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Fractional Walden Rule for Ionic Liquids: Examples from Recent Measurements and a Critique of the So-Called Ideal KCl Line for the Walden Plot[†]

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Temperature-dependent conductivity, viscosity, and density of four ionic liquids (ILs), 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF_4]), 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF_4]), 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([EMIM][NTf_2]), and 1-ethyl-3-methylimidazolium dicyanamide ([EMIM][DCA]), were measured with high precision from +80 °C down to −35 °C, if possible. Fitting parameters for the Vogel−Fulcher−Tammann (VFT) equation were obtained for conductivity and viscosity data, and obtained data were analyzed with the help of the fractional Walden rule and the Walden plot. Excellent linear behavior is observed for all ILs; however, the average slope is not unity as expected for the ideal Walden rule, but 0.92 ± 0.02. The so-called ideal KCl line that is used to compare ILs within the Walden plot is discussed, as literature data for aqueous KCl solutions show that its assumed ideality has to be modified.

Introduction

The Walden plot has been used increasingly in the last years to illustrate the conductivity−viscosity relationship of pure ionic liquids (ILs) and draw conclusions on the extent of, for example, ion association, by comparing the ILs' graph to the graph of a so-called ideal electrolyte solution, typically a 1-molar aqueous KCl solution.[1−8]

In 1906, P. Walden published his empirically discovered relation known as the Walden rule.[9] It states that the product of the limiting molar conductivity Λ_m^0 and the pure solvent's viscosity η is constant for infinitely diluted electrolyte solutions, as expressed by eq 1.

$$\Lambda_m^0 \eta = C = \text{constant} \tag{1}$$

$$\log \Lambda_m^0 = \log C + \log \eta^{-1} \tag{2}$$

It has been found empirically that the Walden rule is often obeyed well, especially by solutions of large and only weakly coordinating ions in solvents with nonspecific ion−solvent interactions. In this case, ion mobility and hence conductivity are solely governed by ion migration, according to the Stokes−Einstein equation; see eq 3.[10,11]

$$D_i^0 = u_i k T \tag{3}$$

where D_i^0 is the diffusion coefficient of an ion i, u_i is its mobility, k is the Boltzmann's constant, and T is the absolute temperature. The mobility is linked to the single ion conductivity λ_i^0 via

$$\lambda_i^0 = z_i F u_i \tag{4}$$

yielding

$$\lambda_i^0 \eta = \frac{e_0 z_i F}{f} \frac{1}{R_i} \tag{5}$$

and for a 1,1-salt

$$\Lambda_m^0 \eta = \frac{e_0 F}{f} \frac{1}{(R_+ + R_-)} = C \tag{6}$$

where e_0 is the elementary charge, z_i the charge of the ion, and F Faraday's constant. f is a factor based on Stokes law ($f = 6\pi$ for perfect stick or $f = 4\pi$ for perfect slip), and R_i is the Stokes radius of the ion, that is, the ionic radius plus a contribution due to solvation of the ion by solvent molecules. R_+ and R_- are the Stokes radii of the cation and anion, respectively. To avoid size variation effects of solubilized ions dissolved in different solvents, these should preferably interact only weakly and/or at least in a similar manner with the electrolytes' ions. This assists comparable ion coordination behavior, and by eliminating specific solvent−solute interactions, the solvents' viscosity is the only key property determining the solutions' conductivity.

Walden's rule is often used to estimate the limiting molar conductivity $\Lambda_m{}^0$ of salts when they cannot be obtained by fits to the conductivity equation. For example, strong association as known for many salts in solvents of low dielectric permittivity often then entails unrealistic Λ^0 values and K_A values. This is a problem of data analysis caused by the large extrapolation of very small Λ_i values at the lowest concentration of a run when compared with the expected Λ^0 value. Improved estimates for Λ^0 are obtained with the help of the Walden rule at constant temperature T, if Λ^0 is known for the electrolyte in another solvent (2) where a small association constant does not prohibit its determination and η is known for both solvents (1,2).

$$\left\{ \frac{\Lambda_0^{(1)}}{\Lambda_0^{(2)}} = \frac{\eta^{(2)}}{\eta^{(1)}} \right\}_T \tag{7}$$

Thereafter, Λ^0 is fixed in the subsequent fitting procedure, and reliable K_A and R[11] values are obtained.

