The Conductivity of Imidazolium-Based Ionic Liquids from (−35 to 195) °C. A. Variation of Cation's Alkyl Chain[†]

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Data for the conductivity (κ) of the ionic liquids [emim][BF_4], [bmim][BF_4], [hmim][BF_4], and [omim][BF_4] from (−35 to 195) °C are reported. The data can be well-fit with the Vogel−Fulcher−Tammann equation. Additionally, molar conductivities (Λ) were determined for the limited temperature range of (5 to 65) °C. Walden plots of these data indicate that the investigated compounds can be classified as "high-ionicity" ionic liquids. It is suspected that the large difference between the present κ values and some of the literature values is mainly due to the neglect of BF_4^- hydrolysis.

Introduction

Room-temperature ionic liquids (RTILs) are salts that are liquid at ambient temperature. Among various outstanding properties,[1−4] the wide liquid range and high thermal stability of these compounds are especially notable because they allow the use of RTILs, either in neat form or in mixtures with proton conductors, as electrolytes in high-temperature fuel cells.[5−7] Such applications require knowledge of RTIL transport properties over a wide temperature range. Surprisingly, systematic studies in this field are scarce.[8−15]

In this contribution, we report data for the electrical conductivity (κ) of several neat alkylmethylimidazolium tetrafluoroborate ionic liquids, namely, 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF_4], CAS no. 143314-16-3), 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4], CAS no. 174501-65-6), 1-hexyl-3-methylimidazolium tetrafluoroborate ([hmim][BF_4], CAS no. 244193-50-8), and 1-methyl-3-octylimidazolium tetrafluoroborate ([omim][BF_4], CAS no. 244193-52-0), covering the temperature range from (−35 to 195) °C. The stability of the RTILs in the investigated temperature range was checked through thermogravimetric analysis. Additionally, the densities (ρ) of the RTILs were determined over a more limited temperature range ($5 \leq t/°C \leq 65$) and used to calculate molar conductivities (Λ). A complementary study of the anion effect on the conductivity of 1-butyl-3-methylimidazolium salts is reported in the companion paper (DOI: 10.1021/je900793r).[16]

Experimental Section

Materials. All of the studied ionic liquids were synthesized in our laboratory. Samples of [emim][BF_4], [bmim][BF_4], and [hmim][BF_4] were taken from the same batches used in a previous mixture study.[17] A detailed description of the synthesis and purification of these compounds is given there.

The following chemicals were used for the preparation of [omim][BF_4]: 1-Methylimidazole (MI; Merck, 0.99 mass fraction purity) was distilled over KOH (Merck, p. a.) under reduced pressure, stored over 4 Å molecular sieves, and redistilled under reduced pressure prior to use. 1-Chlorooctane (1CO; Aldrich, ≥ 0.99 mass fraction purity) was distilled prior to use. The salt $NaBF_4$ (VWR Prolabo, 0.986 mass fraction purity) was used as received.

Synthesis of [omim][BF_4]. The compound was synthesized from MI via 1-methyl-3-octylimidazolium chloride ([omim]Cl). The latter was obtained by adding a slight molar excess ($n_{1CO} \approx 1.1 n_{MI}$) of 1CO to a stirred solution [∼40 % (v/v)] of MI in acetonitrile (Merck, ≥ 0.999 mass fraction purity) under an atmosphere of dry nitrogen. The [omim]Cl thus formed was washed twice with ethyl acetate (Merck, p.a.). [omim][BF_4] was then obtained via anion metathesis from equimolar amounts of [omim]Cl dissolved in dichloromethane (Acros, 0.9999 mass fraction purity) and $NaBF_4$ in aqueous solution (using water purified with a Millipore MILLI-Q purification unit). The organic phase was subsequently washed thrice with small amounts of water to remove traces of NaCl before evaporation of the solvent. All of the preparation steps involving aqueous phases were performed rapidly with materials cooled to approximately 0 °C prior to use to minimize the hydrolysis of BF_4^-. The obtained product was slightly yellowish.

