# Effects of Alkyl Chain Length and Solvents on Thermodynamic Dissociation Constants of the Ionic Liquids with One Carboxyl Group in the Alkyl Chain of Imidazolium Cations

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**ABSTRACT:** Thermodynamic dissociation constants of the Brønsted acidic ionic liquids (ILs) are important for their catalytic and separation applications. In this work, a series of imidazolium bromides with one carboxylic acid substitute group in their alkyl chain ([{(CH<sub>2</sub>)<sub>n</sub>COOH}mim]Br, n = 1,3,5,7) have been synthesized, and their dissociation constants (pK<sub>a</sub>) at different ionic



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strengths have been determined in aqueous and aqueous organic solvents at 0.1 mole fraction (x) of ethanol, glycol, iso-propanol, and dimethyl sulfoxide by potentiometric titrations at 298.2 K. The standard thermodynamic dissociation constants ( $pK_a^T$ ) of the ILs in these solvents were calculated from the extended Debye–Hückel equation. It was found that the  $pK_a$  values increased with the increase of ionic strength of the media and of the addition of organic solvent in water. The  $pK_a^T$  values also increased with the increase of the alkyl chain length of cations of the ILs. In addition, the effect of solvent nature on  $pK_a^T$  values is interpreted from solvation of the dissociation components and their Gibbs energy of transfer from water to aqueous organic solutions.

## 1. INTRODUCTION

In the past two decades, room temperature ionic liquids (ILs) have aroused considerable attention due to their superior physicochemical properties such as no vapor pressure and nonflammability under ambient conditions, wide electrochemical window, high chemical and thermal stability, large electrical conductivity, and unusual solubility for many compounds. Thus, ILs have been widely applied in organic synthesis,<sup>1,2</sup> nanotribology,<sup>3,4</sup> biocatalysis,<sup>5</sup> energetic materials,<sup>6</sup> analytical and separation science,<sup>7,8</sup> and so on.

Among these ILs, those based on the imidazolium cation with carboxylic acid groups in their alkyl chain have been used to selectively dissolve metal oxides<sup>9,10</sup> and metal hydroxides,<sup>11</sup> efficiently catalyze the synthesis of cyclic carbonates,<sup>12,13</sup> and significantly stabilize the metal nanoparticle in aqueous solution.<sup>14</sup> Apparently, these applications are related with the acidic nature of carboxyl group in these ILs. Therefore, knowledge of acid-base property is very important for their potential applications. It is known that thermodynamic dissociation constants are important physicochemical parameters to reflect the acid-base behavior of Brønsted acidic ILs in solutions. However, it is surprising to find that only two articles have been published for the determination of  $pK_{a}$  values of the ILs with carboxyl groups in the alkyl chain of their cations. In this context, Fei et al.<sup>15</sup> reported the  $pK_a$  values of the ionic liquids ([{(CH<sub>2</sub>)<sub>n</sub>COOH}mim]X,  $n = 1, 3; X = Cl, BF_4$ ,  $CF_3SO_3$ ) and  $([{(CH_2)_nCOOH}_2im]X, n = 1,3; X = BF_4,$  $CF_3SO_3$ ) in aqueous solution at the ionic strength of approximate 0.01 mol/L by potentiometric titrations. Geng et al.<sup>16</sup> also measured the  $pK_a$  values of some polycarboxyl imidazolium ILs (such as [{(HOOCCH<sub>2</sub>CHCOOH}eim]Br) in water by the same methodology. These  $pK_a$  values are a

function of IL concentrations because the determinations were not performed at constant ionic strength.

