A New Fragment Contribution-Corresponding States Method for Physicochemical Properties Prediction of Ionic Liquids

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A new fragment contribution-corresponding states (FC—CS) method based on the group contribution method and the corresponding states principle is developed to predict critical properties of ionic liquids (ILs). There are 46 fragments specially classified for ILs considering the ionic features of ILs, and the corresponding fragment increments are determined using the experimental density data. The accuracy of the developed method is verified indirectly via predicting density and surface tension of ILs. The results show that the FC—CS method is reasonable with an average absolute relative deviation less than 4%. With the calculated critical properties, corresponding states heat capacity (CSHC) and corresponding states thermal conductivity (CSTC) correlations are proposed to predict heat capacity and thermal conductivity of ILs, respectively. The predicted results agreed well with the experimental data. The proposed FC—CS method and the two corresponding states correlations are important for design, simulation, and analysis of new ionic liquid processes. © 2012 American Institute of Chemical Engineers *AIChE J,* 59: 1348–1359, 2013
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Introduction

Ionic liquids (ILs), which refer to liquids that are entirely composed of ions, attract increasing interest in both academic research and the industry.[1] The widespread applications of ILs have been reported in numerous and diverse fields such as chemical and biological catalysis reactions,[2,3] electrochemical industry,[4] analytical chemistry,[5] energy and fuel cycle,[6] and separation engineering.[7] With increasing potentials of ionic liquids for industrial applications being explored, knowledge of the physicochemical properties of ILs has become crucial. It was estimated that at least 10^{18} ILs (binary and ternary mixtures are included) can be potentially created[1] with the different combinations of anions and cations and modification of side chains, thus, measuring all the properties of various ILs under a wide range of conditions through experimental techniques is impractical. Alternatively, generalized reliable predictive methods for the physicochemical properties are fundamentally important for the development and design of new IL-based processes.

A brief survey on the current methods for predicting properties of ILs shows that there are four main methods developed (1) models based on quantum chemistry, (2) empirical correlations based on the adjustable parameters for specific IL, (3) the group contribution method (GCM), and (4) correlations based on the concept of corresponding states principle (CSP). Some applications of these four methods are provided in Table 1. The quantitative structure–property relationship (QSPR) method based on *ab initio* calculations was first presented for the prediction of the melting point and liquid density of one kind of energetic IL.[8] Then, Sun et al.[9] calculated another two kinds of ILs using a QSPR approach. The COSMO—RS method, which was originally used in phase equilibrium calculations, was extended for the prediction of the physicochemical properties of ILs, such as density,[10] viscosity, surface tension,[11] vapor pressure and vaporization enthalpy.[12] Although the methods above were derived at the atomic and molecular levels, they are very expensive in computation for large compounds and their accuracy range irregularly. Many studies have used empirical correlations to predict density,[13,14] viscosity, interfacial tension, self-diffusion coefficient, refractive index,[15] and thermal

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Table 1. Summary of Property Prediction of ILs by Four Types of Methods

	Methods Type	[e]Specific Method	Property	T(K)	P(MPa)	Number of ILs	Predictive Deviations	Reference
1	Quantum chemistry-based	QSPR	Melting point	–	–	26	[a]$R > 0.9$	Trohalaki et al.[8]
			Density					
			Melting point	–	–	41	[a]$R > 0.9$	Sun et al.[9]
		COSMO-RS	Density	298	0.1	40	[a]$R > 0.99$	Palomar et al.[10]
			Viscosity	298	0.1	10	–	Torrecilla et al.[11]
			Surface tension	313				
			Vapor pressure	437–517	0.1	4	[b]RD = 10%	Diedenhofen et al.[12]
2	Empirical correlations	$\rho = a + b(T - 273.15)$	Density	292–391	0.1	6	–	Jacquemin et al.[13]
		$\rho = \frac{\rho_0}{1 - C_T \ln((B_T + p)/(B_T + p_0))}$	Density	283–333	0.1-65	5	[c]RRD < 0.009	Guerrero et al.[14]
		$\eta_{calc} = \eta_0 \exp[B/(T - C)]$	Viscosity	283–363	0.1	1	[c]RRD = 1.37 %.	Koller et al.[15]
		$D_{+/-} = D_{0,+/-} \exp\left(-\frac{E_{A,+/-}}{RT}\right)$	Self-diffusion coefficients	313–363	0.1	1	–	Koller et al.[15]
		$n_{calc} = n_0 + n_1 T + \frac{\Delta n}{\Delta \lambda}(\lambda - \lambda_D)$	Refractive index	283–313	0.1	1	[c]RRD = 0.004%	Koller et al.[15]
		$\lambda_{c,calc} = \lambda_0 + \lambda_1 T$	Thermal conductivity	273–353	0.1	10	[d]AARD = 7%	Froeba et al.[16]
3	The group contribution method	$\rho(T,P) = \frac{\rho(T,P_0)}{1 - C \ln[1 + (P - P_0)B(T)]}$	Density	253–473	0.1-300	828	[d]AARD = 0.53%	Paduszynski et al.[18]
		$\ln \eta = A_\eta + \frac{B_\eta}{(T - T_{0\eta})}$	Viscosity	293–393	0.1	29	[d]AARD = 8%	Gardas et al.[19]
		$\kappa = A_\kappa - B_\kappa T$	Thermal conductivity	293–390	0.1	16	[d]AARD = 1.06%	Gardas et al.[19]
4	Corresponding states principle-based equations	$\rho = A/B + (2/7)[A(\ln B)/B)][(T - T_b)/(T_c - T_b)]$	Density	270–360	0.1	146	[d]AARD = 2.6%	Valderrama et al.[28]
		$\gamma = 0.819\left(\frac{T_b - T}{T_b - T_m}\right)\gamma_m + 0.500\left(\frac{T}{T_b}\right)\gamma_m$	Surface tension	278–473	0.1	30	[d]AARD = 2.98%	Mousazadeh et al.[29]
		$\frac{C_p - C_p^0}{R} = 1.586 + \frac{0.49}{1 - T_r} + \omega\left[4.2775 + \frac{6.3(1 - T_r)^{1/3}}{T_r} + \frac{0.4355}{1 - T_r}\right]$	Heat capacities	256–470	0.1	53	[d]AARD = 2.9%	Ge et al.[30]

[a]R: correlation coefficients.
[b]RD: relative deviation.
[c]RRD: relative root-mean-square deviations.
[d]AARD: average absolute relative deviation.
[e]Specific method: meaning and units of notations in each equation can be found in cited references.

