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Solubility of four novel Brønsted-acidic ionic liquids with 8-hydroxyquinoline cation in six alcohols

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ABSTRACT

The equilibrium solubility of four novel Brønsted-acidic ionic liquids (8-hydroxyquinoline phosphate ([HOQu][H_2PO_4]), 8-hydroxyquinoline sulfate ([HOQu][HSO_4]), 8-hydroxyquinoline methanesulfonate ([HOQu][CH_3SO_3]) and 8-hydroxyquinoline *p*-toluenesulfonate ([HOQu][*p*-TSA])) in six lower alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-methyl-1-propanol) was measured at temperatures from (278.15 to 348.15) K using a static method. With increasing temperatures, the solubility of ionic liquids increased and some of them showed "temperature-sensitive" property. The solubility of ionic liquids is closely related to the polarity and molecular structure of the solvents together with the strength of hydrogen bonding between anionic group of ionic liquids and alcohols. The experimental solubility values were well correlated by the modified Apelblat equation and λh equation. The dissolution enthalpy ($\Delta_{\mathrm{disoln}}S$) and dissolution entropy ($\Delta_{\mathrm{disoln}}H$) were determined using the van't Hoff equation and the change of Gibbs free energy ($\Delta_{\mathrm{disoln}}G$) was calculated at $T = 298.15$ K. The results showed that the dissolution process was endothermic and entropy-driven.

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1. Introduction

Ionic liquids (ILs) are room temperature molten salts, which commonly consist of large organic cations and inorganic or organic anions with smaller size and more asymmetrical shape [1,2]. As an emerging class of environmentally friendly "green solvents", ILs have attracted increasing attention in many fields [3,4] due to their particular properties over the past few decades [5–7]. Recently, many Brønsted acidic ILs were synthesized and used as catalysts for esterification and acetalization reactions [8–11]. However, the recovery of ILs is difficult in their applications involving high operation temperature and complex synthesis system. Some attempts [9] have been performed to improve ILs recovery and reuse but the results are not entirely satisfactory, more convenient methods are needed to be developed.

Some ILs has high melting points (some above 373.15 K) at atmosphere pressure [12]. However, their solubility in some solvents could change greatly with a small-scale of temperature variation. Thus, they could serve as homogeneous catalysts to catalyze efficiently reactions at higher temperature or as heterogeneous solid catalysts to simplify their recovery by filtration at lower temperature after reaction [8,10]. For instance, new benzothiazolium-based ILs [11] was reported as self-separation catalysts used to catalyze esterification. Moreover, previous studies [13,14] indicated that the alcohol solutions of ILs could be employed in the extraction or esterification processes and the recovery of ILs is also a non-negligible work. The variation of ILs solubility with solvents species and process conditions (such as temperature) is of primary important prior to their further applications. In order to broaden the application of ILs in alcohol solutions and predicting the solubility of ILs in related mixture, a deep understanding about the values and variation of ILs solubility in a series of lower alcohols is essential.

Recently, four novel Brønsted-acidic ILs based on 8-hydroxyquinoline cation ([HOQu]$^+$) ([HOQu][H_2PO_4], [HOQu][HSO_4], [HOQu][CH_3SO_3] and [HOQu][*p*-TSA]) were synthesized by us and some of them present good reactivity under mild conditions when used as catalysts for the esterification reaction of long-chain fatty acids and ethanol and recoverability by simple filtration after reaction [15]. In this study, four kinds of novel Brønsted-acidic [HOQu]$^+$-based ILs were synthesized referring to the previous work [15], their chemical structures are depicted in Fig. 1. The melting properties of ILs were investigated by differential scanning calorimetry and the solubility of ILs in six lower alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-methyl-1-propanol) was determined by static equilibrium method at temperatures from (278.15 to 348.15) K under atmospheric pressure. The effects of ILs structures and the solvents on the solubility of ILs were explored and discussed. Moreover, the modified Apelblat equation and λh equation were used to correlate the experimental solubility values. The van't Hoff equation was used to investigate the thermodynamic properties of dissolution of ionic liquids in different solvents. The results are supposed to provide useful information for further process and design of novel ILs.

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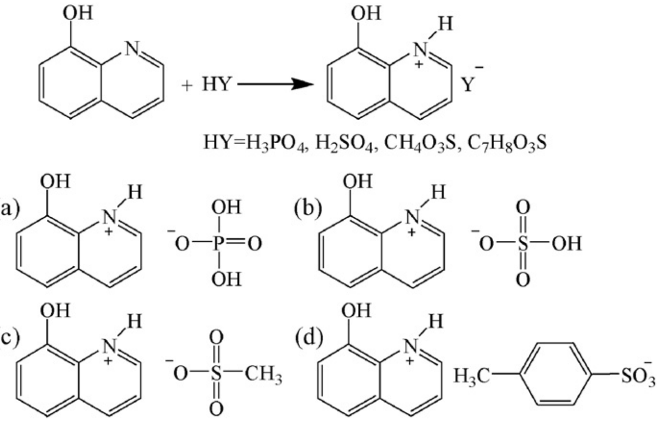

Fig. 1. The synthetic routes and chemical structures of 8-hydroxyquinoline ionic liquids: (a) [HOQu][H_2PO_4], (b) [HOQu][HSO_4], (c) [HOQu][CH_3SO_3], (d) [HOQu][p-TSA].

