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The fluidity of room temperature ionic liquids

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ABSTRACT

The fluidities, $\Phi = \eta^{-1}$, of room temperature ionic liquids (RTILs) as functions of the temperature can be described in terms of the Hildebrand and Lamoreaux approach. This relates the (temperature dependent) fluidity to the (temperature dependent) molar volume V of the RTIL: $\Phi = B[(V - V_0)/V_0]$. The resulting V_0 parameters, signifying the absence of free volume, are 99.0 ± 0.5% of the molar volume at 298.15 K. Counter to expectation, the B parameters increase with the interionic attractive forces. It is shown that the volumetric behavior of the RTILs permits the prediction of the temperature dependence of their viscosities, provided that the latter are not larger than ca. 50 mPa s^{-1}.

1. Introduction

The fluidity of a liquid is the reciprocal of its dynamic viscosity: $\Phi = \eta^{-1}$ and is measured in s mPa^{-1}. The viscosity, hence the fluidity, of only few room temperature ionic liquids (RTILs) obeys the Arrhenius expression, $\Phi = \Phi_0 \exp(E_\Phi/RT)$. The fluidities of most RTILs are better described by the Vogel–Tammann–Fulcher (VTF) [1–3] expression:

$$\Phi = \Phi_0 \exp\left[\frac{K}{T - T_0}\right] \quad (1)$$

with three coefficients, Φ_0, K, and T_0. The VTF expression is in some cases modified by replacement of Φ_0 by $\Phi_0' T^{1/2}$. In the expression proposed by Litovits [4], $(T - T_0)$ in the denominator of the exponent in Eq. (1) is replaced by T^3. Ghatee et al. [5] proposed the expression:

$$\Phi^{0.3} = a + bT \quad (2)$$

for describing the temperature dependence of the fluidity of RTILs.

The present paper explores the application to the RTILs of the expression originally proposed by Hildebrand and Lamoreaux [6,7] for various liquids:

$$\Phi = B\left[\frac{V - V_0}{V_0}\right] \quad (3)$$

relating the (temperature dependent) fluidity to the (temperature dependent) molar volume V of the liquid. This expression makes the fluidity proportional to the fraction of free volume of the liquid, the parameter V_0 denoting that molar volume "at which the molecules are so closely crowded as to prevent viscous flow while still retaining rotational freedom" [6]. Eq. (3) is re-written as:

$$\Phi = -B + \left(\frac{B}{V_0}\right) V \quad (4)$$

yielding a straight line when Φ is plotted against V, from the intercept and slope of which the parameters B and V_0 are readily obtained.

2. Results

A large but not exhaustive database of the viscosities of RTILs as functions of the temperature has been assembled and their reciprocals, their fluidities Φ, have been obtained. The corresponding molar volumes V were obtained from the temperature dependent densities, if available in the same publication. Otherwise they were obtained from the temperature dependence of the densities in a recent compilation by the author [8].

Plots of the data according to Eq. (4) yielded straight lines (with a linear correlation coefficient of ≥0.995) only for *not* highly viscous RTILs. That is, the linear dependence is observed at temperatures well away from their melting temperatures, say above 40 °C, where generally $\Phi \geq 0.02$ s mPa^{-1}, depending on individual cases. With decreasing temperatures the fluidity diminishes below this limit and the lines curve upwards, as shown in Fig. 1 for representative RTILs. The V_0 values are not very sensitive (within ±1 cm^3 mol^{-1}) to where the straight line dependence is cut off, but the B values are not accurate, varying up to 30% according to this place. The resulting coefficients B and V_0 are shown in Table 1.

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Table 1
The coefficients B and V_0 obtained from plots of Eq. (4) of the fluidities against the molar volumes of room temperature ionic liquids.