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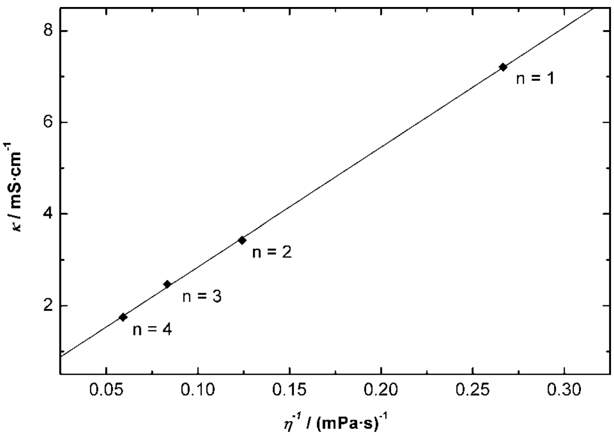

Figure 1. Conductivity of 1 M $LiAsF_6$ in sulfolane/glyme mixtures (1:1) for glymes $n = 1$ to $n = 4$, redrawn from data in ref 16.

If the temperature dependence of conductivity of a given salt is known in a given solvent, a much better estimate of an unknown Λ^0 for high temperatures (T_2) that cannot be obtained by fits due to strong association at high temperatures can be obtained by fits of conductivity data at lower temperatures (T_1) with the help of the Walden rule:

$$\frac{\Lambda_0^{(T_1)}}{\Lambda_0^{(T_2)}} = \frac{\eta^{(T_2)}}{\eta^{(T_1)}} \tag{8}$$

For a recent application of the Walden rule for mixed solvents see refs 12 to 14 and for molten salts, ref 15.

Unexpectedly, the Walden rule can also be used for concentrated electrolyte solutions, as shown in many studies related to lithium-ion battery research.[11] To give an example, in 1:1 sulfolane/glyme mixtures with glymes of different chain length ($CH_3O(C_2H_4O)_nCH_3$, $n = 1, 2, 3, 4$), Dudley et al.[16] obtained for 1 M $LiAsF_6$ a linear relation for specific conductivity and fluidity $\phi = \eta^{-1}$, see Figure 1.

Examples from this group include linear plots of κ_{max} versus $R_+{}^{-1}$ for tetraalkylammonium hexafluorophosphates at every temperature and linear plots of κ_{max} versus μ (the concentration where κ is κ_{max}) at every temperature.[11]

According to eq 2, the relation between solvents' viscosities and electrolytes' limiting molar conductivities can be plotted in a logarithmic plot, the so-called Walden plot. Limiting molar conductivities of an electrolyte in a series of solvents should fall on a straight line with a slope of 1. Different electrolytes of course do not necessarily need to fall on the same line, as their C values, that is, R_+ and R_- values, vary according to eq 6. By introducing an additional exponent α in eq 1, a fractional Walden rule (eqs 9 and 10) can be obtained that allows the slope to vary in the corresponding Walden plot,[5,17,18] and by linear data fitting, the exponent is gathered together with the graph's intercept, log C'.

$$\Lambda_m^0 \eta^\alpha = C' = \text{constant} \tag{9}$$

$$\log \Lambda_m^0 = \log C' + \alpha \log \eta^{-1} \tag{10}$$

If viscosity and conductivity data of neat ILs were measured at the very same temperatures, results can be correlated in the Walden plot in the same manner as for electrolyte solutions. Limiting molar conductivities of pure ILs are obtained according to eq 11 from specific conductivities κ and molar volumes V_m which in turn are obtained from ILs' densities ρ and molar masses M.