Table 2. Predictive Methods for Critical Parameters of ILs

Method	Critical parameters	Number of ILs	Predictive deviations	Authors	Year
Eotvos and Guggenheim surface tension equations	T_c	15	–	Rebelo et al.[32]	2005
		17	–	Kilaru et al.[34]	2007
		34	–	Ghatee et al.[35]	2010
		4	–	Weiss et al.[33]	2010
A modified group contribution method	T_c, P_c, V_c, ω	50	AARD = 5.2%	Valderrama et al.[37]	2007
		294	AARD = 3.9%	Valderrama et al.[38]	2009
		747	AARD = 4.4%	Shen et al.[17]	2011

conductivity[16] of ILs. Their predictive results were highly in accordance with the experimental results, whereas sufficient experimental data under various conditions are required to fit different parameters of expression of each IL. GCM is a kind of semiempirical theory which is extensively used for estimating properties such as critical properties,[17] density,[18] viscosity, electrical conductivity and thermal conductivity[19] of ILs. This method is easy to use, but many of the reported GCMs are based on the groups of molecular compounds. The corresponding states principle proposed by van der Waals in 1873 was particularly helpful for the property estimation of widespread substances.[20] The extended correlations of van der Waals's CSP, including the equation of state, have been applied to successfully predict various properties of molecular compounds and inorganic salts, such as density,[21] vapor pressure, entropy of evaporation, heat capacity, surface tension,[22,23] thermal conductivity,[24] and viscosity.[25–27] However, reports on the application of the CSP to ILs are few. Valderrama et al.[28] proposed an empirical CSP density correlation for ILs which showed greater accuracy compared with 10 generalized CSP correlations for molecular fluids available in other studies. Mousazadeh et al.[29] related the reduced surface tensions to the reduced temperatures using a linear regression relationship based on the CSP. Ge and Hardacre[30] predicted ideal gas heat capacity using the Joback GCM and calculated the liquid heat capacity of ILs using an original CSP correlation. However, the ideal gas heat capacity of ILs cannot be tested using experimental data; thus, the Joback GCM may place a level of uncertainty on the prediction of the liquid heat capacity of ILs. CSP is hampered in its application to ILs mainly because of the absence of critical parameters that are unavailable through direct experimental observations, since ILs generally degrade below their critical temperatures. Critical properties are used not only as the basis for models such as corresponding states correlations for PVT equations of state, but also in composition-dependent mixing rules for the parameters on describing mixtures.[20] Thus, it is imperative to predict the critical properties of ILs through reliable method.

Two methods have been reported for predicting critical properties of ILs, as summarized in Table 2. One is Eotvos and Guggenheim method; the other is the group contribution method. Eotvos[31] and Guggenheim[22] empirical surface tension equations, which describe the behavior of the liquid-vapor interfacial tension γ as a function of temperature (T), provide critical temperature (T_c) via the extrapolation of sufficient $\gamma(T)$ data to the temperature at which $\gamma = 0$. Rebelo et al.[32] tested the adequacy of the two aforementioned equations by predicting the T_c of 90 compounds. Their results showed that both expressions could provide an accurate T_c estimate for most fluids, except the strongly hydrogen-bonded substances and several inorganic molten salts. Moreover, they first extended the two equations to estimate the critical temperature of ILs. Several researchers[33–35] subsequently quoted the Eotvos and Guggenheim equations and calculated the T_c of ILs. These pioneering works provide ideas and methods for predicting the critical temperatures of ILs, whereas the derived values needed further investigations to justify their validity. Weiss et al.[36] pointed out the existence of uncertainties on the direct application of either Eotvos or Guggenheim expression to determine the T_c of ILs. They stated the surface tension of an IL as a function of temperature might exhibit an inflection point, and the extrapolation of surface tension to its vanishing temperature was error-prone. Moreover, the two equations are unavailable for determining the acentric factor (ω), the critical pressure (P_c), and the critical volume (V_c), which are all necessary for the CSP.

The GCM is the main method used for estimating critical properties,[20] and only two articles have devoted themselves to predicting the entire critical parameters of ILs by far. Valderrama and Robles[37] first used a modified GCM based on the well-known Lydersen and Joback and Reid's method to predict the critical properties, normal boiling temperatures, and acentric factors of 50 ILs. The accuracy of their method was justified by calculating the liquid densities through a generalized correlation. Shen et al.[17] developed a GC—PT method which combined the modified Lydersen-Joback-Reid GCM[38] with the Patel-Teja (PT) equation of state to predict the critical parameters of ILs, and they confirmed the results by predicting the densities at higher temperature and pressure conditions using four different density correlations. Undeniably, the studies above[17,38] have given values of critical parameters, at least reliable for the prediction of IL densities. Nevertheless, their suitability for the prediction of other properties remains unknown and the used groups did not contain ionic groups which are the main components in ILs. As Jones et al.[39] pointed out, the T_c values from the work of Valderrama and Robles[37] were likely to be in error because of the noninclusion of the Coulombic energy in IL. Therefore, a more exact predictive method for critical parameters of ILs considering their ionic features should be developed urgently. Thus, generalized equations based on CSP for the calculation of physicochemical properties will be accessible for the fundamental data and industry field.

This study mainly focuses on two respects. In one respect, a FC—CS method is developed to estimate the critical properties, normal boiling temperatures, and acentric factors of ILs. The validity and accuracy of the FC—CS method is verified via the prediction of density and surface tension using CSP equations. In another respect, new heat capacity and thermal conductivity predictive correlations based on the CSP were proposed for ILs as an extended application of the FC—CS method.

Table 3. Summary of Experimental Data

Property	Temperature Range (K)	Pressure Range (MPa)	Number of ILs	Data Points
Density	283.15–313.2	0.1	490	514
Density	273.15–473.15	0.1	519	1907
Density	278.15–428.15	0.1–100	128	3272
Surface tension	273.15–492.5	0.1	112	838
Heat capacity	10–573.1	0.1	26	599
Thermal conductivity	273.15–390	0.1–20	22	138

Database

In this study, all experimental data were extracted from IL Thermo Database,[40] a book,[41] Database software,[42] three main references,[17,30,43] and other accessible studies on the physicochemical properties of ILs. The principle of screening experimental data from a sufficient amount of literature is to discard the data that deviate from other data. For example, the surface tension of 1-Butyl-3-methylimidazolium tetrafluoroborate has been reported in at least 17 various studies.[43] Two experimental data of those studies[44,45] were rejected in the current study because of enormous data discrepancy compared with the others at 298.15 K. All literature sources have been listed in the Supplementary Material to provide direct and comprehensive information. Table 3 summarized the total number of ILs, data points, and the condition of different experimental property data used in this work.

The investigated ILs were mainly based on alkyl-substituted cations, including imidazolium [Im], pyridinium [Py], pyrrolidinium [Pyr], piperidinium [Pip], guanidinium [Gua], phosphonium [P], ammonium [N], sulfonium [S], and different anions, such as tetrafluoroborate [BF_4], hexafluorophosphate [PF_6], halide [X], bis(trifluoromethylsulfonyl)imide [BTI], bis(perfluoroethyl sulfonyl)imide [BETI], alkyl sulfate [RSO_4], dialkylphosphate [R_2PO_4], trifluoromethylsulfonate [TfO], trifluoroacetate [TfA], nitrate [NO_3], dicyanamide [Dca], tricyanomethanide [Tcm], tris(trifluoromethylsulfonyl)methide [Tf_3C], tetrachloroalluminate [$AlCl_4$], tetrachloroironate [$FeCl_4$], tetrachlorogallate [$GaCl_4$], tetrachloroindate [$InCl_4$], trichlorozincate [$ZnCl_3$], and acetate [Ac], among others.

The classification of IL fragments, the molar mass, the global formula, the IUPAC name and the abbreviations of ILs are presented in the Supplementary Material. In addition, all predictive critical properties, density, surface tension, heat capacity, and thermal conductivity are also included in the Supplementary Material. Given this information, any reader can search for the required property data and easily calculate the physicochemical properties of any IL composed of the fragments defined in this study.