Sample Handling. Prior to use, all of the RTILs were dried on a high-vacuum line ($p < 10^{-8}$ bar) for 7 days at approximately 40 °C, yielding water mass fractions of $< 50 \times 10^{-6}$ (coulometric Karl Fischer titration, Mitsubishi Moisturemeter MCI CA-02). Potentiometric titration of RTIL samples in aqueous solution against a standard solution of $AgNO_3$ (Carl Roth) yielded halide mass fractions of $< 50 \times 10^{-6}$ for [bmim][BF_4], [hmim][BF_4], and [omim][BF_4]. Halide impurities could not be detected for [emim][BF_4]. No contaminations were detected in ^1H and ^{19}F NMR analyses.

The dried RTILs were stored in a N_2-filled glovebox. N_2 protection was also maintained during all steps of sample handling, including filling of the cells and the subsequent measurements. The water mass fractions of selected samples determined after finishing the measurement program were still $< 50 \times 10^{-6}$.

Conductivity. Measurements in the low-temperature region ($-35 \leq t/°C \leq 25$; stability < 0.003 K) were performed with equipment developed by Barthel and co-workers[18,19] and described previously.[17] A set of four three-electrode capillary cells with cell constants (C) in the range (25 to 470) m^{-1} was used. For the measurements from ambient to high temperatures

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($25 \leq t/°\mathrm{C} \leq 195$) a new homemade precision thermostat was set up in combination with a cold source (Julabo FP40). This thermostat was stable to < 0.003 K over the entire temperature range. Here a set of four two-electrode capillary cells with C values in the range (1260 to 4613) m^{-1} was used. All of the cells were calibrated with aqueous KCl.[20]

For both setups, the cell resistance [$R(\nu)$] was measured with a manually balanced high-precision conductivity bridge as a function of AC frequency (ν) between 480 Hz and 10 kHz. To eliminate electrode polarization, the conductivity of each sample was obtained as $\kappa = C/R_\infty$, where R_∞ was obtained from the extrapolation $R_\infty = \lim_{\nu\to\infty} R(\nu)$ using the empirical function $R(\nu) = R_\infty + A/\nu^a$; the parameter A was cell-specific, and the exponent a was found to be in the range $0.5 \lesssim a \lesssim 1$.[21]

For all of the measurements, the uncertainty in temperature was ± 0.01 °C (NIST-traceable Pt sensor and bridge, ASL). Repeat measurements of κ for selected samples with the same cells after an accomplished temperature cycle as well as measurements of the same sample with different cells agreed within 0.3 %. When the sources of error (calibration, measurements, impurities) were taken into account, the relative uncertainties in κ and the derived molar conductivity Λ were within 0.5 %. Consideration of the temperature dependence of the cell constant C[18,20,22] revealed only a negligible effect on κ and was accordingly omitted.

Density. To calculate molar concentrations (c), ρ values for the RTILs were determined at $5 \leq t/°\mathrm{C} \leq 65$ with a vibrating tube densimeter (Anton Paar DMA 60 in conjunction with DMA 601HT). The instrument was calibrated with degassed water and purified nitrogen at atmospheric pressure, assuming densities from standard sources.[23] The repeatability of the measurements was $\pm$ 0.001 $\mathrm{kg \cdot m^{-3}}$. Taking into account the sources of error (calibration, measurement, purity of materials), we estimate the uncertainty of ρ to be within $\pm$ 0.05 $\mathrm{kg \cdot m^{-3}}$.

Thermal Analysis. The thermal stabilities of the samples were studied with a thermogravimetric analyzer (PerkinElmer model TGA 7). Samples were measured at a heating rate of 10 $\mathrm{K \cdot min^{-1}}$ over the temperature range $30 \leq t/°\mathrm{C} \leq 600$ with application of a continuous nitrogen flow. The onset point of mass loss, defined as the intersection of the baseline before decomposition and the tangent to the mass-loss-versus-temperature curve, was taken as the decomposition temperature (t_{dec}).

