

Temperature and Concentration Dependence of Conductivities of Some New Semichelatoborates in Acetonitrile and Comparison with Other Borates

Tobias Herzig,[†] Christian Schreiner,[†] Hartmut Bruglachner,[†] Steffen Jordan,[†] Michael Schmidt,[‡] and Heiner J. Gores^{*,†}

Institut für Physikalische und Theoretische Chemie der Universität Regensburg, Universität Regensburg, D-93040 Regensburg, Germany, and Merck KGaA, D-64271 Darmstadt, Germany

Data on the temperature and concentration dependence of conductivities of some new ionic liquids based on the reduced symmetry of the semichelato-borate anion are presented and compared to data for the corresponding symmetrical chelato-borate and tetrafluoroborate salts. The compounds under investigation are the semichelato-borates tetraethylammonium difluoromono[1,2-oxalato(2-)-O,O']borate ([TEA][BF₂OX]) and the new 1-ethyl-3-methylimidazolium difluoromono[1,2-oxalato(2-)-O,O']borate ([EMIM][BF₂OX]), the chelato-borates tetraethylammonium bis[1,2-oxalato(2-)-O,O']borate ([TEA][B(OX)₂]) and the new 1-ethyl-3-methylimidazolium bis[1,2-oxalato(2-)-O,O']borate ([EMIM][B(OX)₂]), and the well-known tetrafluoroborates tetraethylammonium tetrafluoroborate ([TEA][BF₄]) and 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF₄]). The concentration dependence of conductivities of [TEA][BF₂OX], [EMIM][BF₂OX], [TEA][B(OX)₂], [EMIM][B(OX)₂], [TEA][BF₄], and [EMIM][BF₄] in pure acetonitrile was measured at 25 °C, 5 °C, -15 °C, and -35 °C and fitted to the Casteel–Amis equation. Data presented in this work should clarify the influence of reduced symmetry caused by the substitution of two fluorine atoms by the oxalate moiety in the borate anion on its conductivity behavior, especially at low temperatures.

Introduction

Double-layer capacitors (DLCs) are electrochemical devices for electrical energy storage.^{1,2} Their main advantages in comparison to the most important electrical energy storage devices, rechargeable batteries, are a far superior power density (more than 10⁴ W·kg⁻¹ vs about 10² W·kg⁻¹ for lithium-ion batteries) and a better cycleability (more than ca. 10⁵ vs ca. 10³ cycles) without appreciable loss in performance.^{1–4} Two major types of DLCs can be distinguished, with aqueous electrolytes and nonaqueous electrolytes, respectively. DLCs with aqueous electrolytes exhibit superior power density at lower energy density, whereas DLCs with nonaqueous electrolytes exhibit superior energy density but inferior power density due to the larger voltage window but lower conductivity of nonaqueous electrolytes. A search for better electrolytes or electrolytes with special features has been performed by several groups.^{5–10} This work includes synthesis of new salts, electrochemical characterization of electrolytes, DLC performance investigations, and studies of electrolyte conductivities, a key parameter for the power density of DLCs, which is closely related to ESR values as obtained from impedance spectroscopy.

In ref 11, we reported that for the tetraethylammonium salt [TEA][BF₂OX] the lower symmetry of the borate anion leads to a low melting point of 33 °C compared to the high melting point of 382 °C for [TEA][BF₄].¹² Salts with low melting points are known to have typically a very high solubility in many solvents, a feature that is important for double-layer capacitors at low temperatures.

In this work, the influence of structural modifications of the tetrafluoroborate anion on the specific conductivity, especially

Table 1. Specific Conductivities of [TEA][BF₂OX] in AN at Several Temperatures

<i>m</i>	κ_T mS·cm ⁻¹ (25 °C)	κ_T mS·cm ⁻¹ (5 °C)	κ_T mS·cm ⁻¹ (-15 °C)	κ_T mS·cm ⁻¹ (-35 °C)
mol·kg ⁻¹				
3.6	55.26	41.83	29.15	17.83
3.0	56.62	43.76	31.41	20.07
2.4	56.43	43.30	32.54	21.53
1.8	53.03	42.63	32.35	22.51
1.2	44.78	36.64	28.49	20.57
0.6	30.98	25.74	20.46	15.23

at low temperatures, is investigated. It should be primarily clarified what effect the substitution of fluorine atoms by the oxalate moiety has on the specific conductivity and the solubility at various temperatures. Therefore, the bisoxalato-borates [TEA][B(OX)₂] and [EMIM][B(OX)₂], with melting points of (118 and 56) °C,^{11,10} and the new ionic liquids based on the lower symmetric difluoromono[1,2-oxalato(2-)-O,O']borate anion, [TEA][BF₂OX] and [EMIM][BF₂OX], with melting points of (33 and 18) °C¹¹ were synthesized.