Methodology

A FC—CS method

The definition of fragments of ILs. In this study, with the simultaneous consideration of the ionic features and neutral portion of ILs, each IL is divided into three basic elements, namely, cation fragment, anion fragment, and substituent fragment attached to the cation or anion. The definition of fragments is proposed to distinguish with original GCM which is applied to organic compounds. A complete set of 46 fragments, including 7 cation fragments, 18 anion fragments, and 21 substituent fragments were defined. Figure 1 shows the chemical structures of the cation fragments belonging to the ILs investigated in this study. The structures of anion and substituent fragments are presented in the Supplementary Material.

Description of the Method. A new FC—CS method proposed based on a CSP correlation and the GCM consists of six equations (1) the Riedel corresponding states equation[46] (see Eq. 1) for calculating density (ρ), (2) the Joback-Reid GCM[47] (see Eq. 2) for calculating T_b, (3) the GCM modified by Alvarez and Valderrama[48] (see Eq. 3) for calculating T_c, (4) the Lydersen GCM[20] (see Eq. 4) for calculating P_c, (5) the MXXC method[49] (see Eq. 5) for calculating V_c, and (6) the equation (see Eq. 6) deduced in this study from the Clausius-Clapeyron equation and the acentric factor equation of definition[20] for calculating ω. The density calculated by Eq. 1 is based on T_c, V_c and ω, and ω is calculated based on T_b, T_c and P_c. Therefore, the six property parameters can be associated with the FC—CS method which can be described as follows

$$\rho = \frac{M}{V_c}[1 + 0.85(1 - T_r) + (1.6916 + 0.984\omega)(1 - T_r)^{1/3}] \quad (1)$$

$$T_b = 198.2 + \sum_i n_i \Delta T_{b,i} \quad (2)$$

$$T_c = \frac{T_b}{0.5703 + 1.0121 \sum_i n_i \Delta T_{c,i} - \left(\sum_i n_i \Delta T_{c,i}\right)^2} \quad (3)$$

$$P_c = \frac{M}{\left(0.34 + \sum_i n_i \Delta P_{c,i}\right)^2} \quad (4)$$

$$V_c = 28.8946 + 14.75246 \sum n_i \Delta V_{c,i} + \frac{6.03853}{\sum n_i \Delta V_{c,i}} \quad (5)$$

$$\omega = \frac{T_b T_c}{(T_c - T_b)(0.7T_c)} \log\left(\frac{P_c}{P_b}\right) - \left(\frac{T_c}{T_c - T_b}\right) \log\left(\frac{P_c}{P_b}\right) + \log\left(\frac{P_c}{P_b}\right) - 1 \quad (6)$$

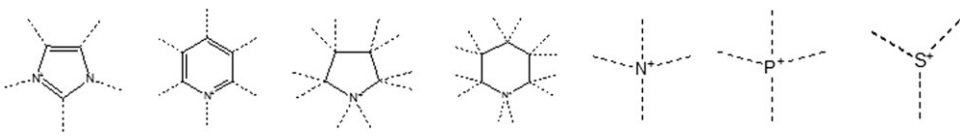

Figure 1. Cation fragments of ILs.

In Eqs. 1–4, n_i represents the number of fragment i that appears in the ILs; $\Delta T_{b,i}$, $\Delta T_{c,i}$, $\Delta P_{c,i}$, and $\Delta V_{c,i}$ denote the fragment increments of fragment i for the normal boiling temperature, critical temperature, critical pressure, and critical volume, respectively. In Eq. 5, P_b is the atmospheric pressure in bar. In Eq. 6, M is the molar mass in g·mol^{-1}, and T_r is the reduced temperature ($T_r = T/T_c$).

Determination of fragment increments

As previously described, 46 fragments were defined for the ILs investigated in this study. Their corresponding fragment increments (namely, $\Delta T_{b,i}$, $\Delta T_{c,i}$, $\Delta P_{c,i}$, and $\Delta V_{c,i}$) for calculating T_b, T_c, P_c, and V_c were performed by optimizing the following objective function

$$O.F. = \min \sum_{i=1}^{N_P} \left(\rho_i^{\text{cal}} - \rho_i^{\text{exp}}\right)^2 \tag{7}$$

The density data used to determine the fragment increments were under the conditions with temperatures of approximately 298 K or 293 K and pressure of 101.325 kPa.

The average absolute relative deviation (AARD) can be defined as follow

$$\text{AARD}\ (\%) = 100 \times \sum_{i=1}^{N_P} \left|\rho_i^{\text{cal}}/\rho_i^{\text{exp}} - 1.0\right|/N_P \tag{8}$$

where N_p represents the total number of data points of density, ρ is the density in g·cm^{-3}, and superscripts "cal" and "exp" denote the calculated values using the FC—CS method and the experimental data, respectively.

Verification of the FC—CS method

Verification of the FC—CS method via density prediction. In order to test the validity of the fragment increments as well as the FC—CS method developed in this study, the liquid densities over a wide range of temperature and pressure were estimated using six different equations, including the Riedel equation (see Eq. 1), VSD equation[50] (see Eq. 9), VSY equation[50] (see Eq. 10), LGM[28](see Eq. 11), Yamada-Gunn equation[51] (YG) (see Eq. 12), and McHaweh equation[52] (MH) (see Eq. 13). These density equations are all based on the CSP. The calculation method for the AARD of the different methods is similar to Eq. 8

$$\rho = \frac{Mp_c}{RT_c}\left(\frac{0.3445 p_c V_c^{1.0135}}{RT_c}\right)^{\Omega}; \quad \Omega = -\left[\frac{1+(1-T_r)^{2/7}}{1+(1-T_{br})^{2/7}}\right] \tag{9}$$

$$\rho = \left(0.01256 + \frac{0.9533M}{V_c}\right)\left[\left(\frac{0.0039}{M} + \frac{0.2987}{V_c}\right)V_c^{1.033}\right]^{\Psi}; \quad \Psi = -\left(\frac{1-T_r}{1-T_{br}}\right)^{2/7} \tag{10}$$

$$\rho = A/B + (2/7)[A(\ln B)/B)][(T-T_b)/(T_c-T_b)] \tag{11}$$

$$A = 0.3411 + 2.0443M/V_c \tag{11a}$$

$$B = (0.5386/V_c + 0.0393/M)V_c^{1.0476} \tag{11b}$$

$$\rho = \frac{M}{V_c}(0.29056 - 0.08775\omega)^{-(1-T_r)^{2/7}} \tag{12}$$

$$\rho(T) = \frac{M}{V_c}(1 + 1.169\tau^{1/3} + 1.818\tau^{2/3} - 2.658\tau + 2.161\tau^{4/3}) \tag{13}$$

$$\tau = 1 - \frac{(T/T_c)}{[1 + m(1 - \sqrt{T/T_c})]^2} \tag{13a}$$

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \tag{13b}$$

where T_{br} is the reduced temperature at the normal boiling point ($T_{br} = T_b/T_c$).

