pH Measurements of Caprolactam Tetrabutyl Ammonium Bromide Ionic Liquids in Solvents

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The pH value of binary systems containing caprolactam tetrabutyl ammonium bromide ionic liquids and solvents (water, ethanol, and 2-propanol) in the range of ionic liquid concentrations from $(5.0 \cdot 10^{-3}$ to 0.80) $mol \cdot L^{-1}$ and temperature range from (296.15 to 325.65) K was measured. The pH values of the solutions of caprolactam and tetrabutyl ammonium bromide ionic liquids are also presented. The results showed that the range of the pH values was from (5.12 to 6.93). The pH value of binary systems consisting of ionic liquids and solvents was found to be dependent on temperature and concentrations of the ionic liquids. The temperature dependency of the pH value was correlated using an empirical equation. The correlations gave satisfactory results.

Introduction

Room-temperature ionic liquids (ILs) are organic salts that are liquid at room temperature and composed of organic cations and organic or inorganic anions. Due to their unique properties such as negligible vapor pressure, high conductivity, excellent thermal properties, stabilities, and wide electrochemical windows, ionic liquids are regarded as green solvents in both industry and academia.[1−3] Ionic liquids are initially utilized in electroplating and electrolysis; however, their application has been expanded greatly, e.g., used as a catalyst for some reactions and as solvents in separation processes.[4,5] Recently, many studies have focused on obtaining specific ILs for a range of applications in industry.[6,7] The areas of application include gas solubility and separations, cellulose processing, catalysis, extraction, and high-temperature pyrochemical processing, etc.[8−10] The best aim of any research is applied to industry, and its industrial application has gained tremendous interest. However, industrial applications of ILs are based on a theoretical foundation which contains physical and chemical properties, e.g., viscosity, thermal stability, conductivity, and surface tension.[11,12]

Zhang studied the physicochemical properties of ILs which were based on nitrile-functionalized imidazolium, pyridinium as cations and chloride, tetrafluoroborate, and dicyanamide as anions, such as spectroscopic, thermal, solubility, electrochemical, tribological, and toxicity.[13] Sesto drew the conclusion that pyrrolidinium and imidazolium ionic liquids had unique properties, and their thermal stabilities were much lower than previously thought.[14] Ayyaz found that the basic physical and transport properties of ILs were vital for process design, and thermal expansion values of ILs were calculated from the development of contacting equipment. He obtained chloride and water contents, density, dynamic viscosity, surface tension, refractive indices, and thermal decomposition of ILs.[15] The pH of ionic liquids is one of the very important physical properties. Bogel-Łukasik has shown the pH of 1-alkyl-3-methylimidazolium chloride in alcohols and found that the range of pH values is from (3.0 to 8.5).[16] Li studied the basicity of several basic ionic liquids quantitatively and found that the basicity of the ionic liquids can be switched repeatedly by bubbling CO_2 and N_2 through the solution alternately.[17]

Water, alcohol, and ionic liquids are often used together during chemical processes as potential successful replacements for conventional media. They are environmentally friendly. It is easy to synthesize the caprolactam tetrabutyl ammonium bromide ionic liquids ([CPL][TBAB], 6:1), and the price of the ILs is very low. Our group believes that the [CPL][TBAB] ionic liquid has great potential as an alternative solvent for the recovery of SO_2 in the industrial process of flue gas desulfurization (FGD).[18] So a better understanding of the pH value of these ILs is necessary and useful. This work measured the pH values of the binary systems of [CPL][TBAB] ionic liquids and solvents (water, ethanol, and 2-propanol).