Experimental Section

All procedures related to electrolyte preparation, conductivity measurement, and cell filling were carried out in a nitrogen-filled glovebox (O₂ and H₂O < 10 ppm) (Mecaplex).

For electrolytic conductivity measurements, solutions of [TEA][BF₂OX], [EMIM][BF₂OX], [TEA][B(OX)₂], [EMIM][B(OX)₂], [TEA][BF₄], and [EMIM][BF₄] were prepared using highly pure acetonitrile (AN) (Merck, selectipur) with a very low water content [(10 to 30) ppm], as checked by coulometric Karl Fischer titration using a Mitsubishi Moisturemeter, model CA-20.

* Corresponding author. E-mail: heiner.gores@chemie.uni-regensburg.de.

[†] Universität Regensburg.

[‡] Merck KGaA.

Table 2. Fit Parameters (Casteel–Amis Equation) of [TEA][BF₂OX] in AN

	25 °C	5 °C	−15 °C	−35 °C
$\kappa_{\max}/\text{mS}\cdot\text{cm}^{-1}$	56.98 ± 0.18	44.43 ± 0.15	32.73 ± 0.13	22.29 ± 0.13
$\mu/\text{mol}\cdot\text{kg}^{-1}$	2.811 ± 0.023	2.555 ± 0.024	2.247 ± 0.032	1.889 ± 0.045
a	0.7157 ± 0.0516	0.7340 ± 0.0520	0.7592 ± 0.0645	0.8081 ± 0.0942
b	−0.0141 ± 0.0079	−0.0120 ± 0.0081	−0.0096 ± 0.0103	−0.0046 ± 0.0156
R^2	0.99993	0.99992	0.99987	0.99969

Table 3. Specific Conductivities of [TEA][B(OX)₂] in AN at Several Temperatures

m mol·kg ^{−1}	κ_T mS·cm ^{−1} (25 °C)	κ_T mS·cm ^{−1} (5 °C)	κ_T mS·cm ^{−1} (−15 °C)	κ_T mS·cm ^{−1} (−35 °C)
2.4	38.44	27.68	17.84	10.11
2.0	38.92	29.07	19.61	11.88
1.6	37.96	29.07	20.65	12.90
1.2	34.76	27.23	19.98	13.30
0.8	27.43	22.33	16.71	11.30
0.4	17.36	14.18	11.04	7.03

Table 4. Fit Parameters (Casteel–Amis Equation) of [TEA][B(OX)₂] in AN

	25 °C	5 °C	−15 °C	−35 °C
$\kappa_{\max}/\text{mS}\cdot\text{cm}^{-1}$	39.13 ± 0.22	29.33 ± 0.07	20.63 ± 0.11	13.27 ± 0.09
$\mu/\text{mol}\cdot\text{kg}^{-1}$	2.018 ± 0.046	1.792 ± 0.010	1.568 ± 0.019	1.365 ± 0.025
a	0.8525 ± 0.1070	0.8872 ± 0.0389	0.8088 ± 0.0865	1.143 ± 0.124
b	−0.0466 ± 0.0354	−0.0450 ± 0.0132	−0.0926 ± 0.0303	−0.0473 ± 0.0442
R^2	0.99976	0.99996	0.99980	0.99958

Table 5. Specific Conductivities of [TEA][BF₄] in AN at Several Temperatures^a

m mol·kg ^{−1}	κ_T mS·cm ^{−1} (25 °C)	κ_T mS·cm ^{−1} (5 °C)	κ_T mS·cm ^{−1} (−15 °C)	κ_T mS·cm ^{−1} (−35 °C)
3.6	63.99	—	—	—
3.0	63.98	—	—	—
2.4	61.70	49.57	37.58	—
1.8	55.81	45.74	35.59	—
1.2	45.73	37.99	30.11	22.30
0.6	32.52	26.75	21.16	18.03

^a Due to the limited solubility of [TEA][BF₄] at lower temperatures, conductivity measurements were not possible at lower temperatures for the more concentrated systems.

