The Conductivity of Imidazolium-Based Ionic Liquids from (248 to 468) K. B. Variation of the Anion[†]

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The effect of the anion, namely dicyanamide, hexafluorophosphate, trifluoroacetate, or trifluoromethanesulfonate, on the conductivity (κ) of 1-*N*-butyl-3-*N*-methylimidazolium-based room-temperature ionic liquids (RTILs) was studied over the temperature range (248 to 468) K. The uncertainty in κ was estimated to be less than 0.5 %. The conductivity values obtained are well-described by the Vogel−Fulcher−Tammann equation. Additionally, densities (ρ) and the corresponding molar conductivities (Λ) are reported for the temperature range (278 to 338) K. The data for Λ and the associated viscosities (η) were found to fit fractional forms of the Walden relationship.

1. Introduction

Over the last several years, ionic liquids (ILs) have gained more and more attention because of their unique properties, such as negligible vapor pressure and high electrical conductivity and thermal stability, coupled with a wide liquid range.[1,2] These properties render ILs, especially room-temperature ILs (RTILs), excellent candidates for potential applications.[3,4] ILs can be applied as solvents in organic reactions or catalysis[5,6] and as media in extraction processes.[7] Other studies concern the use of ILs as electrolytes in batteries,[8] double-layer capacitors, or solar cells.[9,10]

In recent years, progress in the determination of thermodynamic and transport properties of RTILs has been made, with imidazolium-based compounds being in the focus of many studies. Various groups have studied the conductivity (κ) of imidazolium-based RTILs.[11−20] In general, however, the temperature ranges investigated have been rather limited, and the measurements have often been performed at a single frequency (thus neglecting electrode polarization) and/or with commercial samples of limited purity. In this contribution, we report precise conductivity data for the RTILs 1-*N*-butyl-3-*N*-methylimidazolium dicyanamide ([bmim][DCA]), 1-*N*-butyl-3-*N*-methylimidazolium hexafluorophosphate ([bmim][PF_6]), 1-*N*-butyl-3-*N*-methylimidazolium trifluoroacetate ([bmim][TA]), and 1-*N*-butyl-3-*N*-methylimidazolium trifluoromethanesulfonate ([bmim][TfO]) over the temperature range (248 to 468) K. This contribution on the anion dependence of RTIL conductivity complements a companion paper (DOI: 10.1021/je900789j) on the cation dependence of κ for a series of imidazolium tetrafluoroborates.[20]

2. Experimental Section

Chemicals. 1-Methylimidazole (Merck, ≥ 99 %) was distilled from KOH, stored over 4 Å molecular sieves, and redistilled prior to use. 1-Chlorobutane (Fluka, ≥ 99.5 %) was distilled prior to use. Sodium dicyanamide (Fluka, ≥ 96 %) was recrystallized from methanol (Merck, ≥ 99 %). Potassium hexafluorophosphate (Fluorochem, ≥ 99 %) was used as received. 1-Butylimidazole (ABCR, ≥ 99 %), methyl trifluoroacetate (ABCR, ≥ 99 %), and methyl trifluoromethanesulfonate (ABCR, ≥ 98 %) were distilled prior to use.

Synthesis and Sample Handling. [bmim][DCA] and [bmim][PF_6] were obtained by metathesis of 1-*N*-butyl-3-*N*-methylimidazolium chloride ([bmim][Cl]) and appropriate alkali metal salts, following the procedure of Cammarata et al.[21] with slight modifications.[19]

[bmim][TfO] and [bmim][TA] were prepared by slowly adding slight molar excesses (approximately 1:1.1) of methyl trifluoromethanesulfonate and methyl trifluoroactetate, respectively, to solutions of 1-butylimidazole (mass ratio 2:3) in acetonitrile (Merck, ≥ 99.9 %). Excess reactants were removed by vacuum distillation.

