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Studies of Physicochemical and Thermodynamic Properties of the Paramagnetic 1-Alkyl-3-methylimidazolium Ionic Liquids $(EMIm)_2[Co(NCS)_4]$ and $(BMIm)_2[Co(NCS)_4]$[†]

Monika Geppert-Rybczyńska,[*,‡,‖] Jochen K. Lehmann,[‡] Tim Peppel,[§] Martin Köckerling,[§] and Andreas Heintz[‡]

University of Rostock, Institute of Chemistry, Department of Physical Chemistry, Dr.-Lorenz-Weg 1, 18059 Rostock, Germany, and University of Rostock, Institute of Chemistry, Department of Inorganic Chemistry, Albert-Einstein-Str. 3a, 18059 Rostock, Germany

This paper describes selected thermophysical properties of the newly obtained paramagnetic inky, opaque ionic liquid, 1-butyl-3-methylimidazolium tetraisothiocyanato-cobaltate(II) ($(BMIm)_2[Co(NCS)_4]$). Some properties of the homologous ionic liquid (IL), 1-ethyl-3-methylimidazolium tetraisothiocyanato-cobaltate(II) ($(EMIm)_2[Co(NCS)_4]$), have been presented earlier and are discussed here together with those for $(BMIm)_2[(Co(NCS)_4]$. On the basis of experimental densities, kinematic viscosities, conductivities, and surface tensions, some additional parameters have been determined, i.e., expansivity coefficients and surface thermodynamic properties. The influence of structural variation in the 1-alkyl-3-methylimidazolium cation is also discussed.

Introduction

It is well-known that ionic liquids play an increasing role in chemical engineering and physical chemistry as alternative solvents, media for new catalytic processes, electrolytes in flexible solar cells, and electrochemical synthesis of surfaces.[1−6] They are also used as extraction media for selective dissolution of cellulose,[7] as thermofluids, and in many other fields.[2,3,8] More recently, the first paramagnetic ionic liquids have been obtained[9,10] containing the anion $[FeCl_4]^-$. Very recently also the first low viscous paramagnetic ionic liquids have been synthesized (with Co^{2+} ion), and some of their properties as solvent for organic solutes have been studied.[11,12]

In this work, we present some physicochemical and thermodynamic properties and their temperature dependence for the new paramagnetic ionic liquid $(BMIm)_2[Co(NCS)_4]$ (with the ionic charges ratio 1:2) and the comparison of these results with those for $(EMIm)_2[Co(NCS)_4]$ published previously.[12]

Experimental Section

Chemicals. The inky room-temperature ionic liquid $(BMIm)_2[Co(NCS)_4]$ ($M = 569.70\ g\cdot mol^{-1}$) was synthesized as described for $(EMIm)_2[Co(NCS)_4]$ ($M = 513.59\ g\cdot mol^{-1}$).[12] All details concerning the synthesis, purification, and structure have been presented in that reference. Also, the experimental treatment for determining the thermophysical properties in the case of $(BMIm)_2[Co(NCS)_4]$ was similar to that for $(EMIm)_2[Co(NCS)_4]$.[12] $(BMIm)_2[Co(NCS)_4]$ was dried directly before all measurements and degassed under vacuum [(1 to 2) days]. The water mass fraction detected by Karl Fischer titration (TitroLine KF Trace, Schott) was $1.3\cdot 10^{-3}$.

Measurements. Temperature-dependent measurements of the density, ρ, were performed using the vibrating tube densimeter Anton Paar/Austria DMA 602[13,14] in the temperature range from (288.15 to 323.15) K with intervals of 5 K. The measuring set was calibrated at each temperature using bidistilled water and dry air. The Anton Paar DMA 602 device has no internal viscosity correction, so the raw densities were recalculated knowing the viscosities of samples according to the equation provided by the producer ($\Delta\rho/\rho = (-0.5 + 0.55\cdot\sqrt{\eta})\cdot 10^{-4}$). The experimental uncertainty is equal to $\pm\ 2\cdot 10^{-5}\ g\cdot cm^{-3}$.