$$\Lambda_m^0 = \kappa V_m = \kappa \frac{M}{\rho} \tag{11}$$

Experimental Section

Materials. Used ILs 1-ethyl-3-methylimidazolium tetrafluoroborate ($[EMIM][BF_4]$),[19] 1-butyl-3-methylimidazolium tetrafluoroborate ($[BMIM][BF_4]$),[20] 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[EMIM][NTf_2]$),[19] and 1-ethyl-3-methylimidazolium dicyanamide ([EMIM][DCA])[19] were synthesized according to previously published procedures. All used ILs had a water content of less than 30 ppm, checked by Karl Fischer titration (Mettler, Karl Fischer titrator DL18), and the chloride and bromide contents of all used $[BF_4]$ and $[NTf_2]$ ILs were below 30 ppm as well (potentiometric titration with $AgNO_3$; however, this procedure was not possible for [EMIM][DCA] due to the coprecipitation of AgDCA). Storage and handling of ILs was done in an argon-filled glovebox (MBraun, type MB150BG, O_2 and $H_2O < 1$ ppm).

Conductivity Measurements. Conductivity measurements were carried out with an in-house built symmetrical Wheatstone bridge, with Wagner earth, resistance decade, and sine generator as described by Wachter et al.[21] The conductivity cells were filled and sealed gas-tight in the glovebox under argon atmosphere and then transferred to the thermostat bath. Applied cells with cell constants in the range from (38 to 91) cm^{-1} were previously calibrated with aqueous KCl solutions.[22] The electrolyte resistances were measured at frequencies of (1.7, 3.2, 5.1, 6.5, 7.7, and 10.1) kHz, respectively, and extrapolated to infinite frequency. Temperature control for conductivity and viscosity measurements was ensured by using the thermostat assembly described in detail in refs 21 and 23. With this assembly a temperature stability of ± 2 mK was achieved. The actual temperatures of measurements were monitored using an ASL F-250 MkII thermometer (Automatic Systems Laboratories). On the basis of the calibration of individual measuring cells, the estimated uncertainty of the measured specific conductivities is in the range of (0.2 to 0.4) %.

Viscosity Measurements. Viscosities were measured with a modified automated AVS/G capillary viscometer (Schott) as described in ref 24, using a micro-Ubbelohde capillary viscometer (Schott Instruments, type 537 20/II) placed in a Dewar flask that was connected to the high-precision thermostat with a circulation pump, allowing a temperature control of ± 3 mK. In-house built modifications allowed keeping samples under dry nitrogen throughout the whole measurement procedure to prevent any water uptake from air. The manufacturers' original capillary calibrations were confirmed successfully and improved with a certified viscosity standard oil (50 BW, ZMK-Analytik, relative uncertainty 0.32 %) at (20, 23, 25, 30, and 40) °C, with a flow time reproducibility better than ± 0.05 % of the actual time readings for individual calibration runs, with a resolution of 0.01 s.

For the actual measurements, ILs' flow times were measured automatically by the viscometer's control unit for all given temperatures. Obtained viscosities are the average values from (3 to >10) single runs. On the basis of temperature and calibration standard's accuracy and measurement reproducibility, the estimated relative uncertainty of presented viscosities is about 0.5 %.

Density Measurements. ILs' densities were determined with a precision densitometer DMA 60/DMA 602 from Anton Paar in a temperature range from (25 to 60) °C. Temperature control (better than ± 0.02 K) was maintained by a RK 8 KP thermostat

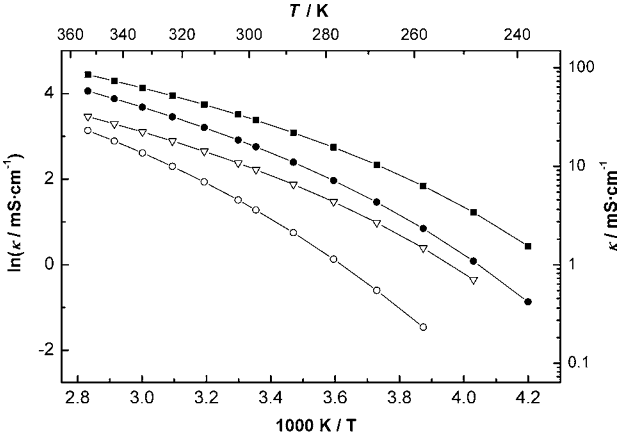

Figure 2. Arrhenius plot for ILs' temperature-dependent conductivity data for ■, [EMIM][DCA]; ●, [EMIM][BF_4]; △, [EMIM][NTf_2]; and ○, [BMIM][BF_4].