Verification of the FC—CS Method via Surface Tension. CSP correlations are successful in the surface tension estimation of a substantial amount of molecular liquids.[53–56] Surface tension values of ILs are similar to most molecular liquids. In this study, two frequently-used corresponding states surface tension correlations were adopted to predict the surface tension of ILs by virtue of the critical parameters obtained using the FC—CS method. The two equations proposed by Brock-Bird[56] and Pitzer[20] are described as follows

$$\sigma = P_c^{2/3} T_c^{1/3}(1-T_r)^{11/9} Q;$$
$$Q = 0.1196[1 + T_{br}\ln(Pc/1.01325)/(1-T_{br})] - 0.279 \tag{14}$$

$$\sigma = P_c^{2/3} T_c^{1/3} \frac{1.86 + 1.18\omega}{19.05}\left[\frac{3.75 + 0.91\omega}{0.291 - 0.08\omega}\right]^{2/3}(1-T_r)^{11/9} \tag{15}$$

The AARD is defined as follows

$$\text{AARD}\ (\%) = 100 \times \sum_{i=1}^{N_P} \left|\sigma_i^{\text{cal}}/\sigma_i^{\text{exp}} - 1.0\right|/N_P \tag{16}$$

CSHC correlation

The CSP correlation of liquid heat capacity (C_p) requires an ideal gas heat capacity value[20] which are not accessible for ILs through experiment. To the best of our knowledge, corresponding states correlation for the liquid heat capacity estimation of IL has not been reported to date. Based on the critical parameters, a new corresponding states heat capacity (CSHC) correlation is proposed as follows

$$C_p = M\omega T^a T_c^b\left[c + \left(\frac{1-T_{br}}{1+T_r}\right)^d\right]/P_c^e \tag{17}$$

$$a = 1.565, \quad b = 0.15, \quad c = -0.00005, \quad d = 4.126, \quad e = 0.7568$$

The constants a, b, c, d, and e were estimated by minimizing the following objective function

$$O.F. = \sum_{i=1}^{N_P}\left(C_{p_i}^{\text{cal}} - C_{p_i}^{\text{exp}}\right)^2 \tag{18}$$

The AARD can be defined as follows

$$\text{AARD}\ (\%) = 100 \times \sum_{i=1}^{N_P}\left|C_{p_i}^{\text{cal}}/C_{p_i}^{\text{exp}} - 1.0\right|/N_P \tag{19}$$

Table 4. Fragment Increments for the FC—CS Method

No.	Fragments	$\Delta T_{b,i}$	$\Delta T_{c,i}$	$\Delta p_{c,i}$	$\Delta V_{c,i}$
Cation fragments					
1	im	89.58	0.07	0.81	3.92
2	pyr	−86.00	0.0911	−0.122	−14.6
3	py	102.46	0.0701	0.7749	2.4475
4	pip	8.49	0.01	−0.52	−13.79
5	N	156.80	0.0899	0.589	4.615
6	P	349.70	0.078	−0.011	9.925
7	S	21.89	0.06	1.43	8.30
Anion fragments					
8	$[BF_4]^-$	102.53	0.14	−0.12	4.37
9	$[PF_6]^-$	195.29	0.1466	0.3072	10.023
10	$[Cl]^-$	96.56	0.127	−0.6717	−1.5871
11	$[Br]^-$	79.49	0.1635	−0.04001	1.081
12	$[I]^-$	155.33	0.161	0.07014	5.725
13	$[NO_3]^-$	84.58	0.1455	−0.3091	0.9915
14	$[Ace]^-$	13.58	0.2545	0.69952	14.13
15	$[BMB]^-$	51.71	0.1282	1.397	22.55
16	$[BMLB]^-$	30.71	0.1322	1.747	27.68
17	$[BOB]^-$	30.51	0.1254	0.977	13.58
18	−CN	57.71	0.1351	−0.59	−3.11
19	$-SO_2-$	40.85	0.1639	−0.4901	−2.7086
20	−P=O	−16.52	0.194	−0.64	−3.983
21	In	19.41	0.3054	4.006	26.91
22	Zn	−7.56	0.438	2.245	17.91
23	Ga	−3.78	0.3202	3.711	24.88
24	Fe	1.22	0.3115	3.718	23.91
25	Al	−11.56	0.3366	3.355	24.257
Substituent fragments					
26	$-CH_3$	41.24	−0.02	0.32	5.93
27	$-CH_2-$	6.17	0.00	0.20	3.42
28	>CH− or $[-CH-]^-$	21.58	0.03	0.05	1.90
29	>C< or $[>C-]^-$	17.41	0.38	1.96	22.13
30	$=CH_2$	7.58	−0.18	1.51	−1.47
31	=CH−	7.25	0.14	−1.48	−1.33
32	=C<	47.58	−1.08	−2.21	−19.31
33	—H (ring)	47.00	0.00	0.21	4.01
34	−O− or $[-O]^-$	22.49	−0.005	0.133	2.6685
35	=O	−205.16	0.058	−0.102	−0.2195
36	—OH	188.50	−0.0062	0.2181	5.614
37	—H(non−ring)	41.89	0.07	0.62	8.53
38	—S or $[-S-]^-$	35.41	0.01	0.30	6.89
39	BF_3	79.15	0.17	−0.22	−0.20
40	benzene ring	−13.58	−0.0694	0.0702	−4.015
41	$[—N—]^-$ or >N−	37.79	0.5992	0.8077	11.114
42	$-NH_2$	70.86	−0.0232	0.2319	2.303
43	C=O	50.86	0.165	−0.7206	−2.883
44	>CF−	−121.56	−0.0323	−0.5344	−2.044
45	$-CF_2-$	17.57	−0.0053	0.3954	5.223
46	$-CF_3$	45.04	−0.0348	0.78925	10.00081

CSTC correlation

Latini method and Sastri method are the two main methods for predicting thermal conductivity (λ) of organic compounds.[20] Latini method was recommended for substances having molar masses between 50 g·mol^{-1} and 250 g·mol^{-1} with an error of less than 10%[20]. However, the molar masses of many ILs are larger than 250 g·mol^{-1}. The Sastri method[20] is a kind of GCM with group parameters that are unavailable for ILs. In this study, a corresponding states thermal conductivity (CSTC) correlation with both the influence of temperature and pressure is developed for ILs as follows

$$\lambda = \left(\frac{11.1}{T^x} + \frac{fT_{br}^y}{gM^z}\right)\left[1 - h\left(\frac{\mathrm{P}}{P_c}\right)^{0.7}\right] \tag{20}$$

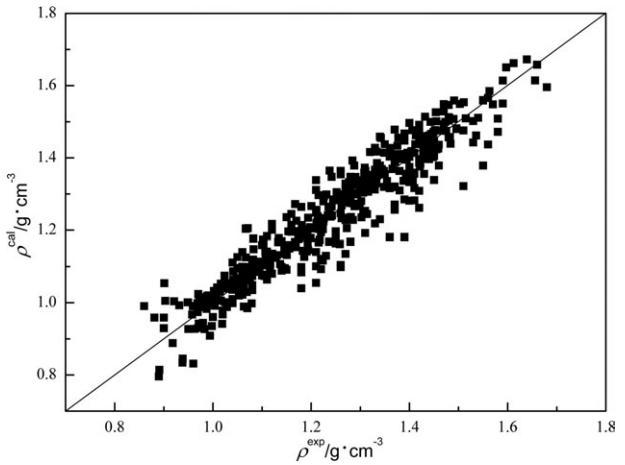

Figure 2. Experimental vs. calculated densities for 514 data of 490 ILs using the FC—CS method.