Kinematic viscosities, ν, were determined with an Ubbelhode viscometer system CT 1150 (Schott−Geräte GmbH, Hofheim, capillary no. III) in the temperature range from (288.15 to 323.15) K, in steps of 5 K. The viscosimeter was calibrated with mineral oils. About 20 mL of sample was used, and the measurements were repeated 5 to 10 times. Also, a time correction for the viscous flow was applied as well. The estimated uncertainty was better than $0.25\ mm^2\cdot s^{-1}$.

Surface tensions, σ, were measured with the DSA 10 Kruss Tensiometer (with Drop Shape Analysis Software) using the pendant drop method. The temperature range was (288.15 to 318.15) K with steps of 5 K. Some of the instrumental details and the experimental procedures have been described previously.[15] For each temperature, the sample was analyzed several times. In our case, uncertainty did not exceed $0.05\ mN\cdot m^{-1}$ for $(BMIm)_2[Co(NCS)_4]$, while for $(EMIm)_2[Co(NCS)_4]$ we achieved earlier uncertainties of $(0.4\ to\ 0.7)\ mN\cdot m^{-1}$.[12] The repeatability for $(BMIm)_2[Co(NCS)_4]$ was the same order as the uncertainties.

Conductivities, κ, were measured with a Microprocessor Conductivity Meter WTW LF 537, equipped with an WTW/Tetracon 96 electrode of a cell constant, equal to $0.605\ cm^{-1}$. The cell was calibrated using a standard aqueous KCl solution and checked by measurements of conductivity of $(EMIm)[NTf_2]$. The maximal difference between our and literature values[16] is not larger than 1 %. The temperatures were measured by a platinum thermometer (placed in the measuring cell) with a

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[*] Corresponding author. E-mail: monikageppert@wp.pl; mong@o2.pl.

[‡] Department of Physical Chemistry.

[§] Department of Inorganic Chemistry.

[‖] Permanent address: University of Silesia, Institute of Chemistry, Department of Physical Chemistry, Szkolna 9, 40-006, Katowice, Poland.

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Table 1. Densities and Kinematic Viscosities of $(BMIm)_2[Co(NCS)_4]$

T / K	ρ^a / $(g \cdot cm^{-3})$	T / K	ν / $(mm^2 \cdot s^{-1})$
288.15	1.22862	288.15	562.32
293.15	1.22534	293.25	374.62
298.15	1.22201	298.15	257.78
303.15	1.21865	303.55	180.03
308.15	1.21516	308.15	135.77
313.15	1.21175	313.15	102.09
318.15	1.20825	318.15	78.00
323.15	1.20481	323.15	61.21

[a] Values after viscosity correction.

Table 2. Surface Tensions and Conductivities of $(BMIm)_2[Co(NCS)_4]$

T / K	σ / $(mN \cdot m^{-1})$	T / K	κ / $(S \cdot m^{-1})$
288.15	50.18 (0.03)[a]	288.2	0.066
293.15	49.84 (0.05)	293.2	0.096
298.15	49.54 (0.05)	298.2	0.134
303.15	49.19 (0.05)	303.4	0.185
308.15	48.92 (0.04)	308.2	0.248
313.15	48.54 (0.04)	313.2	0.325
318.15	48.28 (0.04)	318.2	0.408
		323.1	0.510
		328.2	0.627
		333.2	0.755

[a] Standard deviations of the mean value.

resolution of 0.01 K, but the uncertainty of these temperature measurements was at a level of ± 0.05 K.

Results and Discussion

Results of Measurements and Some Correlations. The physical properties, density, and kinematic viscosity of $(BMIm)_2[Co(NCS)_4]$ were measured from (288.15 to 323.15) K, the conductivity from (288.15 to 333.15) K, and the surface tension from (288.15 to 318.15) K in general steps of 5 K. The experimental values are summarized in Tables 1 and 2.

Densities and surface tensions of $(BMIm)_2[Co(NCS)_4]$ were correlated as a function of temperature

$$\rho/(g \cdot cm^{-3}) = 1.42526 - 6.819 \cdot 10^{-4} \cdot T/K \quad (s = 9 \cdot 10^{-5}\ g \cdot cm^{-3}) \tag{1}$$

$$\sigma/(mN \cdot m^{-1}) = 68.53 - 6.37 \cdot 10^{-2} \cdot T/K \quad (s = 2.6 \cdot 10^{-2}\ mN \cdot m^{-1}) \tag{2}$$

where s is the standard deviation, derived from the regression line.

