Kinetic Properties of Ionic Solutions: Impedance measurements and general resistivity-viscosity relations.

Thesis submitted for the M.Sc. degree

by

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I wish to express my gratitude to Mr. Dimitry Linsky who steadily offered me any possible help and taught me a mastering of laboratory art,

My gratitude to Prof. Voronel for his wise guidance and support, I thank him for his trust in me,

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Glossary of common symbols

\( \eta \) - dynamic viscosity (in Poise [cgs]).
\( \zeta \) - bulk viscosity (in Poise [cgs]).
\( G \) - shear modulus.
\( \rho \) - resistivity in ohm.cm.
\( \sigma \) - conductivity in 1/ohm.cm.  \( \sigma = 1/\rho \).
\( \lambda_i \) - equivalent conductivity of ion \( i \) (conductivity per mole salt: in cm²/ohm.mol).
\( \Lambda \) - sum of equivalent conductivities of the solute.
\( D \) - diffusion coefficient.
\( \varepsilon \) - dielectric constant at zero frequency (dimensionless).
\( f \) - frequency (Hz).
\( \omega \) - angular frequency.
\( \tau \) - characteristic relaxation time.
\( e \) - electron charge (in positive sign).
\( z_i \) - ionicity (charge of an ion divided by \( e \)).
\( \nu_i \) - number of cations/anions per one molecule of salt.
\( a_i \) - activity coefficient (dimensionless).
\( \gamma_i, \gamma_z \) - molar activity coefficient and average \( \gamma_z = [\gamma^+ \gamma^-]^{\nu^+ + \nu^-} \).
\( E \) - electric field.
\( j \) - electric current density.
\( F \) - Faraday number.
\( N_A \) - Avogadro number.
\( n \) - particles density.
\( k_B \) - Boltzmann’s constant.
\( m \) - the “fractional parameter” in eq. (A.1).
\( T \) - temperature in °K (Kelvin).
\( A \% \) - salt equivalents per salt+solvent equivalents.
\( c \) - concentration in mole(equivalent) per cm³.
\( c[molar] \) - concentration in mole(equivalent) per liter.
\( w \%) \) - weight part of solute in the solvent.
molarity - mole(equivalent) solute per liter solution.
molality - mole(equivalent) solute per kilogram solution.

[cgs] - the metric system of cm,gr,sec, erg (energy unit), esu=√erg·cm (charge unit), statvolt (electric field). The Poisson equation for vacuum is in the form: \( \nabla \cdot E = 4\pi \rho \). In this system Resistance is in units of seconds and Capacitance is in units of cm.

ohm = joule.sec/coulomb².
Abstract

Electric impedance measurements at frequencies 20hz to 5Mhz were performed for aqueous solution of LiCl over concentrations 0.1 to 12.8 molar and temperatures of -90°C to 70°C. The impedance of a fused salt-mixture AlBr3/KCl at the eutectic ratio (66.7%-33.3%) was measured at temperatures 80°C to 210°C. Resistivity was extracted and compared to known viscosity data. The results confirm an empirical “fractional law” which is suggested as a modification of the Nernst-Stokes-Einstein law. The general dependencies of resistivity and viscosity on ionic concentration were formulated based on other works and an analysis of LiCl and other ionic solutions (KOH, ZnSO4, and seawater). The dependencies were used to extrapolate part of the viscosity data of LiCl aqueous solution at some concentrations, and to show that the “fractional parameter” is independent of concentration. A theoretical explanation is proposed for the “fractional law” based on a model of geometrical barriers which open for ions by thermal fluctuations and close after a typical relaxation time of structural deformations (a time equals to the ratio between viscosity and the shear modulus). Some standing questions about viscosity, resistivity, diffusion and dielectric coefficients are discussed. The breakdown of the Nernst-Stokes-Einstein law is explained in being grounded on the equipartition theorem which is inapplicable to ionic particles. A result of impedance measurements for the Dead-Sea water is also provided.
I. Introduction

A. Prologue

Recent experiments by A. Voronel et al [56] suggested a new empirical relation between viscosity and electric resistivity:

\[ \rho \propto (\eta)^m \quad m = 0.75 \pm 0.1 \]  

(A.1)

The purpose of this study is to supply further evidence for this relation, with emphasis on spherical ion liquids. It is tested whether \( m \) is a constant, and a question arises how \( m \) depends on the system. Also a theoretical aspect is proposed. We tried to relate different kinetic properties of ionic solutions, and trace the root of their relation. Equation (A.1) is referred here as the “fractional law” since a power \( m \) modifies the classical Nernst-Stokes-Einstein equation.

Nernst-Stokes-Einstein equation is based on the following argument:

Ionic transport is viewed as the motion of hard spheres in a continuum of Newtonian liquid. On the basis of hydrodynamic theory a dragging force acts on the sphere:

\[ F_d = 6\pi \eta r_0 \bar{u} \]  

(A.2)

(\( \bar{u} \) is the sphere velocity, assuming no slip on the boundary. \( r_0 \) is the radius of the spheres, \( \eta \) the viscosity of the liquid).

In a steady motion the active force is proportional to velocity with a ratio determined from the diffusion coefficient according to Einstein’s relation:

\[ \frac{D}{k_B T} = \frac{\bar{u}}{F_d} = \frac{1}{6\pi \eta r_0} \]  

(A.3)

(Using (A.2), resulting in the Stokes-Einstein equation).
The Nernst relation is established between the electric current density and gradients of chemical and electric potentials [29]:

$$j_i = -N_A z_i e D_i \frac{c_{i}}{RT} (\nabla \mu_i - N_A z_i e E) \quad (A.4)$$

($j_i$ the electric current density, $\mu_i$ the chemical potential).

Resistivity equals:

$$\rho_i = \frac{1}{(\partial j_i / \partial E)} = \frac{RT}{c_i D_i N_A e^2 z_i^2} \quad (A.5)$$

and thus from (A.3) and (A.5) a linear relation is virtually expected between resistivity and viscosity. This linear relation was obtained also in a study of hard spheres with Boltzmann distribution of velocities [28].