$$x = 1.091,\ y = 0.552,\ z = 0.5817,\ f = 0.6107,$$
$$g = 0.1369,\ h = 0.007$$

The constants x, y, z, f, g, and h were attained via the minimization of the following objective function

$$O.F. = \sum_{i=1}^{N_P} \left(\lambda_i^{\mathrm{cal}} - \lambda_i^{\mathrm{exp}}\right)^2 \tag{21}$$

The AARD can be defined as follows

$$\mathrm{AARD}\ (\%) = 100 \times \sum_{i=1}^{N_P} \left|\lambda_i^{\mathrm{cal}}/\lambda_i^{\mathrm{exp}} - 1.0\right|/N_P \tag{22}$$

Results and Discussion

Critical properties

The determined fragment increments with respect to the FC—CS method for calculating T_b, T_c, P_c, and V_c are summarized in Table 4. The predicted T_b, T_c, P_c, V_c, ω and ρ using the FC—CS method for 490 ILs are provided in the

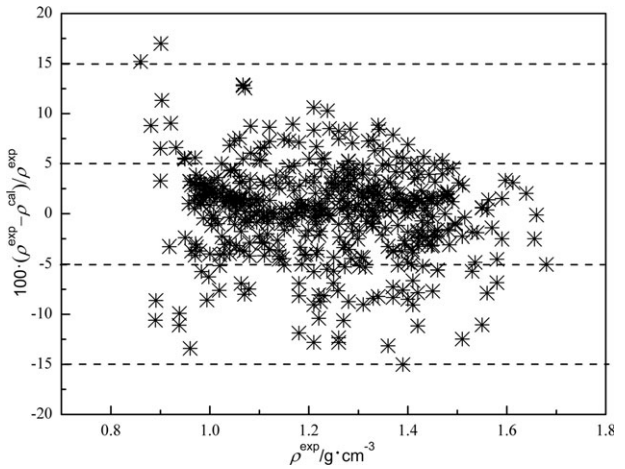

Figure 3. Relative deviations between the experimental and calculated densities as a function of experimental density.

Table 5. Comparison of the Calculated Density Deviations of ILs

Methods	NG[d]	ILs	Points	Min RD[e](%)	Max RD(%)	Overall AARD(%)	Distributions of ARD[f] of the calculated densities of ILs		
							≤5.0%	5.0−10.0%	>10.0%
FC—CS[a]	46	490	514	−15	15.7	3.3	399	93	22
LGM[b]	44	294	294	−20.5	28.1	3.9	222	50	22
GC—PT[c]	47	747	918	−29.9	30.8	4.4	645	189	84

[a]FC—CS: FC—CS Method proposed in this study.
[b]LGM: Linear Generalized Method used in ref. 38.
[c]GC—PT: GC—PT Method presented in ref. 17.
[d]NG: Number of groups/fragments defined to calculate the critical properties.
[e]RD: Relative deviation of density, $\Delta\rho(\%) = (\rho^{cal} - \rho^{exp})/\rho^{exp} \times 100$.
[f]ARD: Absolute relative deviation of density, $|\Delta\rho|(\%) = \left|(\rho^{cal} - \rho^{exp})/\rho^{exp}\right| \times 100$.

worksheet ''Critical Properties'' in the Supplementary Material. Figure 2 shows the comparison of the experimental and correlated densities using the FC—CS method. Figure 3 is the plot of the relative deviations between the calculated and experimental densities as a function of experimental density for all data points used in this study.

As can be seen in Figure 2, the calculated densities using the FC—CS method were in good agreement with the corresponding experimental densities with an overall AARD of 3.3%. As shown in Figure 3, majority of the relative deviations were within ±10% and distributed randomly around the baseline of 0%. These results indicate the validity of the calculated 46 fragment increments. The observed maximum relative deviation was 15.7% for $[P_{666(14)}][Tcm]$ (Trihexyltetradecyl- phosphonium tricyanomethanide) at 293.15 K and 101.3 kPa. Screening of the experimental denstiy was not possible for $[P_{666(14)}][Tcm]$ because of the limited availability of data in literature. However, lower deviations can be found in other compounds with the same $[P_{666(14)}]$ cation or [Tcm] anion. For instance, the deviation was 1.0% for $[C_4MIm][Tcm]$ (1-butyl-3-methyl-imidazolium tricyanomethanide) and 0.1% for $[P_{666(14)}][Ace]$ (tetradecyltrihexylosphonium acesulfamates), demonstrating that such a large deviation for IL $[P_{666(14)}][Tcm]$ is not caused by unsuitable fragment increments.

A comprehensive comparison of the accuracies of different methods, including total number of groups/fragments and ILs, overall AARD, maximum and minimum deviations, and distributions of ARD, are summarized in Table 5. As shown in Table 5, the FC—CS method presented in this study gives lower overall AARD and greater percentage of low deviations. All results suggest that the IL fragments defined in this study are successful in predicting critical points, at least for the ILs studied in this section. The rationality of the critical properties derived using the FC—CS method should be further verified in the light of their potential to correlate with more property data, such as density over a wider condition and surface tension, as will be discussed in the subsequent sections of this study.

Density prediction using six CSP equations

With the fragment increments in Table 4, T_b, T_c, P_c, and V_c of 519 ILs were calculated using Eqs. 1–4. Considering that the fragment increments were derived solely from the density data of ILs at ambient temperature and atmospheric pressure, the densities at higher temperature and pressure should be estimated to verify the prediction performance of the developed FC—CS method. Based on the calculated data, the temperature dependence of the densities were predicted using six density equations, namely, Eq. 1 and Eqs. 9–13. The detailed results, including all calculated data and deviations, are provided in the worksheets named ''Density Dependence of T'' and ''Density Dependence of P and T'' in the Supplementary Material. As shown in Table 6, the six density equations obtained good predictive results for the 1,907 density data points of 519 ILs, especially the Riedel and YG equations with low AARDs of 2.1% and 2.3%, respectively. The AARD for the 3,272 density data points of 128 ILs was only 1.1% for the Riedel equation and 1.3% for the YG equation. The maximum relative deviation of 15.7% was observed for $[P_{666(14)}][Tcm]$ (Trihexyltetradecylphosphonium tricyanomethanide) by Riedel equation, whereas the LGM and the MH equation merely gave relative deviation of 1.8% and 0.9%, respectively, for the same data point. This implies some large deviations are caused by random errors of different predictive equations. Even so, Riedel and

Table 6. Comparison of the Calculated Density Deviations of ILs using Six Equations