RTIL[a]	Ref.	B (s mPa^{-1})	V_0 (cm^3 mol^{-1})
Memim$^+$ $MeSO_4^-$	[9]	2.26	156
Etmim$^+$ BF_4^-	[10]	1.70	152
Etmim$^+$ $MeSO_3^-$	[11]	1.21	165
Etmim$^+$ $EtSO_3^-$	[12]	1.41	188
Etmim$^+$ $N(CN)_2^-$	[12]	3.16	156
Etmim$^+$ $B(CN)_4^-$	[13]	5.39	217
Etmim$^+$ NTF_2^-	[10]	0.18	256
Etmim$^+$ NTF_2^-	[12]	2.17	255
Etmim$^+$ NTF_2^-	[14]	2.22	257
Etmim$^+$ NTF_2^-	[15]	2.20	255
Etmim$^+$ NTF_2^-	[16]	2.81	256
Etmim$^+$ $EtSO_4^-$	[17]	1.95	190
Etmim$^+$ $OcSO_4^-$	[11]	0.44	291
Etmim$^+$ NO_3^-	[18]	2.18	180
Etmim$^+$ $CF_3SO_3^-$	[18]	4.04	188
Prmim$^+$ NTF_2^-	[14]	2.63	293
Prmim$^+$ NTF_2^-	[19]	2.49	296
Bumim$^+$ $MeCO_2^-$	[20]	1.05	188
Bumim$^+$ BF_4^-	[21]	1.89	188
Bumim$^+$ BF_4^-	[18]	1.57	188
Bumim$^+$ BF_4^-	[22]	2.72	189
Bumim$^+$ BF_4^-	[23]	2.21	188
Bumim$^+$ $N(CN)_2^-$	[15]	3.40	192
Bumim$^+$ $N(CN)_2^-$	[22]	5.24	194
Bumim$^+$ PF_6^-	[24]	0.67	207
Bumim$^+$ PF_6^-	[25]	1.23	209
Bumim$^+$ PF_6^-	[21]	1.04	207
Bumim$^+$ PF_6^-	[18]	1.34	206
Bumim$^+$ NO_3^-	[18]	1.07	253
Bumim$^+$ NO_3^-	[26]	1.92	174
Bumim$^+$ $CF_3CO_2^-$	[21]	2.52	207
Bumim$^+$ $CF_3SO_3^-$	[15]	1.83	221
Bumim$^+$ $CF_3SO_3^-$	[21]	1.86	221
Bumim$^+$ $CF_3SO_3^-$	[18]	2.84	222
Bumim$^+$ NTF_2^-	[21]	2.36	290
Bumim$^+$ NTF_2^-	[27]	2.36	291
Bumim$^+$ NTF_2^-	[14]	2.08	290
Bumim$^+$ NTF_2^-	[28]	2.61	290
Bumim$^+$ $(C_2F_5SO_3)_2N^-$	[21]	1.58	345
Pemim$^+$ NTF_2^-	[14]	2.59	309
Hxmim$^+$ BF_4^-	[18]	1.20	281
Hxmim$^+$ $N(CN)_2^-$	[15]	2.72	225
Hxmim$^+$ $CF_3SO_3^-$	[15]	1.51	256
Hxmim$^+$ NTF_2^-	[15]	2.02	348
Hxmim$^+$ PF_6^-	[29]	0.84	240
Hxmim$^+$ PF_6^-	[18]	0.70	335
Hxmim$^+$ NO_3^-	[18]	1.07	253
Hxmim$^+$ $(C_2F_5)_3PF_3^-$	[29]	1.94	395
Ocmim$^+$ BF_4^-	[30]	1.29	258
Ocmim$^+$ BF_4^-	[18]	1.07	329
Ocmim$^+$ BF_4^-	[22]	1.67	259
Ocmim$^+$ PF_6^-	[18]	0.66	377
Dcmim$^+$ BF_4^-	[18]	0.88	370
Bubim$^+$ NTF_2^-	[11]	1.49	310
MePy$^+$ $MeSO_4^-$	[31]	1.69	151
Me(2Et)Py$^+$ $MeSO_4^-$	[31]	1.06	191
Me(3Me)Py$^+$ $MeSO_4^-$	[31]	1.96	167
EtPy$^+$ $EtSO_4^-$	[16]	2.14	189
Et(2Et)Py$^+$ $EtSO_4^-$	[33]	1.19	213
Et(4Me)Py$^+$ NTF_2^-	[31]	2.69	288
Et(3Me)Py$^+$ NTF_2^-	[15]	2.54	289
Pr(3Me)Py$^+$ NTF_2^-	[15]	2.49	308
BuPy$^+$ BF_4^-	[10]	0.74	180
BuPy$^+$ BF_4^-	[32]	2.48	185
BuPy$^+$ NTF_2^-	[10]	0.31	284
BuPy$^+$ NTF_2^-	[28]	2.58	287
Bu(3Me)Py$^+$ BF_4^-	[16]	1.91	204
Bu(3Me)Py$^+$ BF_4^-	[22]	3.12	201
Bu(3Me)Py$^+$ $N(CN)_2^-$	[22]	4.28	206
Bu(3Me)Py$^+$ NTF_2^-	[15]	2.19	325
Bu(3Me)Py$^+$ NTF_2^-	[16]	2.45	309
Bu(4Me)Py$^+$ NTF_2^-	[33]	2.51	325
Bu(3CN)Py$^+$ NTF_2^-	[34]	1.25	303
Hx(3CN)Py$^+$ NTF_2^-	[34]	1.10	338
Hx(4Me)Py$^+$ NTF_2^-	[34]	1.29	338
OcPy$^+$ BF_4^-	[32]	1.35	252
Oc(3CN)Py$^+$ NTF_2^-	[34]	0.94	373
Ocisoquin$^+$ NTF_2^-	[36]	0.87	393
$BuMe_3N^+$ NTF_2^-	[28]	1.78	285
Oc_3MeN^+ NTF_2^-	[12]	0.48	616
PrMePyrr$^+$ NTF_2^-	[14]	1.94	305
BuMePyrr$^+$ NTF_2^-	[14]	1.90	301
BuMePyrr$^+$ NTF_2^-	[15]	1.82	302
BuMePyrr$^+$ NTF_2^-	[28]	1.96	303
BuMePyrr$^+$ $CF_3SO_3^-$	[15]	1.45	233
$MeOCH_2$MePyrr$^+$ NTF_2^-	[37]	2.60	277
PrMePip$^+$ NTF_2^-	[14]	1.70	315
Bu_3MeP^+ $MeSO_4^-$	[35]	0.84	311
Bu_3EtP^+ $Et_2PO_4^-$	[35]	1.21	382
Bu_3OcP^+ Cl^-	[35]	0.29	383
Hx_3TdP^+ $N(CN)_2^-$	[38]	1.11	618
Hx_3TdP^+ $MeSO_3^-$	[38]	0.71	633
Hx_3TdP^+ $NoCO_2^-$	[38]	0.98	754
Hx_3TdP^+ NTF_2^-	[38]	1.15	723