Experimental Methods

Materials. White crystalline caprolactam powder (CAS No. 105-60-2, $C_6H_{11}NO$) was obtained from the Shijiazhuang Refinery, China, the purity of which was up to 99.5 %. Tetrabutyl ammonium bromide (CAS No. 1643-19-2, $C_{16}H_{36}NBr$) was bought from the Jintan Huadong Chemical Research Institute, China, the purity of which was up to 99.5 %. Ethanol and 2-propanol were bought from the Tianjin Kewei Chemical Institute, the purities of which were up to 99.7 %. Water was deionized before use. Three kinds of pH standard buffer solutions were delivered from the Shanghai Rex Co-perfect Instrment Co., Ltd., China, with pH values equal to 4.00 ± 0.01, 6.86 ± 0.01, and 9.18 ± 0.01 that were used for calibration of the pH apparatus. The caprolactam and tetrabutyl ammonium bromide ionic liquid (6:1) was synthesized from 6 mol of caprolactam with 1 mol of tetrabutyl ammonium bromide and characterized in our laboratory following procedures reported elsewhere.[18] The water contamination of the ILs was determined using the Karl Fischer technique. The water content of ILs was < 0.02 mol percent.

pH Measurements of ILs and Solvents. The investigations were carried out over a wide range of concentrations of ionic

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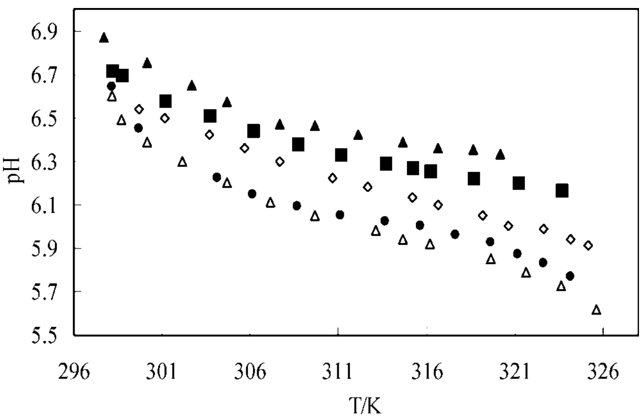

Figure 1. pH values for binary systems [CPL][TBAB] (6:1) (1) + water (2) as a function of temperature: ▲, $x_1 = 9.02 \cdot 10^{-5}$; ■, $x_1 = 3.60 \cdot 10^{-4}$; ◇, $x_1 = 7.21 \cdot 10^{-4}$; ●, $x_1 = 1.44 \cdot 10^{-3}$; Δ, $x_1 = 2.39 \cdot 10^{-3}$.

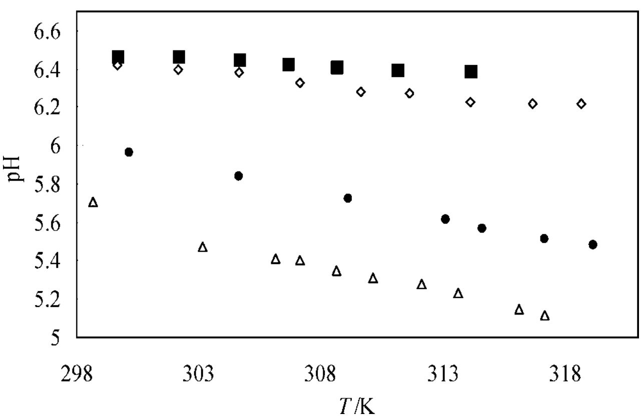

Figure 2. pH values for binary systems [CPL][TBAB] (6:1) (1) + ethanol (2) as a function of temperature: ■, $x_1 = 7.25 \cdot 10^{-5}$; ◇, $x_1 = 2.91 \cdot 10^{-4}$; ●, $x_1 = 4.35 \cdot 10^{-4}$; Δ, $x_1 = 1.16 \cdot 10^{-3}$.