Results and Discussion

Thermal Stability. According to the thermogravimetric analysis, the onset temperature t_{dec} for thermal decomposition decreased with increasing the length of the alkyl chain. The obtained t_{dec} values are 449 °C for [emim][BF_4], 432 °C for [bmim][BF_4], 425 °C for [hmim][BF_4], and 416 °C for [omim][BF_4]. These data suggest that effects on κ due to the decomposition of the RTILs at elevated temperatures can be excluded. This was corroborated by remeasuring κ at 65 °C after finishing the temperature ramp at 195 °C.

Crystallization Temperature of [emim][BF₄]. Surprisingly, [emim][BF_4] crystallized in the conductivity cell at an unknown temperature when the sample was cooled from −25 °C to −35 °C, which is well above the published crystallization temperatures (−63 °C[8] and −58 °C[9]). We believe that this premature crystallization reflects the high purity of our sample and highlights the difficulties associated with synthesizing highly pure [emim][BF_4].

Table 1. Electrical Conductivities (κ) of the Investigated Ionic Liquids[a]

t/°C	$\kappa/\mathrm{S \cdot m^{-1}}$			
	[emim][BF_4]	[bmim][BF_4]	[hmim][BF_4]	[omim][BF_4]
−35	–	0.00212	0.000405	0.0001524
−25	0.1059	0.00778	0.001685	0.000650
−15	0.228	0.0225	0.00544	0.00218
−5	0.423	0.0542	0.01451	0.00605
5	0.703	0.1132	0.0332	0.01441
15	1.076	0.211	0.0672	0.0304
25	1.546	0.352	0.1229	0.0579
35	2.11	0.556	0.207	0.1012
45	2.77	0.821	0.326	0.1647
55	3.51	1.150	0.483	0.252
65	4.34	1.545	0.683	0.368
75	5.23	2.00	0.926	0.512
85	6.20	2.52	1.214	0.688
95	7.22	3.10	1.545	0.895
105	8.29	3.73	1.92	1.134
115	9.41	4.41	2.33	1.403
125	10.56	5.13	2.78	1.701
135	11.75	5.88	3.26	2.03
145	12.97	6.64	3.77	2.38
155	14.22	7.45	4.31	2.75
165	15.48	8.29	4.88	3.15
175	16.75	9.15	5.46	3.56
185	18.03	10.04	6.07	3.99
195	19.3	10.94	6.69	4.44

[a] The relative standard uncertainty of κ is 0.5 %.

Conductivity Data. Table 1 summarizes the measured values of κ, and graphs comparing the present results with literature data are given in Figures 1 through 4. The studied RTILs showed the expected decrease of κ with increasing alkyl chain length as the consequence of increasing viscosity.[11,12,14,15] A previous literature survey of the electrical conductivities of various RTILs at 25 °C revealed significant scatter in the measured values.[17] The discrepancies were ascribed to either sample purity (including BF_4^- hydrolysis) or electrode polarization.

The present κ values, which cover a very wide temperature range, agree quantitatively (i.e., within the given errors) with some of the published data but deviate considerably from others. For [emim][BF_4], [bmim][BF_4], and [hmim][BF_4] at 25 °C, the agreement with our previous values[17] is excellent; the relative deviations $\delta_{\mathrm{Lit}} = 100 \cdot (\kappa - \kappa_{\mathrm{Lit}})/\kappa$ are < 0.45.

[emim][BF_4] was studied by Vila et al.[24,25] over the wide temperature range $-15 \leq t/°\mathrm{C} \leq 160$. Measurements were performed with a commercial conductometer (stated reproducibility < 10 %[24] and 5 %[25]) using samples of stated purity (> 99 %[24,26] and > 98 %[25,26]) as received. The relative deviations between their data and appropriately interpolated values from this investigation are in the range $-12 \leq \delta_{\mathrm{Lit}} \leq 14$ (Figure 1). A commercial sample of > 97 % purity[26] and a conductometer operating at a single frequency were used by Yu et al.[27] While their data are in good agreement with those of Vila et al.[24,25] (Figure 1), they differ in the range $-5.6 \leq \delta_{\mathrm{Lit}} \leq 9.2$ from those presented here. The results of Nishida et al.,[9] also obtained with a commercial conductometer but with a highly pure sample at $-30 \leq t/°\mathrm{C} \leq 25$, are in better but still not satisfactory agreement ($0 \leq \delta_{\mathrm{Lit}} \leq 6$; Figure 1).

