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Measurement and Correlation of Solubility of Benzothiazolium Ionic Liquids in Ethanol + Ethyl Benzoate

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ABSTRACT: The solubilities of benzothazolium-based ionic liquids (ILs) [HBth][BF₄], [HBth][CH₃SO₃], and [HBth][*p*-TSA] in binary ethanol + ethyl benzoate solvents were measured using the equilibrium method with the temperature range from 233.2 to 293.7 K at atmospheric pressure. Results of these measurements were correlated by both λh equation and the modified Apelblat equation. It was found that both models gave satisfactory correlation results. In the λh model, the average relative deviations were 0.7145, 0.7845, and 0.8119% for [HBth][BF₄], [HBth][CH₃SO₃], and [HBth][*p*-TSA], respectively. Interestingly, the parameters of λ and *h* for the λh model and *A*, *B*, and *C* for the modified Apelblat model were simultaneously expressed as functions of solvent composition (x_{sol}) for the first time. Furthermore, solubilities of these three ILs in the binary system were predicted through these two sets of self-created correlation equations with ideal performances. The total average relative deviations were less than 2.2% for both models. These successful in-depth correlations and validated prediction results have guaranteed the accuracy of experimental solubility data and provide us a reliable method for accurate solubility prediction at any temperature with any solvent composition. This developed calculation method in this report lays a foundation for accurate industrial recovery of ILs and gives us valuable guidance for the design of the specific purification process to acquire desired purity of the product in industrial production.

INTRODUCTION

Aromatic esters are very important chemical intermediates with wide applications in the chemical industry and are usually synthesized through acid-catalyzed esterification reactions¹ or synthesized through enzymatic esterification reactions²⁻⁴ with alcohols and benzoic acids as raw materials. Inorganic acids such as H_3PO_4 , H_2SO_4 , and so forth, have been widely applied as catalysts for the esterification.^{5–9} Although high yields were acquired, usage of a large amount of organic solvents and difficulty in the catalyst recovery could result in environmental contamination. Thus, it is necessary to develop novel environmentally friendly, efficient, and recyclable catalysts.

Ionic liquids (ILs), a class of nonmolecular solvents with low melting points, negligible volatility, wide liquid range, and good chemical stability and solubility,^{10,11} have drawn widespread attention of researchers. In the field of synthetic chemistry, they often replace hazardous organic solvents and serve as an environmentally friendly, nonvolatile, and recyclable reaction medium.¹² Many researchers have already successfully applied ILs in the esterification with reduced reaction time and temperature as well as satisfactory recyclability.^{13–17} Later,

Song et al.¹⁸ reported the first esterification of aromatic acid with alcohols catalyzed by "temperature-sensitive" ILs. These functionalized ILs including [HBth][BF₄], [HBth][CH₃SO₃], and [HBth][p-TSA] had very large solubility differences with only small-scale changes of temperature in many alcohols.¹⁹ They exhibited excellent catalytic performances and ideal recoveries. Among them, esterification yield of benzoic acid could reach up to 97.3% in ethanol with [HBth][CH₃SO₃] as the catalyst, which is showing great industrial application potential. Although this temperature-sensitive IL-catalyzed esterification of benzoic acid in ethanol had excellent performances, there still exists some amount of ILs dissolved in the ethanol + ethyl benzoate solution after cooling down to room temperature at the end of the reaction. Due to the high cost of IL and high requirement of product purity,²⁰ it is vitally important

Received: October 18, 2019 Accepted: December 27, 2019





Figure 1. Synthetic routes and molecular structures of [HBth][BF₄], [HBth][CH₃SO₃], and [HBth][*p*-TSA].

Table 1. Provenance and Puri	y of the Chemicals	Used in This Work
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chemical name	source	initial mole fraction purity	purification method	final mole fraction purity	analysis method
[HBth][BF ₄]	prepared in lab	0.95	developed in our lab	≥0.99	HPLC
[HBth][CH ₃ SO ₃]	prepared in lab	0.96	developed in our lab	≥0.99	HPLC
[HBth][p-TSA]	prepared in lab	0.95	developed in our lab	≥0.99	HPLC
ethyl benzoate	Kelon Chemical Reagent Co., Ltd.	≥0.995	no further purification	≥0.995	
ethanol	Kelon Chemical Reagent Co., Ltd.	≥0.995	no further purification	≥0.995	
ethyl acetate	Kelon Chemical Reagent Co., Ltd.	≥0.995	no further purification	≥0.995	

to further crystallize IL out for recycle by cooling the system down to very low temperature. Therefore, accurate solubility data of these ILs in this binary system at low temperature is of vital importance for the guidance of industrial separation.

Herein, we report the solubility data of three ILs ([HBth]-[BF₄], [HBth][CH₃SO₃], and [HBth][*p*-TSA]) in the binary ethanol + ethyl benzoate solvents at low temperature ranging from 233.2 to 293.7 K at atmospheric pressure. These data were ideally fitted by the λh equation and the modified Apelblat equation, respectively. Surprisingly, for the first time, parameters of λ and *h* for the λh model and *A*, *B*, and *C* for the modified Apelblat model were simultaneously expressed as functions of solvent composition (x_{sol}) with satisfactory correlation coefficients (R^2). Furthermore, solubilities of these three ILs at any solvent composition and any temperature could be accurately predicted through both models.