Actual ionic system never contains a single ionic specie. It could be thought that the total conductivity is summed over all ionic species: $$\sigma = \sum_{i} 1/\rho_i \cdot$$ However due to attraction between positive and negative charges each ion is surrounded with an atmosphere of the opposite ion, and additional phenomena have to be regarded: First, it is the local electric field which is changed by so called relaxation field due to a distortion of the ionic atmospheres. Secondly, when two opposite charge bypass each other in their opposite direction of motion, they slow down each other (the electrophoretic effect).

R.Fuoss, based on a pioneering work of Onsager, evaluated the weight of these effects and fitted empirical results to his calculations by using elementary fitting parameters, as the ionic radius and the degree of dissociation (described in chap. K).

Fuoss’ calculations, based on Debye-Huckel theory, are intended to apply for dilute ionic solutions of molecular liquid solvents, not above 1 molar ionic concentration. So this description is irrelevant for ionic melts, which are purely ionic liquids. In concentrated solutions the interaction between close-packed ions involves not only electrostatic forces. But even in a model of electrostatic forces alone Fuoss estimated that above 1 molar the statistics fail and many-body interaction should enter into consideration. The problem of understanding friction is not solved. A new type of mechanism, a dielectric friction is described by Hubbard [21] but still has not reached maturity. Regarding the details above it is quite a remarkable fact that a simple correlation does exist between conductivity and viscosity.
New general formulas for conductivity and viscosity are described in chapter F. Their advantage over other suggested formulas are in being consistent with each other and valid at all temperatures, whereas former formulas were intended for room temperature only. The formulas are good in all the concentration range at the expense of accuracy, which is up to 6%. It may be compared to the formula of Islam et al [23] that use one fitting parameter to reach accuracy of 0.1%, but above a concentration of 4 molar exploding negative values for conductivity are obtained and a relation at other temperature than 25°C is not offered.

Nernst-Stokes-Einstein equation is based on Einstein’s relation and Nernst’s relation which are both limited by an assumption that the equipartition theorem is applicable (described in details in chap. J). However this assumption is not justified for ionic particles, and a new theory of resistivity in ionic solutions is requested. In section III a model of fluctuating geometrical barriers is suggested to explain the “fractional law” using calculations which have been derived for an analogous phenomenon of reaction in proteins.
B. Review of the physical objects

Viscosity

When one mixes water and salt in the laboratory he expects the temperature to change. The reaction can be exothermic (as for LiCl solution) or endothermic (for instance with KBr). Evidently for the salts that make an endothermic reaction with water (i.e. the system absorbs heat and passes to an higher energy state) the product has low viscosity (in compared with water), and for the other salts the vise versa is evident. One learns that viscosity is concerned with the energy of bonds in the liquid.

A principle of how viscosity depends on salt concentration was shown by Satoh&Hayashi:

![Figure B.1](image)

**Fig B.1** Relative viscosity for aq. solutions vs. concentration at 25°C (from [42]).

We see an interesting phenomenon that for solutions of larger ions viscosity decreases in a certain range of concentrations below the viscosity of water. The slope near 0 molar can indicate this effect.
For dilutions of less than 0.1 molar the Jones-Dole formula is found more accurate than a linear law:

$$\frac{\eta}{\eta_{\text{solvent}}} = 1 + a \sqrt{c} + bc$$  \hspace{1cm} (B.1)

It was found (Kaminsky [25]) that the coefficient $a$ in eq. (B.1) depends on ion-ion interaction while the coefficient $b$ depends on solute-solvent interaction. The case of over fluidity $\frac{\eta}{\eta_{\text{solvent}}} < 1$ is explained by that the ions break the structure of the solvent and decrease the correlation length. Data of Jones-Dole b coefficients ([25],[10]) can be compared with data of molar enthalpy of solvation at infinite dilution [CRC] as shown in table B.1, and indeed a correlation appears. But it is known that viscosity in aqueous solutions is determined by the amount of hydrogen bonds (that are the dominant force between water molecules). Hence perhaps the two aspects that determine viscosity is a combination of system energy and amount of degrees of freedom.

Table B.1  Comparing enthalpy of solvation and Jones-Dole b coefficient for aqueous solutions.

<table>
<thead>
<tr>
<th>solute</th>
<th>$\Delta_{\text{sol}}H_0$</th>
<th>b (J-D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>-37.03</td>
<td>0.140</td>
</tr>
<tr>
<td>NaCl</td>
<td>3.88</td>
<td>0.080</td>
</tr>
<tr>
<td>KCl</td>
<td>17.22</td>
<td>-0.015</td>
</tr>
<tr>
<td>KBr</td>
<td>19.87</td>
<td>-0.049</td>
</tr>
<tr>
<td>KI</td>
<td>20.33</td>
<td>-0.075</td>
</tr>
</tbody>
</table>

The simplest scheme of experiment to determine viscosity is sketched in fig B.2.

Fig B.2  Viscosity measurement.
A velocity gradient $\frac{du_z}{dz}$ is formed in the liquid (for example between two mechanical bodies: a rotating cup and a fixed round object), and the shear stress $\sigma_{xy}$ in units of pressure is measured (a force in direction x per area unit projected in direction y).

Another method is based on measuring the speed of flow in a capillary and taking the shear stress from the known gravitational force. The absolute viscosity is:

$$\eta = \frac{\sigma_{xy}}{du_x / dy} \quad \text{(B.2)}$$

$\eta$ in Newtonian liquids is a constant and bears the units of poise = gr/cm s = 0.1 Pa s.

A related empirical method concerns the width of a Brillouin line in optical scattering [55]. The origin of that line is the Doppler shift of light scattered by sound waves created by thermal density fluctuation. The spectrum of these waves is centered around a characteristic frequency which is reciprocally related to the characteristic time of shear relaxation $\tau_s$ (as in chap. G). The width of the line is $2\Gamma k^2$, $k$ is the wave vector of sound, $1/\Gamma k^2$ is the characteristic time of sound attenuation. From the solution of Navier-Stokes equation it is found that [18]:

$$\Gamma = \frac{1}{\tau} \left[ \frac{\lambda}{nC_v} (\gamma - 1) / \gamma + \frac{\eta + \zeta}{d} \right] \quad \text{(B.3)}$$

$\zeta$ is the bulk viscosity, $\lambda$ is thermal conductivity, $d$ is mass density, and $\gamma = C_p / C_v$ is the ratio of specific heats. No simple relation exist between $\zeta$ and $\eta$, but except in supercooled liquids they are of the same order of magnitude.