Previous conductivity measurements for [bmim][BF_4] at temperatures in the range $5 \leq t/°\mathrm{C} \leq 65$ were performed with a sample prepared via the [bmim]Br route[28] (also see ref 17). The higher level of halide impurities for that sample may explain the deviations of $-1.7 \leq \delta_{\mathrm{Lit}} \leq 2.9$ from the present κ values. Comparison to the data of Suarez et al.[29] reveals unexpectedly large discrepancies ($32 \leq \delta_{\mathrm{Lit}} \leq 55$; Figure 2). These authors measured the resistance of a [bmim][BF_4] sample of unstated purity with an HP 4265B universal bridge. Also, the κ values of Vila et al.[25] obtained with a commercial sample (purity > 99 %[26]) deviate considerably ($-24 \leq \delta_{\mathrm{Lit}} \leq 12$). Despite the stated

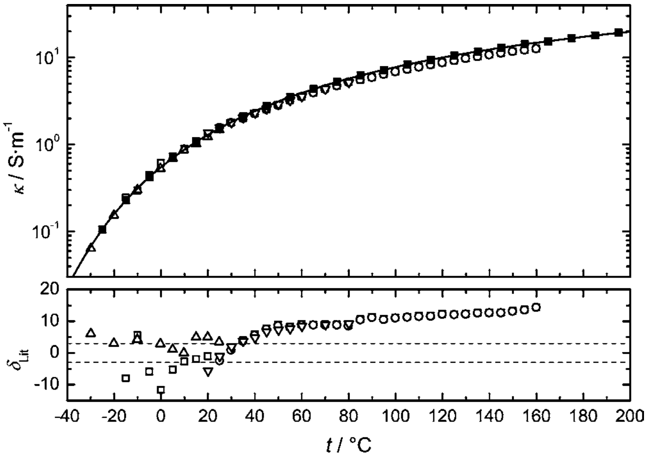

Figure 1. Conductivities (κ) of [emim][BF$_4$] from this study (■) and κ values and their relative deviations (δ_{Lit}) from the present results, obtained from published data of Vila et al. (□[24] and ○[25]), Yu et al.[27] (▽), and Nishida et al.[9] (△). The solid line represents a VFT fit (eq 1) calculated with parameters given in Table 2; the dashed lines indicate an (arbitrary) margin of ± 3 for δ_{Lit}.

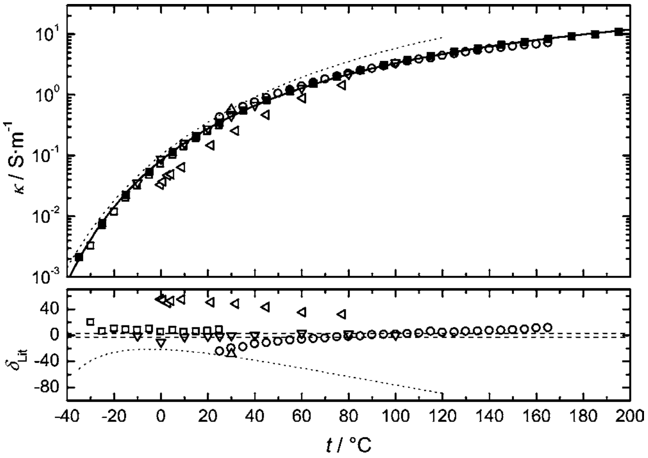

Figure 2. Conductivities (κ) of [bmim][BF$_4$] from this study (■) and κ values and their relative deviations (δ_{Lit}) from the present results, obtained from published data of Suarez et al.[29] (left-pointing open triangles), Nishida et al.[9] (□), Tokuda et al.[31] (▽), Liu et al.[30] (△), and Vila et al.[25] (○). The solid line represents a VFT fit (eq 1) calculated with parameters given in Table 2, and the dotted lines were calculated from VFT parameters given by Leys et al.;[10] the dashed lines indicate an (arbitrary) margin of ± 3 for δ_{Lit}.