2. Experimental

2.1. Materials

All the alcohols used (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-methyl-1-propanol) were of analytical grade and purchased from Kelong Chemical Reagent Co., Ltd. (Chengdu, China). Their mass fraction purities (all above 0.995) were analyzed by a GC 7900 gas chromatography (Techcomp, China) equipped with a TM-1701 column (30 m long, 1 μm I.D., 0.32 mm film thickness) and a flame ionization detector (FID). The provenance and purity of chemicals and self-prepared ILs are listed in Table 1. All the alcohols were used without further purification.

2.2. Synthesis of the ionic liquids

The four ILs consisting of $[HOQu]^+$ cation and different anions were directly synthesized by neutralization of 8-hydroxyquinoline and acids. The synthetic routes are shown in Fig. 1. In the experiment, 7.258 g (0.05 mol) of 8-hydroxyquinoline (C_9H_7NO, AR, >0.995) and 50 mL ethanol was loaded into a 250 mL around-bottom flask in an ice-water bath between (273.15 and 278.15) K. Then 0.05 mol phosphoric acid (H_3PO_4, AR, >0.85) in 20 mL ethanol was charged into the flask slowly under vigorously stirring over a period of 30 min. The reaction lasted for 4 h at room temperature and the resulting mixture was evaporated under reduced pressure to remove ethanol. The crude product was washed three times with 15 mL acetone respectively, and then was purified by recrystallization from mixed solution of ethyl acetate and appropriate ethanol. Finally, the crystals were filtered, and dried by a DZF-6050 drying oven (Gongyi, China) under high vacuum for 24 h to reduce the water content and the volatile compounds to negligible values, then the [HOQu][H_2PO_4] product was obtained with a yield of 0.837. [HOQu][HSO_4], [HOQu][CH_3SO_3] and [HOQu][p-TSA] were prepared under the same procedure except that different acids (sulfuric acid, methanesulfonic acid and p-toluenesulfonic acid) (AR, >0.98) were used, and the corresponding production rate was 0.796, 0.785 and 0.862, respectively. The ILs purities (all above 0.990) were checked by a high-performance liquid chromatography (HPLC) system, which composed of a LC6A isocratic pump (Shimadzu, Japan), a 2000ES evaporative light scattering detector (Alltech, USA) and an in-line Rheodyne valve with a 20 μL sample loop. The LC column was a Waters symmetry C_{18} column (150 mm × 3.9 mm I.D., 5 μm), and mobile phase was 28/72 (v/v) acetonitrile-water solution (no buffer added) with the flow rate of $1\ mL \cdot min^{-1}$. The water content of the ILs individual samples was determined by a ZKF-1 Karl Fischer (KF) Titrator (Super scientech, China) and all found to be <0.00015 mass fractions.

The structures of ILs were confirmed by a combination of 1H-nuclear magnetic resonance (NMR) spectra and Infrared (IR) spectroscopy. 1H NMR spectra were obtained on an AV-400 NMR spectrometer (Bruker Corporation, Germany) in CH_3DO-d_6 with tetramethylsilane (TMS) as an internal standard. IR spectra were recorded on a SPECTRUM 400 Fourier transform infrared spectroscopy (FT-IR) (Perkin-Elmer, USA) absorption spectrometer using potassium bromide (KBr) disc. The spectra data of the ILs are shown in figures S1 to S8 (supplementary information) and agreed with their chemical structures.

2.3. Measurements of melting properties

Information of melting temperature (T_f) of the ILs was provided by a DSC Q20 differential scanning calorimetry (TA Instruments, USA). The calorimeter was calibrated against the melting temperature and enthalpy of fusion of indium. (4 to 10) mg of samples was heated from (293.15 to 493.15) K at the rate of (2 or 5) K min^{-1} in hermetic Al pans, which was purged with high purity nitrogen at a rate of 50 mL min^{-1}. In this study, the onset point of the DSC curve was used as the melting temperature. T_f was determined by averaging the results of four measurements and the outcomes were (451.15, 439.15, 445.15 and 427.15) K for [HOQu][H_2PO_4], [HOQu][HSO_4], [HOQu][CH_3SO_3] and [HOQu][p-TSA], respectively. The standard uncertainty of T_f was ±0.1 K.

2.4. Measurements of solubility

The solubility of ILs in alcohols was determined by static equilibrium method. For each measurement, a three-neck water-jacketed flask fitted with a submersible magnetic stirrer was used to prepare saturated solutions (about 20 mL) of solute, in which excess ILs was dissolved in the alcohol. The temperature of the flask was controlled by circulating water from a DC0506 thermostatic bath (±0.01 K, Hengping Instrument Co., Ltd., China). A digital thermometer (±0.05 K) was used to keep the solution in flask at desired temperature, which was directly inserted into the solution. The solution was heated to a constant temperature with continuous stirring at least 2 h in order to accelerate dissolution equilibrium. Then the stirring was stopped to allow solution to

Table 1
Provenance and mass fraction purity of chemicals studied.