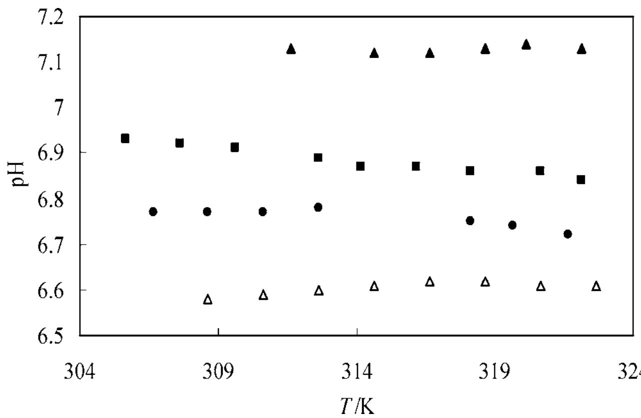

Figure 3. pH values for binary systems ILs ([CPL][TBAB], 6:1) (1) + 2-propanol (2) as a function of temperature: ▲, $x_1 = 3.78 \cdot 10^{-4}$; ■, $x_1 = 1.52 \cdot 10^{-3}$; ●, $x_1 = 2.27 \cdot 10^{-3}$; Δ, $x_1 = 6.05 \cdot 10^{-3}$.

liquid from $(5.0 \cdot 10^{-3}$ to $0.80)$ mol·L^{-1} and in the range of temperatures from (296.15 to 325.65) K. The temperature was controlled using a precision thermometer to determine the temperature with an uncertainty of ± 0.01 K. The mixtures of the pure components, solute, and solvent were weighed using a balance with an uncertainty of ± 0.0001 g. pH was assessed directly by inserting the probe into the mixtures. The pH measurement was carried out with a Mettler-Toledo pH/conductivity meter using a combination pH electrode LE409. The precision of the pH measurements was ± 0.01 pH units. Before each pH value reading, the pH buffer solution was used to check the measurements of the electrode.

Results and Discussion

The pH values of binary systems containing [CPL][TBAB] (6:1) ionic liquids and solvents (water, ethanol, 2-propanol) were measured in a range of ionic liquid concentrations (c) from $(5.0 \cdot 10^{-3}$ to $0.80)$ mol·L^{-1} at temperatures from (296.15 to 325.65) K.

In Figure 1, the pH values of the ionic liquid of binary systems containing ionic liquids and water are shown. As seen from this figure, the pH values decrease with an increase of temperature, and the pH value also decreased with an increase of the concentration of ionic liquid: the higher the concentration that was present, the stronger the temperature dependence of the pH value observed. As shown in Figure 2, the pH values of binary systems containing ionic liquids and ethanol are illustrated. It is clearly seen that the pH values of the studied systems decrease as the concentration increases and increase as the temperature increases. Figure 3 shows the pH values of binary systems containing ionic liquids and 2-propanol. In this figure, the temperature dependence of the pH value was weak. The influence of the concentration of the mixture was obvious, and the pH values decreased as the concentration of the mixture increased.

The change of the pH values with temperature for the IL solutions from Figure 1 to Figure 3 looks nonlinear. For the purpose of comparison and application, the measured pH values of binary systems containing [CPL][TBAB] (6:1) ionic liquids and solvents (water, ethanol, and 2-propanol) were expressed empirically as a function of temperature as follows (eq 1)

$$x_i^{\text{calcd}} = a + b/(T/\text{K}) + c(T/\text{K})^2 + d(T/\text{K})^3 \qquad (1)$$

where T is the absolute temperature, and a, b, c, and d refer to the fit coefficients. The pH values of the solution (x_i^{calcd}) are given in Table 1 to Table 3. The values of the relative deviation (RD) are also given in Table 1 to Table 3. The RD is defined as eq 2.

$$\text{RD} = \frac{|x_i - x_i^{\text{calcd}}|}{x_i} \qquad (2)$$

where x_i^{calcd} represents the pH values calculated from eq 1, and x_i represents the experimental values of the pH values. The values of parameters a, b, c, and d and the root-mean-square deviations (rmsd) are listed in Table 4. The rmsd is defined as eq 3.

$$\text{rmsd} = \left\{ \frac{\sum_{i=1}^{N} [(x_i^{\text{calcd}} - x_i)^2]}{N} \right\}^{1/2} \qquad (3)$$

where x_i is the pH values of the mixture at different temperatures and concentrations. N is the number of experimental points, and the superscript calcd refers to the values calculated from eq 1.