Figures 1 and 2 show the temperature dependence of the density and surface tension of $(BMIm)_2[Co(NCS)_4]$ together with the data obtained earlier for $(EMIm)_2[Co(NCS)_4]$.[12]

From Figures 1 and 2, it is visible that the temperature dependencies of ρ and σ of both ionic liquids are comparable. This fact is not surprising, when compounds differ only in two $-CH_2-$ groups in the hydrocarbon chain of the cation. Both properties, the density and surface tension of $(BMIm)_2[Co(NCS)_4]$, are lower than those of $(EMIm)_2[Co(NCS)_4]$. Thus, this is in general accordance with the data in the literature for 1:1 ionic liquids. For example, for ILs with the same cations as ours but with anions like $[NTf_2]^-$, $[BF_4]^-$, $[GaCl_4]^-$, or $[FeCl_4]^-$, the densities of BMImX are about 5 % lower than for EMImX, while surface tensions are lower by about (10 to 20) %.[9,16−20]

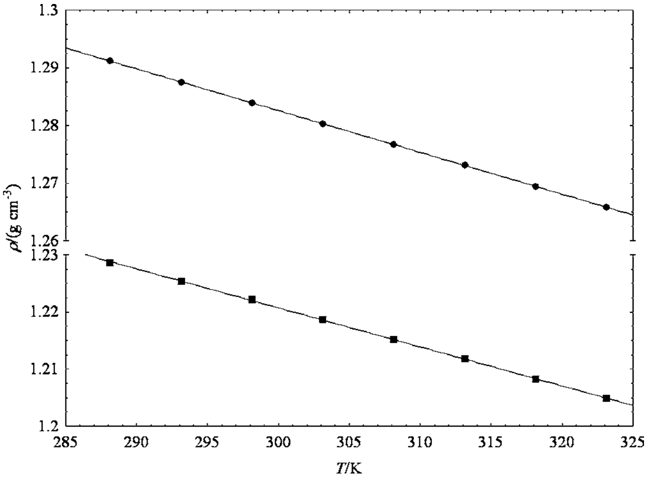

Figure 1. Plot of the temperature dependence of the experimental density: ■, for $(BMIm)_2[Co(NCS)_4]$ obtained in this study; ●, for $(EMIm)_2[Co(NCS)_4]$ taken from ref 12; lines were drawn on the basis of eq 1.

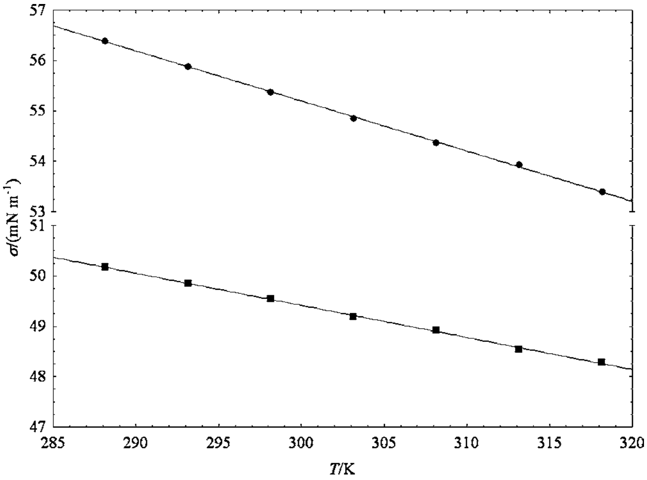

Figure 2. Plot of the temperature dependence of the surface tension: ■, for $(BMIm)_2[Co(NCS)_4]$ obtained in this study; ●, for $(EMIm)_2[Co(NCS)_4]$ taken from ref 12; lines were drawn on the basis of eq 2.