In the present work, we synthesized a series of four imidazolium bromides with one carboxylic acid substituent group in the alkyl chain of their cations, i.e., 1-alkylcarboxylic acid-3-methylimidazolium bromides ([{( $CH_2$ )<sub>n</sub>COOH}mim]-Br, n = 1,3,5,7). For the sake of easy understanding, the chemical structure of these ILs is shown in Figure 1. The  $pK_a$ 

Figure 1. The structures of the four ionic liquids.

values of these ILs at different ionic strengths have been determined by potentiometric titration in aqueous solution and in aqueous organic solvent mixtures at 298.2 K due to its simplicity and accuracy. Ethanol (EtOH), glycol (GL), isopropanol (*i*-PrOH), and dimethyl sulfoxide (DMSO) are selected as organic additives for of the following reasons: (i) they have strong ability to solubilize slightly soluble or insoluble compounds in water and thus have been widely used in analytical and separation processes; (ii) they are fully miscible with water but less polar than water; and (iii) they are potential green solvents based on the classification of Moity and his coworkers.<sup>17</sup> The mole fraction (*x*) of organic compounds in the solvent mixtures is kept at 0.1. The thermodynamic dissociation

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Fable 1. $pK_a$ Values of the ILs 1 and	l 2 in Different Solvents at 298.2 K	as a Function of Ionic Strength (	$(\mathbf{I})$
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			IL 1				IL 2			
$I \ (mol{\cdot}L^{-1})$	$H_2O$	$EtOH + H_2O$	glycol + $H_2O$	i-PrOH + H <sub>2</sub> O	$DMSO + H_2O$	$H_2O$	$EtOH + H_2O$	glycol + $H_2O$	i-PrOH + H <sub>2</sub> O	$DMSO + H_2O$
0.10	2.02	2.25	2.28	2.28	2.46	4.03	4.32	4.27	4.40	4.57
0.30	2.06	2.27				4.05	4.34			
0.50	2.08	2.32	2.32	2.32	2.49	4.08	4.39	4.32	4.45	4.61
0.80	2.11		2.40		2.51	4.12		4.40		4.63
1.0	2.14	2.37	2.44	2.36	2.54	4.15	4.44	4.46	4.49	4.65
1.2			2.47	2.39	2.56			4.48	4.53	4.68
1.5	2.19	2.41	2.51	2.41	2.59	4.21	4.48	4.51	4.55	4.71

constants  $(pK_a^T)$  have been obtained by nonlinear fitting of the extended Debye–Hückel equation. These results have been utilized to understand the effects of the ionic strength of the media, the alkyl chain length of the cations, and the nature of the solvents on the acid–base property of the ILs.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** *N*-methylimidazole (Linhai Kaile Chem. Co., 99%) was distilled before use. 2-Bromoacetic acid (Aladdin Chem. Co. Ltd., 98.5%), ethyl 4-bromobutyrate (Aladdin Chem. Co. Ltd., 95%), 6-bromohexanoic acid (Aladdin Chem. Co. Ltd., 97%), 8-bromooctanoic acid (Alfer Aser, 97%), and hydrobromic acid (Aladdin Chem. Co. Ltd., 48%) were used without further purification. Ethanol (Shanghai Chem. Co.), glycol (Shanghai Chem. Co.), iso-propanol (Tianjin Guangfu Chem. Co.), and dimethyl sulfoxide (Shanghai Chem. Co.) were analytical grade and used after drying over 4 A-type molecular sieves (Shanghai Chem. Co.).

A stock aqueous solution of carbonate-free NaOH (Shanghai Chem. Co, AR) was prepared and standardized with potassium hydrogen phthalate (KHP, PT, Aladdin Chem. Co. Ltd.). The concentration of HCl (Shanghai Chem. Co, AR) was determined by titration with standard aqueous NaOH solution. In order to reduce the experimental error, stock solutions of the ILs were prepared, and their accurate concentrations were determined by potentiometric titration. Dilute solutions were prepared by appropriate dilution of the stock solutions. All the aqueous organic solvents were prepared by weight and the mole fraction of the organic compounds was fixed at 0.1. The ionic strength in all the solutions was adjusted with KCl (Shanghai Chem. Co, AR). Conductivity water with a conductivity of 1.2  $\mu\Omega^{-1}$  cm<sup>-1</sup> was prepared by redistilling the deionized water and subsequently boiled to remove CO<sub>2</sub> before use.