All of the RTILs were dried under high vacuum ($p < 10^{-8}$ bar) at 40 °C for 1 week, yielding (in the case of [bmim][DCA], [bmim][TA], and [bmim][TfO] slightly yellow) liquids with water mass fractions of $< 80 \cdot 10^{-6}$ (as determined by coulometric Karl Fischer titration using a Mitsubishi Moisturemeter MCI CA-02). Potentiometric titration of freshly prepared aqueous RTIL solutions against standardized $AgNO_3$(aq) yielded halide mass fractions of $< 50 \cdot 10^{-6}$ for [bmim][PF_6] and 0.0021 for [bmim][DCA]. No AgCl precipitation was observed when $AgNO_3$(aq) was added to [bmim][TA] or [bmim][TfO]. No contamination was detected by analysis using ^1H, ^{13}C, and (where applicable) ^{19}F NMR spectroscopy. The samples were stored in a N_2-filled glovebox; conductivity cells were filled under a nitrogen atmosphere.

Thermal stability was studied with a thermogravimetric analyzer (PerkinElmer model TGA 7). Samples were heated at a rate of 10 K·min^{-1}, applying a continuous nitrogen flow. Decomposition temperatures (T_{dec}) were taken as the onset of mass loss, defined as the intersection of the baseline before decomposition and the tangent to the mass loss afterward. The obtained T_{dec} values were 566 K for [bmim][DCA]; 710 K for [bmim][PF_6]; 689 K for [bmim][TfO]; and 461 K for [bmim][TA], which are in quite good agreement with literature data (573 K for [bmim][DCA];[22] 706 K for [bmim][PF_6];[13] 682 K[13] and 665 K[22] for [bmim][TfO]; and 449 K for [bmim][TA][13]).

Conductivity. Conductivity measurements were performed over the temperature range (248 to 468) K in steps of 10 K.

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Measurements in the low-temperature region [(248 to 298) K] were carried out with the equipment developed in the laboratory of J. Barthel.[23,24] For the high-temperature region [(308 to 468) K], a precision thermostat combined with a symmetrical Wheatstone bridge with Wagner earth, sine generator, and resistance decade was set up. Both thermostats were stable to < 0.003 K over the investigated temperature range. As bath fluids, silicone oil M5 (Roth) and silicone oil M50 (Roth) were used for the low- and high-temperature regions, respectively. A set of four three-electrode capillary cells with cell constants (a) between (25 and 470) m^{-1} was used for the low-temperature region (≤ 298 K), whereas a set of four two-electrode capillary cells with cell constants ranging from (1260 to 4610) m^{-1} was used at high temperatures. The cells were calibrated with aqueous KCl solutions having molalities ranging from (0.01 to 0.05) $\text{mol}\cdot\text{kg}^{-1}$ according to the procedure described by Barthel et al.[25] The accuracy of the cell constants was better than 0.5 %.

To eliminate electrode polarization effects, resistances (R) were measured at frequencies (ν) between 480 Hz and 10 kHz and extrapolated to $R_\infty = \lim_{\nu\to\infty} R(\nu)$ to yield $\kappa = a/R_\infty$, as described in the companion paper.[20] Repeated measurements on selected samples agreed within $\delta R/R = 0.3$ %. The relative uncertainty of the electrical conductivities was estimated to be < 0.5 %.[20]

Since the experiments covered an extremely wide temperature range, possible changes in the cell constants a had to be considered. The temperature dependence of $a(T)$ is essentially determined by the thermal expansion coefficients of the materials used for cell construction (platinum and Pyrex glass) and by the size and shape of the cell.[23,26] It can be expressed as

$$a(T) = a_0[1 + \beta(T - 298.15\ \text{K})] \tag{1}$$

where a_0 is the cell constant at 298.15 K and β is the temperature coefficient

$$\beta = \frac{1}{a_0}\left(\frac{\text{d}a}{\text{d}T}\right) \tag{2}$$

For capillary cells like those used in the present work, β has been found to be $-3.5\cdot10^{-6}\ \text{K}^{-1}$.[23] Thus, the temperature variation of a was negligible in the present measurements.

