

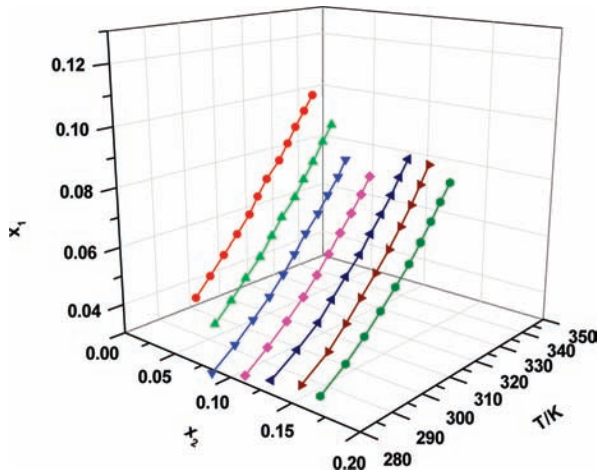
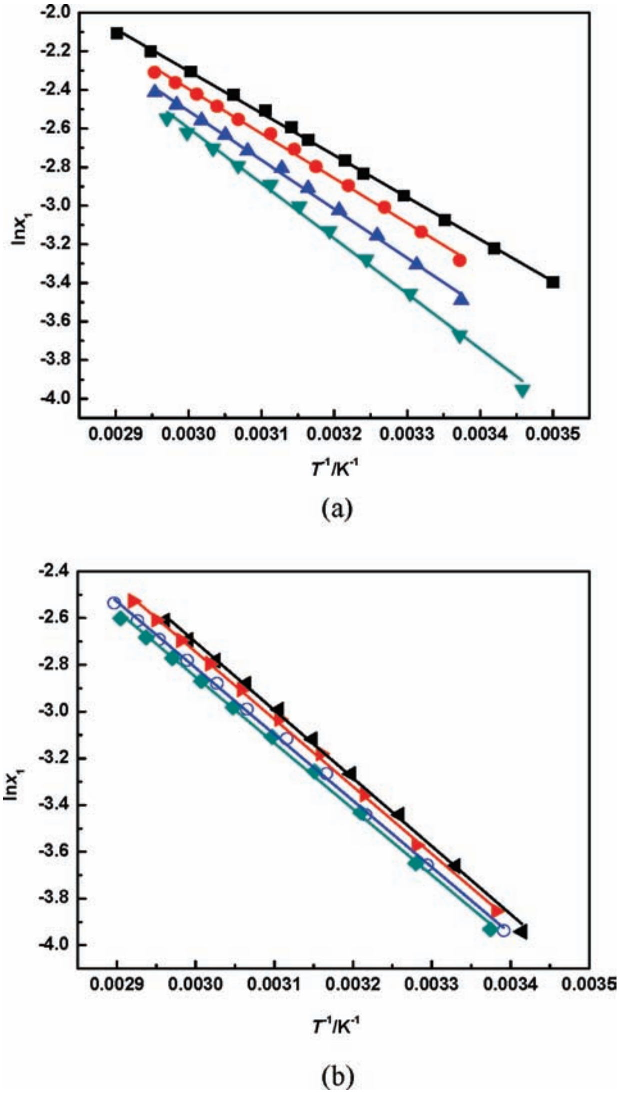


Figure 7. 3-D diagram of solubility of [HTEA]Cl in aqueous hydrochloric acid solutions.

SLE phase diagram, which is of utility for the synthesis process of [HTEA]Cl.



(a)

(b)

Figure 8. Plots of ln x_1 versus $1/T$ for mole fraction solubility of [HTEA]Cl (x_1) in aqueous hydrochloric acid solutions with various concentrations (x_2): (a) ■, $x_2 = 0$; ●, $x_2 = 0.0179$; ▲, $x_2 = 0.0367$; ▼, $x_2 = 0.0550$. (b) Solid triangle pointing right, $x_2 = 0.0748$; solid triangle pointing left, $x_2 = 0.0925$; ○, $x_2 = 0.1163$; ☐, $x_2 = 0.1309$. The line is the values calculated with the modified Apelblat equation.