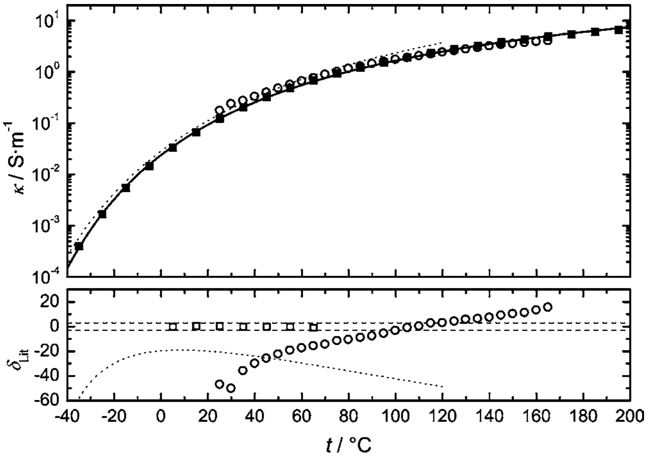

Figure 3. Conductivities (κ) of [hmim][BF$_4$] from this study (■) and κ values and their relative deviations (δ_{Lit}) from the present results, obtained from published data of Hunger et al.[28] (□) and Vila et al.[25] (○). The solid line represents a VFT fit (eq 1) calculated with parameters given in Table 2, and the dotted lines were calculated from VFT parameters given by Leys et al.;[10] the dashed lines indicate an (arbitrary) margin of ± 3 for δ_{Lit}.

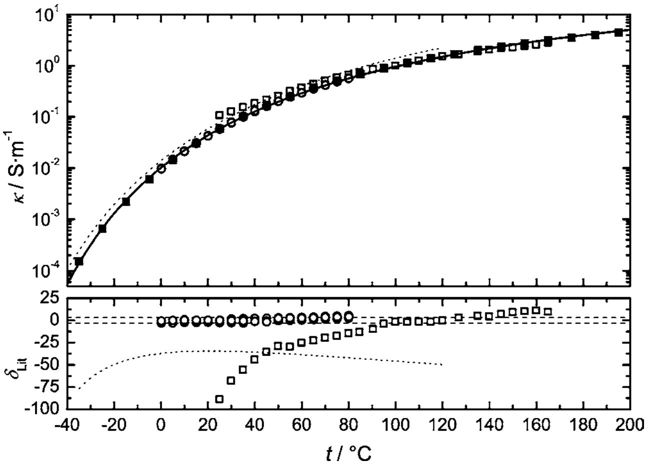

Figure 4. Conductivities (κ) of [omim][BF$_4$] from this study (■) and κ values and their relative deviations (δ_{Lit}) from the present results, obtained from published data of Vila et al.[25] (□) and Kanakubo et al.[13] (○). The solid line represents a VFT fit (eq 1) calculated with parameters given in Table 2, and the dotted lines were calculated from VFT parameters given by Leys et al.;[10] the dashed lines indicate an (arbitrary) margin of ± 3 for δ_{Lit}.

high purity of the sample, the results of Nishida et al.[9] deviate in the range $5.5 \leq \delta_{Lit} \leq 20$, as does the value at 30 °C given by Liu et al.[30] ($\delta_{Lit} = -29$) for a sample of unstated purity. Except for κ at 0 °C, reasonable agreement ($-2.5 \leq \delta_{Lit} \leq 3.0$) was found between our data and those given by Tokuda et al.[31] over the temperature range $-10 \leq t$/°C ≤ 100. The latter were determined from impedance spectroscopy of a pure sample.

The same batch of [hmim][BF$_4$] as in our previous studies[17,28] was used, and consequently, δ_{Lit} is within our claimed accuracy ($-0.30 \leq \delta_{Lit} \leq 0.95$). However, the measurements of Vila et al.[25] (commercial sample with purity > 99 %[26]) deviate considerably from the present results ($-50 \leq \delta_{Lit} \leq 16$; Figure 3).