Methods	Min RD(%)	Max RD(%)	Overall AARD(%)	Distributions of ARD of the calculated densities of ILs			
				≤1.0%	1.0−5.0%	5.0−10.0%	>10.0%
1907 data points in the temperature range of 273.15−473.15 K and pressure of 0.1 Mpa							
Riedel	−15.0	15.7	2.1	721	980	181	25
VSD	−21.9	33.6	4.4	262	1053	417	175
VSY	−24.0	17.9	3.7	305	1056	507	39
LGM	−29.5	17.9	3.8	301	1066	477	63
YG	−16.4	45.3	2.3	737	940	191	39
MH	−36.5	7.1	5.8	116	789	797	205
3272 data points in the temperature range of 278.15−428.15 K and pressure range of 0.1−100 MPa							
Riedel	−4.9	5.0	1.1	1665	1607	0	0
VSD	−6.6	10.2	3.6	293	2131	845	3
VSY	−9.4	3.7	2.9	541	2194	537	0
LGM	−5.3	12.5	3.1	474	2230	544	24
YG	−5.0	4.9	1.3	1581	1690	1	0
MH	−12.0	2.4	4.8	220	1725	1173	154

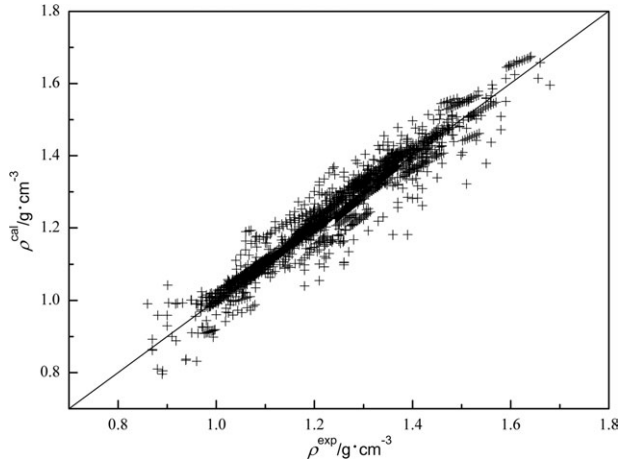

Figure 4. Experimental vs. calculated densities using the Riedel equation for 1,907 data of 519 ILs.

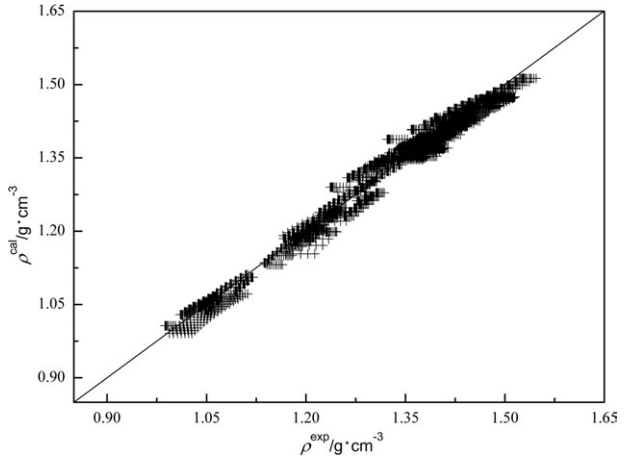

Figure 6. Experimental vs. calculated densities using the Riedel equation for 3,272 data of 128 ILs.

YG equation are recommended to predict density based on critical properties derived from the FC—CS model, because they usually obtain more accurate predictive results in most cases. Some deflected experimental data may also cause large deviations. For example, three different relative deviations can be found for [C_4Py][BTI] (1-butylpyridinium bis (trifluoromethylsulfonyl)imide). Among them, the largest is −6.5% which is caused by the inaccuracy of experimental data when compared with the other two of −3.2% and −3.3%. However, relative deviations of ILs composed of alanine based cation and nitrate anion are larger than 12% using all the six density equations. So the FC—CS method is not recommended to be used for this kind of IL. On the whole, large deviations can mainly be attributed to two factors, namely (1) random error of a density prediction equation, and (2) the inaccuracy of the experimental data.

As shown in Figure 4, the calculated densities for 519 ILs were randomly distributed along the diagonal $\rho^{cal} = \rho^{exp}$. Figure 5 clearly shows that majority of the deviations were within ±5%, and the deviations were distributed randomly around the baseline of 0%. Similar results can be found for 128 ILs over a wide pressure range, as shown in Figures 6 and 7. The results suggest that the FC—CS method is valid and the derived critical properties can be successfully applied to predict density of ILs using different corresponding states correlations.

Surface tension prediction using two CSP equations

The surface tensions of 112 ILs at varying temperatures were predicted using the Brock-Bird equation (see Eq. 14), and Pitzer equation (see Eq. 15), to further validate the calculated critical properties using the FC—CS method. Figures 8a and 8b show the comparisons of the experimental and calculated surface tensions using the Brock-Bird and Pitzer equations, respectively. The 838 experimental surface tension data of 112 pure ILs were found to be in accordance with the predicted values using the Brock-Bird and Pitzer equations with overall AARDs of 3.7% and 3.6%, respectively. The maximum deviations of the Brock-Bird and Pitzer equations were −12.3% and −25.9% for [N_{8881}][BTI] (trioctyl(methyl)ammonium bis(trifluoromethylsulfonyl)imide) and [$(NH_2)C_4C_1$im][BF_4] (1-(4-Aminobutyl)-3-methylimidazolium dicyanamide), respectively. The maximum deviations are probably caused by the random error of different predictive equations, because the other equation gives low RD of −3.7% and −8.1%, respectively. The results further indicate that the FC—CS method is reliable and the obtained critical properties can be used satisfactorily in predicting surface tension using different corresponding states correlations.

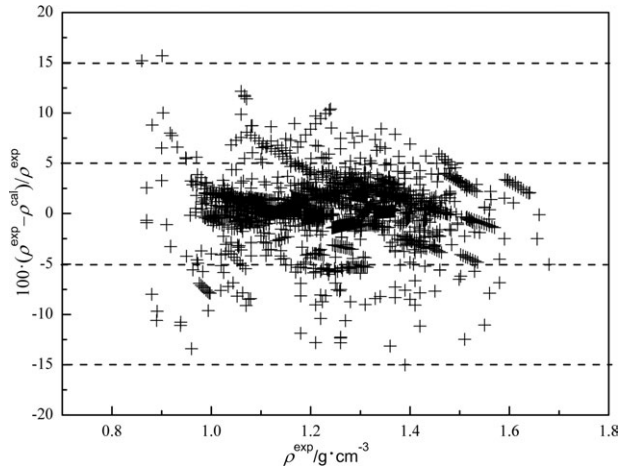

Figure 5. Relative deviations between the experimental and calculated densities for the same data set as in Figure 4.

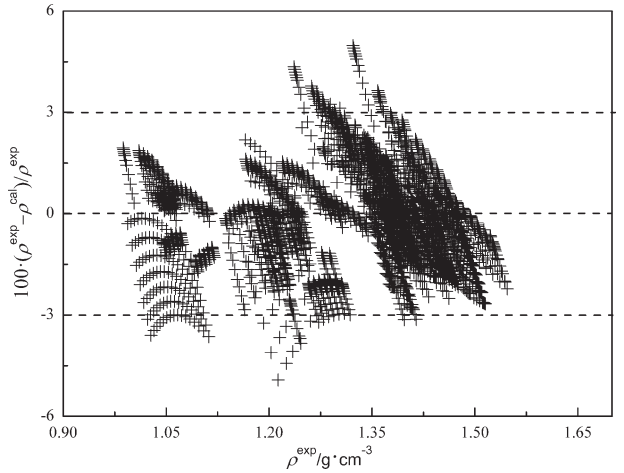

Figure 7. Relative deviations between the experimental and calculated densities for the same data set as in Figure 6.