Table 3. Parameters of the Modified Apelblat Equation (Equation 5) for [HTEA]Cl (1) in Aqueous Hydrochloric Acid Solutions with Different Concentrations of HCl (2)

x_2	a	b	rmsd
0.000	4.236	−2179.482	0.001071
0.0179	4.547	−2313.932	0.001055
0.0367	5.106	−2538.412	0.000918
0.0550	5.975	−2857.758	0.001302
0.0748	6.026	−2909.892	0.000805
0.0952	5.906	−2883.372	0.004044
0.1163	5.715	−2842.659	0.003508
0.1309	5.627	−2826.393	0.000638

Calculation of Dissolution Enthalpy. Dissolution enthalpy ΔH_{Sol} is a relevant thermodynamic measure for the degree of interaction of the solvent and the solute molecules. The value of dissolution enthalpy can indicate solid−liquid interfacial energy, which is a significant physical property influencing nucleation and growth of crystals.[15,16]

On the basis of the principle of solid/liquid equilibrium, when a solid is dissolved in a solvent and forms an ideal solution, the chemical potential of the solute i can be expressed as[17]

$$\mu_i = \mu_i^* + RT \ln x_i \tag{7}$$

where μ_i, μ_i^*, x_i, R, and T stand for the chemical potential of the pure solid, chemical potential of the solute in ideal solution, the mole fraction in the solution, the gas constant, and absolute temperature, respectively. However, for nonideal solutions, the equilibrium relation can be rearranging as

$$\mu_i = \mu_i^* + RT\ln(\gamma_i x_i) \tag{8}$$

where γ_i is the activity coefficient of solute in solution. Rearranging, we obtain

$$\ln(\gamma_i x_i) = -\frac{\mu_i^*}{RT} + \frac{\mu_i}{RT} \tag{9}$$

In accordance with the phase rule, the temperature and pressure can be varied independently. When the pressure is held constant, the partial derivative of activity to T can be obtained

$$\left(\frac{\partial \ln(\gamma_i x_i)}{\partial T}\right)_P = \frac{H_i - h_i}{RT^2} \tag{10}$$

H_i is the partial molar enthalpy of the component in the ideal solution, and h_i is its enthalpy per mole as the pure solid, both referring to the temperature T. the equation may therefore be rewritten as

$$\left(\frac{\partial \ln(\gamma_i x_i)}{\partial T}\right)_p = \left(\frac{\partial \ln \gamma_i}{\partial T}\right)_p + \left(\frac{\partial \ln x_i}{\partial T}\right)_p = \frac{\Delta H_{\mathrm{Sol}}}{RT^2} \tag{11}$$

where ΔH_{Sol} is the dissolution enthalpy of the component i. If γ_i has low temperature dependence and can be neglected, eq 11 can be simplified to

$$\left(\frac{\partial \ln x_i}{\partial T}\right)_p = \frac{\Delta H_{\mathrm{Sol}}}{RT^2} \tag{12}$$