[a] Mim, 3-methylimidazole-1-; bim, 3-butylimidazole-1-; NTF_2, bis(trifluoromethyl-sulfonyl)amide; Py, pyridine, Pyrr, pyrridoline; Pip, piperidine; Td, tetradecyl.

3. Discussion

The upwards curvature of the plots of Eq. (4) at low temperatures, demonstrated in Fig. 1 for representative RTILs, means that the Hildebrand concept of fluidity breaks down under such conditions and the ions of the RTIL cannot rotate freely any more. However, above ca. 40 °C the $\Phi = f(V)$ curves are linear as stipulated by this concept. The V_0 values recorded in Table 1 are 99.0 ± 0.5% of the molar volume at 25 °C, which may therefore be taken as the molar volume at which the ions are closely crowded, making viscous flow difficult while the ions still retain rotational freedom.

Little can be said about the B values shown in Table 1. For a series of cations, say the 1-alkyl-3-methylimidazolium ones, with a given anion the B values tend to diminish as the cation becomes larger and its V_0 values increase. The products BV_0 are very roughly constant. 350 ± 40 for the tetrafluoroborate salts, 250 ± 20 for the hexafluorophosphate salts and 670 ± 100 for the bis(trifluoromethylsulfonyl)amide salts. When a B value is outside

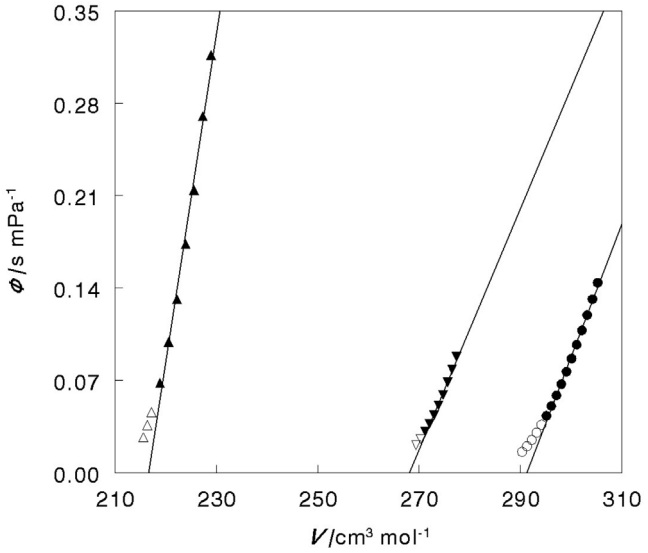

Fig. 1. Plots of the fluidity against the molar volume at a range of temperatures for Etmim$^+$ $B(CN)_4^-$ (▲) with data from [12], Bumim$^+$ NTF_2^- (▼) with data from [17], and Et(3Me)Py (●) with data from [14]. Filled symbols conform to a straight line with a linear correlation coefficient ≥0.995, empty symbols do not.