EXPERIMENTAL SECTION

Chemicals and Apparatus. Benzothiazole (CAS number 95-16-9) of analytical grade was supplied by Xilong Chemical Factory in Shantou City, Guangdong. Tetrafluoroboric acid (CAS number 16872-11-0), methanesulfonic acid (CAS number 75-75-2), ethyl benzoate (CAS number 93-89-0), ptoluenesulfonic acid (CAS number 104-15-4), ethyl acetate (CAS number 141-78-6), anhydrous ethanol, and so forth, were purchased from Chengdu Kelon Chemical Reagent Co., Ltd., with analytical grade or above. All used water was ultrapure water obtained from an ultrapure water purification system (0.4)mm filter) manufactured by Millipore Co., Ltd. (Bedford, MA, USA). A RE-3000B rotary evaporator (Shanghai Yarong Biochemical Instrument Co., Ltd., China) was applied for vacuum evaporation. Melting points were measured by an XRC-1 melting point apparatus (Sichuan University Instrument Co., Ltd.). Mass values were measured by an electronic balance (ESJ200-4A, Longteng Electronics Co., Ltd., Shenyang, China) with an uncertainty of ± 0.0001 g. ¹H NMR and ¹³C NMR spectra were recorded on an AV-400 spectrometer (Bruker

Corporation, Germany) in DMSO- d_6 with tetramethylsilane (TMS) as an internal standard. ¹H NMR spectra were recorded at 400 MHz, and ¹³C NMR spectra were recorded at 100 MHz. The electrospray ionization mass spectrometry (ESI-MS) spectra were recorded on a ZQ 4000 mass spectrometer (Waters Corporation, USA). An LC20-AT high-performance liquid chromatography (HPLC) instrument (Shimadzu Co., Japan) consisting of a diode array detector was used for the analysis and quantitation of targeted IL. A Welchrom C18 column (4.6 × 250 mm, 5 μ m) was used as the HPLC analytical column.

Synthesis and Purification of ILs. The synthesis of ILs was according to the reported literature.¹⁹ Briefly, 0.5 mol accurate amount of benzothiazole was dissolved in 100 mL of anhydrous ethanol and placed in a round-bottom flask equipped with a magnetic stirrer in an ice bath. Equal molar of fluoroboric acid (methanesulfonic acid or *p*-toluenesulfonic acid) dissolved in about 40 mL of ethanol was added dropwise into the roundbottom flask under adequate stirring for about 1 h. Afterward, the mixture was continuously stirred for 12 h at room temperature. Ethanol was removed by evaporation under vacuum to give the crude product as a white solid. It was then washed three or four times by ethyl acetate and recrystallized in anhydrous ethanol to give the final pure product, which was dried for more than 12 h under vacuum at 343 K. The ILs were characterized by ¹H NMR, ¹³C NMR, and ESI-MS (the detail is shown in the Supporting Information). The synthetic route of ILs is shown in Figure 1. Melting points were determined as 398 K for benzothiazolium tetrafluoroborate ([HBth][BF₄]), 378 K for benzothiazolium methanesulfonate ([HBth][CH₃SO₃]), and 393 K for benzothiazolium p-toluene sulfonate ([HBth]-[p-TSA]).¹⁹ All these three purified ILs have mole fraction purities higher than 99% determined by HPLC. The provenance of main used chemicals and their purities are given in Table 1.

Solubility Measurement. The solubility of ILs was measured by a static equilibrium method as presented in Figure 2. The concentration determination of ILs was conducted by the



Figure 2. Apparatus for determination of solubilities of $[HBth][BF_4]$, $[HBth][CH_3SO_3]$, and [HBth][p-TSA]. (1) Preprogrammed automatic temperature controller, (2) thermostat with ethanol as medium, (3) rubber plug, (4) mercury thermometer, (5) sample connection, (6) crystallizer, and (7) magnetic stirrer.

HPLC method. First, HPLC separation conditions were investigated and determined. Then, a certain amount of pure IL was accurately weighed and dissolved in certain solvent in a 100 mL volumetric flask. Afterward, gradient solutions were prepared by diluting the original one and injected into the HPLC in turn to generate the chromatogram. The external standard curve was obtained by linear regression with the peak area as the vertical coordinate and concentration of IL as the horizontal coordinate. Afterward, solvents with different compositions were carefully prepared and added into a crystallizer (self-made). A thermostatic refrigeration recycler (Gongyi Yuhua Instrument Co., Ltd., China) with an uncertainty of ± 0.05 K was started to keep the system at a desired constant temperature. An excess amount of pure IL was subsequently added in and stirred for at least 4 h to reach the equilibrium. The solution was then settled for more than 2 h to guarantee that extra IL was completely precipitated at the bottom of the solution. A little drop of upper clear liquid was carefully withdrawn by a pipette into a previously weighed EP tube with the main body of liquid not disturbed as possible as we could. Then, the solution-containing EP tube was accurately weighed. The solution mass (m) equaled to the total mass minus the mass value of the empty EP tube. The mass values of solvents ethyl benzoate and ethanol were defined as m_1 and m_2 , respectively. The solution was then diluted into a certain volume and analyzed by HPLC to acquire the solute mass (m_A) from an external standard method. The optimal HPLC conditions on the C₁₈ column were determined as the mobile phase of water-methanol (50:50, v/v) at a flow rate of 1.0 mL min^{-1} with 20 μ L injection volume. The column effluents were monitored at 284 nm for [HBth][p-TSA] and 250 nm for [HBth][BF₄] and [HBth][CH₃SO₃], which were the maximum UV adsorption wavelengths of them.

RESULTS AND DISCUSSION

The molar fraction solubility was determined by eqs 1-3.

$$m - m_{\rm A} = m_1 + m_2 \tag{1}$$

$$x_{\rm sol} = \frac{\frac{m_1}{M_1}}{\frac{m_1}{M_1} + \frac{m_2}{M_2}}$$
(2)

$$x = \frac{\frac{m_{\rm A}}{M_{\rm A}}}{\frac{m_{\rm A}}{M_{\rm A}} + \frac{m_{\rm 1}}{M_{\rm 1}} + \frac{m_{\rm 2}}{M_{\rm 2}}}$$
(3)

where M_{A} , M_1 , and M_2 represent the molecular weights of the solute, ethyl benzoate, and ethanol, respectively. x_{sol} is the molar fraction of ethyl benzoate in the binary solvent system. x is the molar fraction solubility of IL.