Substituting eq 5 for $\ln x_i$, the following equation can be obtained

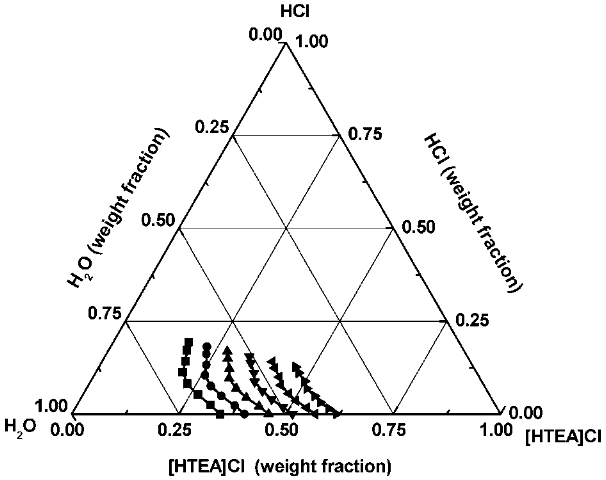


Figure 9. Phase diagram of the system [HTEA]Cl−HCl−H$_2$O at various temperatures: ■, 300 K; ●, 310 K; ▲, 320 K; ▼, 330 K; solid triangle pointing right, 340 K; solid triangle pointing left, 350 K.

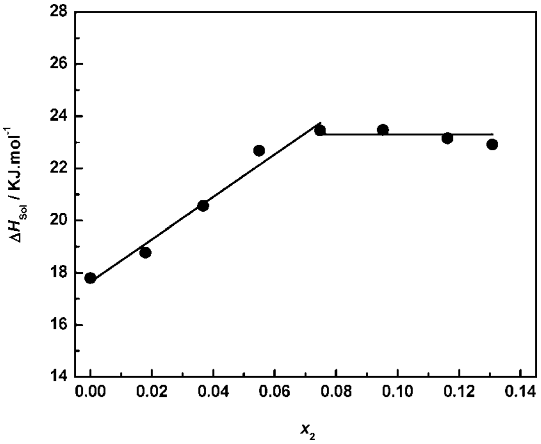


Figure 10. Dissolution enthalpy ΔH_{Sol} versus the concentration of hydrochloric acid x_2.

$$\left(\frac{\partial \ln x_i}{\partial T}\right)_p = \left(\frac{\partial\left(a + \frac{b}{T}\right)}{\partial T}\right)_P = -\frac{b}{T^2} \tag{13}$$

By combining eq 12 and eq 13, we obtain

$$-\frac{b}{T^2} = \frac{\Delta H_{\mathrm{Sol}}}{RT^2} \tag{14}$$

Finally, the dissolution enthalpy can be expressed as

$$\Delta H_{\mathrm{Sol}} = -bR \tag{15}$$

The values of ΔH_{Sol} determined by eq 15 are presented in Figure 10. It can be seen that ΔH_{Sol} increases with increasing concentration of aqueous hydrochloric acid when x_2 is lower than 0.075. However, it remains constant with the value of about 23.3 kJ·mol^{-1} when x_2 is more than 0.075.

Conclusions

The solubilities of [HTEA]Cl in water and hydrochloric acid with concentrations from (1.01 to 8.37) mol·kg^{-1} have been successfully determined by a dynamic method. Solubility of [HTEA]Cl in hydrochloric acid increases with increasing temperature. However, the common ion effect makes the solubilities of [HTEA]Cl in hydrochloric acid decrease with increasing concentration of hydrochloric acid solutions. The molality-based solubility product (assuming activity coefficients of unity) was obtained by correlating the solubility data of [HTEA]Cl in deionized water. Experimental data of solubilities in aqueous hydrochloric acid were correlated by the modified Apelblat equation, and the calculated solubilities showed good agreement with the experimental data. On the basis of the two-parameter Apelblat equation, molar dissolution enthalpy ΔH_{Sol} of [HTEA]Cl in aqueous hydrochloric acid was calculated.

Literature Cited

(1) Domanska, U.; Zolek-Tryznowska, Z.; Krolikowski, M. Thermodynamic Phase Behavior of Ionic Liquids. *J. Chem. Eng. Data* **2007**, *52*, 1872–1880.
(2) Domanska, U.; Casa, M. L. Solubility of Phosphonium Ionic Liquid in Alcohols, Benzene, and Alkylbenzenes. *J. Phys. Chem. B* **2007**, *111*, 4109–4115.

(3) Belveze, L. S.; Brennecke, J. F.; Stadtherr, M. A. Modeling of Activity Coefficients of Aqueous Solutions of Quaternary Ammonium Salts with the Electrolyte-NRTL Equation. *Ind. Eng. Chem. Res.* **2004**, *43*, 815–825.