Table 6. Fit Parameters (Casteel–Amis Equation) of [TEA][BF₄] in AN^a

	25 °C	5 °C	−15 °C	−35 °C
$\kappa_{\max}/\text{mS}\cdot\text{cm}^{-1}$	64.48 ± 0.21	49.95 ± —	37.59 ± —	—
$\mu/\text{mol}\cdot\text{kg}^{-1}$	3.211 ± 0.056	2.655 ± —	2.445 ± —	—
a	0.4546 ± 0.0611	0.3539 ± —	0.4263 ± —	—
b	−0.0431 ± 0.0092	−0.0881 ± —	−0.0873 ± —	—
R^2	0.99991	1	1	—

^a Because of the limited solubility of [TEA][BF₄] at low temperatures, there were not enough data points to fit at −35 °C. For the same reason, at (−15 and 5) °C, no reasonable errors for the fit parameters can be given, as the number of data points is the same as the number of free fit parameters.

Table 7. Specific Conductivities of [EMIM][BF₂OX] in AN at Several Temperatures

m mol·kg ^{−1}	κ_T mS·cm ^{−1} (25 °C)	κ_T mS·cm ^{−1} (5 °C)	κ_T mS·cm ^{−1} (−15 °C)	κ_T mS·cm ^{−1} (−35 °C)
3.6	59.63	45.30	31.71	19.51
3.0	59.31	45.10	33.34	21.57
2.4	56.38	44.70	33.27	22.48
1.8	50.80	41.00	31.28	21.92
1.2	42.01	33.45	26.07	18.87
0.6	29.05	22.56	17.25	12.31

Synthesis, analysis, and physical and electrochemical properties of [EMIM][B(OX)₂], [TEA][BF₂OX], and [EMIM][BF₂OX] are given elsewhere.^{10,11} [TEA][B(OX)₂] was synthesized according to the synthesis of [EMIM][B(OX)₂].^{10,13} [EMIM][BF₄] was synthesized via an established method,¹⁴ and [TEA][BF₄] was used as received from Merck (selectipur grade).

Conductivity measurements have been carried out with an in-house built Wheatstone bridge, with Wagner earth, and a set of U-type cells with platinum electrodes as described else-

where.¹⁵ Cell constants covering the range from (27 to 89) cm^{−1} were calibrated precisely with standard methods (aqueous KCl solutions).

Resistances of the semichelato-borates [TEA][BF₂OX] and [EMIM][BF₂OX], the chelato-borates [TEA][B(OX)₂] and [EMIM][B(OX)₂], and the tetrafluoroborates [TEA][BF₄] and [EMIM][BF₄] were measured at frequencies of 3.5 kHz, 5.0 kHz, 6.5 kHz, and 8.0 kHz, respectively, and extrapolated to infinite frequency to get exact values (0.01 % range).

Table 8. Fit Parameters (Casteel–Amis Equation) of [EMIM][BF₂OX] in AN

	25 °C	5 °C	−15 °C	−35 °C
$\kappa_{\max}/\text{mS}\cdot\text{cm}^{-1}$	59.77 ± 0.03	46.15 ± 0.12	33.57 ± 0.06	22.56 ± 0.03
$\mu/\text{mol}\cdot\text{kg}^{-1}$	3.395 ± 0.011	3.044 ± 0.034	2.688 ± 0.012	2.288 ± 0.008
a	0.5483 ± 0.0078	0.6457 ± 0.0496	0.7733 ± 0.0307	0.9109 ± 0.0219
b	−0.0285 ± 0.0012	−0.0314 ± 0.0075	−0.0247 ± 0.0047	−0.0204 ± 0.0034
R^2	1	0.99994	0.99998	0.99999

Table 9. Specific Conductivities of [EMIM][B(OX)₂] in AN at Several Temperatures¹⁰

m mol·kg ^{−1}	κ_T mS·cm ^{−1} (25 °C)	κ_T mS·cm ^{−1} (5 °C)	κ_T mS·cm ^{−1} (−15 °C)	κ_T mS·cm ^{−1} (−35 °C)
2.42	41.35	29.92	19.53	10.84
2.00	41.52	30.71	20.72	12.14
1.40	40.07	30.55	21.55	13.53
1.03	36.27	28.33	20.69	13.70
0.58	27.92	22.37	16.93	11.82
0.30	18.70	15.23	11.80	8.52

Table 10. Fit Parameters (Casteel–Amis Equation) of [EMIM][B(OX)₂] in AN¹⁰

	25 °C	5 °C	−15 °C	−35 °C
$\kappa_{\max}/\text{mS}\cdot\text{cm}^{-1}$	41.69 ± 0.12	30.97 ± 0.08	21.53 ± 0.02	13.74 ± 0.02
$\mu/\text{mol}\cdot\text{kg}^{-1}$	2.050 ± 0.046	1.766 ± 0.014	1.463 ± 0.006	1.163 ± 0.007
a	0.7940 ± 0.0376	0.7993 ± 0.0264	0.8058 ± 0.0126	0.8181 ± 0.0161
b	0.0148 ± 0.0147	0.0200 ± 0.0106	0.0252 ± 0.0052	0.0305 ± 0.0069
R^2	0.99994	0.99997	0.99999	0.99998