**2.2. Synthesis of the ILs.** All the ILs, except for IL 2, were synthesized in acetonitrile or tetrahydrofuran through the reaction of *N*-methylimidazole with excess bromine substituted carboxylic acid under reflux at about 65 °C. After the reaction, solvents were removed by rotary evaporation, and then the crude products of the ILs 1, 3, and 4 were washed with acetonitrile, acetone, and diethyl ether, respectively. The IL 2 was prepared in a similar procedure described in the literature.<sup>15</sup> These ILs were dried under vacuum at 50 °C for 3–4 days in the presence of  $P_2O_5$ . The melting points of the ILs 1, 2, 3, and 4 were 182.4, 99.6, 109.5, and 124.6 °C, respectively, as measured by a NETZSCH 204  $F_1$  differential scanning calorimetry. <sup>1</sup>H NMR spectra of the ILs were determined by a Bruck AV-400 spectrometer.

**2.3. Determination of the Dissociation Constants.** All titrations of the aqueous ILs solution and calibration of the electrode were performed on an ORION 720A digital pH

meter, equipped with a pH combined electrode in a waterjacketed glass vessel. The temperature in the glass vessel was kept at 298.2  $\pm$  0.1 K by circulating water from a thermostat. Purified argon was passed through the solution to reduce the adverse effect of carbon dioxide during titrations.

Before determination of the  $pK_a$  values, calibration of the electrode system was performed by using the procedure described in the literature.<sup>18</sup> After calibration of the electrode, the titration of IL solution with aqueous NaOH was conducted under the same experimental conditions. The dilute IL solutions prepared in water and in the mixed solvents were titrated with 0.01 mol/L of NaOH. During the titrations, all the titrands and titrants had the same ionic strength and solvent composition. The volume of the titrant and the corresponding potential of the cell were recorded after a suitable time interval (around 2–3 min). The  $pK_a$  values of the ILs were determined in triplicate, and the standard error was within 0.02  $pK_a$  unit.

## 3. RESULTS AND DISCUSSION

**3.1.** Dissociation Constants and Thermodynamic Dissociation Constants of the ILs. Dissociation equilibrium of the ILs in solution can be described in terms of the following single process:

$$R^{+}(CH_{2})_{n}COOH + SH \rightleftharpoons R^{+}(CH_{2})_{n}COO^{-} + SH_{2}^{+}$$
(1)

where SH represents a solvent, and  $\text{SH}_2^+$  denotes a solvated proton, and  $\text{R}^+(\text{CH}_2)_n\text{COOH}$  and  $\text{R}^+(\text{CH}_2)_n\text{COO}^-$  refer to the acid and conjugate base forms of the ILs, respectively. According to the above equilibrium, the dissociation constant can be expressed by

$$K_{a} = [R^{+}(CH_{2})_{n}COO^{-}][SH_{2}^{+}]/[R^{+}(CH_{2})_{n}COOH]$$
(2)

At any point of the titration, the mass and charge balance are expressed by the equations:

$$C_{[\mathbb{R}^{+}(\mathrm{CH}_{2})_{n}\mathrm{COOH}]Br} = C_{Br}^{-}$$

$$= [\mathbb{R}^{+}(\mathrm{CH}_{2})_{n}\mathrm{COOH}]$$

$$+ [\mathbb{R}^{+}(\mathrm{CH}_{2})_{n}\mathrm{COO}^{-}] \qquad (3)$$

$$[Na^{+}] + [SH_{2}^{+}] + [R^{+}(CH_{2})_{n}COOH] = [S^{-}] + [Br^{-}]$$
(4)

In these equations, *C* stands for the total concentration of each IL at any moment of titration. From eqs 2, 3, and 4, we have

$$pK_{a} = -lg[SH_{2}^{+}] - lg\{([Na^{+}] + [SH_{2}^{+}] - [S^{-}]) \\ /(C - [Na^{+}] - [SH_{2}^{+}] + [S^{-}])\}$$
(5)