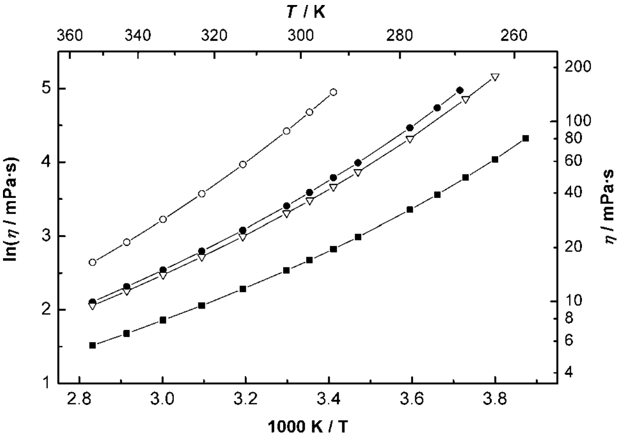

Figure 3. Arrhenius plot for ILs' temperature-dependent viscosity data for ○, [BMIM][BF_4]; ●, [EMIM][BF_4]; △, [EMIM][NTf_2]; and ■, [EMIM][DCA].

from LAUDA and controlled by a temperature sensor close to the measuring cell. Measured densities were fitted highly accurately with a second-order polynom to inter- and extrapolate ILs' densities as required for data evaluation over the whole temperature range. The estimated relative uncertainties of the measured densities are below 0.01 %.

Results and Discussion

Detailed measurement data are given in the Supporting Information. Figure 2 shows the Arrhenius plot for the ILs' temperature-dependent conductivities and Figure 3 for their viscosities, respectively. All data are in good agreement with the literature.[25−27]

Both plots show that investigated ILs deviate from Arrhenius like behavior, so the Vogel−Fulcher−Tammann (VFT) equation[28−31] was used to fit the data. Table 1 summarizes the VFT fit parameters for viscosity data (eq 12) and conductivity data (eq 13), respectively. These parameters allow precise interpolation of viscosity and conductivity in the given temperature range and a fairly good extrapolation beyond these limits too.

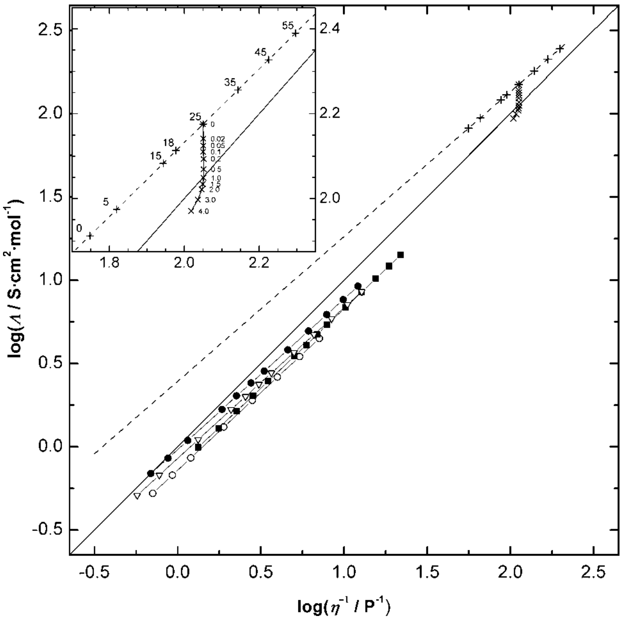

Figure 4. Walden plot of temperature-dependent conductivities and viscosities for ILs (●, [EMIM][BF_4]; △, [EMIM][NTf_2]; ■, [EMIM][DCA]; ○, [BMIM][BF_4]); temperature-dependent conductivity data of infinitely diluted aqueous KCl solutions from (0 to 55) °C with corresponding pure water's viscosity (+) and its linear extrapolation (dashed line),[33] and conductivities and viscosities of aqueous KCl solutions at 25 °C in the concentration range (0 to 4) mol·L^{-1} (×).[34] Numerical values next to data points in the insert represent the concentration (mol·L^{-1}) for aqueous KCl solutions and temperature (°C) for infinitely diluted aqueous KCl solutions, respectively. The straight solid line through the origin with a slope of 1 represents the so-called ideal KCl line; see text.