Generally, densities and surface tensions of both ionic liquids under study resemble the values for ρ and σ of $EMIm[BF_4]$ and $BMIm[BF_4]$. At 298.15 K, densities of $EMIm[BF_4]$ and $BMIm[BF_4]$ are (1.280 38 and 1.202 19) $g \cdot cm^{-3}$, respectively,[17] and surface tensions are (54.50 and 43.6) $mN \cdot m^{-1}$.[19,20] It is also remarkable that $(EMIm)_2[Co(NCS)_4]$ as well as $(BMIm)_2[Co(NCS)_4]$ have surface tensions lower than that of water (71.8 $mN \cdot m^{-1}$ at 298 K[21]) but higher than for many other ionic liquids; their values are even higher than those of ILs containing metals in the anion, i.e., $EMIm[GaCl_4]$ ($\sigma = 50$ $mN \cdot m^{-1}$ (room temperature)[18]).

The temperature dependencies of the absolute viscosity ($\eta = \nu \cdot \rho$) and the conductivity κ can be described using the Vogel−Fulcher−Tamman equation (VTF)[22−24]

$$\eta = \eta_0 \cdot \exp(B/(T - T_0)) \tag{3}$$

$$\kappa = \kappa_0 \cdot \exp(-B'/(T - T_0')) \tag{4}$$

where η_0, κ_0, B, B', T_0, and T_0' are fit parameters, collected in Table 3.

Table 3. Fit Parameters of the VTF Equations Applied to the Absolute Viscosity, Equation 3, and the Ionic Conductivity, Equation 4, of $(BMIm)_2[Co(NCS)_4]$

η_0 (mPa·s)	B K	T_0 K	r
0.08 ± 0.03	952 ± 87	182.5 ± 5.2	0.9999
κ_0 (S·m^{-1})	B' K	T'_0 K	r
90 ± 15	631 ± 39	208 ± 5	0.9999

In Figures 3 and 4, the absolute viscosities and conductivities of $(BMIm)_2[Co(NCS)_4]$ are presented as a function of T together with η data for $(EMIm)_2[Co(NCS)_4]$ taken from our previous work.[12]

Figures 3 and 4 show that absolute viscosities of $(BMIm)_2[Co(NCS)_4]$ are significantly higher than those of $(EMIm)_2[Co(NCS)_4]$; the opposite behavior has been observed for the conductivities. Generally, 1-ethyl- and 1-butyl-3-methylimidazolium ionic liquids vary in their viscosities. The range of η values goes from 32.6 mPa·s at 298.15 K for $(EMIm)[NTf_2]$[16] to 1110 mPa·s at 298.15 K for BMImI.[25] So the result obtained for $(BMIm)_2[Co(NCS)_4]$ (315.46 mPa·s at 298.15 K) fits into this range. However, for ionic liquids containing a metal in a univalent anion, viscosities are usually lower, like 43 mPa·s (at 298.15 K) for $BMIm[FeCl_4]$.[9]

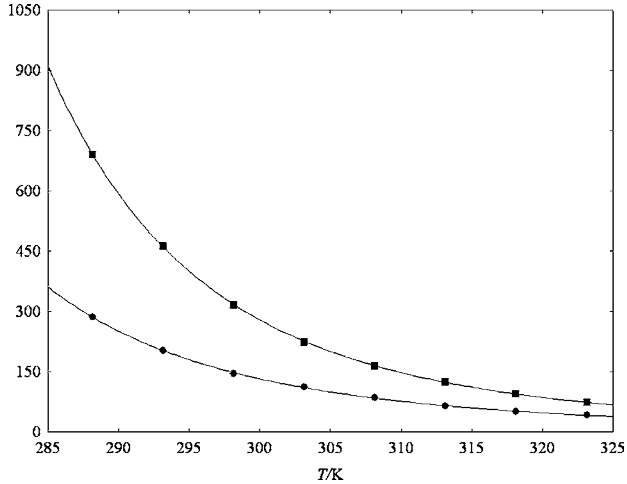

Figure 3. Absolute viscosity against T: ■, for $(BMIm)_2[Co(NCS)_4]$; ●, for $(EMIm)_2[Co(NCS)_4]$ taken from ref 12; lines were drawn on the basis of eq 3.