Table 2. pK <sub>a</sub> Values of the ILs 3 ar	4 in Different Solvents at 298.2	K as a Function of Ionic S	strength (I)
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			IL 3		IL 4						
$I \ (mol \cdot L^{-1})$	$H_2O$	$EtOH + H_2O$	glycol + $H_2O$	i-PrOH + H <sub>2</sub> O	$DMSO + H_2O$	$H_2O$	$EtOH + H_2O$	glycol + $H_2O$	i-PrOH + H <sub>2</sub> O	$DMSO + H_2O$	
0.10	4.36	4.75	4.68	4.91	4.99	4.56	5.00	4.84	5.24	5.19	
0.30		4.77					5.03				
0.50	4.39	4.82	4.71	4.94	5.03	4.60	5.06	4.87	5.28	5.22	
0.80	4.42		4.76		5.05	4.62		4.94		5.24	
1.0	4.45	4.86	4.80	4.98	5.07	4.64	5.08	4.97	5.31	5.26	
1.2	4.48		4.82	5.00	5.10	4.66		4.99	5.33	5.28	
1.5	4.50	4.89	4.85	5.04	5.13	4.69	5.10	5.03	5.36	5.31	

Table 3.  $pK_a^T$  Values of the ILs in Different Solvents at 298.2 K, and the *b* Value in eq 13 and Their Standard Error (RSD)

	IL 1			IL 2			IL 3			IL 4		
solvent	$pK_a^T$	Ь	RSD (%)	$pK_a^T$	Ь	RSD (%)	$pK_a^T$	Ь	RSD (%)	$pK_a^T$	Ь	RSD (%)
H <sub>2</sub> O	1.93	0.089	0.5	3.93	0.10	1.0	4.26	0.08	1.4	4.47	0.06	1.0
glycol + $H_2O$	2.16	0.14	1.9	4.15	0.15	2.1	4.56	0.10	1.8	4.72	0.11	1.7
$EtOH + H_2O$	2.14	0.08	1.2	4.20	0.08	1.4	4.64	0.07	1.2	4.90	0.033	0.62
i-PrOH + H <sub>2</sub> O	2.15	0.06	1.1	4.27	0.07	1.2	4.78	0.05	1.7	5.11	0.04	1.6
$DMSO + H_2O$	2.35	0.07	1.4	4.47	0.07	1.2	4.89	0.07	1.2	5.09	0.04	1.8

Table 4. pK<sub>a</sub><sup>T</sup> Values of the ILs and Some Carboxylic Acids in Aqueous Solution at 298.2 K

	$pK_a^T$		$pK_a^T$		$pK_a^T$		$pK_a^T$
IL 1	1.93	IL 2	3.93	IL 3	4.26	IL 4	4.47
acetic acid	4.75	butyric acid	4.81	hexanoic acid	4.88	octanoic acid	4.89
$\Delta p K_{a}^{T}$	2.82	$\Delta p K_{a}^{T}$	0.88	$\Delta p K_{a}^{T}$	0.62	$\Delta p K_{a}^{T}$	0.42
2-chloroacetic acid	2.82	4-chlorobutyric acid	4.52				

When the titration was carried out at the pH value below 7 against a solution of 0.01 mol/L of IL, the value of  $[S^-]$  can be neglected.<sup>19</sup> Thus,

$$pK_{a} = -lg[SH_{2}^{+}] - lg\{([Na^{+}] + [SH_{2}^{+}]) \\ /(C - [Na^{+}] - [SH_{2}^{+}])\}$$
(6)

During the titration of each IL solution, the unknown values of  $lg[SH_2^+]$  could be obtained by the following equation:

$$lg[SH_2^+] = (E - E^{0'})/s$$
(7)

where *E* is a measured electrode potential in the titration, *s* and  $E^{0'}$  are the slope and the formal electrode potential, which could be obtained by a linear correlation between electrode potential *E* recorded and  $[SH_2^+]$  calculated on the basis of the titration of HCl with NaOH. By using a series of volume and concentration data of titrant and titrand, the value of  $pK_a$  has been calculated, and the results are listed in Tables 1 and 2. It can be seen that  $pK_a$  values increase with the increase of ionic strength. Such a trend is identical with that of the protonated triethanolamine,<sup>20</sup> but different from monocarboxylic acids.<sup>21,22</sup> Therefore, it seems likely that the ILs with carboxyl group in their alkyl chain of cations could not be simply regarded as the traditional carboxylic acids.