Chemicals	Provenance	CAS	Mass fraction purity	Purification method	Analytical method
Methanol	Kelong Chemical Reagent Co., Ltd.	67-56-1	≥0.995	None	GC
Ethanol	Kelong Chemical Reagent Co., Ltd.	64-17-5	≥0.995	None	GC
1-Propanol	Kelong Chemical Reagent Co., Ltd.	71-23-8	≥0.995	None	GC
2-Propanol	Kelong Chemical Reagent Co., Ltd.	67-63-0	≥0.995	None	GC
1-Butanol	Kelong Chemical Reagent Co., Ltd.	71-36-3	≥0.995	None	GC
2-Methyl-1-propanol	Kelong Chemical Reagent Co., Ltd.	78-83-1	≥0.995	None	GC
Benzoic acid	Kelong Chemical Reagent Co., Ltd.	65-85-0	≥0.995	None	GC
[HOQu][H_2PO_4]	Prepared in laboratory		≥0.990	Recrystallization	HPLC
[HOQu][HSO_4]	Prepared in laboratory		≥0.990	Recrystallization	HPLC
[HOQu][CH_3SO_3]	Prepared in laboratory		≥0.990	Recrystallization	HPLC
[HOQu][p-TSA]	Prepared in laboratory		≥0.990	Recrystallization	HPLC

settle down at list 2 h until the upper layer was clear. About 1 mL upper clear saturated solution was sampled by the pre-heated/cooled syringes (5 mL) with filters (0.2 μm) and extruded into a previously weighed vial determined by an ESI200-4 A analytical balance (±0.0001 g, Longteng Electronics Co., Ltd., China). The vial with the sample solution was closed quickly and weighed, and the mass of the sample solution determined accordingly. Then the sample solution was diluted by a factor ranging from 1:10 to 1:100 (v:v) in alcohol which was used as solvent, depending on the solubility of the ILs in the study. The concentration of the ILs in ILs-saturated solution was determined by an UV2800S UV–Vis spectrophotometer (Shunyuhengping Instrument Co., Ltd., China) using calibration curves established previously. The maximum wavelength of [HOQu][H_2PO_4], [HOQu][HSO_4], [HOQu][CH_3SO_3] and [HOQu][*p*-TSA] at the UV–Vis spectrophotometric calibration curves were determined as (315, 309, 309 and 309) nm, respectively. The DSC Q20 differential scanning calorimetry (TA Instruments, USA) was used to rapidly analyze the ionic liquids individual samples before and after each experiment, and no sign of degradation was observed.

The solubility results at each individual temperature were determined as the average of at least four independent measurements. The mole fraction solubility of ILs in six lower alcohols (x_i) was calculated as follows:

$$x_i = \frac{m_1/M_1}{m_1/M_1 + (m - m_1)/M_2} \tag{1}$$

where m (g) and m_1 (g) represent the mass of the sample and the solute, respectively; M_1 (g mol^{-1}) and M_2 (g mol^{-1}) represent the molecular mass of solute and the solvent, respectively.

In order to check the accuracy of the measurement method, the solubility of benzoic acid in 2-propanol obtained by the measurement method in this work was compared with the literature data [16] at atmosphere pressure and the results are listed in Table 2. The UV maximum wavelength used of determination of solubility of benzoic acid in 2-propanol was 272 nm. The average relative deviation (*ARD*) between the experimental solubility and the literature data was 0.0033, which is calculated by Eq. (2). This indicates that above experimental procedure was reliable and accurate for solubility measurement.

$$ARD = (1/N)\sum_{i=1}^{N}\left(\left|\chi_i^{lit} - \chi_i^{exp}\right|/\chi_i^{exp}\right) \tag{2}$$

where *N* is the number of experimental points, *xlit i* and *xexp i* represent the literature and the experimental mole fraction solubility, respectively.

Table 2
Comparison between the experimental mole fraction solubility (x_i) of benzoic acid in 2-propanol of this work and those reported in the literature at atmosphere pressure (p = 0.1 MPa).[a,b]

T/K	x_i		*ARD*[d]
	Literature values[c]	Experimental values	
288.15	0.1595	0.1587	0.0033
303.45	0.2146	0.2153	
312.80	0.2525	0.2516	
317.85	0.2780	0.2792	
328.20	0.3251	0.3245	
333.20	0.3465	0.3473	
338.15	0.3735	0.3745	
343.10	0.4107	0.4121	

[a] Standard uncertainties u are u(T) = ±0.05 K, u(x_i) = ±0.01 x_i and u(p) = ±2 kPa.
[b] Standard uncertainty u was calculated using standard deviation (SD), x_i is the mole fraction solubility of benzoic acid at the system temperature T.
[c] Reference [16].
[d] $ARD = (1/N)\sum_{i=1}^{N}(|\chi_i^{lit} - \chi_i^{exp}|/\chi_i^{exp})$.