The solubilities of three benzothiazolium-based ILs were determined in the temperature range of 233.2 to 293.7 K. First of all, we determined the solubilities in ethanol and compared these results with the previous literature¹⁹ in the Supporting Information. Then, the solvent compositions (x_{sol}) were defined as 0.25, 0.33, 0.50, 0.67, and 1.00 in the main text. As demonstrated in Tables 2–4, solubility data of these ILs in different solvent compositions were measured and correlated by the λh equation and the modified Apelblat equation. The λh model is a semiempirical equation proposed by Buchowski et al.²¹ and is given as eq 4.

$$\ln\left[1 + \lambda\left(\frac{1}{x} - 1\right)\right] = \lambda h\left(\frac{1}{T} - \frac{1}{T_m}\right) \tag{4}$$

where *x* is the molar fraction solubility of IL, *T* represents the absolute temperature of the system, and $T_{\rm m}$ is the melting point of the solute, which was previously experimentally determined. λ and *h* are two adjustable parameters obtained from correlation of the experimental solubility data. The value of λ can reflect the nonideal feature of the system and could be interpreted as the average association degree of the solute molecule in the solution system, whereas *h* is related to the enthalpy of solution.²²

The modified Apelblat equation $^{23-25}$ is shown as eq 5.

$$\ln x = A + \frac{B}{T} + C \ln T \tag{5}$$

where *x* and *T* similarly represent molar fraction solubility of IL and absolute temperature of the system, respectively. Parameters *A*, *B*, and *C* were empirical constants obtained from correlation of experimental solubility data. The values of *A* and *B* reflect the variation in the solution activity coefficient and provide an indication of the effect of solution nonideality on the solute solubility.²⁶

The experimental solubility data shown in Tables 2–4 could be ideally correlated by both λh model and Apelblat model. The calculated solubility data and the relative deviations (RDs) defined by eq 6 are also presented in Tables 1–3. The average relative deviation (ARD) is defined by eq 7. For the λh model, the ARDs were 0.7145% for [HBth][BF₄], 0.7845% for [HBth][CH₃SO₃], and 0.8119% for [HBth][*p*-TSA]. Intuitional comparisons between experimental data and the calculated ones are shown in Figures 3–5. All model parameters, correlation coefficients (R^2), and root-mean-square deviations (rmsd) defined by eq 8 were obtained and are listed in Table 5.

$$RD = \frac{|x^{exp} - x^{cal}|}{x^{exp}} \times 100\%$$
(6)

$$ARD = \frac{1}{N} \sum_{i}^{N} \frac{|x_i^{exp} - x_i^{cal}|}{x_i^{exp}} \times 100\%$$
(7)

rmsd =
$$\left[\sum_{i=1}^{N} \frac{(x^{\exp} - x^{cal})^2}{N}\right]^{0.5}$$
 (8)

As can be seen from the curves in Figures 3-5, [HBth][BF₄], [HBth][CH₃SO₃], and [HBth][*p*-TSA] had similar solubility values in the binary ethanol + ethyl benzoate systems. Generally, these three ILs were slightly soluble in ethanol and almost

Table 2. Experimental a	nd Calculate	d Solubiliti	ss of [HBth	[][BF4] in I	Sthanol + F	Ethyl Benzo	oate from	T = 293.7 t	o 233.2 K	at 100 kPa	a-c			
models	T (K)	293.7	288.5	283.3	278.4	273.2	268.4	263.6	258.5	253.4	248.3	243.1	238.3	233.2
						$x_{\rm sol} = 0.25$								
<i>Ah</i> model	$x^{\mathrm{exp}} \times 10^3$	12.54	10.86	9.192	7.883	6.664	5.664	4.810	4.027	3.312	2.752	2.241	1.851	1.522
	$x^{ m cal} imes 10^3$	12.65	10.80	9.197	7.864	6.653	5.670	4.813	4.022	3.342	2.759	2.254	1.856	1.499
	RD%	0.8772	0.5525	0.05440	0.2410	0.1651	0.1059	0.06237	0.1242	0.9058	0.2544	0.5801	0.2701	1.511
modified Apelblat model	$x^{ m cal} imes 10^3$	12.59	10.77	9.169	7.849	6.626	5.643	4.786	3.998	3.322	2.745	2.246	1.856	1.505
	RD%	0.3987	0.8287	0.2502	0.4313	0.5702	0.3708	0.4990	0.7201	0.3019	0.2544	0.2231	0.2701	1.117
						$x_{\rm sol} = 0.33$								
<i>Ah</i> model	$x^{\mathrm{exp}} imes 10^3$	9.251	8.146	7.024	6.017	5.272	4.513	3.931	3.372	2.85	2.469	2.066	1.728	1.472
	$x^{ m cal} imes 10^3$	9.305	8.081	7.003	6.106	5.264	4.577	3.967	3.394	2.891	2.450	2.058	1.743	1.451
	RD%	0.5837	0.7979	0.2990	1.479	0.1517	1.418	0.9158	0.6524	1.439	0.7695	0.3872	0.8681	1.427
modified Apelblat model	$x^{ m cal} imes 10^3$	9.267	8.063	6.992	6.095	5.251	4.562	3.950	3.377	2.875	2.438	2.051	1.742	1.457
	RD%	0.1730	1.019	0.4556	1.296	0.3983	1.086	0.4833	0.1483	0.8772	1.2556	0.7260	0.8102	1.019
						$x_{\rm sol} = 0.50$								
<i>Ah</i> model	$x^{ m exp} imes 10^3$	5.424	4.824	4.311	3.868	3.423	3.037	2.722	2.427	2.113	1.874	1.63	1.439	1.254
	$x^{ m cal} imes 10^3$	5.449	4.845	4.305	3.848	3.411	3.048	2.719	2.402	2.117	1.861	1.625	1.430	1.243
	RD%	0.4609	0.4353	0.1392	0.5171	0.3506	0.3622	0.1102	1.030	0.1893	0.6937	0.3067	0.6254	0.8772
modified Apelblat model	$x^{ m cal} imes 10^3$	5.413	4.830	4.301	3.850	3.416	3.053	2.724	2.409	2.125	1.871	1.639	1.447	1.265
	RD%	0.2028	0.1244	0.2320	0.4654	0.2045	0.5268	0.07348	0.7417	0.5679	0.1601	0.5521	0.5559	0.8772
						$x_{\rm sol} = 0.67$								
<i>Ah</i> model	$x^{\mathrm{exp}} \times 10^3$	2.320	2.097	1.910	1.723	1.520	1.389	1.270	1.124	1.030	0.9090	0.8214	0.7307	0.6465
	$x^{\rm cal} imes 10^3$	2.345	2.109	1.896	1.715	1.541	1.395	1.261	1.132	1.014	0.9063	0.8066	0.7226	0.6410
	RD%	1.078	0.5722	0.7330	0.4643	1.382	0.4320	0.7087	0.7117	1.553	0.2970	1.802	1.109	0.8507
modified Apelblat model	$x^{\rm cal} imes 10^3$	2.310	2.088	1.885	1.710	1.540	1.397	1.266	1.140	1.024	0.9198	0.8232	0.7424	0.6645
	RD%	0.4310	0.4292	1.309	0.7545	1.316	0.5760	0.3150	1.423	0.5825	1.188	0.2191	1.601	2.784
						$x_{\rm sol} = 1$								
<i>λh</i> model	$x^{\mathrm{exp}} \times 10^4$	4.672	4.304	3.913	3.639	3.338	3.091	2.844	2.571	2.359	2.215	2.029	1.821	1.713
	$x^{\rm cal} imes 10^4$	4.685	4.286	3.924	3.614	3.313	3.058	2.823	2.592	2.379	2.182	1.997	1.837	1.680
	RD%	0.2783	0.4182	0.2811	0.6870	0.7490	1.068	0.7384	0.8168	0.8478	1.490	1.577	0.8786	1.926
modified Apelblat model	$x^{\mathrm{cal}} imes 10^4$	4.656	4.272	3.918	3.610	3.310	3.054	2.818	2.587	2.374	2.180	1.998	1.844	1.694
	RD%	0.3425	0.7435	0.1278	0.7969	0.8388	1.197	0.9142	0.6223	0.6359	1.580	1.528	1.263	1.109
^a Standard uncertainties $u(.)$	r) = 0.05 K and hanol + ethyl	$I_{u}(P) = 0.05$ benzoate syst	kPa and relations, and $x_{\rm sol}$	ative standard is the molar	l uncertainti fraction of	es $u_{\rm r}(x_i) = 0$ ethyl benzos	.031 and u_r (ate in the b	x_{sol}) = 0.015. inary solvent	b_{x_i} is the m	iole fraction	solubility of	f ILs at the s	system temp	erature T.