Table 11. Specific Conductivities of [EMIM][BF₄] in AN at Several Temperatures

m mol·kg ^{−1}	κ_T mS·cm ^{−1} (25 °C)	κ_T mS·cm ^{−1} (5 °C)	κ_T mS·cm ^{−1} (−15 °C)	κ_T mS·cm ^{−1} (−35 °C)
5.00	66.79	51.67	37.25	24.10
4.00	65.32	51.86	38.71	26.33
3.00	60.75	49.18	37.71	26.64
2.00	51.41	42.48	33.44	24.51
1.00	34.58	29.08	23.42	17.74

Table 12. Fit Parameters (Casteel–Amis Equation) of [EMIM][BF₄] in AN

	25 °C	5 °C	−15 °C	−35 °C
$\kappa_{\max}/\text{mS}\cdot\text{cm}^{-1}$	66.80 ± 0.01	52.04 ± 0.03	38.69 ± 0.06	26.82 ± 0.07
$\mu/\text{mol}\cdot\text{kg}^{-1}$	5.125 ± 0.014	4.417 ± 0.020	3.817 ± 0.017	3.270 ± 0.029
a	0.8026 ± 0.0032	0.7873 ± 0.0137	0.7705 ± 0.0300	0.7409 ± 0.0521
b	0.0004 ± 0.0002	−0.0018 ± 0.0010	−0.0048 ± 0.0022	−0.0096 ± 0.0039
R^2	1	1	0.99999	0.99997

Table 13. Specific Conductivity Maxima, κ_{\max} , of [TEA][BF₂OX], [TEA][B(OX)₂], [TEA][BF₄], [EMIM][BF₂OX], [EMIM][B(OX)₂], and [EMIM][BF₄] in AN (Casteel–Amis)

$\kappa_{\max}/\text{mS}\cdot\text{cm}^{-1}$	25 °C	5 °C	−15 °C	−35 °C
([TEA][BF ₂ OX])	56.98 ± 0.18	44.43 ± 0.15	32.73 ± 0.13	22.29 ± 0.13
([TEA][B(OX) ₂])	39.13 ± 0.22	29.33 ± 0.07	20.63 ± 0.11	13.27 ± 0.09
([TEA][BF ₄])	64.48 ± 0.21	49.95 ± −	37.59 ± −	−
([EMIM][BF ₂ OX])	59.77 ± 0.03	46.15 ± 0.12	33.57 ± 0.06	22.56 ± 0.03
([EMIM][B(OX) ₂])	41.69 ± 0.12	30.97 ± 0.08	21.53 ± 0.02	13.74 ± 0.02
([EMIM][BF ₄])	66.80 ± 0.01	52.04 ± 0.03	38.69 ± 0.06	26.82 ± 0.07

Temperature was controlled to ± 0.005 K with the help of a thermostat coupled to a cryostat (for details see refs 15 and 16).

The conductivity cells containing ~3 mL of electrolyte solution (with AN as solvent) were filled in the glovebox, closed gastight with glass stopcocks, and then transferred to the thermostating bath.^{15,16}

The thermostat was checked with an F-250 MkII thermometer from Automatic Systems Laboratories (Milton Keynes, UK). The appertaining platinum thermometer was calibrated by WYCO (ROMSAY) according to UKAS with an accuracy of ± 10 mK. The temperature and concentration dependence of conductivity was then measured at (25, 5, −15, and −35) °C. The resistances were converted to specific conductivities κ as a function of molal concentration m and temperature T .

Results and Discussion

Conductivity data were fitted with the help of the empirical Casteel–Amis (CA) equation (eq 1).¹⁷

$$\kappa = \kappa_{\max} \left(\frac{m}{\mu} \right)^a \exp \left[b(m - \mu)^2 - \frac{a}{\mu} (m - \mu) \right] \quad (1)$$

In eq 1, κ_{\max} is the conductivity maximum attained at a given temperature and the corresponding molal concentration μ . a and b are empirical fit parameters without physical meaning (for details of the fitting procedure and its limitations, see ref 18). The nonlinear fits were carried out with Microcal Origin.