**Diffusion coefficient**

Many indirect experimental methods are used to evaluate the diffusion coefficient in ionic solutions. Usually a simple boundary condition is imposed at the set time: two volumes with different concentrations that come into contact. A restricting porous membrane is sometimes held between the volumes. Since neutrality constraint is imposed (by nature) an equal amount of ions from each type diffuse to the less concentrated volume. The evolution of the system with time is described by:

$$c(y,t) = \frac{c_1 + c_2}{2} + \frac{c_2 - c_1}{\sqrt{\pi}} \int_0^{\sqrt{4Dt}} \exp(-s^2)ds \quad \text{(B.4)}$$
The concentrations at two points of $y$ is measured [40] with time and fitted to eq. (B.4). The result is interpreted as the diffusion coefficient of the salt and can be related to each of the ionic species (in binary systems) as follows ([CRC-P.Vanysek], [38]):

Since electric current is absence in the diffusion process which implies that the velocities of the two ionic species are the same:

$$u = -\frac{D_+}{RT} \nabla \mu_+ = -\frac{D_-}{RT} \nabla \mu_-$$

The total chemical potential gradient $\nabla \mu = \nabla \mu_+ + \nabla \mu_-$ in ideal solution is related to concentration gradient by:

$$\nabla \mu = (\nu_+ + \nu_-)RT \ln c$$

Therefore:

$$cu = -\frac{(\nu_+ + \nu_-)D_+D_-}{\nu_+D_- + \nu_-D_+} \frac{RT}{c} \nabla c$$

and the diffusion coefficient of the salt is:

$$D_{\text{salt}} = \frac{(\nu_+ + \nu_-)D_+D_-}{\nu_+D_- + \nu_-D_+} = \frac{(z_+ + z_-)D_+D_-}{z_+D_+ + z_-D_-}$$

(Note that $z_+ / z_- = \nu_- / \nu_+$.)

Some electrochemical methods enable to estimate the specific diffusion coefficient of one ionic specie, but are binding to use appropriate electrodes and supporting electrolyte and a voltage to activate a reaction. One needs to provide a sharp step voltage or alternatively to use low frequency impedance spectroscopy and isolate the Warburg component [29]. More detailed account of diffusion measuring techniques is found in [24-a].

The following results of diffusion coefficient measurements in aqueous solutions (using diaphragm-cell method [47]) appear to decouple from the results of viscosity as shown in fig. B.1. The increase in diffusion coefficient with concentration is most surprising by itself, since viscosity increases.
**Fig. B.3.** Diffusion coefficients of aqueous solutions at 25°C vs. concentration (picture from [47]).

**Resistivity**

In early studies of resistivity of ionic solutions the AC resistance (modulus of impedance) was measured at around 1000 Hz and divided by the cell constant to get resistivity. A better method is to model the equivalent circuit of the sample and isolate the required component (as shown in chapter D). The way we extract resistance from impedance is done simply by drawing a cole-cole plot (-\text{Im}\{Z\} vs. \text{Re}\{Z\} where Z is the complex impedance) and finding the point on the real axis where the plot approach a minimal imaginary value. This method is justified to use in our laboratory from the analysis shown in chapter D (Impedance treatment).
II. Experimental section

C. Experimental details

Impedance measurement principle

The measuring cell is shown in figure C.1(a). It consists of a sealed parallel glass tube (ap. 10 mm i.d.) filled with an ionic solution, and four electrodes (Platinum 0.5 mm wires) implanted through the wall. A four-probe method was used. The wires are connected through screened cables to an AC-bridge (LCR meter HP4284A), which measures impedance at 22 frequencies from 20 hz to 1 Mhz. The voltage is set to minimum (5 mv) to prevent any electrochemical reaction. Specific resistivity was extracted using a method discussed in Chap. D. It was found that there is no essential difference between measuring specific resistivity in either the 2,3 or 4-probe system. However the results vary by a minor factor which is due to a geometrical edge effect near the electrodes. The four-probe system was chosen because it is the best for eliminating edge effects. An experiment in which two-probe systems were constructed with different pairs of the four electrodes showed that, as expected, the resistivity is proportional to the length of the liquid column between the pairs.

The cell constant was calibrated with KCl solution of concentration 76.58 gr/1 kg water at 25 °C [CRC]. The constant was found in agreement with the geometry of the cell. For the cell in the cryogenic system the constant was 10.62, and for the cell in the warming system the constant was 10.90.
Solution preparation

The LiCl solutions were prepared from Merck pro-analysis LiCl and deionized water (resistivity above 10 MΩ.cm, TAU school of chemistry). The content of moisture was estimated as 0.7% by comparing to a dry sample that was prepared by heating to 250°C and then vacuum drawing for half an hour. In order to reach the required concentration the components were weighed before and after dissolving (so the water that evaporates during the release of heat could be taken into account).

Cryostat (Temperatures: 25°C to -90°C)

The experimental glass tube was enclosed in two metal shells. The outer one is a brass vacuum can which is filled with 1 atm Helium to reduce temperature gradients and to eliminate gas condensation. It was put in a liquid nitrogen dewar, about 10-30 cm above the liquid level; in this way it cooled only by the cold vapours and thermal insulation (the rate never exceeds 2°C/min). Inside the brass can there was a cylindrical copper shell that...
covers the glass tube. A thin wire heating coil (260Ω, 60v) was wound around the copper shell. The heating power was delivered by a temperature controller (Omega CN76000), and the temperature detector (Platinum RTD-100) was placed on the copper shell. A second temperature detector of the same kind was placed inside a glass socket which entered the solution from the seal. The temperature of the latter was displayed on the computer screen. Each measurement was completed when the readings from the two temperature detectors agreed within accuracy of 0.1°C. We waited from half an hour (at temperatures above minus(-) 22°C) up to 10 hours (for lower temperatures) for stabilisation at each temperature point before taking the measurement. It was checked a few times that when a second measurement was taken 48 hours later it showed the same resistivity. Although, below the solidus line (fig E.1) the measurements are expected to depend on time and rate of cooling.