[omim][BF$_4$] (Figure 4) was also studied by Vila et al.[25] Again, their data deviate strongly from our results ($-89 \leq \delta_{Lit} \leq 11$). On the other hand, generally quantitative agreement with the κ values determined by Kanakubo et al.[13] is found. These authors, claiming an uncertainty of ± 3 % from the average of three independent data sets, also eliminated the effects of electrode polarization. Only at the highest temperatures did the relative deviations increase to $\delta_{Lit} < 5.7$.

In addition to the data discussed above, Figures 2, 3, and 4 also show conductivities calculated from Vogel−Fulcher−Tammann parameters published by Leys et al.,[10] who determined $\kappa = f(T)$ for a series of imidazolium-based RTILs via dielectric spectroscopy over a frequency range of 1 Hz to 10 MHz. Significant deviations from the present results are obvious.

Two main reasons might explain the unsatisfactory agreement between the present κ values and most of the literature data.

Table 2. Parameters of the VFT Fits (eq 1) to the Electrical Conductivities (κ) and the Standard Uncertainties of the Overall Fits (σ_{fit})

	[emim][BF$_4$]	[bmim][BF$_4$]	[hmim][BF$_4$]	[omim][BF$_4$]
$\ln(A_\kappa/\text{S}\cdot\text{m}^{-1})$	4.951	5.112	5.187	5.179
B_κ/K	−607.5	−806.6	−983.9	−1119
$T_{0,\kappa}$/K	163.7	167.0	163.3	158.6
$B_\kappa/T_{0,\kappa}$	−3.712	−4.830	−6.038	−7.059
$10^2\cdot\sigma_{fit}$	0.3	3	5	5

Table 3. Densities (ρ) and Molar Conductivities (Λ) of the Investigated Ionic Liquids over the Temperature Range $5 \le t/°\mathrm{C} \le 65$[a]

	ρ/kg·m^{-3}				$10^4\cdot\Lambda$/S·m^2·mol^{-1}			
t/°C	[emim][BF$_4$]	[bmim][BF$_4$]	[hmim][BF$_4$]	[omim][BF$_4$]	[emim][BF$_4$]	[bmim][BF$_4$]	[hmim][BF$_4$]	[omim][BF$_4$]
5	1293.75	1215.43	1159.81	1116.79	1.076	0.211	0.0727	0.0364
15	1288.03	1209.33	1153.14	1110.36	1.654	0.394	0.1481	0.0772
25	1280.07	1202.08	1146.18	1103.60	2.39	0.666	0.273	0.1480
35	1272.48	1194.78	1139.15	1096.82	3.29	1.053	0.462	0.260
45	1265.12	1187.79	1132.31	1090.04	4.33	1.562	0.731	0.426
55	1256.89	1180.62	1125.18	1083.22	5.53	2.20	1.091	0.657
65	1250.24	1173.51	1118.54	1076.46	6.87	2.98	1.551	0.963

[a] The standard uncertainty of ρ is 0.05 kg·m^{-3}; the relative standard uncertainty of Λ is 0.5 %.

One reason is the measurement of κ itself. Most groups used commercial instruments that neglect (conductometers working at a single frequency) or inappropriately treat (dielectric spectroscopy with parallel-plate capacitors) electrode polarization. The best agreement was found with the data of Tokuda et al.[31] and Kanakubo et al.,[13] who corrected for this effect. The second reason is certainly the quality of the samples: although several authors used highly pure samples with stated purities, some did not. However, this alone is not sufficient to explain the large discrepancies between the different data sets. The generally claimed (published) degrees of (im)purity should not have such a large impact on κ.[17] A more likely cause is hydrolysis of the BF_4^- anion (during either sample preparation or the conductivity measurement itself), an effect which is generally overlooked.[17]

Glass Formation of the RTILs. Generally, transport properties Y (e.g., κ, η^{-1}, etc.) of glass-forming liquids above their glass-transition temperatures (T_g) can be described by the Vogel−Fulcher−Tammann (VFT) equation,

$$\ln(Y) = \ln(A_Y) + \frac{B_Y}{(T - T_{0,Y})} \tag{1}$$

where A_Y and B_Y are fit parameters and $T_{0,Y}$ is the so-called VFT temperature.[32]