Density. To calculate molar conductivities (Λ), densities (ρ) of the RTILs were determined over the temperature range (278 to 338) K using a vibrating-tube densimeter (Anton Paar DMA 60). The instrument was calibrated at each measurement temperature with purified dry nitrogen and degassed Millipore water using precise density values from the literature.[27] The uncertainty in ρ was estimated to be < 0.05 kg m^{-3}. The relative uncertainty of Λ was thus estimated to be < 0.5 %.

3. Results and Discussion

The conductivity data obtained for the four RTILs are summarized in Table 1. [bmim][DCA] was investigated over the full temperature range (248 to 468) K, whereas [bmim][PF_6] and [bmim][TfO] could only be studied between (268 and 468) K because samples crystallized in the conductivity cells upon cooling to 258 K. For [bmim][TA], data between (248 and 368) K are reported, since the formation of bubbles was observed above 375 K. This effect may be related to a partial degradation of [bmim][TA] at these temperatures, although TGA experiments yielded a decomposition temperature of $T_{\text{dec}} = 461$ K. As even small amounts of impurities, including degradation products, can have significant effects on the conductivity of [bmim][TA], we have abstained from reporting κ values for T > 368 K.

Table 1. Conductivities (κ) of the Investigated RTILs

	$\kappa/\text{S}\cdot\text{m}^{-1}$			
T/K	[bmim][DCA]	[bmim][PF_6]	[bmim][TfO]	[bmim][TA]
248.15	0.0483			0.00858
258.15	0.1180			0.0244
268.15	0.242	0.0164	0.0539	0.0569
278.15	0.433	0.0385	0.1038	0.1144
288.15	0.702	0.0792	0.1808	0.205
298.15	1.052	0.1465	0.290	0.333
308.15	1.483	0.248	0.436	0.504
318.15	1.991	0.390	0.621	0.723
328.15	2.57	0.578	0.848	0.988
338.15	3.22	0.815	1.117	1.301
348.15	3.93	1.102	1.426	1.658
358.15	4.69	1.440	1.775	2.06
368.15	5.41	1.825	2.16	2.50
378.15	6.34	2.26	2.60	
388.15	7.26	2.74	3.04	
398.15	8.19	3.25	3.52	
408.15	9.15	3.81	4.03	
418.15	10.12	4.39	4.56	
428.15	11.12	5.01	5.12	
438.15	12.10	5.65	5.69	
448.15	13.09	6.31	6.28	
458.15	13.75	7.00	6.88	
468.15	14.54	7.69	7.50	

The present data for [bmim][DCA] (Figure 1) are in reasonable agreement with the κ value given by Yoshida et al. for 298 K.[16] However, they are systematically lower than those reported by Hunger et al.,[28] with relative deviations [$\delta_{\text{Lit}} = 100\cdot(\kappa - \kappa_{\text{Lit}})/\kappa$] given by $|\delta_{\text{Lit}}| \leq 11.3$ (Figure 1). A possible reason is the amount of halide impurities, for which ref 28 reported a mass fraction of 0.005, whereas that of the present sample is only 0.0021 (corresponding to a mole fraction of 0.02). Since the halide content of the present sample was still rather high, it is suspected that (currently unavailable) very pure [bmim][DCA] would have a notably lower conductivity.

For [bmim][PF_6] (Figure 2), conductivity data were reported by Widegren et al.[14] between (288.15 and 323.15) K, Suarez et al.[12] between (273.50 and 349.50) K, and Yu et al.[29] between (303.20 and 353.20) K. Furthermore, Kanakubo et al.[30] reported κ values obtained with two different cell types, namely, low-pressure cells used between (298.15 and 353.12) K and high-pressure cells covering (298.15 to 343.16) K. Whereas the data