3. Results and discussion

3.1. Solubility and ILs structures

The mole fraction solubility values of [HOQu][H_2PO_4], [HOQu][HSO_4], [HOQu][CH_3SO_3], and [HOQu][*p*-TSA] in six alcohols (methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-methyl-1-propanol) in the temperature range from (278.15 to 348.15) K are listed in Table 3, respectively. It could be found that the solubility of ILs increased with increasing temperature. It was interesting to observe that the obvious solubility variation could occur within a narrow temperature range. For instance, the solubility of [HOQu][*p*-TSA] in 2-propanol was rapidly doubled from 0.0127 to 0.0253 within the very small temperature range from (323.15 to 333.15) K, that means the solubility is very sensitive to temperature change. This behavior refers to "temperature-sensitive" property of solubility [17,18]. This may be attributed to the temperature dependence of acid-dissociation and ion-pair formation. Namely, the acid-dissociation and ion-pair formation of ionic liquids were increased and decreased with increasing temperature, respectively. According to Table 3, the temperature-sensitive region of the solubility behavior varies apparently in different alcohols and [HOQu][*p*-TSA] has the most significantly "temperature-sensitive" behavior in all investigated alcohols. The temperature-sensitivity makes these ILs can be easily dissolved in solution as homogeneous catalyst or extraction auxiliary reagent at high working temperature, then they can easily crystallize or precipitate from the mixtures at low temperature after reaction or extraction process.

As the electronegativity of anionic group increases, the hydrogen bonding between the solvent molecule and the anionic group becomes stronger [19–21]. The results show a large difference in the mole fraction solubilities of the four [HOQu]$^+$-based ILs as with different anions, and the tendence of the solubility of ILs in one solvent at the same temperature is roughly [HOQu][H_2PO_4] < [HOQu][HSO_4] < [HOQu][CH_3SO_3] < [HOQu][*p*-TSA], which could be affected by the strength of hydrogen bonding between alcohol and anionic group of ILs. For instance, Fig. 2 shows that the solubilities of the four ILs in 1-propanol were along with the trend of [HOQu][H_2PO_4] < [HOQu][HSO_4] < [HOQu][CH_3SO_3] < [HOQu][*p*-TSA], thus the order of the strength of hydrogen bonding could be [H_2PO_4]$^-$ < [HSO_4]$^-$ < [CH_3SO_3]$^-$ < [*p*-TSA]$^-$.

Solvent polarity will decrease with the increase of the alkyl straight chain length or carbon number of alcohols (e.g. methanol > ethanol > 1-propanol > 2-propanol > 1-butanol > 2-methyl-1-propanol). Normally, the hydrogen bonding interaction between solvent molecules and anionic groups becomes weaker with the decreasing polarity of solvent, which is not beneficial for the dissolution of ILs [22]. The results show that the solubility of an ILs in different solvents decreases roughly along with the decreasing polarity of solvents especially in the four straight chain fatty alcohols (including methanol, ethanol, 1-propanol, 1-butanol), except that the solubility of [HOQu][HSO_4] and [HOQu][*p*-TSA] follows the order as 2-methyl-1-propanol > 2-propanol. For example, as shown in Fig. Fig. 3, the exception of [HOQu][*p*-TSA] solubility could be attributed to the branched-chain that exists in the structure of alcohols.

3.2. Correlation of the experimental data

Considering the "temperature-sensitive" property is of great significance for the separation and reusage of [HOQu]$^+$-based ILs from reaction mixtures. Therefore, correlation of the solubility data of ILs in solvents is necessary for the prediction of the solubility of ILs at other operation temperatures. Generally, the temperature dependence of the solubility of a solute in solvents can be modeled in three ways, including empirical correlation, non-activity coefficient method and activity coefficient method. In this work, according to the (solid + liquid) phase equilibrium theory and supposing that the enthalpy of solution varies with temperature linearly, the modified Apelblat equation [23,

Table 3
Mole fraction solubilities (x_i) of the four ILs in six alcohols between $T = (278.15$ and $348.15)$ K at atmosphere pressure ($p = 0.1$ MPa).[a,b]