$$\eta = \eta_0 \exp\left(\frac{B}{T - T_0}\right) \tag{12}$$

$$\kappa = \kappa_0 \exp\left(\frac{-B'}{T - T_0'}\right) \tag{13}$$

Suffice to mention here that ideal glass transition temperatures T_0 obtained from fits of data to eq 12 and 13 respectively will generally not yield the same T_0, as conductivity data in contrast to viscosity data is containing another contribution from temperature-dependent ion association. The fact that T_0 values of our four studied ILs from two methods scarcely differ can be tentatively explained by assuming a small association.

Calculation of ILs' molar conductivities according to eq 11 allows us to draw the Walden plot (Figure 4) and linear data fitting according to eq 10. Presented data in the Walden plot show an excellent linear correlation between neat ILs' conductivities and viscosities with an average slope of $\alpha = 0.922 \pm 0.022$ and intercepts $\log(C'/\mathrm{S\cdot cm^2\cdot mol^{-1}})$ ranging from −0.02 to −0.14; see Table 2.

Obtained fit parameters therefore allow accurate calculation of ILs' viscosity from their conductivity which is usually

Table 1. Fitting Parameters for VFT Equations, Equations 12 and 13, Describing ILs' Viscosity and Conductivity, Respectively

	η_0	B	T_0	κ_0	B'	T_0'
IL	10^{-2} mPa·s	K	K	mS·cm^{-1}	K	K
[EMIM][BF_4]	24.82 ± 1.82	661.60 ± 17.19	165.27 ± 1.51	1421.82 ± 15.51	607.92 ± 3.43	163.23 ± 0.43
[BMIM][BF_4]	11.11 ± 0.74	897.36 ± 18.35	167.60 ± 1.41	1461.37 ± 58.95	739.31 ± 12.37	175.02 ± 1.25
[EMIM][NTf_2]	22.72 ± 0.29	684.36 ± 2.94	160.20 ± 0.25	656.86 ± 9.82	571.60 ± 4.64	164.25 ± 0.61
[EMIM][DCA]	29.27 ± 1.07	524.49 ± 8.01	163.65 ± 0.83	1217.44 ± 16.05	511.92 ± 4.06	160.82 ± 0.59

Table 2. Linear Fitting Parameters for Fractional Walden Plots According to Equation 10[a]

IL	A	$\log(C'/\mathrm{S \cdot cm^2 \cdot mol^{-1}})$
$[EMIM][BF_4]$	$0.90419 \pm 7.7 \cdot 10^{-4}$	$-0.01655 \pm 4.8 \cdot 10^{-4}$
$[BMIM][BF_4]$	$0.93024 \pm 8.4 \cdot 10^{-4}$	$-0.14099 \pm 4.1 \cdot 10^{-4}$
$[EMIM][NTf_2]$	$0.90588 \pm 1.2 \cdot 10^{-3}$	$-0.06951 \pm 7.8 \cdot 10^{-4}$
[EMIM][DCA]	$0.94946 \pm 7.5 \cdot 10^{-4}$	$-0.12221 \pm 6.4 \cdot 10^{-4}$

[a] Standard deviations for all linear fits in the Walden plot were in the range of about 0.1 %, with $R^2 > 0.99999$.

measured far more easily and quickly in high accuracy than viscosity. The deviation of measured viscosities from calculated viscosities obtained from corresponding conductivities and eq 10 is below 0.6 %. For these purposes, the fractional Walden rule and the Walden plot are quite useful tools.

However, further interpretation of ILs' plots with respect to their deviation from the so-called ideal KCl line is at least a bit questionable, as pointed out in the following section.