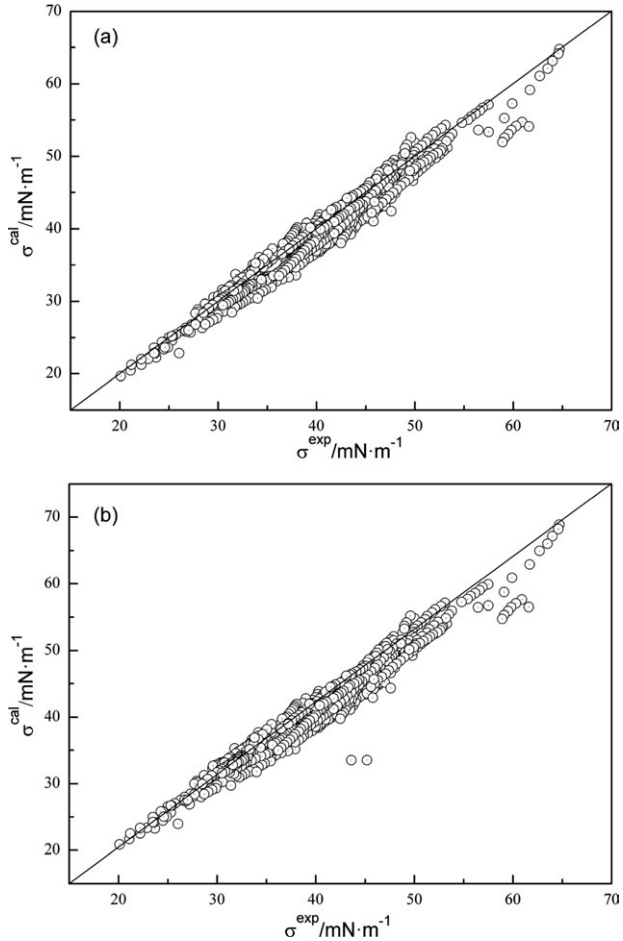

Figure 8. Experimental vs. calculated surface tensions of 112 ILs within the temperature range of 273.15 K to 492.5 K using the (a) Brock-Bird equation, and (b) Pitzer equation.

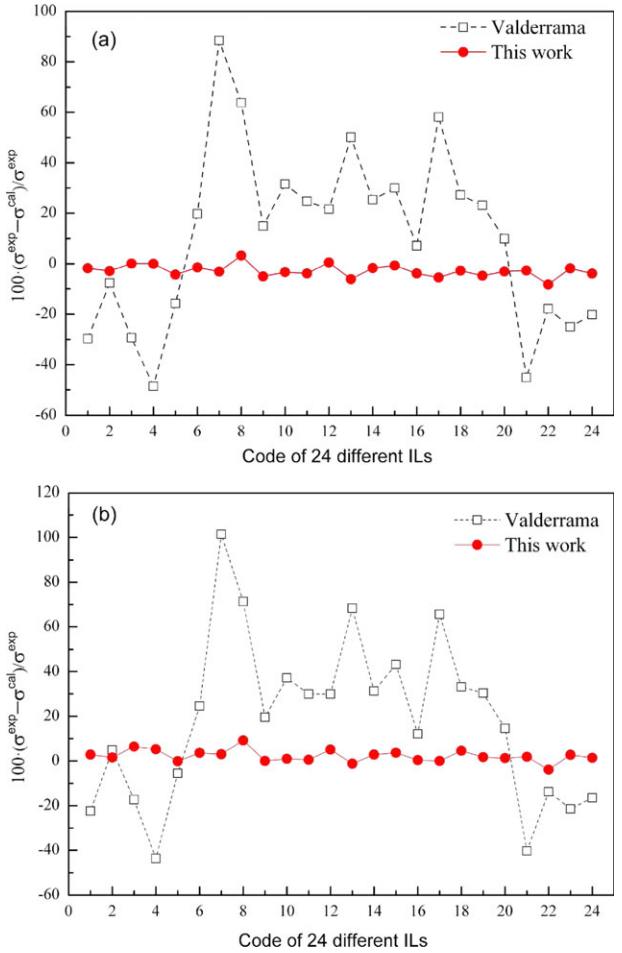

Figure 9. Critical properties from Valderrama and the current study led to different deviations between the experimental and calculated surface tension data using the (a) Brock-Bird equation, and (b) Pitzer equation.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The surface tension of 24 ILs were calculated using the Brock-Bird and Pitzer equations based on the critical properties obtained by Valderrama[38] and the FC—CS method, respectively to compare the performances of the two methods. Figure 9a and 9b show the relative deviation RD (%) of surface tension based on different critical properties sources. Detailed results are shown in the worksheet named "Comparison with Valderrama" in the Supplementary Material. The maximum relative deviations of FC—CS method and Valderrama in calculating surface tension were −8.3% and 88.5%, respectively. The results indicate that the FC—CS method was improved for predicting critical properties of ILs.

Applicability for mixtures of ILs

Experimental density data of 13 kinds of binary ILs were obtained from literature,[57–59] and their critical properties and

Table 7. The Calculated Density Deviations of Binary ILs Mixtures by Riedel Equation

Binary mixtures	x_1 (mole fration)	T/K	Points	Min RD (%)	Max RD (%)	AARD (%)
[C_6MIm][BF_4](1) + [C_2MIm][BF_4](2)	0.0978–0.9455	298	13	−0.2	0.4	0.3
[C_4MIm][BF_4](1) + [C4MIm][$MeSO_4$](2)	0.1209–0.9683	308	14	−0.1	0.2	0.1
[C_4MIm][BF_4](1) + [C_6MIm][BF_4](2)	0.1083–0.946	301	10	−3.2	4.6	2.1
[C_4MIm][PF_6](1) + [C_4MIm][BF_4](2)	0.0568–0.945	303	12	0.2	0.3	0.3
[omim][BF_4](1) + [omim] [Cl](2)	0.2–0.8	303–333	20	−0.3	0.3	0.2
[hmim][BF_4](1) + [hmim][Cl](2)	0.2–0.8	303–333	16	−0.2	0.3	0.2
[hmim][PF_6](1) + [hmim][Cl](2)	0.2–0.8	303–333	16	−0.1	0.6	0.3
[C_1MPyr][BTI](1) + [C_4MPyr][BTI](2)	0.1–0.4	273–373	4	−0.8	1.3	0.8
[C_1MPyr][BTI](1) +[C_5MPyr][BTI](2)	0.1–0.3	283–373	3	0	2.2	0.8
[C_2MPyr][BTI](1) +[C_3MPyr][BTI](2)	0.1–0.5	283–373	5	−0.9	1.1	0.7
[C_2MPyr][BTI](1) +[C_4MPyr][BTI](2)	0.1–0.5	273–373	5	−1.1	1.2	0.8
[C_2MPyr][BTI](1) +[C_5MPyr][BTI](2)	0.1–0.5	273–373	5	−0.3	1.6	0.8
[C_3MPyr][BTI](1) +[C_5MPyr][BTI](2)	0.1–0.9	273–373	5	−1.7	1.6	0.7
Total	0.0568–0.9683	273–373	128	−0.7	1.2	0.6

densities were predicted. The predicted values display well agreement with experimental data, as shown in Table 7. The results suggest the FC—CS method is also applicable for mixtures of ILs. More details of the calculation can be found in "Mixtures of ILs" of Supplementary Material.