T/K	10^3x_i			
	$[HOQu][H_2PO_4]$	$[HOQu][HSO_4]$	$[HOQu][CH_3SO_3]$	[HOQu][*p*-TSA]
Methanol				
278.15	1.8822	94.515	32.900	74.031
283.15	1.9455	114.24	39.742	85.924
288.15	2.0666	137.14	47.273	98.792
293.15	2.2705	165.24	57.234	113.10
298.15	2.6023	203.26	67.708	128.81
303.15	2.9651	239.40	79.574	149.44
308.15	3.4442	288.89	91.176	167.35
313.15	4.0548	346.83	102.63	192.94
318.15	4.7712	409.01	117.24	214.26
323.15	5.6976	487.73	133.15	244.51
Ethanol				
278.15	0.6872	5.2814	6.5606	11.201
283.15	0.7761	6.6975	7.8740	13.957
288.15	0.9051	8.5420	9.5025	17.624
293.15	1.0484	10.876	11.576	22.320
298.15	1.2250	13.692	14.143	28.742
303.15	1.3650	17.307	17.800	38.198
308.15	1.5920	21.651	22.249	49.405
313.15	1.8671	26.693	27.501	66.300
318.15	2.1610	32.198	34.689	86.789
323.15	2.5202	39.243	43.613	114.12
1-Propanol				
278.15	0.4514	2.2396	3.5422	6.3360
283.15	0.5206	2.3408	4.2770	8.1192
288.15	0.6062	2.5591	5.1144	10.465
293.15	0.7105	2.7651	6.1132	13.559
298.15	0.8160	3.0906	7.3599	17.643
303.15	0.9596	3.5222	9.1214	23.041
308.15	1.1128	4.1362	11.290	30.247
313.15	1.2956	4.8408	14.037	39.547
318.15	1.5143	5.7330	17.485	51.810
323.15	1.7824	6.8243	21.663	67.887
328.15	2.0822	8.2334	27.290	88.949
333.15	2.4557	9.9985	34.708	115.70
2-Propanol				
278.15	0.3250	1.0405	2.0106	1.9787
283.15	0.3859	1.1096	2.3823	2.1574
288.15	0.4482	1.2055	2.8430	2.4373
293.15	0.5221	1.3061	3.4002	2.8525
298.15	0.6239	1.4170	4.1658	3.4298
303.15	0.7454	1.5741	5.1009	4.2527
308.15	0.8896	1.7251	6.2868	5.4148
313.15	1.0724	1.9009	7.7976	7.0909
318.15	1.2629	2.1117	9.7236	9.4208
323.15	1.5192	2.3400	12.194	12.720
328.15	1.8083	2.5809	15.345	17.866
333.15	2.1587	2.9085	19.365	25.259
1-Butanol				
278.15	0.3521	1.3058	2.6477	4.6852
288.15	0.4912	1.4814	3.8256	7.0046
298.15	0.6679	1.7138	5.6382	10.994
308.15	0.9432	2.1252	8.3876	17.947
318.15	1.3017	2.6957	12.633	30.262
328.15	1.7963	3.5222	19.108	51.910
338.15	2.5508	4.6803	28.744	89.931
348.15	3.4972	6.4664	43.645	159.82
2-Methyl-1-propanol				
278.15	0.2571	1.3041	1.8394	3.5054
288.15	0.3574	1.4028	2.9090	4.8998
298.15	0.4986	1.5832	4.5897	7.3356
308.15	0.6977	1.8647	7.2148	11.638
318.15	0.9883	2.2778	11.287	19.442
328.15	1.3659	2.8726	17.545	33.482
338.15	1.9272	3.7243	27.127	59.371
348.15	2.6916	4.9438	41.378	106.16

[a] Standard uncertainties u are u(T) = ±0.05 K, u(x_i) = ±0.01 x_i or ±0.0001 (whichever was greater) and u(p) = ±2 kPa.

[b] Standard uncertainty u was calculated using standard deviation (SD), x_i is the mole fraction of the solubility of ILs at the system temperature T.

24] and λ*h* equation (also known as Buchowski-Ksiazczak equation) [23] were used to correlate the solubility data of ILs in alcohols as a function of temperature.

A frequently used semi-empirical equation is the so-called Apelblat equation [25,26]:

$$\ln x_i = A + \frac{B}{(T/K)} + C\ln(T/K) \tag{3}$$

in which *A*, *B*, and *C* are the empirical parameters, which could be regressed from the experimental solubility data by multivariable least-square method. The constants *A* and *B* provide an indication of the effect of solution non-idealities on the solubility of the solute and represent the solute activity coefficient of variation, and the *C* value represents the effect of temperature on the fusion enthalpy (ΔH_f, kJ·mol^{-1}), which is a deviation of heat capacity (ΔC_P, J·K^{-1}·mol^{-1}).

ΔC_P refers to the difference in heat capacity at constant pressure between the solid form and the hypothetical super-cooled liquid form of the compound at the solution temperature, this is a parameter that cannot be measured. It is customary to approximate it using the difference between the heat capacity at the melting point, namely, the difference between the heat capacity of the liquid and solid forms of the compound at its melting point. A common assumption of assigning a fair value to ΔC_P is that ΔC_P is equal to the entropy of fusion (ΔS_f, J·K^{-1}·mol^{-1}) [27,28], where

$$\Delta S_f = \Delta H_f / T_f \tag{4}$$

where ΔH_f (kJ·mol^{-1}) is the enthalpy of fusion and T_f (K) is the melting point of solute.

ΔH_f was determined by differential scanning calorimeter in this work, the ΔC_P of ILs were calculated from the ΔH_f and T_f, and the outcomes were (186.332, 170.341, 180.314 and 168.345) J·K^{-1}·mol^{-1} for $[HOQu][H_2PO_4]$, $[HOQu][HSO_4]$, $[HOQu][CH_3SO_3]$ and [HOQu][*p*-TSA], respectively.