In fact, the thermodynamic dissociation constant is only dependent on temperature and can be formulated by

$$K_{a}^{T} = K_{a} \times \gamma_{R^{+}(CH_{2})_{n}COO^{-}} \times \gamma_{SH_{2}^{+}} / \gamma_{R^{+}(CH_{2})_{n}COOH}$$
(8)

where  $\gamma_i$  represents activity coefficient of the species *i*. Taking the logarithms on both sides of eq 8, this equation would be changed into

$$pK_{a}^{T} = pK_{a} \times \lg \gamma_{R^{+}(CH_{2})_{n}COOH} - \lg \gamma_{R^{+}(CH_{2})_{n}COO^{-}} - \lg \gamma_{SH_{2}^{+}}$$
(9)

where  $\gamma_{R^+(CH_2),aCOO^-}$  can be regarded as 1, and in the electrode calibration, the lg  $\gamma_{(SH_2^+)}$  value is already contained in the  $E^{0'}$  term based on eq 7, and is thus included in the values of p $K_a$ . In this case, we have

$$pK_a^1 = pK_a + \lg \gamma_{R^+(CH_2)_n COOH}$$
(10)

According to the extended Debye-Hückel equation:<sup>23</sup>

$$\lg \gamma_{\mathrm{R}^{+}(\mathrm{CH}_{2})_{\mathrm{n}}\mathrm{COOH}} = -A\sqrt{I}/(1+B\mathring{a}\sqrt{I}) + bI$$
(11)

where a is the ion-size parameter, and A and B are Debye– Hückel parameters, which are related with the dielectric constant ( $\varepsilon$ ) of the solvents and the thermodynamic temperature (T) in the following way:<sup>24</sup>

$$A = 1.8246 \cdot 10^{6} / (\varepsilon T)^{3/2} \qquad B = 50.29 / (\varepsilon T)^{1/2}$$
(12)

Thus, eq 10 can be transformed to eq 13:

$$pK_{a} = pK_{a}^{T} - A\sqrt{I}/(1 + Ba\sqrt{I}) + bI$$
(13)

The dielectric constants of the mixed solvents studied in the present work were obtained by interpolation from the experimental data reported by Åkerlöf<sup>25</sup> and Khoo.<sup>26</sup> Thus, the values of  $pK_a^T$  were calculated by using nonlinear least-squares regression. It was found that using the a value of 10 nm gave the maximum correlation coefficient (*R*) and the minimum standard error. Therefore, all the  $pK_a^T$  values of the ILs in water and in the aqueous organic solvents were calculated with a =10 nm, and the results were collected in Table 3.

Table 5. Dielectric Constant ( $\varepsilon$ ) of Different Aqueous Organic Solvents (x = 0.1) and the Values of  $\Delta G_t^0$ ,  $\Delta G_t^0(H^+)$ , and  $\Delta d\{\Delta G_t^0[R^+(CH_2)_nCOO^-] - \Delta G_t^0[R^+(CH_2)_nCOOH]\}$  from Water to the Mixed Solvents at 298.2 K (in KJ·mol<sup>-1</sup>)

			IL1		IL2		IL3		IL4	
solvent	dielectric constant $(\varepsilon)$	$\Delta G_{\mathrm{t}}^{\ 0}(\mathrm{H}^{\scriptscriptstyle +})$	$\Delta G_{ m t}^{0}$	$\Delta d$	$\Delta G_{ m t}^{\ 0}$	$\Delta d$	$\Delta G_{ m t}^{\ 0}$	$\Delta d$	$\Delta G_{ m t}^{\ 0}$	$\Delta d$
$glycol + H_2O$	70.4	-0.86	1.31	2.17	1.26	2.12	1.71	2.57	1.43	2.29
$EtOH + H_2O$	65.7	-2.37	1.20	3.57	1.54	3.91	2.17	4.54	2.45	4.79
i-PrOH + H <sub>2</sub> O	59.4	-3.74	1.26	5.00	1.94	5.68	2.97	6.71	3.65	7.39
$DMSO + H_2O$	76.4	-6.65	2.40	9.05	3.08	9.73	3.60	10.2	3.54	10.2