Heat capacity

Based on the critical properties calculated above, 599 liquid heat capacity data of 26 ILs that cover a wide temperature range (10 K to 573.10 K) were estimated using the CSHC correlation(see Eq. 17) proposed in this study. The calculated liquid heat capacities agree well with the corresponding experimental data with an overall AARD of 3.8%, as shown in Figure 10. Although the obtained AARD was higher than the AARD of 2.9% reported by Ge et al.[30] the temperature range of the data points was wider, i.e., the CSHC equation can be applied under broader conditions. All relative deviations of the 599 calculated data points were within ±10.0%, of which 64% were within ±5.0 and 36% were between ±(5.0 and 10.0) %. Moreover, the maximum deviations were 9.9% observed for [C_4MIm][Br] (1-Butyl-3-methylimidazolium Bromide) at an extremely low temperature (110 K). The detailed results are described in the worksheet "Heat capacity" in the Supplementary Material.

Thermal conductivity

Almost all available thermal conductivity data in literature were collected, including 22 ILs within the temperature range of 273.15 K to 390 K and 0.1 MPa to 20 MPa pressure. The thermal conductivities of the 22 ILs were between 0.117 and 0.205, which were near 0.10 $W \cdot m^{-1} \cdot K^{-1}$ to 0.17 $W \cdot m^{-1} \cdot K^{-1}$ range of most organic liquids below the normal boiling point.[20] The CSTC correlation (see Eq. 20) was proposed to predict the dependence of thermal conductivity on temperature and pressure. Figure 11 shows the relative deviations between the calculated and experimental data as a function of experimental value for all data points used in the current study. As shown in Figure 11, all deviations were within ±10%, and were distributed randomly around the baseline of 0%, among which 74% were within ±5.0, and 26% were between ±(5.0 and 10.0) %. The detailed results are described in the worksheet "Thermal conductivity" in the Supplementary Material.

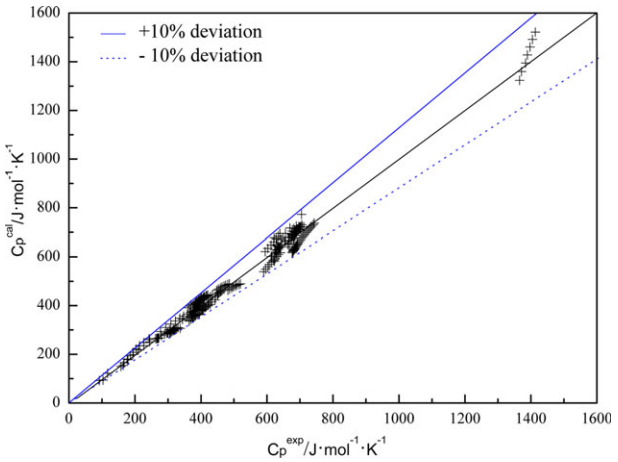

Figure 10. Comparison between the predicted and experimental heat capacities of 26 ILs within the temperature ranges of 10 K to 573.1 K.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

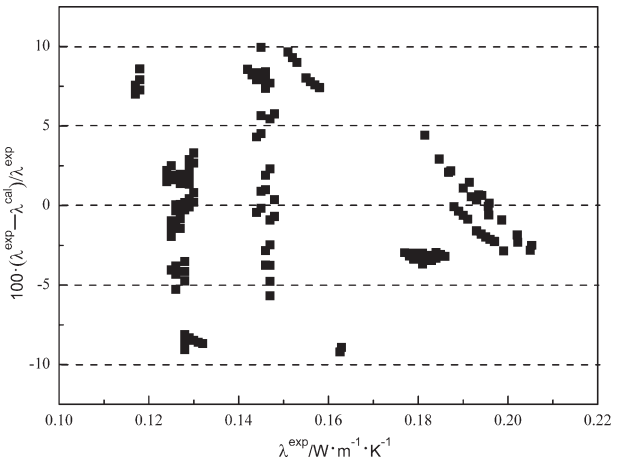

Figure 11. Relative deviations between the experimental and calculated thermal conductivities of 26 ILs.

Conclusions

This study developed a FC—CS method on the basis of 46 fragments for the prediction of the normal boiling temperatures, critical properties, and acentric factors of ILs. The fragment increments were determined using the experimental density data of 490 pure ILs under ambient temperature and atmospheric pressure. It shows the FC—CS method provides more reliable prediction results than the original GCM with neutral groups, given that both the temperature and pressure dependence of the density and surface tension of ILs can be correlated well using different equations. Those results imply that the definition of fragments and the estimated critical properties of pure ILs are reasonable. Furthermore, the method is able to be applied for mixtures of ILs.

The heat capacity and thermal conductivity of ILs can be successfully predicted using the CSHC and CSTC correlations proposed in this study by virtue of critical parameters calculated by the FC—CS method, at least for the ILs investigated. Compared with any other reported methods, the correlations exhibited general feasibility since they were obtained based on the CSP.

The methods and correlations proposed in this study take advantage of both the convenience of GCM and the generalized applicability of CSP, and will be useful for the acquisition of physicochemical properties for ILs at least investigated here. The FC—CS method will allow new IL fragment to be defined to predict critical properties of other ILs when their experimental density data are available. With the derived critical properties, more CSP correlations and equations of state can be developed to play a fundamental role in exploiting new process using ILs.

Acknowledgments

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Notation

Symbols

C_p = liquid heat capacity, $J \cdot mol^{-1} \cdot K^{-1}$
M = molar mass, $g \cdot mol^{-1}$
N_p = total number of data points
P_b = normal boiling pressure, 1.01325 bar

P_c = critical pressure, bar
T_b = normal boiling temperature, K
T_{br} = reduced temperature at the normal boiling point
T_c = critical temperature, K
T_r = reduced temperature
V_c = critical volume, $cm_3 \cdot mol^{-1}$

Abbreviations

AARD = average absolute relative deviation
CSP = corresponding states principle
CSHC = corresponding states heat capacity correlation proposed
CSTC = corresponding states thermal conductivity correlation proposed
GCM = group contribution method
FC—CS = fragment contribution—corresponding states
IL = ionic liquid
LGM = near generalized model by Valderrama et al.
MH = Mchaweh et al. equation
QSPR = quantitative structure–property relationship
RD = relative deviation
VSD = Valderrama and Abu-Sharkh SD equation
VSY = Valderrama and Abu-Sharkh SY equation
YG = Yamada and Gunn equation

Greek letters

ρ = density, $g \cdot cm^{-3}$
σ = surface tension, $mN \cdot m^{-1}$
λ = liquid thermal conductivity, $W \cdot m^{-1} \cdot K^{-1}$
ω = acentric factor

Subscripts

cal = calculated property
exp = experimental property

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