First of all, there is no theoretical foundation justifying the comparison of pure ILs' conductivity and viscosity to that of any (semi)diluted electrolyte solution, both aqueous or nonaqueous, and aqueous KCl in particular. Secondly, the choice of 1 M aqueous KCl as the "ideal" solution to compare to ILs' data seems to be arbitrary. Typically, KCl as a standard electrolyte for aqueous systems is used because of its similar values for the cation's and anion's specific limiting molar conductivities, but this is of no importance for comparison to the ILs. So, if one still likes to agree on KCl as some sort of arbitrary comparison standard, a infinitely diluted KCl solution would be more reasonable as electrolyte theories are far more developed for that than for any concentrated solutions. The only advantage of 1 M KCl is that it coincidentally gives a nice data point at 25 °C in the Walden plot, with $\log(\Lambda/\mathrm{S \cdot cm^2 \cdot mol^{-1}}) \approx 2.05$ and $\log(\eta^{-1}/\mathrm{P}^{-1}) \approx 2.05$, as can be seen in the insert in Figure 4. So by taking this single point in those units (with the viscosity in Poise, $1\ \mathrm{P} = 0.1\ \mathrm{Pa \cdot s}$ or $1\ \mathrm{cP} = 1\ \mathrm{mPa \cdot s}$), it is possible to draw the "ideal line" with the assumed slope of $\alpha = 1$ through origin.

But, thirdly, the assumption of ideal behavior for that, for example, $\alpha = 1$, has not been supported. The way to construct the "ideal KCl line" by constructing a line with a slope just assumed to be 1 and through only one "carefully" selected data point is quite arguable. Literature data[32] for infinitely diluted aqueous KCl solutions at several temperatures show clearly that in this case the slope α in the Walden plot equals not 1 but about 0.87 actually (cf. Figure 4).

Deviations from the Walden rule are discussed in terms of ionicity of the ILs; compare ref 8 and the literature cited therein. The decrease of "ionicity" (i.e., by association) entails an increasing deviation from the Walden rule. This correlation can even be improved by taking Stokes radii of ions into account;[8] compare to eq 6.

Conclusions

This work presents temperature-dependent conductivity and viscosity data for some neat ILs and briefly discusses the somehow questionable foundation for the comparison of ILs with the so-called ideal KCl line in the Walden plot, based on actual KCl solution literature data instead of simplified and arbitrary assumptions. Given results show that the fractional Walden rule's exponent α, as derived from the slope of the linear correlation of conductivity and viscosity data points in the Walden plot, is not unity but around 0.92. This agrees with the general findings in literature, where α is most often found to be somewhere in the range of 0.8 ± 0.1.[32] Obviously, this much more seems to be the typical behavior, not that of a hypothetical ideal KCl line with its slope assumed to be 1. As shown by simple and straightforward literature data analysis, infinitely diluted aqueous KCl itself behaves not ideally but shows a slope of 0.87 in the Walden plot, so it is clearly deviating from unity too. The Walden plot gives a good representation of ILs' key data and their fit serves surprisingly excellently for the calculation of viscosity from conductivity and vice versa. Instead of focusing on deviations from arbitrary lines, we would like to encourage further investigation of possible fundamental meanings of slope and intercept in the Walden plot by theoretical means, honoring the strikingly excellent correlation of ILs' data according to the fractional Walden rule.

While the comparison of aqueous electrolyte solutions with pure room temperature molten salts seems to be not very plausible, it might be of interest to correlate these Walden parameters to other IL properties or theories. Theories describing the liquid state of ILs are emerging nowadays, and hopefully the relationship between their conductivity and viscosity and other parameters will be understood finally.[8] ILs are, as their name perfectly says, purely ionic liquids and therefore the very other extreme to (diluted) electrolyte solutions. While the complicated case of diluted electrolytes is still not handled very well theoretically, we hope that pure ILs as the other extreme to diluted electrolyte solutions might be more accessible to theoretical description in the near future. Electrolyte solutions often suffer from changes in solvation and ion interaction upon temperature shifts often preventing the use of the Walden rule.

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Supporting Information Available:

Measured temperature-dependent conductivity, viscosity, and density data for given ILs. This information is available free of charge via the Internet at http://pubs.acs.org/.

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