Experimental specific conductivity data, $\kappa_T = f(m)$, of [TEA][BF₂OX], [TEA][B(OX)₂], [TEA][BF₄], [EMIM]-[BF₂OX], [EMIM][B(OX)₂], and [EMIM][BF₄] in AN at several

Table 14. Molality Maxima, μ , of [TEA][BF₂OX], [TEA][B(OX)₂], [TEA][BF₄], [EMIM][BF₂OX], [EMIM][B(OX)₂], and [EMIM][BF₄] in AN (Casteel–Amis)

	μ		μ	
	mol·kg ⁻¹ (25 °C)	mol·kg ⁻¹ (5 °C)	mol·kg ⁻¹ (-15 °C)	mol·kg ⁻¹ (-35 °C)
([TEA][BF ₂ OX])	2.811 ± 0.030	2.555 ± 0.024	2.247 ± 0.032	1.889 ± 0.045
([TEA][B(OX) ₂])	2.018 ± 0.046	1.792 ± 0.010	1.568 ± 0.019	1.365 ± 0.025
([TEA][BF ₄])	3.211 ± 0.056	2.655 ± —	2.445 ± —	—
([EMIM][BF ₂ OX])	3.395 ± 0.011	3.044 ± 0.034	2.688 ± 0.012	2.288 ± 0.008
([EMIM][B(OX) ₂])	2.050 ± 0.046	1.766 ± 0.014	1.463 ± 0.006	1.163 ± 0.007
([EMIM][BF ₄])	5.125 ± 0.014	4.417 ± 0.020	3.817 ± 0.017	3.270 ± 0.029

Table 15. Values for the Walden Analogous Expression, $B = 10^3 \eta_0 (\kappa_{\max} / \mu)$, for [TEA][BF₂OX], [TEA][B(OX)₂], [TEA][BF₄], [EMIM][BF₂OX], [EMIM][B(OX)₂], and [EMIM][BF₄] in AN

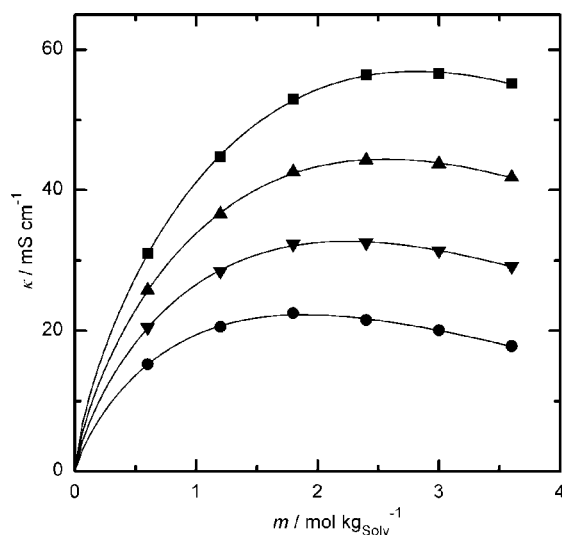
$\theta / ^\circ\text{C}$	B (25 °C)	B (5 °C)	B (-15 °C)	B (-35 °C)
[TEA][BF ₂ OX]	7.040	7.321	7.701	7.154
[TEA][B(OX) ₂]	6.734	6.891	6.956	5.894
[TEA][BF ₄]	6.974	7.921	8.128	—
[EMIM][BF ₂ OX]	6.114	6.383	6.603	5.978
[EMIM][B(OX) ₂]	7.063	7.383	7.781	7.163
[EMIM][BF ₄]	4.527	4.960	5.359	4.973

molalities, m , and temperatures, T , are listed in Tables 1, 3, 5, 7, 9, and 11. Corresponding fit parameters, the specific conductivity maximum κ_{\max} , the molal concentration μ of the electrolyte at κ_{\max} , and empirical fit parameters a and b are listed in Tables 2, 4, 6, 8, 10, and 12 together with appertaining standard deviations and R^2 . The number of figures given for the parameters κ_{\max} , μ , a , and b is needed to obtain a sufficient accordance of measured and calculated values. A fitted plot of κ_T vs molality m is given in Figure 1 as an example to show the quality of the Casteel–Amis fits. A summary of specific conductivity maxima κ_{\max} and the according molality maxima of all investigated salts is listed in Tables 13 and 14.