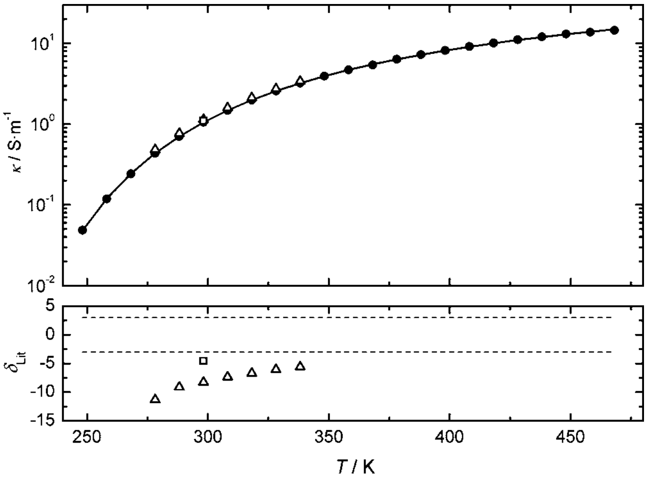

Figure 1. Specific conductivities (κ) of [bmim][DCA] from this study (●) along with literature κ values and their relative deviations from the present data [$\delta_{\text{Lit}} = 100\cdot(\kappa - \kappa_{\text{Lit}})/\kappa$]: △, Hunger et al.;[28] □, Yoshida et al.[16] The solid line is a fit of κ using eq 3 (see Table 2); dashed lines indicate an (arbitrary) $\delta_{\text{Lit}} = \pm$ 3 margin.

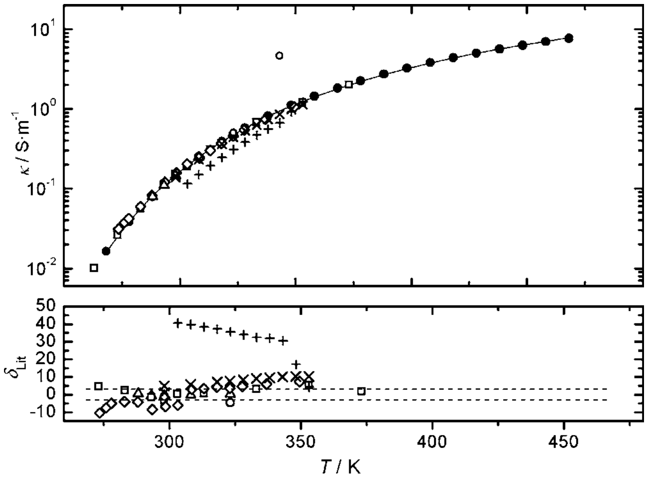

Figure 2. Specific conductivities of [bmim][PF$_6$] from this study (●) along with literature κ values and their relative deviations from the present data [$\delta_{Lit} = 100 \cdot (\kappa - \kappa_{Lit})/\kappa$]: △, Widegren et al.;[14] □, Tokuda et al.;[15] ◇, Suarez et al.;[12] +, Yu et al.;[29] ○, high pressure cell, and ×, low pressure cell, from Kanakubo et al.[30] The solid line is a fit of κ using eq 3 (see Table 2); dashed lines indicate an (arbitrary) $\delta_{Lit} = \pm\ 3$ margin.

Table 2. Parameters of the VFT Fits (Equation 1) with the Corresponding Standard Uncertainties of the Fit [σ_y, where $y = \ln(\kappa/\text{S}\cdot\text{m}^{-1})$]

	[bmim] [DCA]	[bmim] [PF$_6$]	[bmim] [TfO]	[bmim] [TA]	[bmim] [BF$_4$]^a
A/S·m^{-1}	104.3	131.1	95.1	103.5	166.0
B/K	−572.0	−818.1	−767.2	−737.3	−806.6
T_0/K	173.7	177.4	165.6	169.8	167.0
$100 \cdot \sigma_y$	1.0	1.6	0.3	0.7	3

[a] Data from ref 20.

of Widegren et al. are in excellent agreement with our results ($-0.6 \leq \delta_{Lit} \leq 0.6$), the values of Suarez et al. deviate considerably ($-10.4 \leq \delta_{Lit} \leq 7.5$). The conductivities reported by Yu et al. are systematically lower, with $\delta_{Lit} \leq 40.4$, whereas the κ values determined by Kanakubo et al. with their low-pressure cells are lower ($\delta_{Lit} \leq 10.3$) and those obtained with the high-pressure cells are higher ($\delta_{Lit} \leq -4.5$); the value reported for 343.16 K with $\delta_{Lit} = -390.7$ seems to be an outlier. The conductivities published by Tokuda et al.[15] for the temperature range (273.15 to 373.15) K also agree well with the present results ($-3.4 \leq \delta_{Lit} \leq 5.2$), except for the point at 263.15 K ($\delta_{Lit} = -144.9$).