**Warming set-up**  (Temperatures: 25°C to 70°C)

A second experimental cell was placed in a copper shell heated by a heavy thermal wire. As in the first cell two temperature detectors were used to assure stabilised and uniform temperature (not exceeding 1°C gradient). It was used to determine resistivity in aqueous solutions.

**The experiment in AlBr3/KCl melt**

Resistivity measurement in ionic melts is a difficult experiment. Common salts as alkaly-halogens are melted at temperatures above 700°C, what excludes the use of common glass cell. In this experiment a semi-ionic/semi-polar AlBr3 salt was used, which melts at 97°C. A mixture of AlBr3 with 33.3% KCl forms an eutactic point and melts at 75°C. Pure AlBr3 is not conductive (specific resistivity above 3 MΩ.cm) but it dissolves other ionic salts and is analogous to water. Using a measuring temperature range of 80°C to 210°C a change of two orders of magnitude in resistivity (and viscosity) was observed.
A technical difficulty with AlBr₃ is that it reacts violently with moisture and oxygen (and produces HBr vapors). The handling of the material has been made in nitrogen filled glove box. The materials were Alderich’s AlBr₃ 99.99% and Alderich’s anhydrous KCl in an Argon filled ampoule. When heated together in a glass tube a foam was created which escaped the cell and spoiled the mixture. The same thing happened when the material packages were opened only for a few seconds to the atmosphere of the glove box. A different approach was taken: The AlBr₃ powder was melted individually and solidified in the tube (perhaps some moisture evaporated, also no bubbles remained trapped in the liquid). Then KCl grains were added on top of the solid AlBr₃ (inside the glove box) and then sealed and the tube was heated again in the facility shown in fig C.2. The wider end of the tube was used for precaution but was found unnecessary. The salt dissolved slowly and allowed to mix and casually swayed for 5 hours at 190°C before the first measurement was taken.

The experiment lasted 48 hours. The cell was immersed in NaCl for temperature stabilization; however it is seriously recommended not to repeat that: The NaCl salt expands at ap. 250°C and caused some glass tubes to crack. NaCl is not helpful in experiments of high temperatures. The high heat capacity of the cell and its environment required to operate the temperature controller driven by a computer. A software was written to slowly change the temperature orders to the controller according to the actual temperature readings. The all procedure was automated and 14 readings were taken continuously at decreasing temperature set points. No interpolation is used in the presented results (table H.4). A measurement was taken only when the temperature readings remained within ±0.3°C near the set point for 4 minutes or when the readings showed to fluctuate around the set point for 2 min.

The cell constant for this experiment is 15.6 (using aqueous KCl calibration). I.D.~8 mm. In the end of the experiment the solid looked black, perhaps because of a reaction with the glass. There is some probability for a minor amount of contamination from the silicon greas near the joints.
Fig C.2  Experimental setup for fused AlBr₃/KCl.
D. Impedance treatment

Extraction of resistivity from impedance data was done graphically taking the real part value of one cluster of points in the complex plane nearest to the real axis, as shown in fig D.2 for R[bulk]. In this chapter we discuss a further analysis of the impedance data.

Theory

The impedance spectrum is classically modeled using the following equivalent circuit:

![Classical equivalent circuit model](image)

**Fig D.1 Classical equivalent circuit model**

![Cole plot](image)

**Fig D.2 A typical Cole plot for the equivalent circuit in fig D.1.**

For the left half circle C_{stray} is dominant and for the right half circle C[dl] is dominant. In between R[bulk] is found, which is the resistance of the bulk of the solution.
In terms of the discussion in chapter I the complex conductivity of the solution is constant: \( \sigma^*(\omega) = \sigma_0 = [\text{cell const}] / R[\text{bulk}] \).

C[dl] is the double layer capacitance of the electrodes (explained with the Stern model [14]).

R[F] is concerned with the rate of electrochemical reaction that passes charge to one of the electrodes. The rate is exactly zero when the voltage is lower than the reversible voltage \( (\Delta \phi_{\text{rev}} = -\Delta G^0 / zF) \) i.e. when the reaction is disabled from a thermodynamical view. Above the reversible voltage the rate depends on the area of the electrode, the activation energy of the reaction, the overpotential (and empirical parameter: the symmetry factor), concentration and temperature [14].

Cstray depends on the features of the measuring equipment and on the sample. This component is added when the equipment is unable to supply the necessary current for the first response to a step of potential in ionic solution.

\( Z_W \) is the Warburg impedance \( Z_W = k_w (1-i) \omega^{-1/2} \) which describes the effect of diffusion controlled reaction at very low frequencies [14]. This component is analyzed only in systems of supported electrolyte, i.e. a system that consists of a dilute ionic solute (which react on the electrodes) and a concentrated electrolyte (not reacting) so that \( E = 0 \) and \( \Delta \mu \neq 0 \) as appeared in eq. (A.4).

In this experiment the voltage amplitude was limited to a low value: 5mV. In aqueous LiCl solution an electrochemical reaction occurs only above 1.23 V, which is the electrolysis of water (and above 1.38 V: Cl₂ can be produced but is not observed). We could suppose that in the experiment \( R[F]=\infty \). However in aqueous LiCl a value \( R[F]=100\text{K}\Omega \) was derived from the results, and it may be explained by a local high field on the surface of the electrode.
The measurement results of impedance using the HP4284A device was fitted to the following equivalent circuit:

![Equivalent Circuit Diagram](image)

**Fig D.3** Equivalent circuit for HP4284A with ionic solution.

The values of $C[E]$ (stray/equipment capacitance) are around $10^{-9}$ F, and $R[E]$ around 1000 ohm. (When an electronic resistor was sampled the results were almost independent of frequency and these components were omitted, as explained above). The value of $C[dl]$ for the experimental cell is around 1mF (in the four-probe configuration). $R[F]=100K\Omega$. When other values were found they were shown in the graphs in figs D.5-D-10.