From Tables 13 and 14, it can be seen that in AN the maxima of specific conductivities, κ_{\max} , and the corresponding molalities, μ , of the tetraethylammonium salts decrease in the order of [TEA][BF₄] > [TEA][BF₂OX] > [TEA][B(OX)₂]. Thereby, κ_{\max} values of [TEA][BF₂OX] are more similar to those of [TEA][BF₄] than to those of [TEA][B(OX)₂]. At -35 °C, due to the limited solubility of [TEA][BF₄] at low temperatures, there were not enough data points to fit. [TEA][BF₂OX] did not precipitate in any investigated system, in contrast to [TEA][BF₄], which already precipitates at 5 °C at a concentration of 3.0 mol·kg⁻¹. The reason for the higher solubility of [TEA][BF₂OX] is the low interaction in the crystal lattice between cations and anions resulting in the low melting point of 33 °C, which is mainly caused by the reduced anion symmetry of [BF₂OX]⁻ vs the highly symmetrical [BF₄]⁻ anion. [TEA][B(OX)₂] did not precipitate at any investigated temperature and concentration as well, but κ_{\max} values of [TEA][B(OX)₂] cannot compete with those of [TEA][BF₄] and [TEA][BF₂OX] (cf. Table 13). The possible reason for this is the larger anion size of [TEA][B(OX)₂], which is a limiting factor for the ion mobility in the solution and thereby for its conductivity.^{19,20}

It can be summarized that the standard electrolyte, [TEA][BF₄], shows the best results for specific conductivities, κ_{\max} , at temperatures down to -15 °C. However, for low temperature applications (-35 °C), the specific conductivity maxima of [TEA][BF₂OX] are superior to those of [TEA][BF₄] due to the better solubility of [TEA][BF₂OX].

The maxima of specific conductivities in AN, κ_{\max} , and the corresponding molalities, μ , of the 1-ethyl-3-methylimidazolium salts decrease in the order of [EMIM][BF₄] > [EMIM][BF₂OX] > [EMIM][B(OX)₂] at any temperatures. Again, the κ_{\max} values

**Figure 1.** Specific conductivity κ_T vs molality m of [TEA][BF₂OX] in AN, $\kappa = f(m)$: ■, 25 °C; ▲, 5 °C; ▼, -15 °C; ●, -35 °C.

of the low symmetric [BF₂OX] salt are more similar to those of [EMIM][BF₄] than to the [EMIM][B(OX)₂] values (cf. Table 13, and [TEA][BF₂OX] vs [TEA][BF₄] and [TEA][B(OX)₂]).

Although, compared to the tetraethylammonium salts the 1-ethyl-3-methylimidazolium salts exhibit slightly higher specific conductivities at any temperatures, the main advantage of the tetraethylammonium salts is their easy availability with a much higher purity grade. Thereby, the tetraethylammonium salts ([TEA][BF₄], [TEA][BF₂OX], and [TEA][B(OX)₂]) can be synthesized by direct synthesis methods, which can exclude any halide impurities,^{10,11,13} whereas [EMIM][BF₄] and [EMIM][BF₂OX] are mostly prepared by metathesis reactions, making halide removal difficult.²¹

The importance of viscosity as a factor of a nonspecific hindrance of transport is illustrated in Table 15. A Walden analogous expression (eq 2), the product of the solvent viscosity η_0 and the mobility function at $m = \mu(\kappa_{\max}/\mu)$, is used to show the effect of the solvent viscosity η_0 and its temperature dependence.¹⁹ For η_0 of AN at various temperatures, see ref 22.

$$B = \eta_0 (\kappa_{\max} / \mu) \quad (2)$$

B -values of [TEA][BF₂OX], [TEA][B(OX)₂], [EMIM][BF₂OX], [EMIM][B(OX)₂], and [EMIM][BF₄] electrolyte solutions in AN calculated by eq 2 show roughly constant values approximately in the range 6 to 7. Only [EMIM][BF₄] shows a larger deviation; this deviation may be tentatively explained by a stronger ion–ion interaction. In contrast to [TEA] in [TEA][BF₄], the charge of the cation [EMIM] is not shielded by alkyl chains. Substitution of fluorine ligands by oxalate as in [EMIM][B(OX)₂] reduces this effect completely, whereas partial substitution as in [EMIM][BF₂OX] shows an intermediate behavior. The tentative explanation given here will be substanti-

ated by conductivity measurements at low concentrations to determine association constants.