Another common method to estimate the value of heat capacity is expressed as follows, the values of partial molar enthalpy of solution (ΔH_S, kJ·mol^{-1}) can be estimated by combining Eqs. (3) with (5), and yields Eq. (6) [29,30].

$$\Delta H_S = RT^2 (d\ln x_i / dT) \tag{5}$$

$$\Delta H_S = -BR + CRT \tag{6}$$

where *R* is the gas constant 8.314 × 10^{-3} kJ·mol^{-1}·K^{-1}.

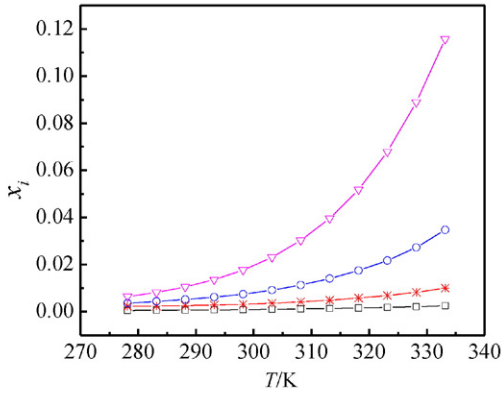

Fig. 2. Mole fraction solubility of ILs in 1-propanol as a function of temperature from (278.15 to 333.15) K: —□—, $[HOQu][H_2PO_4]$; —✳—, $[HOQu][HSO_4]$; —○—, $[HOQu][CH_3SO_3]$; —▽—, [HOQu][*p*-TSA].

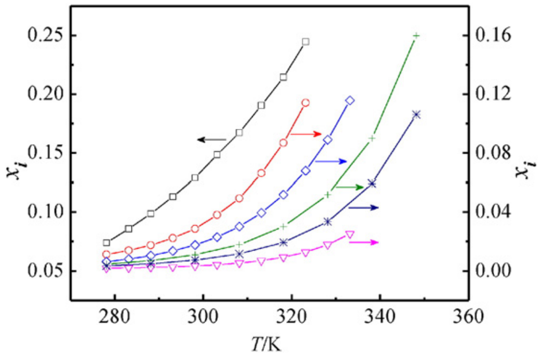

Fig. 3. Mole fraction solubility of [HOQu][*p*-TSA] in six alcohols as a function of temperature: —□—, methanol; —○—, ethanol; —◇—, 1-propanol; —▽—, 2-propanol; —+—,1-butanol; —✳—, 2-methyl-1-propanol.

The heat capacities of solution ($\Delta C_{P,\,S}$, $J \cdot mol^{-1}$) of ILs in alcohols were estimated by Eq. (7) obtained by differentiating Eq. (6), and gives Eq. (8) [31].

$$\Delta C_{P,S} = d \ln x_i / dT \tag{7}$$

$$\Delta C_{P,S} = CR \tag{8}$$

This method is based on the assumption that the solubility curves of ILs ($\ln x_i$ vs.$1/T$) in these alcohols are practically straight. The result shows that when Eq. (3) was used to correlate the solubility data of ILs in alcohols, there is a linear correlation between $\Delta C_{P,\,S}$ and ΔH_S at a certain temperature, and $\Delta C_{P,\,S}$ is independent of temperature.

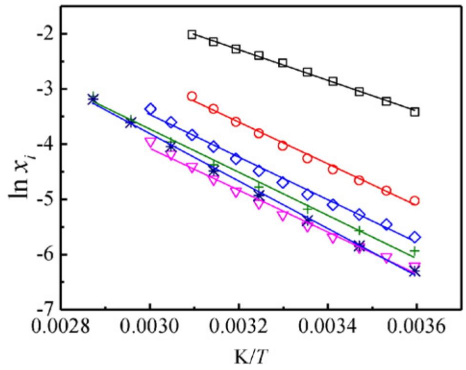

Fig. 4. van't Hoff plot of $\ln x_i$ of [HOQu][CH_3SO_3] in various solvents: methanol,□; ethanol, ○; 1-propanol, ◇; 2-propanol, ▽; 1-butanol, +; 2-methyl-1-propanol, ✳; calculated by equation ((14)), solid line.

The solubility of the ILs as a function of temperature was also correlated by the λ*h* equation, which was originally proposed by Buchowski et al. [32] and practically could be applicable for most solid-liquid equilibrium systems to give excellent correlation results with just two adjustable parameters [33,34]. The λ*h* equation is described as:

$$\ln[1 + \lambda(1/x_i - 1)] = \lambda h[(1/T) - (1/T_m)] \tag{9}$$

where *x* is the mole fraction solubility of ILs in alcohols at temperature *T* (K), T_m (K) refers to the melting point of the solute, λ and *h* are two adjustable parameters to be determined by fitting the solubility data. The

Table 4
Parameters of Eq. (3) and Eq. (9) correlated from experimental data for the four ILs in various alcohols.