Fitting the results to a basic equivalent circuit was not possible without assuming some phase-shift parameters as marked in fig D.3. The following revisions were made:

$Z\{C[dl]\} = \frac{1}{i\omega C[dl]}$  \quad \Rightarrow \quad Z\{C[dl]\} = \frac{1}{i^{\delta[dl]}\omega C[dl]}$

$Z\{C[E]\} = \frac{1}{i\omega C[E]}$  \quad \Rightarrow \quad Z\{C[E]\} = \frac{1}{i^{\delta[E]}\omega^{\delta[\omega]} C[E]}$

$Z \{R[E]\} = R[E]$  \quad \Rightarrow \quad Z \{R[E]\} = i^{\delta \cdot R[E]}$
In fig D.4, a graph of $\tau_{\text{EIS}}/T$ vs. $\rho/T$ which shows a linear behavior indicates a steadiness in the value of $C[E]$. $\tau_{\text{EIS}}$ is the reciprocal value of the frequency of the point at the half circle maximum relating to stray capacitance (i.e. the maximum in the left half circle, as in fig. D.2 $\tau_{\text{EIS}} = (1/20000) \text{ s}$). The values of $\tau_{\text{EIS}}$ were extracted from empirical Cole plots at different temperatures and concentrations. As expected $\tau_{\text{EIS}} = C[E] \cdot R_{\text{bulk}}$ hence $\tau_{\text{EIS}} \propto \rho$.

![Diagram of a graph showing a linear relationship between $\log_{10}(\tau/\rho)$ and $\log_{10}((\rho/T) [\text{ohm cm/ok}])$. The graph includes markers with percentages and a trend line.](21)

**Fig D.4** Analysis of the equipment effect (percents indicate molal concentration ratio).

Different types of behaviors in impedance results are shown in the following graphs. In each case a function could be fitted successfully (smooth curve) using the fitting parameters as discussed above. The fitted parameter $R$ (bulk resistance) correlates with the real part value of a cluster of points that appears nearest to the real axis. Thus we checked that our method to extract resistivity from impedance data is right.
Fig D.5  Cole plot for LiCl: bulk resistance 5200 ohm

Fig D.6  Cole plot for LiCl: bulk resistance 235.5 Kohm
Fig D.7 Cole plot for LiCl: bulk resistance 187.2 ohm

Fig D.8 Cole plot for fused AlBr3/KCl: bulk resistance 847.5 ohm
Fig D.9  Cole plot for LiCl: bulk resistance 88.6 ohm

Fig D.10  Cole plot for LiCl: bulk resistance 100.0 ohm
E. Summary of results

Tables E.1, E.4 and E.7-9 summary resistivity data extracted from original impedance measurements. The empiric data in tables E.2, E.3, E.5 were made from other sources.

Table E.1 is based on a local interpolation of the results to enable concise presentation. The original temperature points are not farther than 1°C from the interpolation points. The interpolation is made using a line of $\log(\rho / T)$ vs. $1 / T$ in according to the Arrhenius law.

The error is estimated around 0.1% for a regular liquid (outside the supercooled or freezing region in the phase diagram [fig. E.1]). Every set of impedance measurements was repeated three to five times at the same temperature in intervals of two minutes, and the estimated error is based on a comparison between the extracted resistivity results.

Empiric viscosity data [35] and extrapolated data (for demonstration) are shown in table E.3. The extrapolation is done via eqs (F.6) (F.7) according to resistivity (conductivity) data from table E.1, and the coefficients $A_1, B_1, A_2, B_2$ (for LiCl) that are discussed in the next chapter.

We use percent (or dimensionless) units to represent the concentration of the samples. A% is the ratio between equivalent number of salt molecules and the sum of salt and solvent equivalent numbers. In empiric formulas it is better (in statistical fittings) to use the concentration c (in equivalent number per volume) as a variable. The conversion formulas between the different representations are shown in table E.6.
<table>
<thead>
<tr>
<th>Δ% T°C</th>
<th>0.2%</th>
<th>1%</th>
<th>3%</th>
<th>6%</th>
<th>8%</th>
<th>10%</th>
<th>11%</th>
<th>13%</th>
<th>14.8%</th>
<th>15.8%</th>
<th>18%</th>
<th>21%</th>
<th>24%</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>4.607</td>
<td></td>
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<td>66</td>
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<td>11.11</td>
<td>4.825</td>
<td>2.995</td>
<td>2.827</td>
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</tr>
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<td>41</td>
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<td>15.17</td>
<td>15.45</td>
<td>18.0</td>
<td>19.2</td>
<td>22.99</td>
<td>31.75</td>
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<td>-22</td>
<td>23.29</td>
<td>20.76</td>
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<td>19.71</td>
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<td>23.6</td>
<td>25.4</td>
<td>30.71</td>
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<td>-47</td>
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<td>114.2</td>
<td>74.93</td>
<td>74.17</td>
<td>77.73</td>
<td>91.88</td>
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<td>-52</td>
<td>256.1</td>
<td>175.2</td>
<td>106.5</td>
<td>104.9</td>
<td>109.9</td>
<td>132.3</td>
<td>142.4</td>
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<td>-57</td>
<td>405.4</td>
<td>275.4</td>
<td>173.7</td>
<td>158.4</td>
<td>166.0</td>
<td>200.2</td>
<td>215.2</td>
<td>280.0</td>
<td>705.9</td>
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<td>-62</td>
<td>683.8</td>
<td>468</td>
<td>337.6</td>
<td>244.4</td>
<td>256.4</td>
<td>316.4</td>
<td>332.3</td>
<td>444.3</td>
<td>1206</td>
<td></td>
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<td>-68</td>
<td>1341</td>
<td>911</td>
<td>658.2</td>
<td>538.8</td>
<td>461.0</td>
<td>595.1</td>
<td>620.4</td>
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<td>-72</td>
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<td>1549</td>
<td>1125</td>
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<td>936.8</td>
<td>969.2</td>
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<td>2004</td>
<td>1549</td>
<td>1109</td>
<td>1605</td>
<td>1692</td>
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<td>-80</td>
<td>4559</td>
<td>3614</td>
<td>2289</td>
<td>1917</td>
<td>2795</td>
<td>3029</td>
<td>3938</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>-85</td>
<td>8898</td>
<td>8346</td>
<td>4915</td>
<td>3793</td>
<td>6092</td>
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<tr>
<td>-90</td>
<td>18386</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>16118</td>
</tr>
</tbody>
</table>
Table E.2  Relative viscosity for LiCl aqueous solution at 25°C [42,35,59]