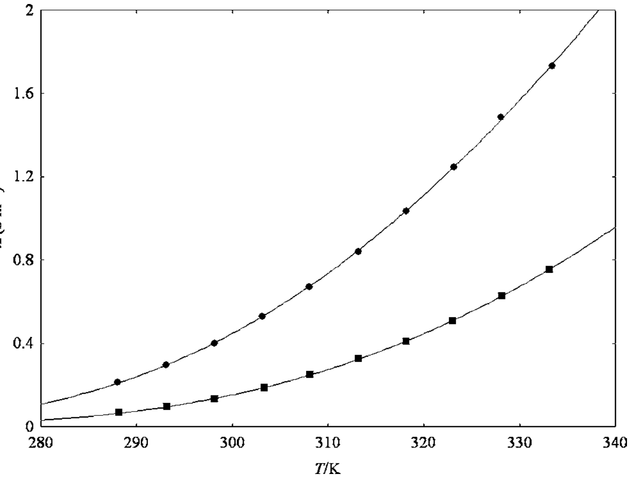

Figure 4. Conductivity against T: ■, for $(BMIm)_2[Co(NCS)_4]$; ●, for $(EMIm)_2[Co(NCS)_4]$ taken from ref 12; lines were drawn on the basis of eq 4.

The conductivities of $(BMIm)_2[Co(NCS)_4]$ are lower than those of $(EMIm)_2[Co(NCS)_4]$ and also a little bit lower than the conductivities of ILs with metal (i.e., 0.89 S·m^{-1} at 298.15 K for $BMIm[FeCl_4]$[9]) or other 1-ethyl- and 1-butyl-3-methylimidazolium ionic liquids (0.35 S·m^{-1} at 298.15 K for $BMIm[BF_4]$[17]).

Finally, it can be said that elongation of the alkyl chain in 3-methylimidazolium-based IL (from EMIm to BMIm) is associated with lower density, higher viscosity, and lower surface tension as well as lower conductivity. The viscosities are higher and electrical conductivities lower, respectively, than those of 1:1 ionic liquids, most probably due to larger size and stronger association of 1:2 ionic liquids, as $(RMIm)_2[Co(NCS)_4]$.

Volumetric and Surface Properties. On the basis of the temperature dependence of density, the thermal expansion coefficient was calculated according to the equation

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = -\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_p \qquad (5)$$

Because all ionic liquids have a very weak variation of α with the temperature, it is generally good enough to regard this coefficient at 298.15 K. For $(BMIm)_2[Co(NCS)_4]$, it is equal to $5.58 \cdot 10^{-4}$ K^{-1}, whereas for $(EMIm)_2[Co(NCS)_4]$, using the density data given in Peppel et al.,[12] $\alpha = 5.64 \cdot 10^{-4}$ K^{-1}. Generally, thermal expansion coefficients of many imidazolium, pyridinum, and pyrrolidinium ILs are very similar and vary from $(5.1 \text{ to } 6.2) \cdot 10^{-4}$ K^{-1}.[26] These values are smaller than α of many traditional solvents (i.e., for 1-propanol at 298.15 K, $\alpha = 10.04 \cdot 10^{-4}$ K^{-1}),[27] but for some of them, like for 1,4-butanediol, the thermal expansion coefficient is also small: $5.69 \cdot 10^{-4}$ K^{-1}.[28] It is quite probable that this small variation of the thermal expansivity of ILs arises from the presence of strong interactions between ions, which are not very sensitive to the temperature.

Surface tension of many liquids almost linearly decrease with the temperature, according to the Eötvös equation

$$\sigma V^{2/3} = k \cdot (T_c - T) \qquad (6)$$

where V is the molar volume of the liquid; T_c is the critical temperature; and k is an empirical constant. k found by a plot of $\sigma V^{2/3}$ versus temperature is $(2.736 \pm 0.060) \cdot 10^{-7}$ J·mol$^{-2/3}$·K^{-1} for $(BMIm)_2[Co(NCS)_4]$ and $(4.283 \pm 0.046) \cdot 10^{-7}$ J·mol$^{-2/3}$·K^{-1} for $(EMIm)_2[Co(NCS)_4]$. An average value of k found for many typical substances is about $2.45 \cdot 10^{-7}$ J·mol$^{-2/3}$·K^{-1},[29] regardless of their polarity. On the other side, for ILs containing a metal complex anion, values of k are close to $1.7 \cdot 10^{-7}$ J·mol$^{-2/3}$·K^{-1}.[30] The higher value of k obtained for $(EMIm)_2[Co(NCS)_4]$ is probably a particular property of 1:2 ionic liquids.