Finally, the ratios $\kappa_{\max}([\text{EMIM}][\text{BF}_2\text{OX}])/\kappa_{\max}([\text{TEA}][\text{BF}_2\text{OX}])$ (1.03 ± 0.02) and $\kappa_{\max}([\text{EMIM}][\text{B}(\text{OX})_2])/\kappa_{\max}([\text{TEA}][\text{B}(\text{OX})_2])$ (1.04 ± 0.02) are found to be constant, independent from temperature, and are equal. The ratio $\kappa_{\max}([\text{EMIM}][\text{BF}_4])/\kappa_{\max}([\text{TEA}][\text{BF}_4])$ is also approximately constant at temperatures between (25 and -15) °C (1.04 ± 0.01).

Conclusion

To summarize, conductivities of some new ionic liquids with a semichelato-borate anion, tetraethylammonium difluoromono[1,2-oxalato(2-)-O,O']borate, and 1-ethyl-3-methylimidazolium difluoromono[1,2-oxalato(2-)-O,O']borate were measured in the temperature range (-35 to $+25$) °C in steps of 20 °C. The obtained specific conductivity maxima are compared with those of the according chelato-borates, the tetraethylammonium bis[1,2-oxalato(2-)-O,O']borate, and the new 1-ethyl-3-methylimidazolium bis[1,2-oxalato(2-)-O,O']borate and the well-known tetrafluoroborates, tetraethylammonium tetrafluoroborate and 1-ethyl-3-methylimidazolium tetrafluoroborate. The maxima of specific conductivities, κ_{\max} , and the according molalities, μ , of the 1-ethyl-3-methylimidazolium salts decrease in the order $[\text{EMIM}][\text{BF}_4] > [\text{EMIM}][\text{BF}_2\text{OX}] > [\text{EMIM}][\text{B}(\text{OX})_2]$ at any temperatures in AN as expected. A comparison of specific conductivity maxima of the pure tetraethylammonium borates, $[\text{TEA}][\text{BF}_2\text{OX}]$, $[\text{TEA}][\text{B}(\text{OX})_2]$, and $[\text{TEA}][\text{BF}_4]$, in AN shows that the specific conductivities of up to 64.48 $\text{mS}\cdot\text{cm}^{-1}$ at 25 °C decrease in the sequence: $[\text{TEA}][\text{BF}_4] > [\text{TEA}][\text{BF}_2\text{OX}] > [\text{TEA}][\text{B}(\text{OX})_2]$ at temperatures down to -15 °C.

Due to its better solubility, $[\text{TEA}][\text{BF}_2\text{OX}]$ may be useful as an alternative electrolyte for low temperature applications in electrochemical energy storage devices such as in double-layer capacitors.

Acknowledgment

The authors are grateful to Prof. B. E. Conway for suggestions. Prof. B. E. Conway acknowledges the opportunity of working at the University of Regensburg for a short time in the summer of 2002 sponsored by the Vielberth-Regensburger-Universitätsstiftung. Professor Brian E. Conway passed away on July 8, 2005, at his home in Ottawa, Canada.