<table>
<thead>
<tr>
<th>c [molar]</th>
<th>0.000</th>
<th>0.714</th>
<th>1.189</th>
<th>1.666</th>
<th>2.123</th>
<th>2.608</th>
<th>3.078</th>
<th>3.540</th>
<th>4.016</th>
<th>4.485</th>
</tr>
</thead>
<tbody>
<tr>
<td>η / η[H₂O]</td>
<td>1.000</td>
<td>1.119</td>
<td>1.188</td>
<td>1.265</td>
<td>1.343</td>
<td>1.433</td>
<td>1.517</td>
<td>1.634</td>
<td>1.735</td>
<td>1.879</td>
</tr>
</tbody>
</table>

Table E.3  Viscosity of LiCl aqueous solution (in Poise).

<table>
<thead>
<tr>
<th>Temp [°C]</th>
<th>empiric viscosity data [35]</th>
<th>extrapolated data via eqs. (F.6,F.7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.0490</td>
<td>0.034</td>
</tr>
<tr>
<td>10</td>
<td>0.0735</td>
<td>0.046</td>
</tr>
<tr>
<td>0</td>
<td>0.1009</td>
<td>0.060</td>
</tr>
<tr>
<td>-10</td>
<td>0.1458</td>
<td>0.082</td>
</tr>
<tr>
<td>-20</td>
<td>0.224</td>
<td>0.121</td>
</tr>
<tr>
<td>-30</td>
<td>0.375</td>
<td>0.190</td>
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<tr>
<td>-40</td>
<td>0.700</td>
<td>0.327</td>
</tr>
<tr>
<td>-50</td>
<td>1.498</td>
<td>0.636</td>
</tr>
<tr>
<td>-60</td>
<td>3.85</td>
<td>1.455</td>
</tr>
<tr>
<td>-70</td>
<td>12.8</td>
<td>3.94</td>
</tr>
<tr>
<td>-75</td>
<td>26.5</td>
<td>6.8</td>
</tr>
<tr>
<td>-80</td>
<td>61.5</td>
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<td>163</td>
<td>64.1</td>
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<td>-90</td>
<td>490</td>
<td>178</td>
</tr>
<tr>
<td>-95</td>
<td>1780</td>
<td>560</td>
</tr>
<tr>
<td>-100</td>
<td>7.9E+3</td>
<td>2110</td>
</tr>
<tr>
<td>-105</td>
<td>4.8E+4</td>
<td>1.01E+4</td>
</tr>
<tr>
<td>-110</td>
<td>4.0E+5</td>
<td>6.8E+4</td>
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<tr>
<td>-115</td>
<td>5.7E+6</td>
<td>6.0E+5</td>
</tr>
<tr>
<td>-120</td>
<td>1.29E+8</td>
<td>7.7E+6</td>
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</table>
Table E.4   Resistivity of fused AlBr3(66.7%)/KCl(33.3%)

<table>
<thead>
<tr>
<th>Temp[°C]</th>
<th>80</th>
<th>90</th>
<th>100</th>
<th>110</th>
<th>120</th>
<th>130</th>
<th>140</th>
</tr>
</thead>
<tbody>
<tr>
<td>ρ [ohm.cm]</td>
<td>44</td>
<td>33.5</td>
<td>28.7</td>
<td>23.0</td>
<td>19.5</td>
<td>16.77</td>
<td>14.02</td>
</tr>
<tr>
<td>exp. error</td>
<td>5%</td>
<td>3%</td>
<td>2%</td>
<td>1%</td>
<td>0.5%</td>
<td>0.5%</td>
<td>0.5%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temp[°C]</th>
<th>150</th>
<th>160</th>
<th>170</th>
<th>180</th>
<th>190</th>
<th>200</th>
<th>210</th>
</tr>
</thead>
<tbody>
<tr>
<td>ρ [ohm.cm]</td>
<td>12.46</td>
<td>11.01</td>
<td>9.99</td>
<td>9.15</td>
<td>8.38</td>
<td>7.59</td>
<td>7.05</td>
</tr>
<tr>
<td>exp. error</td>
<td>0.5%</td>
<td>0.5%</td>
<td>0.5%</td>
<td>0.5%</td>
<td>0.2%</td>
<td>0.2%</td>
<td>0.2%</td>
</tr>
</tbody>
</table>

compared resistivity data: AlBr3/KCl

Table E.5  Viscosity and density of fused AlBr3(66.7%)/KCl(33.3%)   [24-b].

<table>
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<tr>
<th>Temp[°C]</th>
<th>80</th>
<th>90</th>
<th>100</th>
<th>110</th>
<th>120</th>
<th>130</th>
<th>140</th>
</tr>
</thead>
<tbody>
<tr>
<td>η [Poise]</td>
<td>0.41603</td>
<td>0.29599</td>
<td>0.22068</td>
<td>0.16927</td>
<td>0.13678</td>
<td>0.11166</td>
<td>0.09286</td>
</tr>
<tr>
<td>d [gr/cm³]</td>
<td>2.731</td>
<td>2.717</td>
<td>2.702</td>
<td>2.688</td>
<td>2.674</td>
<td>2.659</td>
<td>2.645</td>
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</table>