3.2. Effect of Cationic Alkyl Chain Length on the Dissociation Constants of the ILs. From Tables 1-3, we can clearly see that at a given solvent and a given ionic strength, the values of  $pK_a$  and  $pK_a^T$  increase with the increase of alkyl chain length of the ILs. Similar trend has been reported for the dissociation constants of saturated fatty acids in aqueous solution.<sup>27</sup> This result can be interpreted from the fact that the longer alkyl chain may produce inductive effect, resulting in the enhanced electrostatic attraction between oxygen and hydrogen in carboxyl group and the decreased ability to release proton. It is interesting to note from Table 4 that the  $pK_a^T$  values for the ILs in water are smaller than those of carboxylic acids with the same alkyl chain length. This certainly results from the presence of an imidizolium ring in the ILs, the positive charge of which reduces the electrostatic interaction of the oxygen atom with hydrogen atom in carboxyl group, thus increasing acidity of the ILs. With the increase of alkyl chain length, such an effect becomes smaller, which leads to a decreased difference in  $pK_a^T$ value  $(\Delta p K_a^T)$  between the IL and the corresponding carboxylic acid in water, as indicated by the data in Table 4.

In addition, to qualitatively evaluate the ability of electronwithdrawing of the imidizolium ring, the  $pK_a^T$  values of 2chloroacetic acid and 4-chlorobutylic acid in aqueous solution are also included in Table 4 for comparison. It can be seen that  $pK_a^T$  values of the ILs 1 and 2 are respectively smaller than those of 2-chloroacetic acid and 4-chlorobutyric acid. This suggests that electron-withdrawing ability of the positive charge on the imidizaolium ring is much stronger than that of the chlorine atom in the chlorinated carboxylic acids.

**3.3. Solvent Effects on Dissociation Constants of the ILs.** It is evident from Tables 1–3 that  $pK_a^T$  and  $pK_a$  values of the ILs in aqueous organic solutions become greater than that in water under the same conditions. A similar trend has been reported for monocarboxylic acids such as acetic acid, benzoic acid, and others.<sup>28</sup> This indicates that acid—base property of the ILs changes with addition of organic solvents in water, and the dissociation of the acidic ILs is not favorable in the presence of organic solvent. It is known that the change in thermodynamic dissociation constants results from the difference in the thermodynamic properties of the species participated in dissociation reaction in water and in mixed solvents. Thus, the difference in  $pK_a^T$  value of the ILs in two different solvents is closely related to the standard Gibbs energy of transfer,  $\Delta G_t^0$ , for the dissociation reaction of the ILs:<sup>29</sup>

$$\Delta G_{t}^{0} = 2.303 RT[pK_{a}^{T}(S) - pK_{a}^{T}(W)]$$
(14)

In the above equation,  $pK_a^T(S)$  and  $pK_a^T(W)$  are the standard thermodynamic dissociation constants of ILs in mixed solvent and in water, respectively. According to this equation, if all participation of the solvent in eq 1 is disregarded,  $\Delta G_t^0$  can be represented by the following equation:<sup>29</sup>

$$\Delta G_t^0 = \Delta G_t^0(\mathrm{H}^+) + \Delta G_t^0[\mathrm{R}^+(\mathrm{CH}_2)_n \mathrm{COO}^-] - \Delta G_t^0[\mathrm{R}^+(\mathrm{CH}_2)_n \mathrm{COOH}]$$
(15)