Table 3. Experimental :	and Calculate	ed Solubilit	ies of [HB1	th][CH ₃ SO	3] in Ethan	ol + Ethyl I	Benzoate f	rom T = 29	3.7 to 233.	2 K at 100	kPa ^{a-c}			
models	T (K)	293.7	288.5	283.3	278.4	273.2	268.4	263.6	258.5	253.4	248.3	243.1	238.3	233.2
						$x_{\rm sol} = 0.25$								
$\lambda h \mod$	$x^{\rm exp} \times 10^3$	11.16	9.907	8.815	7.889	6.994	6.207	5.547	4.881	4.336	3.829	3.391	2.972	2.649
	$x^{ m cal} imes 10^3$	11.21	9.930	8.803	7.860	6.968	6.231	5.568	4.934	4.366	3.854	3.386	2.997	2.624
	RD%	0.4480	0.2322	0.1361	0.3676	0.3717	0.387	0.3786	1.086	0.6919	0.6529	0.1474	0.8412	0.9438
modified Apelblat model	$x^{\rm cal} imes 10^3$	11.18	9.934	8.816	7.870	6.969	6.223	5.552	4.913	4.343	3.835	3.375	2.997	2.639
	RD%	0.1792	0.2725	0.01134	0.2408	0.3574	0.2578	0.09014	0.6556	0.1614	0.1567	0.4718	0.8412	0.3775
						$x_{\rm sol} = 0.33$								
$\lambda h \mod$	$x^{\rm exp} \times 10^3$	7.697	6.758	6.034	5.359	4.739	4.245	3.721	3.291	2.915	2.532	2.253	1.982	1.731
	$x^{ m cal} imes 10^3$	7.742	6.830	6.029	5.361	4.731	4.212	3.747	3.303	2.906	2.551	2.228	1.960	1.704
	RD%	0.5846	1.065	0.08286	0.03732	0.1688	0.7774	0.6987	0.3646	0.3087	0.7504	1.110	1.110	1.560
modified Apelblat model	$x^{\rm cal} imes 10^3$	7.638	6.774	6.001	5.348	4.727	4.214	3.752	3.314	2.923	2.575	2.261	2.003	1.759
	RD%	0.7665	0.2368	0.5469	0.2053	0.2532	0.7303	0.8331	0.6989	0.2744	1.698	0.3551	1.060	1.618
						$x_{\rm sol} = 0.50$								
$\lambda h \mod$	$x^{\mathrm{exp}} \times 10^3$	3.495	3.104	2.743	2.376	2.092	1.836	1.658	1.448	1.272	1.084	0.9417	0.8251	0.7124
	$x^{ m cal} imes 10^3$	3.511	3.080	2.703	2.390	2.095	1.854	1.639	1.434	1.252	1.091	0.9440	0.8234	0.7093
	RD%	0.4578	0.7732	1.458	0.5892	0.1434	0.9804	1.146	0.9669	1.572	0.6458	0.2442	0.2060	0.4351
modified Apelblat model	$x^{ m cal} imes 10^3$	3.479	3.064	2.694	2.384	2.091	1.849	1.634	1.430	1.250	1.091	0.9478	0.8314	0.7222
	RD%	0.4578	1.289	1.786	0.3367	0.04780	0.7081	1.448	1.243	1.730	0.6458	0.6478	0.7635	1.376
						$x_{\rm sol} = 0.67$								
<i>λh</i> model	$x^{\mathrm{exp}} \times 10^3$	1.581	1.349	1.204	1.057	0.8984	0.8072	0.7032	0.6139	0.5383	0.4593	0.3893	0.3439	0.2972
	$x^{\rm cal} imes 10^3$	1.555	1.358	1.186	1.044	0.9103	0.8015	0.7045	0.6130	0.5319	0.4601	0.3954	0.3425	0.2928
	RD%	1.581	1.349	1.204	1.057	0.8984	0.8072	0.7032	0.6139	0.5383	0.4593	0.3893	0.3439	0.2972
modified Apelblat model	$x^{\rm cal} imes 10^3$	1.559	1.364	1.192	1.048	0.9119	0.8009	0.7022	0.6096	0.5281	0.4566	0.3928	0.3412	0.2932
	RD%	1.392	1.112	0.9967	0.8515	1.503	0.7805	0.1422	0.7004	1.895	0.5879	0.8990	0.7851	1.346
						$x_{ m sol} = 1$								
$\lambda h \mod l$	$x^{\mathrm{exp}} imes 10^4$	3.218	2.781	2.393	2.067	1.784	1.526	1.338	1.117	0.9524	0.7876	0.6942	0.5742	0.4836
	$x^{\rm cal} imes 10^4$	3.202	2.754	2.367	2.050	1.757	1.520	1.312	1.118	0.9492	0.8024	0.6726	0.5686	0.4729
	RD%	0.4972	0.9709	1.087	0.8224	1.513	0.3932	1.943	0.08953	0.3360	1.879	3.111	0.9753	2.213
modified Apelblat model	$x^{\rm cal} imes 10^4$	3.193	2.754	2.369	2.051	1.755	1.517	1.307	1.113	0.9445	0.7991	0.6716	0.5703	0.4776
	RD%	0.7769	0.9709	1.003	0.7741	1.626	0.5898	2.317	0.3581	0.8295	1.460	3.256	0.6792	1.241
^a Standard uncertainties $u($. ^c The solvents are binary e	T) = 0.05 K an thanol + ethyl	$d \ u(P) = 0.0$ benzoate sys	5 kPa and re tems, and x_i	elative standa sol is the mol	rd uncertaint ar fraction of	ies $u_r(x_i) = 0$. ε ethyl benzos	.031 and $u_{ m r}$ ate in the b	$(x_{sol}) = 0.015$ oinary solvent	b_{x_i} is the m	ole fraction	solubility of	f ILs at the s	iystem temp	erature <i>T</i> .