<table>
<thead>
<tr>
<th>Temp[°C]</th>
<th>150</th>
<th>160</th>
<th>170</th>
</tr>
</thead>
<tbody>
<tr>
<td>η [Poise]</td>
<td>0.07936</td>
<td>0.06854</td>
<td>0.05994</td>
</tr>
<tr>
<td>d [gr/cm³]</td>
<td>2.631</td>
<td>2.616</td>
<td>2.602</td>
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</table>
Table E.6 Conversion between different representations of concentration

\[
A\% = \frac{Wt\%}{M_S} \left[ \frac{18}{18 + (1 - \frac{M_S}{18}) Wt\%} \right] 100\%
\]

\[
c[molar] = \frac{d \cdot 1000}{18 \left( \frac{100\%}{A\%} - 1 \right) + M_S}
\]

\[
R = \frac{[H_2O]_{mole}}{[Salt]_{mole}} = \frac{100\% \cdot A\% - 1}{A\%}
\]

(M_S - the molecular mass of the solvent, d - density in gm/cm³)

Table E.7 Impedance measurements in H2O/LiCl

<table>
<thead>
<tr>
<th>A%</th>
<th>d** [gr/cm³]</th>
<th>c [molar]</th>
<th>Ea[°K] ****</th>
<th>files</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2%</td>
<td>-</td>
<td>0.111</td>
<td>1818</td>
<td>h629s</td>
</tr>
<tr>
<td>1%</td>
<td>1.010*</td>
<td>0.553</td>
<td>1823</td>
<td>h625s</td>
</tr>
<tr>
<td>3%</td>
<td>1.035*</td>
<td>1.658</td>
<td>-</td>
<td>h623s</td>
</tr>
<tr>
<td>6%</td>
<td>1.070*</td>
<td>3.30</td>
<td>1851</td>
<td>e524s,</td>
</tr>
<tr>
<td>8%</td>
<td>1.0920</td>
<td>4.38</td>
<td>1850</td>
<td>e511s</td>
</tr>
<tr>
<td>10%</td>
<td>1.1138</td>
<td>5.45</td>
<td>-</td>
<td>e503s</td>
</tr>
<tr>
<td>11%</td>
<td>1.130*</td>
<td>6.01</td>
<td>-</td>
<td>e203s, e203m(2-p)***</td>
</tr>
<tr>
<td>13%</td>
<td>1.1480</td>
<td>7.05</td>
<td>1838</td>
<td>e426s, h622s</td>
</tr>
<tr>
<td>14.8%</td>
<td>1.1675</td>
<td>8.00</td>
<td>1905</td>
<td>e601s, h601s</td>
</tr>
<tr>
<td>15.8%</td>
<td>1.1831</td>
<td>8.55</td>
<td>1917</td>
<td>e225s, h621s</td>
</tr>
<tr>
<td>18%</td>
<td>1.2046</td>
<td>9.68</td>
<td>2017</td>
<td>e310s, h617s</td>
</tr>
<tr>
<td>21%</td>
<td>1.2376</td>
<td>11.24</td>
<td>2116</td>
<td>e401s, h702s</td>
</tr>
<tr>
<td>24%</td>
<td>1.274*</td>
<td>12.82</td>
<td>2310</td>
<td>h721s, h721s</td>
</tr>
</tbody>
</table>

* from Landolt

** measurements at 25°C.

*** in two-probe measurement.

**** activation energy for 35-70°C as in Arrhenius law.

Table E.8 Impedance measurements in AlBr3/KCl

AlBr3(66.7%)/KCl(33.3% ) file: e928s

Table E.9 Impedance measurements in Dead-Sea water at 25°C

<table>
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<th></th>
<th>ρ = 5.28 ohm.cm</th>
<th>file: ef98s</th>
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</thead>
<tbody>
<tr>
<td>North</td>
<td>ρ = 5.33 ohm.cm</td>
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</tr>
<tr>
<td>South</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig E.1  Phase diagram for H₂O/LiCl  (from [8])

Fig E.2  Phase diagram for AlBr₃/KCl  (from [24-b])
F. Analysis

Suryanarayana’s equation [52] might be the only equation so far to describe conductivity of solutions at high concentrations (up to 1 molar below saturation). A concentration potential is defined: \( c_p = c / c_0 \) (\( c_0 \) is the saturation concentration). The equation is stated:

\[
\frac{\sigma}{c_p} = b + a \frac{(1 - c_p)}{\eta_p} \tag{F.1}
\]

(where \( \eta_p = \eta / \eta_0 \) is the relative viscosity, \( \eta_0 \) the viscosity of pure solvent).

A modification of the original Suryanarayana’s equation is suggested:

\[
\frac{\sigma}{c_p} = b(T) + a(T) \frac{\exp(-c / c_0)}{\eta} \tag{F.2}
\]

Where \( c_0 \) is not necessarily the saturation concentration. This modification is found necessary (see fig. F.1) when we arrive to eq. (F.7) with \( \exp(-c / c_0) \) instead of \( (1 - c / c_0) \). This exponential form appeared also in other works [48].

Su and Maksimova [50] determined fitting parameters for 22 different salt solutions of water using the formula:

\[
\frac{\sigma}{c} = b_1(T) - a_1(T) \sqrt{c} \tag{F.3}
\]

They tested the temperature dependency over the range 20°C-90°C and were mistaken to find linear behavior. Another interesting suggestion was their formula for viscosity:

\[
\eta = a_2 \eta_{\text{H}_2\text{O}} + b_2 \tag{F.4}
\]

which describes temperature dependency of 16 salt solutions that were tested.

By analyzing the available empiric data besides the new results for aqueous LiCl the following formulas were found:

A modified Suryanarayana’ equation:

\[
\frac{\sigma}{c / c_0} = b(T) + a(T) \frac{e^{-c/c_0}}{\eta} \tag{F.5}
\]
Conductivity vs. concentration law:

\[
T \frac{\sigma}{c} = B_1(T) - A_1(T) \cdot \sqrt{c}
\]  \hspace{1cm} (F.6)

From eq. (F.5) and (F.6) we find viscosity vs. concentration law:

\[
T \frac{e^{-c/c_0}}{\eta(T)} = B_2(T) - A_2(T) \cdot \sqrt{c}
\]  \hspace{1cm} (F.7)

The parameters of eqs. (F.6) and (F.7) are fitted to empiric data in the following pages.

---

**Fig. F.1.** Relative viscosity of aqueous KI. Smooth line: fitted with eq. F.7. \(c_0=3.5\) molar. Doted line: fitted with eqs. F.1. + F.6. \(c_0=3.5\). It shows the need to modify eq. F.1. to F.2.