Neglecting their lowest temperature, where our data were extrapolated using eq 3, the conductivities reported by Tokuda et al.[15] for [bmim][TfO] (Figure 3) over the temperature range (263.15 to 373.15) K are in very good agreement with the present data ($|\delta_{Lit}| \leq 3.8$). On the other hand, the κ values of Yu et al.[29] deviate considerably ($\delta_{Lit} \leq 36$), as does the result of Bonhôte et al.[11] for 293 K ($\delta_{Lit} \leq -60$).

For [bmim][TA], comparison is only possible with the conductivity data of Tokuda et al.[15] over the temperature range (263.15 and 373.15) K and the value at 293 K from Bonhôte et al.[11] (Figure 4). While the former are all systematically smaller ($\delta_{Lit} \leq 10.4$),[15] the latter is larger by 22 %.[11]

Similar to supercooled systems,[31] the conductivity of the present RTILs can be well-described by the empirical Vogel−Fulcher−Tammann (VFT) equation:

$$\ln(\kappa/\text{S}\cdot\text{m}^{-1}) = \ln(A/\text{S}\cdot\text{m}^{-1}) + \frac{B}{T - T_0} \qquad (3)$$

with fit parameters A, B, and T_0, where the latter is the so-called VFT temperature.[26] The values obtained for A, B, and

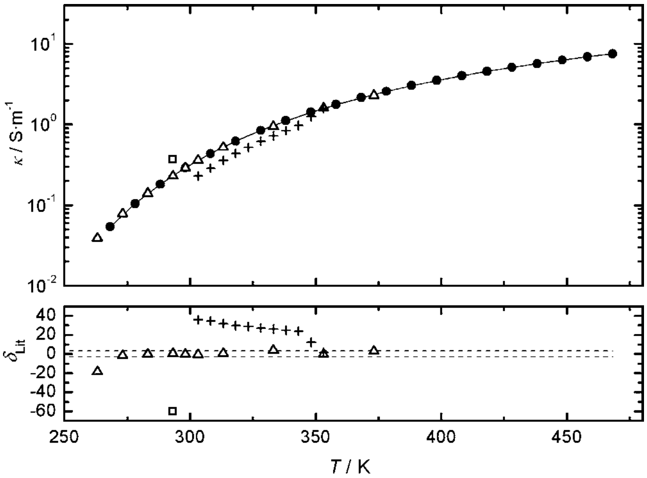

Figure 3. Specific conductivities of [bmim][TfO] from this study (●) along with literature κ values and their relative deviations from the present data [$\delta_{Lit} = 100 \cdot (\kappa - \kappa_{Lit})/\kappa$]: △, Tokuda et al.;[15] +, Yu et al.;[29] □, Bonhôte et al.[11] The solid line is a fit of κ using eq 3 (see Table 2); dashed lines indicate an (arbitrary) $\delta_{Lit} = \pm\ 3$ margin.