Table 4. Experimental a	nd Calculate	d Solubilitie	s of [HBth	i [<i>p</i> -TSA] i	n Ethanol	+ Ethyl Be	nzoate fro	m T = 293	.7 to 233.2	K at 100	kPa ^{a-c}			
models	T (K)	293.7	288.5	283.3	278.4	273.2	268.4	263.6	258.5	253.4	248.3	243.1	238.3	233.2
						$x_{\rm sol} = 0.25$								
<i>λh</i> model	$x^{\mathrm{exp}} imes 10^3$	10.36	9.201	8.225	7.523	6.632	6.047	5.471	4.861	4.331	3.837	3.457	3.029	2.673
	$x^{ m cal} imes 10^3$	10.31	9.234	8.267	7.446	6.660	6.002	5.404	4.826	4.302	3.826	3.387	3.018	2.662
	RD%	0.4826	0.3587	0.5106	1.024	0.4222	0.7442	1.225	0.7200	0.6696	0.2867	2.025	0.3632	0.4115
modified Apelblat model	$x^{\rm cal} imes 10^3$	10.35	9.288	8.325	7.500	6.705	6.039	5.433	4.849	4.322	3.847	3.411	3.049	2.703
	RD%	0.09653	0.9455	1.216	0.3057	1.101	0.1323	0.6946	0.2469	0.2078	0.2606	1.331	0.6603	1.122
						$x_{\rm sol} = 0.33$								
$\lambda h \mod$	$x^{\mathrm{exp}} \times 10^3$	7.015	6.241	5.567	5.021	4.457	4.056	3.648	3.263	2.879	2.587	2.339	2.088	1.831
	$x^{\rm cal} imes 10^3$	6.978	6.250	5.598	5.046	4.516	4.073	3.670	3.281	2.927	2.606	2.310	2.061	1.820
	RD%	0.5274	0.1442	0.5569	0.4979	1.324	0.4191	0.6031	0.5516	1.667	0.7344	1.240	1.293	0.6008
modified Apelblat model	$x^{\rm cal} imes 10^3$	6.929	6.225	5.585	5.037	4.509	4.066	3.663	3.274	2.923	2.606	2.315	2.074	1.842
	RD%	1.226	0.2564	0.3233	0.3187	1.167	0.2465	0.4112	0.3371	1.528	0.7344	1.026	0.6705	0.6008
						$x_{\rm sol} = 0.50$								
$\lambda h \mod$	$x^{ m exp} imes 10^3$	2.939	2.627	2.306	2.108	1.924	1.719	1.575	1.381	1.262	1.124	0.9872	0.8816	0.8030
	$x^{\rm cal} imes 10^3$	2.895	2.600	2.336	2.112	1.896	1.716	1.552	1.393	1.248	1.116	0.9939	0.8911	0.7913
	RD%	1.497	1.028	1.301	0.1898	1.455	0.1745	1.460	0.8689	1.109	0.7117	0.6787	1.078	1.457
modified Apelblat model	$x^{\rm cal} imes 10^3$	2.900	2.611	2.348	2.123	1.905	1.723	1.556	1.395	1.250	1.118	0.9977	0.8969	0.8003
	RD%	1.327	0.6091	1.821	0.7116	0.9875	0.2327	1.206	1.014	0.9509	0.5338	1.064	1.735	0.3362
						$x_{\rm sol} = 0.67$								
<i>λh</i> model	$x^{\rm exp} imes 10^3$	1.232	1.120	0.9897	0.9060	0.8115	0.7342	0.6695	0.5997	0.5393	0.4893	0.4391	0.3961	0.3584
	$x^{\rm cal} imes 10^3$	1.222	1.102	0.9940	0.9023	0.8141	0.7401	0.6725	0.6068	0.5469	0.4922	0.4412	0.3981	0.3561
	RD%	0.8117	1.607	0.4345	0.4084	0.3204	0.8036	0.4481	1.184	1.409	0.5927	0.4783	0.5049	0.6417
modified Apelblat model	$x^{\rm cal} imes 10^3$	1.239	1.117	1.006	0.9113	0.8194	0.7422	0.6717	0.6036	0.5420	0.4862	0.4348	0.3920	0.3508
	RD%	0.5682	0.2679	1.647	0.5850	0.9735	1.090	0.3286	0.6503	0.5006	0.6336	0.9793	1.035	2.121
						$x_{\rm sol} = 1$								
$\lambda h \mod l$	$x^{\mathrm{exp}} imes 10^4$	2.221	2.013	1.849	1.652	1.521	1.368	1.261	1.139	1.017	0.9175	0.8431	0.7579	0.6907
	$x^{\rm cal} imes 10^4$	2.240	2.024	1.831	1.666	1.508	1.375	1.253	1.134	1.026	0.9264	0.8338	0.7553	0.6786
	RD%	0.8555	0.5464	0.9735	0.8475	0.8547	0.5117	0.6344	0.4390	0.8850	0.9700	1.103	0.3431	1.752
modified Apelblat model	$x^{ m cal} imes 10^4$	2.240	2.030	1.837	1.672	1.512	1.376	1.253	1.133	1.023	0.9241	0.8324	0.7555	0.6813
	RD%	0.8555	0.8445	0.6490	1.211	0.5917	0.5848	0.6344	0.5268	0.5900	0.7193	1.269	0.3167	1.361
^a Standard uncertainties $u(7)$ ^c The solvents are binary et	⁻) = 0.05 K and hanol + ethyl b	u(P) = 0.05 penzoate syste	kPa and rela ms, and $x_{\rm sol}$	tive standarc is the mola	l uncertainti r fraction of	es $u_r(x_i) = 0$. ethyl benzo:	.031 and u_r (ate in the b	$(x_{sol}) = 0.015$ inary solven	b_{x_i} is the r	nole fractior	a solubility o	f ILs at the	system temp	erature T.