where  $\Delta G_t^0(\mathrm{H}^+)$ ,  $\Delta G_t^0[\mathrm{R}^+(\mathrm{CH}_2)_n\mathrm{COO}^-]$ , and  $\Delta G_t^0[R^+(CH_2)_nCOOH]$  stand for the standard Gibbs energies of transfer for H<sup>+</sup>, R<sup>+</sup>(CH<sub>2</sub>)<sub>n</sub>COO<sup>-</sup> and R<sup>+</sup>(CH<sub>2</sub>)<sub>n</sub>COOH from water to the mixed solvents. Among these terms, the  $\Delta G_t^0$ values can be obtained from our standard dissociation constant values according to eq 14, and the  $\Delta G_t^0(H^+)$  values have been calculated from the experimental data of Khoo<sup>26</sup> and Wells<sup>30,31</sup> by interpolation. Then the difference between  $\Delta G_t^0[R^+(CH_2)_nCOO^-]$  and  $\Delta G_t^0[R^+(CH_2)_nCOOH]$ ,  $\Delta d_t$  can be calculated, and the results are given in Table 5. The negative  $\Delta G_t^0$  (H<sup>+</sup>) values indicate that the proton is more stable in the mixed solvents than in water. This can be understood from the much higher values of Kamlet–Taft  $\beta$  parameter of DMSO ( $\beta$ = 0.76), *i*-PrOH ( $\beta$  = 0.95), EtOH ( $\beta$  = 0.77) and glycol ( $\beta$  = 0.52) than that of water ( $\beta = 0.18$ ),<sup>32</sup> which has been established as a measure of the hydrogen bond accepting ability or the hydrogen bond basicity of liquid solvents and a higher  $\beta$ parameter value indicates a stronger hydrogen bond basicity of the solvent. However, the positive  $\Delta G_t^0$  values show that the solvent effect on the proton does not account for the increase of  $pK_a^T$  values in the aqueous organic solution, and the solvent effect on the charged ions  $R^+(CH_2)_nCOOH$  and its conjugated base  $R^+(CH_2)_n COO^-$  plays a dominant role in the standard Gibbs energy of transfer for the dissociation reaction of the ILs. Unfortunately, the exact values of transfer energies for both of them are not available in literature. Therefore, we have to qualitatively demonstrate the solvent effect in thermodynamic dissociation constants.

It is noted from Table 5 that the values of  $\{\Delta G_t^0[R^+(CH_2)_nCOO^-] - \Delta G_t^0[R^+(CH_2)_nCOOH]\}$  are increasingly positive in the aqueous organic solutions with the sequence: DMSO > i-PrOH > EtOH > GL. The positive values indicate that values of  $\Delta G_t^0[R^+(CH_2)_nCOO^-]$  are greater than those of  $\Delta G_t^0[\mathbb{R}^+(\mathbb{CH}_2)_n\mathbb{COOH}]$  when the two species transfer from water to the mixed solvents. In other words, compared to the cationic form  $R^+(CH_2)_nCOOH$ , the ampholyte  $R^+(CH_2)_n COO^-$  is stabilized more strongly in water. Actually, due to the presence of two opposite charges,  $R^{+}(CH_2)_n COO^{-}$  can be treated as a dipole ion similar to amino acid. Previous investigations showed that solvent property had a significant impact on the existence form of amino acids. Hughes et al.<sup>33</sup> reported that the ratio of dipolar ion to uncharged form of the amino acids decreased from  $10^4 - 10^5$  in water to 2–40 in DMSO, suggesting that water is a favorable solvent for dipolar ion of the amino acids. They ascribed this difference to the stronger solvation of the carboxylate anion in water than in DMSO. Doğan et al.<sup>34</sup> also reported that this ratio is in the range of  $10^{3.5}-10^5$  in aqueous ethanol mixtures (20-80%) ethanol by volume), and the microscopic protonation constant

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 $(k_{22})$  of amino acids increases due to the weaker solvation of dipolar ions by ethanol. From these investigations, it is reasonable to suggest that the solvation of dipolar ion of amino acids is mainly determined by the solvation of the carboxylate anion because water or alcohol may provide stronger hydrogen bonding to stabilize these anions. However, it should be emphasized that unlike H<sup>+</sup> solvation, solvation of carboxylate anion is dependent on the hydrogen bond donating capacity of the solvents, which can be characterized by the Kamlet–Taft  $\alpha$  parameter. It is known that the  $\alpha$  parameter for DMSO, *i*-PrOH, EtOH, glycol, and water is 0, 0.76, 0.83, 0.90 and 1.17, respectively.<sup>32</sup> The greater the  $\alpha$  parameter, the stronger the hydrogen bond donating capacity of the solvent. Therefore, it is clear that the solvation strength of carboxylate anion by the studied solvents decreases in the order  $H_2O > GL$ > EtOH > *i*-PrOH > DMSO. This indicates that Gibbs energies for the transfer of carboxylate anion and thus  $R^+(CH_2)_nCOO^$ from water to the studied solvents are positive, and the  $\Delta G_t^0[R^+(CH_2)_nCOO^-]$  values should decrease in the order DMSO > i-PrOH > EtOH > GL.