From Table 1 to Table 3, we believe that the experimental values of the pH values represented well the pH values calculated from eq 1. This empirical equation can be applied

Table 1. pH Values, x_i^{calcd}, of Binary Systems Containing Ionic Liquid ([CPL][TBAB], 6:1) and Water

T/K	$x_i^{\text{calcd}\ a}$	RD	T/K	$x_i^{\text{calcd}\ b}$	RD	T/K	$x_i^{\text{calcd}\ c}$	RD	T/K	$x_i^{\text{calcd}\ d}$	RD	T/K	$x_i^{\text{calcd}\ e}$	RD
297.65	6.88	0.15	298.15	6.72	0	299.65	6.55	0.15	298.15	6.62	0.30	298.15	6.56	0.60
300.15	6.74	0.15	298.65	6.7	0	301.15	6.49	0.15	299.65	6.48	0.47	298.65	6.52	0.46
302.65	6.64	0.15	301.15	6.59	0.15	303.65	6.41	0.16	304.15	6.22	0	300.15	6.41	0.31
304.65	6.57	0	303.65	6.51	0	305.65	6.36	0	306.15	6.14	0.16	302.15	6.3	0
307.65	6.49	0.31	306.15	6.44	0	307.65	6.3	0	308.65	6.09	0	304.65	6.19	0.16
309.65	6.45	0.15	308.65	6.38	0	310.65	6.23	0.17	311.15	6.05	0	307.15	6.11	0
312.15	6.41	0.16	311.15	6.33	0	312.65	6.18	0	313.65	6.02	0	309.65	6.05	0
314.65	6.38	0.16	313.65	6.29	0	315.15	6.13	0	315.65	6	0	313.15	5.98	0
316.65	6.36	0	315.15	6.27	0	316.65	6.1	0	317.65	5.97	0.17	314.65	5.95	0.17
318.65	6.35	0	316.15	6.26	0	319.15	6.04	0.17	319.65	5.92	0.17	316.15	5.93	0.17
320.15	6.33	0	318.65	6.23	0.16	320.65	6.01	0.17	321.15	5.88	0.17	319.65	5.85	0
			321.15	6.2	0	322.65	5.97	0.33	322.65	5.83	0	321.65	5.79	0
			323.65	6.17	0	324.15	5.94	0	324.15	5.77	0	323.65	5.72	0.17
						325.15	5.92	0.17				325.65	5.63	0.17

[a] $x_1 = 9.02 \cdot 10^{-5}$. [b] $x_1 = 3.60 \cdot 10^{-4}$. [c] $x_1 = 7.21 \cdot 10^{-4}$. [d] $x_1 = 1.44 \cdot 10^{-3}$. [e] $x_1 = 2.39 \cdot 10^{-3}$.

Table 2. pH Values, x_i^{calcd}, of Binary Systems Containing Ionic Liquid ([CPL][TBAB], 6:1) and Ethanol

T/K	$x_i^{\text{calcd}\ a}$	RD	T/K	$x_i^{\text{calcd}\ b}$	RD	T/K	$x_i^{\text{calcd}\ c}$	RD	T/K	$x_i^{\text{calcd}\ d}$	RD
297.65	6.49	0	297.15	6.42	0	296.15	6.22	0.16	296.65	5.83	0.17
299.65	6.48	0	299.65	6.42	0	300.15	5.99	0.50	298.65	5.69	0.35
302.15	6.47	0	302.15	6.4	0	304.65	5.82	0.34	303.15	5.49	0.37
304.65	6.45	0	304.65	6.37	0.16	309.15	5.71	0.17	306.15	5.41	0
306.65	6.43	0	307.15	6.33	0	313.15	5.62	0.18	307.15	5.38	0.37
308.65	6.41	0	309.65	6.29	0.16	314.65	5.58	0.18	308.65	5.35	0
311.15	6.40	0	311.65	6.26	0.16	317.15	5.52	0.18	310.15	5.32	0.19
314.15	6.39	0	314.15	6.23	0	319.15	5.47	0.18	312.15	5.27	0.19
			316.65	6.22	0				313.65	5.23	0
			318.65	6.22	0				316.15	5.15	0
									317.15	5.12	0

[a] $x_1 = 7.25 \cdot 10^{-5}$. [b] $x_1 = 2.91 \cdot 10^{-4}$. [c] $x_1 = 4.35 \cdot 10^{-4}$. [d] $x_1 = 1.16 \cdot 10^{-3}$.