(4) Hojjati, H.; Sheikhzadeh, M.; Rohani, S. Control of Supersaturation in a Semibatch Antisolvent Crystallization Process Using a Fuzzy Logic Controller. *Ind. Eng. Chem. Res.* **2007**, *46*, 1232–1240.

(5) Zhang, L.; Gui, Q.; Lu, X.; Wang, Y.; Shi, J.; Lu, B. C.-Y. Measurement of Solid-Liquid Equilibria by a Flow-Cloud-Point Method. *J. Chem. Eng. Data* **1998**, *43*, 32–37.

(6) Kwok, K. S.; Chan, H. C.; Chan, C. K.; Ng, K. M. Experimental Determination of Solid-Liquid Equilibrium Phase Diagrams for Crystallization-Based Process Synthesis. *Ind. Eng. Chem. Res.* **2005**, *44*, 3788–3798.

(7) Cheng, W.; Li, Z. Controlled Supersaturation Precipitation of Hydromagnesite for the $MgCl_2$-Na_2CO_3 System at Elevated Temperatures: Chemical Modeling and Experiment. *Ind. Eng. Chem. Res.* **2010**, *49*, 1964–1974.

(8) Domanska, U.; Bogel-Lukasik, E. Solubility of Benzimidazoles in Alcohols. *J. Chem. Eng. Data* **2003**, *48*, 951–956.

(9) Song, C. Y.; Ding, H.; Zhao, J. H.; Wang, J. S.; Wang, L. C. Solubilities of Isonicotinic Acid in (Methanol, Ethanol, 1-Propanol, 2-Propanol, and 1,2-Propanediol, Respectively) from (289.65 to 358.75) K. *J. Chem. Eng. Data* **2009**, *54*, 1120–1122.

(10) Li, Z.; Demopoulos, G. P. Development of an Improved Chemical Model for the Estimation of $CaSO_4$ Solubilities in the HCl - $CaCl_2$ - H_2O System up to 100 °C. *Ind. Eng. Chem. Res.* **2006**, *45*, 2914–2922.

(11) Annunziata, O.; Payne, A.; Wang, Y. Solubility of Lysozyme in the Presence of Aqueous Chloride Salts: Common-Ion Effect and Its Role on Solubility and Crystal Thermodynamics. *J. Am. Chem. Soc.* **2008**, *130*, 13347–13352.

(12) Li, Z.; Demopoulos, G. P. Effect of NaCl, $MgCl_2$, $FeCl_2$, $FeCl_3$, and $AlCl_3$ on Solubility of $CaSO_4$ Phases in Aqueous HCl or HCl + $CaCl_2$ Solutions at 298 to 353 K. *J. Chem. Eng. Data* **2006**, *51*, 569–576.

(13) Wang, L.-S.; Liu, Y.; Wang, R. Solubilities of Some Phosphaspirocyclic Compounds in Selected Solvents. *J. Chem. Eng. Data* **2006**, *51*, 1686–1689.

(14) Kotula, I.; Marciniak, B. Solubilities of Naphthalene and Acenaphthene in Chloro Derivative Solvents. *J. Chem. Eng. Data* **2001**, *46*, 783–787.

(15) Tulashie, S. K.; Lorenz, H.; Seidel-Morgenstern, A. Potential of Chiral Solvents for Enantioselective Crystallization. 2. Evaluation of Kinetic Effects. *Cryst. Growth Des.* **2009**, *9*, 2387–2392.

(16) Omar, W.; Ulrich, J. Solid Liquid Equilibrium, Metastable Zone, and Nucleation Parameters of the Oxalic Acid -Water System. *Cryst. Growth Des.* **2006**, *6*, 1927–1930.

(17) Prausnitz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 3rd ed.; Prentice Hall: NJ, 1999.

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