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The isothermal compressibility and surface tension product of room temperature ionic liquids

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ABSTRACT

The isothermal compressibilities, κ_T, and surface tensions, σ, of room temperature ionic liquids (RTILs) were obtained from the literature. The products, $\kappa_T\sigma$, were compared, in analogy with high-melting ionic liquids (molten salts) and liquid metals, with expectations from the scaled particle theory, the correlation lengths, and the dependence on the cohesive energy density, but poor agreement was found. This behavior is ascribed to the 'loose' packing of the ions in the RTILs, due to the large, generally non-spherical ions making up these ionic liquids.

1. Introduction

The products of the isothermal compressibilities, κ_T, of liquids and their surface tensions, σ, provide interesting regularities. According to the scaled particle theory (SPT) for liquids in general these products follow the expressions [1,2]:

$$\kappa_T\sigma = a(2-3y+y^3)/4(1+2y)^2 \tag{1}$$

and

$$y = (N_A\pi/6)a^3/V \tag{2}$$

where a represents the diameter of the hard spheres to which the SPT pertains, y is their packing fraction, and V is the molar volume of the liquid. At temperatures near the triple point the $\kappa_T\sigma$ product is approximately proportional to the correlation length of the liquid L, which is defined so that $\exp(-r/L)$ is the damping factor of the pair correlation function $g_{ij}(r)$ [3]:

$$\kappa_T\sigma \simeq 0.07L \tag{3}$$

The semi-empirical expression $\kappa_T\sigma \approx 10$ pm has then been derived [4].

The products $\kappa_T\sigma$ of molten salts have recently been evaluated by the author [5] at somewhat above their melting points, namely $1.1T_m$, representing a corresponding temperature for the surface tension of molten alkali metal halides [6] and for the compressibilities of a variety of molten salts [7]. For this kind of ionic liquids the products $\kappa_T\sigma$ are a function of independent values of their cohesive energy densities, *ced*, and the charges of the ions, z_A of the anion and z_C of the cation [5]:

$$\kappa_T\sigma = z_A z_C(z_A + z_C)[p + q/ced + r\cdot ced] \tag{4}$$

with $r = 0$. The products $\kappa_T\sigma$ of molten metals have also recently been evaluated by the author [8] at their melting points, and were found to follow Eq. (4) with $z_A = z_C = 1$ and $q = 0$ and $r < 0$. That is, for both these kinds of liquids the product $\kappa_T\sigma$ diminishes with increasing cohesive energy densities.

It is interesting to explore the corresponding products $\kappa_T\sigma$ of room temperature ionic liquids (RTILs) and to see whether and to what extend they follow these regularities.

2. Isothermal compressibility and surface tension product of RTILs

The isothermal compressibilities, κ_T [9,21–41], of room temperature ionic liquids (RTILs) have been evaluated from $\rho(p,T)$ data available in several publications as $\kappa_T = \rho^{-1}(\partial\rho/p)_T$, summarized by the author in [9,10] and by others [11,12]. The surface tension, σ [9,42–62], of RTILs has been reviewed in [9,13–15] and are available for 298.15 K as well as their temperature dependences. However, both the isothermal compressibilities, κ_T, and the surface tensions, σ, are known for some 50 room temperature ionic liquids (RTILs) only, and these quantities as well as their products $\kappa_T\sigma$, all at 298.15 K, are presented in Table 1. The products $\kappa_T\sigma$ vary from 9.9 pm to 21.7 pm, roughly a twofold span, compared with

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Table 1
The isothermal compressibilities κ_T, the surface tensions σ, their products $\kappa_T\sigma$, the molecular volumes v [13], the cohesive energy densities *ced* [9], and the internal pressures P_{int} [14] of room temperature ionic liquids at 298.15 K.