Literature Cited

- Conway, B. E. *Electrochemical Supercapacitors*; Kluwer Academic/Plenum Publishers: New York, 1999.
- Kötz, R.; Carlen, M. Principles and applications of electrochemical capacitors. *Electrochim. Acta* **2000**, *45*, 2483–2498.
- Kötz, R.; Bartschi, M.; Buchi, F.; Gallay, R.; Dietrich, P. HY.POWER - A Fuel Cell Car Boosted with Supercapacitors. Proceedings of the 12th International Seminar on Double Layer Capacitors and Similar Energy Storage Devices, Deerfield Beach, USA, Dec 9–11 **2002**.
- Schnewly, A.; Bartschi, M.; Hermann, V.; Sartorelli, G.; Gallay, R.; Kötz, R. BOOSTCAP Double-Layer Capacitors for Peak Power Automotive Applications, *Proceedings of the Second International ADVANCED AUTOMOTIVE BATTERY Conference (AABC)*, Las Vegas, NV, Feb. 2002.
- McEwen, A. B.; McDevitt, S. F.; Koch, V. R. Nonaqueous Electrolytes for Electrochemical Capacitors: Imidazolium Cations and Inorganic Fluorides with Organic Carbonates. *J. Electrochem. Soc.* **1997**, *144*, L84–L86.
- McEwen, A. B.; Ngo, H. L.; LeCompte, K.; Goldman, J. L. Electrochemical Properties of Imidazolium Salt Electrolytes for Electrochemical Capacitor Applications. *J. Electrochem. Soc.* **1999**, *146*, 1687–1695.
- Ue, M.; Takeda, M.; Toriumi, A.; Kominato, A.; Hagiwara, R.; Ito, Y. Application of Low-Viscosity Ionic Liquid to the Electrolyte of Double-Layer Capacitors. *J. Electrochem. Soc.* **2003**, *150*, A499–A502.
- Sato, T.; Masuda, G.; Takagi, K. Electrochemical properties of novel ionic liquids for electric double layer capacitor applications. *Electrochim. Acta* **2004**, *49*, 3603–3611.
- Kim, Y. J.; Matsuzawa, Y.; Ozaki, S.; Park, K. C.; Kim, C.; Endo, M.; Yoshida, H.; Masuda, G.; Sato, T.; Dresselhaus, M. S. High Energy-Density Capacitor Based on Ammonium Salt Type Ionic Liquids and Their Mixing Effect by Propylene Carbonate. *J. Electrochem. Soc.* **2005**, *152*, A710–A715.
- Bruglachner, H.; Jordan, S.; Schmidt, M.; Schwake, A.; Conway, B. E.; Barthel, J.; Geissler, W.; Gores, H. J. New Electrolytes for Electrochemical Double Layer Capacitors. Synthesis and Electrochemical Properties of 1-Ethyl-3-methylimidazolium bis[1,2-oxalato(2-)-O,O']borate. *J. New Mater. Electrochem. Syst.* **2006**, *9*, 209–220.
- Herzig, T.; Schreiner, C.; Gerhard, D.; Wasserscheid, P.; Gores, H. J. Characterisation and Properties of New Ionic Liquids with the Difluoromono[1,2-oxalato(2-)-O,O']borate Anion. *J. Fluorine Chem.* **2007**, *128*, 612–618.
- Xu, K.; Ding, M. S.; Jow, T. R. Quaternary Onium Salts as Nonaqueous Electrolytes for Electrochemical Capacitors. *J. Electrochem. Soc.* **2001**, *148*, A267–A274.
- Ebina, T.; Uno, H.; Ishizawa, S.; Nanbu, N.; Sasaki, Y. Use of Tetraethylammonium Bis(oxalato)borate as Electrolyte for Electrical Double-layer Capacitors. *Chem. Lett.* **2005**, *34*, 1014–1015.
- Wachter, P.; Schreiner, C.; Zistler, M.; Gerhard, D.; Wasserscheid, P.; Gores, H. J. A microelectrode study of triiodide diffusion coefficients in mixtures of room temperature ionic liquids, useful for dye-sensitized solar cells. *Microchim. Acta* **2007**, in print, DOI 10.1007/s00604-007-0803-2.
- Barthel, J.; Wachter, R.; Gores, H. J. *Modern Aspects of Electrochemistry*; Bockris, J. O'M.; Conway, B. E., Eds.; Plenum: NY, 1979; Vol. 13, pp 1–79.
- Wachter, R.; Barthel, J. Studies on the temperature dependence of properties of electrolyte solutions. Part II. Conductivity determination over a large temperature range. *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 634–642.
- Casteel, F.; Amis, E. S. Specific Conductance of Concentrated Solutions of Magnesium Salts in Water-Ethanol System. *J. Chem. Eng. Data* **1972**, *17*, 55–59.
- Barthel, J.; Gores, H. J.; Schmeer, G. The temperature dependence of the properties of electrolyte solutions. III. Conductance of various salts at high concentrations in propylene carbonate at temperatures from -45 °C to $+25$ °C. *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 911–920.
- Barthel, J.; Wachter, R.; Gores, H. J. Temperature Dependence of Conductance of Electrolytes in Nonaqueous Solutions. In *Modern Aspects of Electrochemistry*; Bockris, J. O'M, Conway, B. E., Eds.; Plenum: NY, 1979; Vol. 13, pp 1–79.
- Barthel, J.; Gores, H. J. *Solution Chemistry: A Cutting Edge in Modern Electrochemical Technology*, in: *Chemistry of Nonaqueous Solutions. Current Progress*; Mamantov, G., Popov, A. I., Eds.; VCH: NY, 1994; pp 1–148, Chapter 1.
- Hagiwara, R.; Ito, Y. Room temperature ionic liquids of alkylimidazolium cations and fluoroanions. *J. Fluorine Chem.* **2000**, *105*, 221–227.
- Wolf, R. R.; Conductance measurements of lithium and tetraethylammonium electrolytes in butylene carbonate and acetonitrile. Ph. D. Thesis, University of Regensburg, 1996.

Received for review September 12, 2007. Accepted November 29, 2007. The authors are grateful to Merck, KgaA, Darmstadt and to the Deutsche Forschungsgemeinschaft (DFG Priority Project Ionic Liquids SPP 1191) for funding.

JE700525H