Figure 3. Experimental molar fraction solubilities of [HBth][BF₄] in ethanol + ethyl benzoate ($x_{sol} = 0.25, 0.33, 0.50, 0.67, and 1.00$). Dashed lines represent the correlation results based on the λh model.



Figure 4. Experimental molar fraction solubilities of [HBth][CH₃SO₃] in ethanol + ethyl benzoate ($x_{sol} = 0.25$, 0.33, 0.50, 0.67, and 1.00). Dashed lines represent the correlation results based on the λh model.



Figure 5. Experimental molar fraction solubilities of [HBth][*p*-TSA] in ethanol + ethyl benzoate ($x_{sol} = 0.25, 0.33, 0.50, 0.67$, and 1.00). Dashed lines represent the correlation results based on the λh model.

insoluble in ethyl benzoate. The solubilities of them gradually increased when the molar ratio of ethanol to ethyl benzoate increased. For all cases, the solubility values have a decreasing trend in the temperature dropping process. Considering this report and the previous literature,¹⁹ it is obvious that the solubilities of all the three ILs decreased more sharply and were more temperature-sensitive with the drop of temperature when the molar ratio of ethanol in the binary solvents was higher. If pure ethyl benzoate was served as the solvent, solubility values were low and not sensitive to temperature.

From an industrial point of view, the system temperature of the esterification reaction was necessarily required to drop below room temperature and even further to crystallize out more considerable amount of IL. Also, higher purity of the ethyl benzoate product was achieved with more recovery of IL catalysts. These experimental solubility data could give us valuable guidance in the practical purification process.

Interestingly, parameters of λ and h (λh model) can be described as a function of solvent composition (x_{sol}) for [HBth][BF₄], [HBth][CH₃SO₃], and [HBth][*p*-TSA]. This is a wonderful linear relationship between the logarithm value of λ (or h) and x_{sol} . For all three ILs (Figure 6), which are demonstrated as eqs 9 and 10 for [HBth][BF₄], eqs 14 and 15 for [HBth][CH₃SO₃], and eqs 19 and 20 for [HBth][*p*-TSA] with all the correlation coefficients (R^2) higher than 0.999. Surprisingly, parameters of A, B, and C (modified Apelblat model) can also be expressed as a function of x_{sol} for these three ILs (Figure 7). A, B, and C were quadratically correlated with w with satisfactory performances. The functional expressions are presented as eqs 11-13 for [HBth][BF₄], eqs 16-18 for [HBth][CH₃SO₃], and eqs 21–23 for [HBth][p-TSA]. Similarly, excellent quadratic fittings are acquired with all the correlation coefficients (R^2) higher than 0.995. To the best of our knowledge, this is the first time to simultaneously express the parameters of λ and h (λ h model) and the parameters of A, B, and C (modified Apelblat model) as functions of solvent compositions (x_{sol}) with ideal performances. With these selfcreated in-depth correlations in hand, we were able to predict the solubility of IL in these binary solvents at any temperature with any solvent composition.