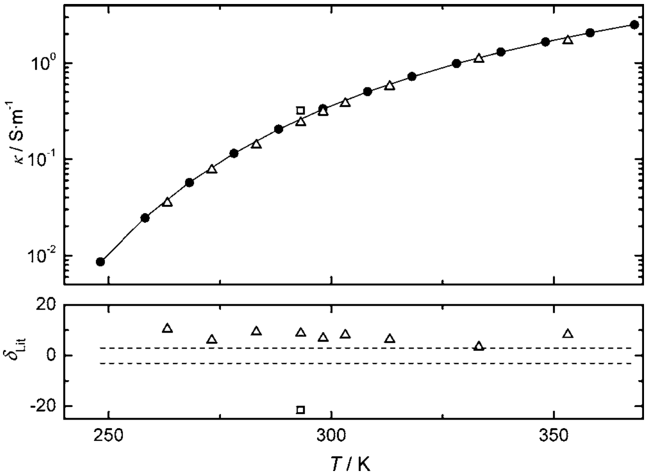

Figure 4. Specific conductivities of [bmim][TA] from this study (●) along with literature κ values and their relative deviations from the present data [$\delta_{Lit} = 100 \cdot (\kappa - \kappa_{Lit})/\kappa$]: △, Tokuda et al.;[15] □, Bonhôte et al.[11] The solid line is a fit of κ using eq 3 (see Table 2); dashed lines indicate an (arbitrary) $\delta_{Lit} = \pm\ 3$ margin.

T_0, which are similar to those for [bmim][BF$_4$],[20] are summarized in Table 2 together with the corresponding uncertainties of the fit [σ_y, where $y = \ln(\kappa/\text{S}\cdot\text{m}^{-1})$]. The fitted curves are shown as solid lines in Figures 1 through 4; deviations of the experimental data from the fits are too small to be shown in the lower panels of Figures 1 through 4.

Consistent with the literature,[27] the VFT temperatures (Table 2) are (20 to 30) K below the glass transition temperatures (T_g) determined using differential scanning calorimetry: 179 K[16] and 183 K[22] for [bmim][DCA]; 196 K,[13] 197 K,[22] and 196 K[32] for [bmim][PF$_6$]; 191 K[15] for [bmim][TfO], and 195 K[13] for [bmim][TA]. Tokuda and co-workers reported T_0 values of 174 K for [bmim][PF$_6$], 162 K for [bmim][TfO], and 172 K for [bmim][TA].[13] In view of the different temperature ranges of the two studies, the agreement of these T_0 values with the VFT temperatures of Table 2 is very good and reflects the generally excellent agreement of the experimental conductivities from the two investigations. In contrast to the behavior of the [C$_n$mim][BF$_4$] compounds studied in the companion paper,[20] where a linear dependence of the strength parameter B/T_0 on n, the number of carbon atoms in the N-alkyl chain, was observed,

Table 3. Densities (ρ) and Molar Conductivities (Λ) of the Investigated RTILs

	[bmim][DCA]		[bmim][PF$_6$]		[bmim][TfO]		[bmim][TA]	
	ρ	$10^4\cdot\Lambda$	ρ	$10^4\cdot\Lambda$	ρ	$10^4\cdot\Lambda$	ρ	$10^4\cdot\Lambda$
T/K	kg·m^{-3}	S·m^2·mol^{-1}	kg·m^{-3}	S·m^2·mol^{-1}	kg·m^{-3}	S·m^2·mol^{-1}	kg·m^{-3}	S·m^2·mol^{-1}
278.15	1072.22	0.830	1383.38	0.079	1313.19	0.228	1230.37	0.235
288.15	1066.15	1.352	1376.92	0.163	1305.51	0.399	1223.40	0.422
298.15	1059.62	2.038	1368.35	0.304	1297.43	0.644	1215.48	0.692
308.15	1053.35	2.89	1359.96	0.518	1289.31	0.974	1207.71	1.053
318.15	1047.26	3.90	1351.63	0.820	1281.61	1.398	1200.23	1.519
328.15	1040.87	5.07	1343.16	1.222	1273.62	1.920	1192.56	2.09
338.15	1034.72	6.39	1334.73	1.735	1265.83	2.54	1185.09	2.77

no general trends in A, B, T_0, or B/T_0 with variation of the anion of the [bmim]$^+$ RTILs could be found.