Cation[a]	Anion[b]	κ_T/GPa^{-1}	Ref.	σ/mN m^{-1}	Ref.	κ_T σ/pm	v/nm^3	*ced*/MPa	P_{int}/MPa
$[C_2mim]^+$	BF_4^-	0.375	[38]	54.4	[42]	20.4	0.231	682	496
	PF_6^-	0.399	[38]	54.0	[43]	21.5	0.263	774	492
	$[OAc]^-$	0.338	[38]	38.1	[44]	12.9	0.230	656	732
	$[NTF_2]^-$	0.380	[9]	36.1	[45]	13.7	0.382	503	366
	$[C_1SO_4]^-$	0.336	[21]	62.9	[46]	21.1	0.259	786	573
	$[C_2SO_4]^-$	0.262	[24]	48.8	[47]	12.8	0.286	728	487
	$CF_3SO_3^-$	0.435	[23]	40.4	[48]	17.6	0.278	656	397
	SCN^-	0.299	[24]	53.1	[49]	15.9	0.223	635	509
$[C_3mim]^+$	$[NTF_2]^-$	0.482	[29]	35.9	[42]	17.3	0.405	811	355
$[C_4mim]^+$	Cl^-	0.451	[38]	48.2	[50]	21.7	0.245	582	470
	BF_4^-	0.404	[38]	46.9	[42]	18.9	0.277	655	448
	PF_6^-	0.412	[9]	47.5	[50]	19.6	0.309	667	439
	$[NTF_2]^-$	0.498	[36]	34.9	[44]	17.4	0.428	472	351
	$[C_1SO_4]^-$	0.375	[25]	43.3	[51]	16.2	0.305	674	427
	$[C_8SO_4]^-$	0.492	[9]	41.7	[45]	20.5	0.494	357	373
	$CF_3SO_3^-$	0.432	[9]	25.2	[48]	10.9	0.324	598	401
	$N(CN)_2^-$	0.415	[9]	45.8	[50]	19.0	0.287	662	375
$[C_5mim]^+$	$[NTF_2]^-$	0.471	[29]	35.9	[52]	16.9	0.451	427	354
$[C_6mim]^+$	BF_4^-	0.446	[38]	39.2	[50]	17.5	0.323	548	402
	PF_6^-	0.411	[38]	43.4	[50]	17.8	0.355	554	420
	$[NTF_2]^-$	0.560	[26]	33.8	[42]	18.9	0.484	410	351
	Cl^-	0.344^j	[39]	47.5	[50]	16.3	0.291	811	474
$[C_7mim]^+$	$[NTF_2]^-$	0.543	[9]	27.8	[9]	15.1	0.497	435	410
$[C_8min]^+$	BF_4^-	0.425	[38]	30.7	[50]	13.0	0.364	456	384
	PF_6^-	0.409	[38]	33.9	[53]	13.9	0.401	499	387
	$[NTF_2]^-$	0.540	[9]	27.8	[54]	15.0	0.520	400	348
	Cl^-	0.389	[27]	31.9	[50]	12.4	0.337	509	433
	$N(CN)_2^-$	0.415	[9]	36.9	[43]	15.3	0.379	609	
$[C_{10}mim]^+$	$[NTF_2]^-$	0.334	[9]	29.6	[55]	9.9	0.566	372	317
$[C_3py]^+$	BF_4^-	0.333	[28]	51.0	[56]	17.0	0.247		515
$[C_4py]^+$	BF_4^-	0.250	[29]	50.9	[56]	12.7	0.271	902	648
	$CF_3SO_3^-$	0.449	[29]	34.8	[57]	15.7	0.318	488	385
$[C_4(3M)py]^+$	BF_4^-	0.369	[40]	44.8	[56]	16.5	0.247	706	443
	$N(CN)_2^-$	0.354	[40]	43.0	[9]	15.2	0.257	738	489
$[C_8(3M)py]^+$	BF_4^-	0.430	[28]	36.5	[9]	15.7	0.390		418
$[N_{1114}]^+$	$[NTF_2]^-$	0.389	[9]	38.1	[58]	14.8	0.422	734	550
$[C_3mpyrro]^+$	$[NTF_2]^-$	0.495	[30]	33.9	[59]	16.8	0.419	475	395
$[C_4mpyrrp]^+$	$[NTF_2]^-$	0.507	[30]	35.4	[60]	17.9	0.443	445	388
$[P_{66614}]^+$	Cl^-	0.586	[31]	33.4	[52]	19.6	0.852	396	341
	Br^-	0.561	[32]	29.3	[9]	16.4	0.861		340
	$[NTF_2]^-$	0.612	[31]	30.1	[61]	18.4	1.035	303	354
	$N(CN)_2^-$	0.492	[33]	31.7	[61]	15.6	0.894	342	405
	$[FAP]^-$	0.589	[62]	29.0	[62]	17.1	1.169		332

[a] The alkyl groups are at the 1-position of mim = 3-methylimidazolium, py = pyridinium, pyrro = pyrrolidinium.
[b] NTF_2 = bis(trifluoromethylsulfonyl)imide, FAP = tris(pentafluoroethyl-trifluorophosphate.

a sixfold span for high temperature molten salts [5] and a fourfold span for liquid metals [8].

Values of the cohesive energy densities, *ced*, of these RTILs (that are all uni-univalent) and their molecular volumes, v, are also shown in Table 1. The volumes v of the individual constituent ions of RTILs have been reported [16], and their diameters should then be $(6v_{ion}/\pi)^{1/3}$ so that the mean diameter for application of Eqs. (1) and (2) of the SPT is $a_{mean} = [(6v_C/\pi)^{1/3} + (6v_A/\pi)^{1/3}]/2$. The values of a_{mean} range from 556 pm for a small RTIL Etmim$^+$Cl$^-$ to 792 for a large one Ocmim NTF_2 among the RTILs represented in Table 1. The packing fraction of RTILs was found to be independent of the natures of the constituent ions and is $y = 0.6875 \pm 0.0055$ [16]. Therefore, Eq. (1) is transformable for all the RTILs tested to:

$$\kappa_T\sigma = (0.01163 \pm 0.00050)a_{mean} \tag{5}$$

and should increase with the sizes of the ions making up the RTIL. The resulting $\kappa_T\sigma$ products according to the SPT and Eq. (5) are in the range from 6 to 10 pm and are about one half only of the experimental ones.

A plot of the $\kappa_T\sigma$ products according to Eq. (4) yields a rather poor correlation, with $R_{corr} = 0.215$ and $p = 9.5 \pm 1.0$, $q = 600 \pm 480$, and $r \sim 0$ for the 34 RTILs for which all the required variables are known (Table 1). That is, contrary to molten salts and liquid metals, the $\kappa_T\sigma$ products do not diminish appreciably with increasing cohesive energy densities, *ced*, or even with decreasing sizes of the ions, v, but are fairly constant, within 16 ± 6 pm, as shown in Fig. 1.

Accordingly, the correlations valid for liquids in general, Eqs. (1), (2), and (5), and for high-melting ionic liquids in particular, Eq. (4), are not followed by the room temperature ionic liquids at all well. It should be remembered, however, that the span of values of the $\kappa_T\sigma$ products of RTILs is short, a factor of two only, hence quantitative correlations would be difficult to observe.

3. Discussion

Although there are many papers dealing with the isothermal compressibility and with the surface tension of room temperature ionic liquids individually, there are very few sources where both quantities are dealt with simultaneously under similar conditions (298.15 K and ambient pressure assumed in the present paper). Group contributions to the thermophysical properties of the RTILs,