As expected, the present κ data are also reasonably well described by eq 1 using the parameter values summarized in Table 2. Consistent with the literature,[32] the characteristic temperatures $T_{0,\kappa}$ obtained from fitting the values in Table 1 with eq 1 are (20 to 30) K below the T_g values determined via differential scanning calorimetry. For the present RTILs, the following T_g values can be found in the literature: (172.0[10] and 181[9]) K for [emim][BF$_4$]; (176,[33] 177.9,[10] 185.77,[34] 188,[9,35] 190,[31] 192,[29] and 202[36]) K for [bmim][BF$_4$]; (187.6[10] and 194[37]) K for [hmim][BF$_4$]; and (189.7[10] and 192[37]) K for [omim][BF$_4$]. Values for $T_{0,\kappa}$ were published by Kanakubo et al.,[13] Vila et al.,[25] and Leys et al.[10] As expected from the previous comparison of the conductivity data (Figures 1 through 4), only the result of Kanakubo et al.[13] for [omim][BF$_4$] ($T_{0,\kappa} = 166.88$ K) is in reasonable agreement with the present value (Table 2). While no general trend in the variation of $T_{0,\kappa}$ (and T_g) was found, the strength parameter $B_\kappa/T_{0,\kappa}$[32] decreases linearly with increasing number of C atoms in the alkyl chain (intercept −2.60 ± 0.07; slope −0.562 ± 0.012).

Molar Conductivities. Table 3 lists the molar conductivities, Λ, of the investigated RTILs over the temperature range $5 \le t/°\mathrm{C} \le 65$. For their calculation, reliable values of the molar concentration c and thus for the density ρ of the ionic liquids were required. As discussed previously,[17] the damping effect of viscous samples leads to systematic errors in the determination of ρ with vibrating-tube densimeters. To estimate the magnitude of the damping error, our data (Table 3) were compared to the values of Harris et al.,[12] who used an instrument with built-in viscosity correction (Anton Paar DMA 5000). The absolute deviations $\rho - \rho_{\mathrm{Lit}} < 1.1$ kg·m^{-3} clearly exceed the uncertainty of our densimeter and decrease with increasing temperature (decreasing viscosity), indicating that viscous damping of the vibrating tube is indeed the main cause. Accordingly, we corrected the raw ρ values as described by Heintz et al.[38] using the viscosity data of Harris et al.[12] This correction produced densities closer to the published data, but the absolute deviation still remained unacceptably high (<0.6 kg·m^{-3}). Since reliable viscosity data and/or more sophisticated correction procedures are currently not available, we refrain from giving corrected ρ values in Table 3. Nevertheless, this data can be used in the calculation of molar conductivities, since values of Λ calculated from corrected and uncorrected densities differ by less than 0.07 %, which is less than the relative uncertainty of κ and Λ (0.5 %).

For the investigated RTILs, Λ increases continuously with increasing temperature (a consequence of decreasing viscosity) and decreasing length of the alkyl chain (Figure 5). The temperature dependence of Λ is again well-described by the VFT equation (eq 1). The derived parameters are listed in Table 4, as they may be useful to readers for interpolation. It should be noted, however, that quantitative agreement between these values and the parameters deduced from a fit to $\kappa = f(T)$ (Table 2) cannot be expected because of the much more limited

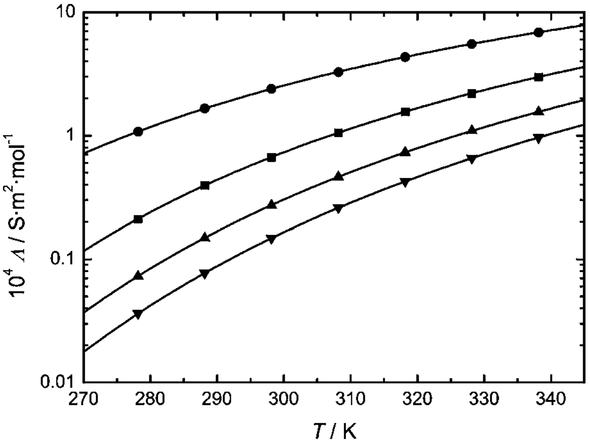

Figure 5. Molar conductivities (Λ) as functions of thermodynamic temperature (T): ●, [emim][BF$_4$]; ■, [bmim][BF$_4$]; ▲, [hmim][BF$_4$]; ▼, [omim][BF$_4$]. Lines are VFT fits (eq 1) calculated with parameters given in Table 4.