According to the previously reported  $\Delta G_t^{0}(i)$  values for the transfer of cations and anions from water to aqueous organic solvents, it is generally known that the  $\Delta G_t^0(i)$  is positive for anions, and negative for most of cations.<sup>35</sup> The  $\Delta G_t^0(H^+)$ values presented in Table 5 confirm this observation. Similarly, we may infer that the  $\Delta G_t^0[\mathbb{R}^+(CH_2)_nCOOH]$  values would be negative for the transfer of  $R^+(CH_2)_nCOOH$  from water to the mixed solvents. Based on the study of Popovych,<sup>36</sup> cations in all polar solvents are solvated by interaction with the negative end of the solvent dipoles to form coordination bonds with the lone pair electrons from oxygen, nitrogen, and sulfur atoms. For a given cation, the electron density at the oxygen atom of organic solvents is mainly responsible for the magnitude of cation solvation. DMSO and i-PrOH molecules have similar molecular structures, and their difference lies in the S=O group in DMSO and the C-OH group in *i*-PrOH. The existence of the S=O group results in a higher electron density on the oxygen atom in DMSO compared with the C-OH group in *i*-PrOH molecules. Therefore, solvation of  $R^+(CH_2)_nCOOH$  species in DMSO-water would be stronger than that in aqueous *i*-PrOH solution, thus leading to greater  $-\Delta G_t^0[R^+(CH_2)_nCOOH]$ values for the transfer from water to aqueous DMSO solvent. Due to the inductive effect of alkyl group of alcohol molecules, the electron density at the oxygen atom decreases in the order i-PrOH > EtOH > GL. Thus, values of  $\Delta G_t^0[\mathbb{R}^+(\mathbb{CH}_2)_n\mathbb{COOH}]$  are increasingly negative in the order GL < EtOH<*i*-PrOH < DMSO. On the other hand, considering the acidic nature of  $R^+(CH_2)_nCOOH$ , its solvation in different solvents can also be estimated by the Kamlet–Taft  $\beta$  parameter of the solvents, and the same conclusion can be obtained for the transfer of  $R^+(CH_2)_n$ COOH from water to aqueous organic solutions. In this way, the  $\{\Delta G_t^0[R^+(CH_2)_nCOO^-] \Delta G_t^0[R^+(CH_2)_nCOOH]$  values in different aqueous solutions listed in Table 5 can be qualitatively interpreted.

At this stage, it seems reasonable to conclude that  $\{\Delta G_t^0[R^+(CH_2)_nCOO^-] - \Delta G_t^0[R^+(CH_2)_nCOOH]\}$  values not only compensate the  $\Delta G_t^0(H^+)$  term but also determine the sign of the total  $\Delta G_t^0$  term. The interaction of both  $R^+(CH_2)_nCOOH$  and its conjuated base with solvent molecules in the mixed solvents are largely responsible for the observed changes of  $pK_a^T$  values with the addition of organic solvents in water.

## 4. CONCLUSION

In this work, four imidazolium bromides with one carboxylic acid substitute group in their alkyl chain have been synthesized, and their dissociation constants and thermodynamic dissociation constants have been determined in water and aqueous organic solvents at 0.1 mole fraction of ethanol, glycol, isopropanol, and dimethyl sulfoxide by potentiometric titrations at 298.2 K. It was found that the values of  $pK_a$  increased with the increase of ionic strength of the media, the addition of organic solvent in water, and the alkyl chain length of cations of the ILs. The acidity of these ILs in water is stronger than that of carboxylic acids with the same alkyl chain length, and the acidbase property of the ILs studied here is analogous to that of protonated amino acid. From the viewpoint of chemical thermodynamics, the solvation of the charged ions  $R^{+}(CH_{2})_{\mu}COOH$  and its conjugated base  $R^{+}(CH_{2})_{\mu}COO^{-}$  is predominant for the solvent effect in the thermodynamic dissociation constants of the ILs. These findings suggest that the dissociation constants of these ILs can be tuned by changing the alkyl chain length of cations of the ILs, using appropriate additives such as alcohol and DMSO and/or modulating of ionic strength of the media to meet the needs of practical application.

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### Notes

The authors declare no competing financial interest.

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