To calculate the molar conductivity, defined as $\Lambda = \kappa\cdot M\cdot\rho^{-1}$, where M is the molar mass of the RTIL, ρ values were measured between (278.15 and 338.15) K with a vibrating-tube densimeter. A viscosity correction[33] was not applied to the raw data for the reasons detailed in the companion paper.[20] The values obtained for ρ and Λ are summarized in Table 3.

According to Voronel et al.[34] and Veliyulin et al.,[35] fractional Walden relations of the form

$$\kappa\cdot T \propto D \propto \left(\frac{T}{\eta}\right)^t \qquad (4)$$

where D is the diffusion coefficient and η is the viscosity, are typical for ionic melts, with exponent values of $t \approx 0.8$ claimed to be universal. For imidazolium-based ILs, Kanakubo et al.[30] and Harris et al.[36] recently applied fractional Walden relations of the form

$$\Lambda\cdot T \propto \left(\frac{T}{\eta}\right)^t \qquad (5)$$

Both groups found good fits over the temperature ranges studied and obtained exponent values of $t \approx 0.9$ independent of pressure and temperature. For the RTILs [bmim][PF$_6$], [bmim][TfO], and [bmim][TA], for which fluidities (η^{-1}) are available,[13] fractional Walden plots according to eq 5 are shown in Figure 5. Good fits were obtained, with t values of 0.86 for [bmim][PF$_6$], 0.88 for [bmim][TfO], and 0.86 for [bmim][TA]. The present exponent for [bmim][PF$_6$] compares well with the value t = 0.91 reported by Kanakubo et al.[30] No significant effect of the anion on the exponent could be observed.

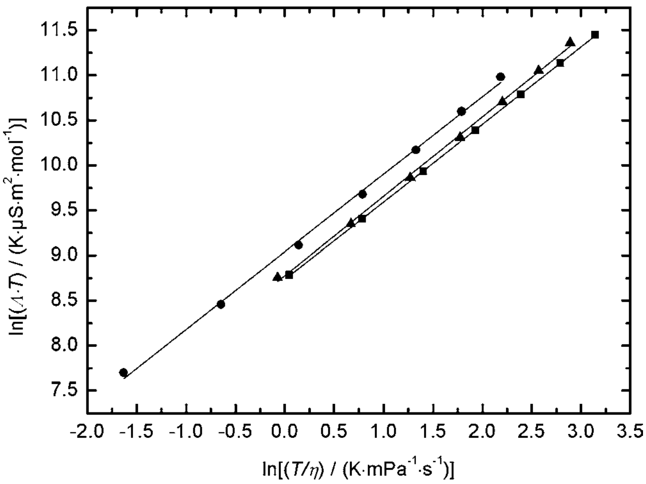

Figure 5. Fractional Walden plots [ln($\Lambda\cdot T$) vs ln(T/η)] for the following RTILs: ●, [bmim][PF$_6$]; ▲, [bmim][TfO]; □, [bmim][TA]. Required viscosities were calculated using VFT parameters from ref 13. Solid lines represent linear least-squares fits of the form $\ln[(\Lambda\cdot T)/(\text{K}\cdot\mu\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1})] = t\cdot\ln[(T/\eta)/(\text{K}\cdot\text{mPa}^{-1}\cdot\text{s}^{-1})] + C$.

4. Conclusion

In this study, where we benefited from the excellent thermal stability and wide liquid range of RTILs, the effect of different anions on the conductivity of highly pure [bmim]$^+$ RTILs has been investigated over the exceptionally wide temperature range (248 to 468) K, supplementing a companion paper on the cation dependence of κ for imidazolium-based RTILs. At a given temperature, the conductivity decreases in the order [bmim][DCA] > [bmim][TA] > [bmim][TfO] > [bmim][PF$_6$]. The temperature dependence is well-described by the VFT equation. While our data compare favorably with some literature results, significant deviations from others were noted. For the limited temperature range (278 to 338) K, where fluidities are available for [bmim][PF$_6$], [bmim][TfO], and [bmim][TA], the molar conductivity data were found to fit fractional forms of the Walden relationship. No systematic effect of the anion on the exponent t could be observed.

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