Table 4. Parameters of the VFT Fits (eq 1) of the Molar Conductivities (Λ) and the Standard Uncertainties of the Overall Fits (σ_{fit})

	[emim][BF$_4$]	[bmim][BF$_4$]	[hmim][BF$_4$]	[omim][BF$_4$]
ln (A_Λ/S·m^2·mol^{-1})	−3.672	−3.235	−2.905	−2.691
B_Λ/K	−639.0	−833.0	−1025	−1179
$T_{0,\Lambda}$/K	161.2	167.5	163.3	158.3
$10^3\cdot\sigma_{\mathrm{fit}}$	0.4	2	3	3

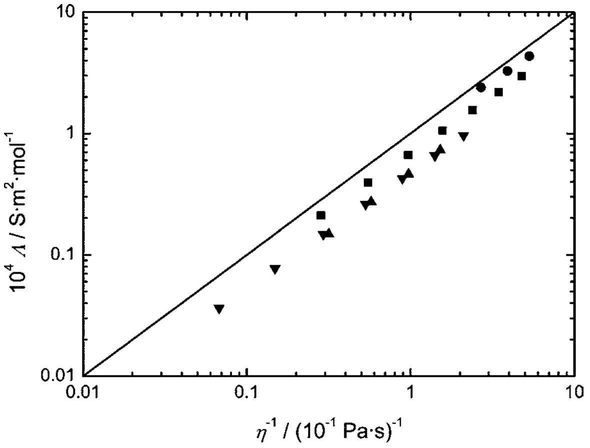

Figure 6. Walden plot for the RTILs: ●, [emim][BF$_4$]; ■, [bmim][BF$_4$]; ▲, [hmim][BF$_4$]; ▼, [omim][BF$_4$]. The solid line represents the "ideal" KCl line.

temperature range. As expected, our values of Λ agree well with the data published by Kanakubo et al.[13] ($-3.0 \leq \delta_{\mathrm{Lit}} \leq 4.0$) and Tokuda et al.[39] (Λ calculated from fit parameters given there; $-4.0 \leq \delta_{\mathrm{Lit}} \leq -2.5$).

The connection between viscosity (η) and molar conductivity is known as the Walden Rule,[40]

$$\Lambda \cdot \eta = \text{constant} \tag{2}$$

and is commonly displayed as a log−log plot of Λ versus fluidity (η^{-1}). Using selected viscosity data[11,12,14,41] yields the correlations shown in Figure 6. In contrast to some examples found in the literature,[40,42,43] the present data are fairly close to the "ideal" KCl line, which represents a completely dissociated electrolyte, so the studied compounds may be classified as "high-ionicity" RTILs. The deviations, which are connected to the degree of correlation in the motions of cations and anions, follow the series [emim]$^+$ < [bmim]$^+$ < [hmim]$^+$ ≈ [omim]$^+$ and may reflect the increasing degree of nanosegregation in these RTILs.[44]

Conclusions

Conductivities of the RTILs [emim][BF$_4$], [bmim][BF$_4$], [hmim][BF$_4$], and [omim][BF$_4$] over an extended temperature range ($-35 \leq t/°\mathrm{C} \leq 195$) have been reported. Our results conform with some of the published data, but large deviations from most of the available literature data are evident. We suppose inappropriate measurement protocols, including the neglect of BF$_4^-$ hydrolysis, to be the major reason for these discrepancies.

Additionally, the densities were measured over the temperature range $5 \leq t/°\mathrm{C} \leq 65$ and used to calculate molar conductivities. The temperature-dependent values $\kappa = f(T)$ and $\Lambda = f(T)$ were well-described by the VFT equation.

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