The relationships between model parameters and x_{sol} for [HBth][BF₄] are listed as follows:

 $\ln \lambda = -7.1596x_{\rm sol} - 0.72113 \left(R^2 = 0.9995 \right) \tag{9}$

$$\ln h = 5.5425x_{\rm sol} + 8.8223 \left(R^2 = 0.9992\right) \tag{10}$$

$$A = 51.494 x_{\rm sol}^2 - 106.72 x_{\rm sol} - 5.6065 \ (R^2 = 0.9985)$$
(11)

$$B = -4108.9x_{\rm sol}^{2} + 8054.4x_{\rm sol} - 2830.7 \ (R^{2} = 0.9960)$$
(12)

$$C = -6.8657 x_{\rm sol}^{2} + 13.511 x_{\rm sol} + 2.0395 \ (R^{2} = 0.9986)$$
(13)

The relationships between model parameters and x_{sol} for [HBth][CH₃SO₃] are listed as follows:

$$\ln \lambda = -3.8343 x_{\rm sol} - 3.0324 \ (R^2 = 0.9994) \tag{14}$$

$$\ln h = 4.3737 x_{\rm sol} + 10.046 \left(R^2 = 0.9999 \right) \tag{15}$$

$$A = 14.077 x_{\rm sol}^{2} - 9.7048 x_{\rm sol} - 61.728 \ (R^{2} = 0.9993)$$
(16)

Table 5. Model Parameters for Three ILs at Different Solvent Compositions $(x_{sol})^{a-c}$

		λh equation	ion			modified	Apelblat equa	tion	
$x_{\rm sol}$	λ	h	R^2	10 ⁵ rmsd	A	В	С	R^2	10 ⁵ rmsd
				[HBth][BF ₄]				
0.25	0.08610	26,600	0.9996	3.716	-28.670	-1114.11	4.943	0.9996	3.516
0.33	0.04300	44,800	0.9993	4.316	-35.763	-576.339	5.815	0.9994	3.894
0.5	0.01350	103,140	0.9996	1.471	-46.096	200.990	7.073	0.9997	1.121
0.67	0.004014	278,100	0.9996	1.309	-53.775	675.790	7.990	0.9996	1.338
1	0.0003810	1,750,000	0.9995	0.2433	-60.890	1125.098	8.691	0.9995	0.2562
				[HBth][CH ₃ SO ₃]				
0.25	0.01811	69,410	0.9995	2.95	-63.245	921.129	9.787	0.9997	1.858
0.33	0.01390	96,920	0.9994	2.973	-63.414	888.857	9.769	0.9994	2.875
0.5	0.007242	203,100	0.9994	1.751	-63.123	744.317	9.666	0.9995	2.166
0.67	0.003581	439,000	0.9996	1.084	-61.848	564.762	9.408	0.9996	1.009
1	0.001050	1,823,000	0.9995	0.1805	-57.368	100.006	8.619	0.9995	0.193
				[HBth]	[p-TSA]				
0.25	0.0186	64,000	0.9993	4.464	-52.554	592.358	8.089	0.9992	4.705
0.33	0.0122	95,900	0.9993	3.034	-54.055	653.376	8.246	0.9992	3.348
0.5	0.00453	241,200	0.9994	2.072	-56.588	755.976	8.477	0.9994	2.006
0.67	0.00164	602,700	0.9994	0.7000	-58.411	819.657	8.610	0.9994	0.6840
1	0.000272	3,397,000	0.9995	0.1147	-60.858	919.133	8.680	0.9995	0.1153

 ${}^{a}\lambda$ and *h* are parameters of the λh equation, and *A*, *B*, and *C* are parameters of the modified Apelblat equation. ${}^{b}R^{2}$ is the correlation coefficient. ${}^{c}_{rmod} = \left[\sum_{k}^{N} (x^{exp} - x^{cal})^{2}\right]^{0.5}$



Figure 6. Linear fitting of $\ln \lambda$ and $\ln h$ with x_{sol} .



Figure 7. Quadratic fitting of modified Apelblat model parameters (*A*, *B*, and *C*) with x_{sol} .

$$B = -749.67x_{\rm sol}^2 - 167.64x_{\rm sol} + 1016.4 \ (R^2 = 0.9994)$$
(17)

$$C = -2.0553x_{\rm sol}^{2} + 1.009x_{\rm sol} + 9.6636 \ (R^{2} = 0.9993)$$
(18)

The relationships between model parameters and x_{sol} for [HBth][*p*-TSA] are listed as follows:

$$\ln \lambda = -5.6717 x_{\rm sol} - 2.5627 \left(R^2 = 0.9995 \right)$$
(19)

$$\ln h = 5.3133x_{\rm sol} + 9.7334 \left(R^2 = 0.9999\right) \tag{20}$$

$$A = 9.2364 x_{\rm sol}^2 - 22.503 x_{\rm sol} - 47.571 \ (R^2 = 0.9990)$$
(21)

$$B = -365.60x_{\rm sol}^{2} + 885.27x_{\rm sol} + 397.96 \ (R^{2} = 0.9962)$$
(22)

$$C = -1.4271x_{\rm sol}^{2} + 2.5568x_{\rm sol} + 7.5480 \ (R^{2} = 0.9972)$$
(23)

To validate our calculation method, solubilities of [HBth]-[BF₄], [HBth][CH₃SO₃], and [HBth][*p*-TSA] at certain temperature with certain solvent composition (x_{sol}) in the range of 233.2 to 293.7 K were predicted through in-depth correlations of both λh model (eqs 9, 10, 14, 15, 19, and 20) and Apelblat model (eqs 11-13, 16-18, and 21-23) at the same time. Seven solubility-unknown points with given values of x_{sol} and T were selected to conduct the solubility measurement and calculate the prediction values through two different models for all three ILs. The prediction results are presented in Table 6. It can be seen that the prediction values obtained from two different ways of estimation are close and both have satisfactory accuracy. The relative deviations were in acceptable ranges of 0.2541-3.309% for [HBth][BF₄], 0.4232-1.234% for [HBth]- $[CH_3SO_3]$, and 0.1941–1.582% for [HBth][p-TSA] for both models. This prediction accuracy could meet the demand of industrial crystallization of [HBth][BF₄], [HBth][CH₃SO₃], and [HBth][*p*-TSA].