Solvents	Apelblat equation				λ*h* equation		
	A^a	B/K	C/K^{-1}	$10^2 rmsd^b$	λ^c	h/K	$10^2 rmsd$
[HOQu][H_2PO_4]							
Methanol	−474.838	19,018.841	71.100	0.0031	0.039	6149.474	0.0193
Ethanol	−156.031	4466.574	23.576	0.0013	0.020	124,963.884	0.0026
1-Propanol	−158.799	4447.203	24.006	0.0005	0.020	141,784.647	0.0027
2-Propanol	−191.552	5622.898	29.016	0.0007	0.026	125,838.523	0.0024
1-Butanol	−140.460	3450.740	21.339	0.0013	0.026	125,472.333	0.0037
2-Methyl-1-propanol	−146.031	3632.042	22.158	0.0005	0.021	157,578.402	0.0029
[HOQu][HSO_4]							
Methanol	−94.501	1364.809	15.500	0.1876	36.997	124.572	1.1220
Ethanol	−0.359	−3610.721	1.436	0.0192	1.067	3780.192	0.0140
1-Propanol	−440.313	17,494.237	65.971	0.0034	0.065	43,568.546	0.0348
2-Propanol	−168.326	5845.526	24.953	0.0009	0.005	288,217.428	0.0036
1-Butanol	−308.313	12,042.819	45.908	0.0016	0.018	127,776.336	0.0214
2-Methyl-1-propanol	−309.962	12,426.616	45.955	0.0001	0.008	206,634.178	0.0180
[HOQu][CH_3SO_3]							
Methanol	130.512	−8347.359	−18.466	0.0719	1.495	1865.015	0.1228
Ethanol	−328.827	11,278.067	50.328	0.0146	1.485	2807.884	0.0723
1-Propanol	−311.424	10,610.741	47.553	0.0084	0.892	4871.180	0.0665
2-Propanol	−326.122	11,270.553	49.642	0.0017	0.479	8996.103	0.0359
1-Butanol	−208.471	6080.486	32.101	0.0058	0.656	6692.854	0.0613
2-Methyl-1-propanol	−145.338	2795.35	22.918	0.0122	0.762	6149.972	0.0345
[HOQu][p-TSA]							
Methanol	−33.641	−616.690	5.909	0.1108	1.927	1344.913	0.1699
Ethanol	−407.252	14,067.127	62.576	0.0753	7.561	722.010	0.1962
1-Propanol	−256.971	7273.102	40.112	0.0385	5.349	1062.889	0.1501
2-Propanol	−826.606	33,510.665	124.357	0.0035	1.373	4448.365	0.0854
1-Butanol	−374.816	12,920.507	57.388	0.0182	6.211	1071.831	0.3185
2-Methyl-1-propanol	−484.106	18,050.527	73.479	0.1034	3.691	1777.271	0.2092

[a] A, B and C are parameters of Apelblat equation, Apelblat equation: $\ln\chi_i = A + (B/T) + C\ln(T/K)$.

[b] $rmsd = \left[(1/N)\sum_{i=1}^{N}(\chi_i^{cal} - \chi_i)^2\right]^{1/2}$.

[c] λ and h are parameters of λh equation, λh equation: $\ln[1 + \lambda(1/x_i - 1)] = \lambda h[(1/T) - (1/T_m)]$.

Table 5
Dissolution enthalpy, entropy of the four ILs in difference alcohols and the Gibbs free energy of solution at $T = 298.15$ K.

Solvents	Methanol	Ethanol	1-Propanol	2-Propanol	1-Butanol	2-Methyl-1-propanol
[HOQu][H$_2$PO$_4$]						
$\Delta_{\mathrm{disoln}}H$ (kJ·mol^{-1})	18.8811	21.5815	23.6749	26.6364	26.4169	27.0296
$\Delta_{\mathrm{disoln}}S$ (J·K^{-1}·mol^{-1})	14.5146	16.6937	20.5896	28.3832	28.2360	27.7962
$\Delta_{\mathrm{disoln}}G$ (kJ·mol^{-1})	14.5536	16.6043	17.5362	18.1740	17.9983	18.7422
[HOQu][HSO$_4$]						
$\Delta_{\mathrm{disoln}}H$ (kJ·mol^{-1})	27.3472	33.5985	21.2689	14.4597	18.3565	16.3977
$\Delta_{\mathrm{disoln}}S$ (J·K^{-1}·mol^{-1})	78.4883	77.0799	24.2070	5.6743	9.4173	3.3871
$\Delta_{\mathrm{disoln}}G$ (kJ·mol^{-1})	3.9459	10.6172	14.0515	12.7679	15.5487	15.3878
[HOQu][CH$_3$SO$_3$]						
$\Delta_{\mathrm{disoln}}H$ (kJ·mol^{-1})	23.2543	31.5849	32.2849	31.8227	32.2982	35.8641
$\Delta_{\mathrm{disoln}}S$ (J·K^{-1}·mol^{-1})	55.4028	71.0697	66.7257	61.7414	65.7962	75.8885
$\Delta_{\mathrm{disoln}}G$ (kJ·mol^{-1})	6.7359	10.3954	12.3907	13.4145	12.6811	13.2379
[HOQu][p-TSA]						
$\Delta_{\mathrm{disoln}}H$ (kJ·mol^{-1})	19.7840	38.8571	40.9107	35.7884	40.6954	39.4375
$\Delta_{\mathrm{disoln}}S$ (J·K^{-1}·mol^{-1})	49.4242	101.4807	104.1412	74.3180	99.9426	92.5930
$\Delta_{\mathrm{disoln}}G$ (kJ·mol^{-1})	5.0482	8.6007	9.8610	13.6305	10.8975	11.8309

parameter regression was performed by minimization of the following objective function using the Levenberg-Marquardt method:

$$\min f(\lambda, h) = \sum_{N} \left[\left(x_i^{cal} - x_i \right) / x_i \right]^2 \tag{10}$$

where N denotes the number of data points for each solvent, *xcal i* represents the solubility calculated from Eqs. (3) and (9), and x_i represents the experimental solubility values.