From the temperature dependence of the surface tension (eq 2), the surface entropy is calculated by $S_a = (\partial\sigma/\partial T)_p$ and the surface enthalpy by $H_a = \sigma - T \cdot (\partial\sigma/\partial T)_p$.[31] The surface entropy of $(BMIm)_2[Co(NCS)_4]$ is $63.7 \cdot 10^{-6}$ J·m^{-2}·K^{-1} and of $(EMIm)_2[Co(NCS)_4]$ is $99.43 \cdot 10^{-6}$ J·m^{-2}·K^{-1}. Both values are higher than S_a for other ILs containing a metal complex anion, i.e., for $BMIm[FeCl_4]$ ($55.8 \cdot 10^{-6}$ J·m^{-2}·K^{-1})[32] or for $PMIm[InCl_4]$ ($58.29 \cdot 10^{-6}$ J·m^{-2}·K^{-1})[30] but is in the same order as for molten alkali halogenide salts (i.e., $91 \cdot 10^{-6}$ J·m^{-2}·K^{-1}) such as RbCl (calculated on the basis of data given by ref 33) or for some alcohols (i.e., $98 \cdot 10^{-6}$ J·m^{-2}·K^{-1} for ethanol[34]).

Table 4. Surface Enthalpies of $(BMIm)_2[Co(NCS)_4]$ and $(EMIm)_2[Co(NCS)_4]$

	$H_a \cdot 10^3/(J \cdot m^{-2})$	
T/K	$(BMIm)_2[Co(NCS)_4]$	$(EMIm)_2[Co(NCS)_4]$
288.15	31.82	27.74
293.15	31.17	26.73
298.15	30.55	25.72
303.15	29.88	24.71
308.15	29.29	23.72
313.15	28.59	22.78
318.15	28.01	21.75

Table 5. Molar Conductivities Λ of $(BMIm)_2[Co(NCS)_4]$ and $(EMIm)_2[Co(NCS)_4]$

T	$\Lambda \cdot 10^4/(S \cdot m^2 \cdot mol^{-1})$	T	$\Lambda \cdot 10^4/(S \cdot m^2 \cdot mol^{-1})$
K	$(BMIm)_2[Co(NCS)_4]$	K	$(EMIm)_2[Co(NCS)_4]$
288.2	0.305	288.1	0.847
293.2	0.446	293.1	1.183
298.2	0.626	298.2	1.600
303.4	0.865	303.2	2.114
308.2	1.163	308.1	2.707
313.2	1.528	313.2	3.389
318.2	1.924	318.2	4.188
323.1	2.411	323.2	5.060
328.2	2.973	328.1	6.050
333.2	3.590	333.5	7.069

Surface enthalpies of $(BMIm)_2[Co(NCS)_4]$ and $(EMIm)_2[Co(NCS)_4]$ are collected in Table 4.

These values are significantly lower than those of other ionic liquids containing metal atoms in the anion (i.e., for PMIm[$InCl_4$], $H_a = 60.82 \cdot 10^{-3}$ J·m^{-2},[30] or for BMIm[$FeCl_4$], $H_a = 62.6 \cdot 10^{-3}$ J·m^{-2} at 298.15 K[32]) or other methylimidazolium-based salts like EMIm[NTf_2] ($56.63 \cdot 10^{-3}$ J·m^{-2} at 298.15 K[35]). Such small values, as for $(BMIm)_2[Co(NCS)_4]$ and $(EMIm)_2[Co(NCS)_4]$, were observed before for some ionic liquids like BMIm[$MeSO_4$] and EMIm[$EtSO_4$], (25.77 and 31.06)·10^{-3} J·m^{-2} at 303.15 K.[36]

Another interesting quantity, which can be derived from our data, is the molar conductivity: $\Lambda = \kappa \cdot M \cdot \rho^{-1}$, where M is the molar mass of the IL. For both ionic liquids, $(BMIm)_2[Co(NCS)_4]$ and $(EMIm)_2[Co(NCS)_4]$ results of Λ are collected in Table 5.