To summarize, excellent in-depth correlations and prediction performances were obtained for three benzothiazolium ionic liquids [HBth][BF₄], [HBth][CH₃SO₃], and [HBth][*p*-TSA]. As far as we know, this is the first report to simultaneously correlate two sets of model parameters with solvent composition. Consequently, the same set of physical property data were satisfactorily predicted by two different methods. Results obtained from two different models were highly consistent with each other. They greatly reduced the uncertainty of estimation and increased the credibility of the prediction value from a theoretical and logical point of view. Previously, the λh equation and the modified Apelblat equation were also applied to correlate the solubility data of easy-made imidazolium ILs^{20,27} and pyridinium ILs²⁸ in many solvents, but none of them could generate further correlation for widespread prediction.

Table 6. Solubility Predictions for ILs at 100 kPa^{a-c}

			λh equ	ation	modified equa	Apelblat tion
$x_{\rm sol}$ (%)	T(K)	$x^{exp} \times 10^3$	$x^{cal} \times 10^3$	RD (%)	$x^{cal} \times 10^3$	RD (%)
			[HBth][BF4	r]		
0.30	235.0	1.657	1.695	2.293	1.605	3.138
0.40	245.0	1.968	1.973	0.2541	1.960	0.4065
0.50	255.0	1.959	1.953	0.3063	2.019	3.063
0.60	265.0	1.783	1.724	3.309	1.824	2.300
0.70	275.0	1.452	1.404	3.306	1.489	2.548
0.80	285.0	1.094	1.081	1.188	1.126	2.925
0.90	295.0	0.7986	0.8014	0.3506	0.8054	0.8515
		[H	HBth][CH ₃ S	O ₃]		
0.30	235.0	2.129	2.115	0.6576	2.1409	0.5589
0.40	245.0	1.654	1.661	0.4232	1.663	0.5441
0.50	255.0	1.296	1.308	0.9259	1.304	0.6173
0.60	265.0	1.041	1.036	0.4803	1.032	0.8646
0.70	275.0	0.8186	0.8249	0.7696	0.8239	0.6474
0.80	285.0	0.6567	0.6629	0.9441	0.6625	0.8832
0.90	295.0	0.5429	0.5387	0.7736	0.5362	1.234
		[HBth][p-TS	A]		
0.30	235.0	2.228	2.200	1.257	2.217	0.4937
0.40	245.0	1.705	1.711	0.3519	1.713	0.4692
0.50	255.0	1.313	1.302	0.8378	1.303	0.7616
0.60	265.0	0.9691	0.9742	0.5263	0.9789	1.011
0.70	275.0	0.7213	0.7199	0.1941	0.7263	0.6932
0.80	285.0	0.5246	0.5272	0.4956	0.5329	1.582
0.90	295.0	0.3821	0.3842	0.5496	0.3867	1.204

"Standard uncertainties u(T) = 0.05 K and u(P) = 0.05 kPa and relative standard uncertainties $u_r(x_i) = 0.031$ and $u_r(x_{sol}) = 0.015$. ^b x_i is the mole fraction solubility of ILs at the system temperature *T*. "The solvents are binary ethanol + ethyl benzoate systems, and x_{sol} is the molar fraction of ethyl benzoate in the binary solvent.

Therefore, excellent performances for these three ILs in this report are probably due to the particular molecular properties of benzothiazolium portion in the IL structures, which may also have intrinsic relationship with their temperature-sensitive properties. Further research of molecular simulation is around the corner in the near future.

CONCLUSIONS

The solubilities of benzothazolium-based ionic liquids [HBth]-[BF₄], [HBth][CH₃SO₃], and [HBth][p-TSA] in binary ethanol + ethyl benzoate solvents were measured using the equilibrium method with the temperature range from 233.2 to 293.7 K at atmospheric pressure. The experimental solubility data were correlated by both λh equation and the modified Apelblat equation with ideal correlation results ($R^2 > 0.999$). Particularly, in the λh model, the average relative deviations were satisfactorily obtained as 0.7145, 0.7845, and 0.8119% for [HBth][BF₄], [HBth][CH₃SO₃], and [HBth][*p*-TSA], respectively. All of these three ILs were showing stronger temperaturesensitive property when the molar ratio of ethanol to ethyl benzoate was higher. To our surprise, the parameters of λ and hfor the λh model and A, B, and C for the Apelblat model were simultaneously expressed as functions of solvent composition (x_{sol}) for the first time. Furthermore, these two sets of selfcreated in-depth correlation equations were successfully applied to predict the solubilities of these three ILs in the binary system with satisfactory performances. The relative deviations of the prediction results were in acceptable ranges of 0.2541-3.309%

for [HBth][BF₄], 0.4232–1.234% for [HBth][CH₃SO₃], and 0.1941–1.582% for [HBth][*p*-TSA] for both models. The total average relative deviations were less than 2.2% for both models. These successful in-depth correlations and validated prediction results have guaranteed the accuracy of experimental solubility data and provide us a reliable method for accurate solubility prediction at any temperature with any solvent composition. The developed calculation method in this report could give us valuable guidance for the design of the specific purification process to acquire desired purity of the product in industrial production.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jced.9b00997.

Profiles of IL characterization (¹H NMR, ¹³C NMR, and ESI-MS spectra) (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding

This work was supported by the National Natural Science Foundation of China (grant nos. 81803486 and 21676170), China Postdoctoral Science Foundation (grant no. 2018M633385), and Sichuan Science and Technology Program (grant no. 2019YJ0030).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (grant nos. 81803486 and 21676170), China Postdoctoral Science Foundation (grant no. 2018M633385), and Sichuan Science and Technology Program (grant no. 2019YJ0030).

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