Table 3. pH Values, x_i^{calcd}, of Binary Systems Containing Ionic Liquid ([CPL][TBAB], 6:1) and 2-Propanol

T/K	$x_i^{\text{calcd}\ a}$	RD	T/K	$x_i^{\text{calcd}\ b}$	RD	T/K	$x_i^{\text{calcd}\ c}$	RD	T/K	$x_i^{\text{calcd}\ d}$	RD
305.65	6.93	0	305.65	6.93	0	304.65	6.77	0	308.65	6.58	0
307.65	6.92	0.14	307.65	6.92	0	306.65	6.77	0	310.65	6.59	0
309.65	6.91	0.14	309.65	6.91	0	308.65	6.77	0	312.65	6.60	0
312.65	6.89	0	312.65	6.89	0	310.65	6.78	0.15	314.65	6.61	0
316.15	6.87	0	314.15	6.87	0.15	314.15	6.75	0.15	316.65	6.62	0
318.15	6.87	0.15	316.15	6.87	0	316.15	6.74	0	318.65	6.62	0.15
320.65	6.86	0	318.15	6.86	0	318.15	6.72	0	320.65	6.61	0.15
322.15	6.86	0	320.65	6.86	0.15				322.65	6.61	0
			322.65	6.84	0.15						

[a] $x_1 = 3.78 \cdot 10^{-4}$. [b] $x_1 = 1.52 \cdot 10^{-3}$. [c] $x_1 = 2.27 \cdot 10^{-3}$. [d] $x_1 = 6.05 \cdot 10^{-3}$.

Table 4. Parameters of Equation 1 and rmsd of Equation 3 for the pH Value in [CPL][TBAB] ILs of Different Solvents

solvent	mol fraction	$a(\cdot 10^{-3})$	$b(\cdot 10^{-6})$	$c(\cdot 10^{-8})$	$d(\cdot 10^{-10})$	rmsd$(\cdot 10^{2})$
water	$9.02 \cdot 10^{-5}$	−0.805	0.777	−2.484	2.650	0.953
	$3.60 \cdot 10^{-4}$	−0.538	0.521	−1.669	1.786	0. 92
	$7.21 \cdot 10^{-4}$	−0.350	0.335	−1.057	1.119	0.886
	$1.44 \cdot 10^{-3}$	−3.396	3.191	−9.983	10.413	1.143
	$2.39 \cdot 10^{-3}$	−2.398	2.255	−7.054	7.362	1.581
ethanol	$7.25 \cdot 10^{-5}$	1.229	−1.122	3.432	−3.495	0
	$2.91 \cdot 10^{-4}$	1.842	−1.698	5.229	−5.365	0.547
	$4.35 \cdot 10^{-4}$	−1.632	1.525	−4.741	4.919	1.541
	$1.16 \cdot 10^{-3}$	−3.046	2.822	−8.707	8.962	1.168
2-propanol	$3.78 \cdot 10^{-4}$	0.518	−0.478	1.485	−1.538	0
	$1.52 \cdot 10^{-3}$	0.173	−0.154	0.474	−0.486	0.577
	$2.27 \cdot 10^{-3}$	−0.3	0.27	0.785	0.760	0.535
	$6.05 \cdot 10^{-3}$	0.740	0.695	−2.152	2.22	0.5

over a wide range of temperatures as it correlated well to the experimental results.

Conclusions

In conclusion, we stated that the pH values of binary systems containing ILs which were synthesized by [CPL][TBAB] (6:1) and solvents (water, ethanol, and 2-propanol) were determined over a wide range of temperatures and concentrations of the binary systems. As we expected, the addition of ILs to different solvents permits us to find the required range of pH values from 5.12 to 6.93. Moreover, the pH value of the solution decreases with an increase of temperature and the concentration of ILs. The temperature dependency of the pH value was correlated using an empirical equation. The result of this work can be applied to numerous industrial applications since pH data are essential information for their rational design.

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