These correlations can be evaluated with the root-mean-square deviations (*rmsd*), average absolute deviation (*AAD*) and squared correction coefficient (r^2) defined as follow:

$$rmsd = \left[(1/N) \sum_{i=1}^{N} (\chi_i^{cal} - \chi_i)^2 \right]^{1/2} \tag{11}$$

$$AAD = (1/N) \sum_{i=1}^{N} \left| \chi_i^{cal} - \chi_i \right| \tag{12}$$

$$r^2 = 1 - \sum \left(\chi_i - \chi_i^{cal} \right)^2 / \sum (\chi_i - \overline{\chi_i})^2 \tag{13}$$

where N is the number of experimental points.

The parameters of Eqs. (3) and (9) were correlated from experimental data for the four ILs in different alcohols, and the results are presented in Table 4, together with the *rmsd* and *AAD* which are defined as Eqs. (11) and (12), respectively. The optimized parameters along with the total calculated average *rmsd*, *AAD* and r^2 are 0.000285, 0.000166, 0.999831, respectively for the Apelblat equation and 0.076730, 0.001011, 0.994269, respectively for the λh equation. These indicate that both equations are satisfactorily correlates the solubility values of ILs in alcohols with temperature variation and the Apelblat equation can provide more ideal correlation results.

3.3. Thermodynamic properties of solutions

For real solutions, the logarithm of molar fraction solubility of a solute ($\ln x_i$) is a linear function of the reciprocal of the absolute temperature ($1/T$), which could be described as the van't Hoff equation (Eq. (14)) [35,36].

$$\ln x_i = -\frac{\Delta_{\mathrm{disoln}}H}{RT} + \frac{\Delta_{\mathrm{disoln}}S}{R} \tag{14}$$

where x_i is molar fraction solubility, $\Delta_{\mathrm{disoln}}H$ (kJ·mol^{-1}) and $\Delta_{\mathrm{disoln}}S$ (J·K^{-1}·mol^{-1}) are the apparent molar enthalpy of dissolution and the apparent molar entropy of dissolution, respectively. The $\Delta_{\mathrm{disoln}}H$ value reflects the temperature dependence of solubility and differs from the true calorimetric enthalpy of solution because the van't Hoff equation neglects the change in activity with composition.

The Gibbs free energy of solution can be calculated by the Gibbs-Helmoholtz equation [37]:

$$\Delta_{\mathrm{disoln}}G = \Delta_{\mathrm{disoln}}H - T\Delta_{\mathrm{disoln}}S. \tag{15}$$

In this work, Eq. (14) was used to reveal the dependence of mole fraction solubility to the temperature. In Fig. 4, for instance, the van't Hoff plots were obtained from the linear fit of $\ln x_i$ of [HOQu][CH$_3$SO$_3$] versus $1/T$ using Eq. (14). The dissolution enthalpy and entropy of ILs were calculated from the slope and interception of these plots and listed in Table 5, together with the change of Gibbs free energy calculated at $T = 298.15$ K using Eq. (15). According to the results, the positive $\Delta_{\mathrm{disoln}}H$ and $\Delta_{\mathrm{disoln}}S$ revealed that the dissolution of ILs in each solvent within the experimental temperature range was an endothermic and entropy-driven process. The dissolution of ILs exhibits a positive Gibbs free energy change. Moreover, low $\Delta_{\mathrm{disoln}}H$ value corresponds to higher solubility, which indicated that low $\Delta_{\mathrm{disoln}}H$ value is more conducive to dissolution. These results are critical for the optimization of the dissolution and crystallization processes of related ILs.

4. Conclusions

The solubility of four novel Brønsted-acidic [HOQu]$^+$-based ILs in six lower alcohols were measured at temperatures from (278.15 to 348.15) K. [HOQu][*p*-TSA] shows the most significantly “temperature-sensitive” behavior among four ILs. The solubilities varied roughly with the polarity and molecular structures of the solvents, as well as with the strength of hydrogen bonding between alcohols and anionic groups. The experimental data were correlated by the modified Apelblat equation and λh equation and both with good agreement. The dissolution enthalpies, entropies of the four ILs in six alcohols and the Gibbs free energy of solution at $T = 298.15$ K were calculated based on the solubility results and the dissolution process was proved to be endothermic and entropy-driven. The results in this work can provide useful information for further process of the application of ILs and their purification after catalytic reaction or extraction.

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Appendix A. Supplementary data

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