As for the conductivities, values of Λ of $(BMIm)_2[Co(NCS)_4]$ and $(EMIm)_2[Co(NCS)_4]$ are not very high. For example, EMIm[$FeCl_4$] and BMIm[$FeCl_4$] have larger values of (4.4 and 2.2)·10^{-4} S·m^2·mol^{-1} at 298.15 K, respectively.[10]

Another interesting relationship is the Walden Product (so-called fractional Walden rule)

$$\Lambda_0 \eta^b = C \tag{7}$$

where Λ_0 is the limiting molar conductivity; C is a specific constant; and b is often close to unity. The theoretical basis of this equation and its use were described very often in the past, recently also by refs 10, 37, and 38 in the context of ionic liquids. Here we try to test eq 7 using Λ_0 and η taken from their dependence on temperature for the pure ionic liquids.

The linearized form

$$\lg \Lambda_0 = \lg C' + b \cdot \lg \eta^{-1} \tag{8}$$

is plotted in Figure 5 for $(BMIm)_2[Co(NCS)_4]$ and $(EMIm)_2[Co(NCS)_4]$.

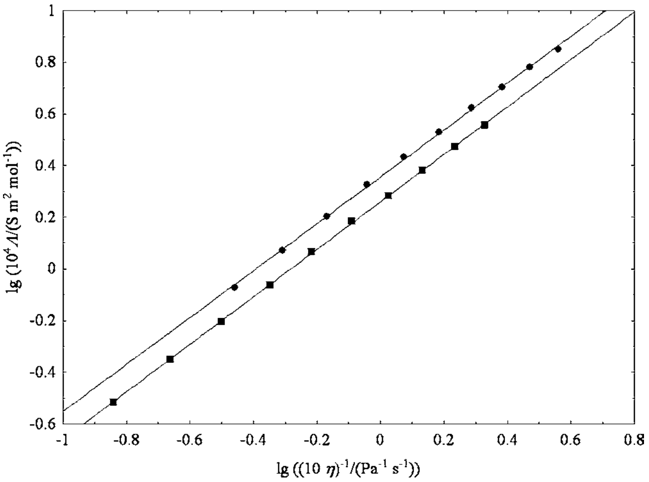

Figure 5. Fractional Walden plot: ■, for $(BMIm)_2[Co(NCS)_4]$ from data obtained in this study; ●, for $(EMIm)_2[Co(NCS)_4]$ on the basis of data taken from ref 12 (η obtained from VTF polynomial); lines represent eq 8.

From the linear regression analysis, the slopes $b = (0.920 \pm 0.004)$ for $(BMIm)_2[Co(NCS)_4]$ and (0.908 ± 0.008) for $(EMIm)_2[Co(NCS)_4]$, so they are in agreement with the results reported for 1-ethyl- or 1-butyl-methylimidazolium salts of $[BF_4]^-$, $[NTf_2]^-$, $[DCA]^-$, $[PF_6]^-$, and $[TA]^-$ anions, where $b \approx 0.9$ has been found.[37,38] The practical consequence of the results obtained is that the viscosities can be estimated easily when the molar conductivities are known (using eq 8).

After analysis of selected properties of paramagnetic inky ionic liquids $(BMIm)_2[Co(NCS)_4]$ and $(EMIm)_2[Co(NCS)_4]$, it can be concluded that they resemble the typical imidazolium-based ionic liquids like EMIm[BF_4] or BMIm[BF_4] rather than those containing a metal in the anion like BMIm[$FeCl_4$]. They have higher viscosities and surface tensions (as well as different surface properties) and lower conductivities than BMIm[$FeCl_4$], PMIm[$InCl_4$], and EMIm[$GaCl_4$]. However, their conductivity–viscosity behavior (Walden Plot) compares closely to the corresponding plots of some 1-ethyl- or 1-butyl-methylimidazolium salts. After all, shortening the length of the alkyl chain in 3-methylimidazolium-based ILs (from BMIm to EMIm) changes their properties in the expected way.

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