The procedure of analysis was to take the linear fittings for \(\sigma/c\) vs. \(\sqrt{c}\) and for \(e^{-c/c_0}/\eta\) vs. \(\sqrt{c}\) and estimate the slopes and the errors. Then the temperature dependence of the parameters was found, and fitted (the best) to a Vogel-Tammann- Fulcher (VTF) form. The sensitivity on \(T_0\) is not high but it was found around the value of the glass transition temperature of aqueous solution \(T_0 = -130 \pm 5^{\circ}C\) (which is the glass transition of “Naive water”, i.e. water without long range correlations). The term “prediction error” means the final error in predicting the result of conductivity or viscosity. For \(A_1, A_2, B_1, B_2\) it is the higher between the error of the linear fit in concentration and of the linear fit for the VTF form in temperature. The prediction error for the the fractional parameter is a ratio that equals the deviation of the results from a fitted line in a ln-ln plot \((\Delta \ln(x) = \Delta x / x)\).
H2O/LiCl: (data from the tables E.1, E.2, E.3)

Only the results above the liquidus line were fitted. The fitted parameters are shown with the relevant prediction error. (see figs F.3 a,b and the last page in this chapter).

\[ c_0 = 10 \text{ molar} \cdot 1 \cdot 10^{-3}, \quad T_0 = -130^\circ\text{c} \]

test limits: \(-75^\circ\text{c}\) to \(25^\circ\text{c}\)

1) 0.1 - 12.8 molar. 2) 8 - 9.7 molar (3 points).

\[ A_1(T) = e^{15.63} \cdot e^{-495/(T-T_0)} \quad \pm 5\% \]

\[ B_1(T) = e^{13.47} \cdot e^{-497/(T-T_0)} \quad \pm 6\% \]

\[ A_2(T) = e^{15.41} \cdot e^{-517/(T-T_0)} \quad \pm 5\% \]

\[ B_2(T) = e^{13.23} \cdot e^{-521/(T-T_0)} \quad \pm 5\% \]

Table F.1 is based on these formulas when viscosity data is extrapolated below 14.8% concentration.

**Table F.1 Fractional coefficient for H2O/LiCl**

<table>
<thead>
<tr>
<th>c [molar]</th>
<th>m [fractional coef]</th>
<th>prediction error</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 - 10</td>
<td>0.89±0.01</td>
<td>2.8-4% (-75to25°C)</td>
</tr>
</tbody>
</table>

H2O/KOH: (data from [30])

\[ c_0 = 10 \text{ molar} \cdot 1 \cdot 10^{-3}, \quad T_0 = -130^\circ\text{c} \]

test limits: \(-60^\circ\text{c}\) to \(60^\circ\text{c}\)

\[ A_1(T) = e^{16.24} \cdot e^{-455/(T-T_0)} \quad \pm 5\% \]

\[ B_1(T) = e^{14.35} \cdot e^{-466/(T-T_0)} \quad \pm 4\% \]

\[ A_2(T) = e^{16.18} \cdot e^{-570/(T-T_0)} \quad \pm 6\% \]

\[ B_2(T) = e^{14.08} \cdot e^{-586/(T-T_0)} \quad \pm 6\% \]

**Table F.2 Fractional coefficient for H2O/KOH**

<table>
<thead>
<tr>
<th>c [molar]</th>
<th>m [fractional coef]</th>
<th>prediction error</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.8</td>
<td>0.77±0.01</td>
<td>4% (-60to60°C)</td>
</tr>
<tr>
<td>5.5</td>
<td>0.84±0.01</td>
<td>2% (-60to60°C)</td>
</tr>
<tr>
<td>6.4</td>
<td>0.86±0.01</td>
<td>1% (-60to60°C)</td>
</tr>
<tr>
<td>8.6</td>
<td>0.83±0.01</td>
<td>3% (-60to60°C)</td>
</tr>
<tr>
<td>9.3</td>
<td>0.80±0.01</td>
<td>4% (-60to60°C)</td>
</tr>
</tbody>
</table>
H2O/ZnSO4: (data from [51])

Here the exact saturation concentration was used for $c_0$.

test limits: 35°C to 60°C

$$c_0 = 3.8 - 5.2 \text{ molar} \cdot 1 \times 10^{-3}, \quad T_o = -130^0\text{c}$$

$$A_2(T) = e^{4.59} \cdot e^{-1392/(T-T_o)} \quad \pm 3\%$$

$$B_2(T) = e^{2.20} \cdot e^{-1426/(T-T_o)} \quad \pm 3\%$$

Sea-Water (data from [57])

The salinity of sea water is roughly the mass of dissolved solids in grams - per 1000 grams of solution. The accurate conversion from salinity $S$ to $c_{[\text{molar}]}$ (the concentration of halides in the solution Cl$, being the majority of anions, I$ and Br$) is as follows:

$$c_{[\text{molar}]} = \frac{1}{1.80655} \cdot \frac{1}{35.45} \cdot [\text{gr / cm}^3] \cdot S[\%]$$

The results are accordingly (see fig F.4):

$$c_0 = 10 \text{ molar} \cdot 1 \times 10^{-3}, \quad T_o = -130^0\text{c}$$

test limits: 0°C to 35°C, 0.16 - 0.67 molar

$$A_1(T) = e^{17.42} \cdot e^{-600/(T-T_o)} \quad \pm 2\%$$

$$B_1(T) = e^{14.38} \cdot e^{-576/(T-T_o)} \quad \pm 2\%$$

$$A_2(T) = e^{17.07} \cdot e^{-734/(T-T_o)} \quad \pm 0.3\%$$

$$B_2(T) = e^{14.57} \cdot e^{-636/(T-T_o)} \quad \pm 0.1\%$$

**Table F.3 Fractional coefficient for sea water**

<table>
<thead>
<tr>
<th>c [molar]</th>
<th>m [fractional coef]</th>
<th>prediction error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.16</td>
<td>0.906±0.001</td>
<td>0.1% (0-35°C)</td>
</tr>
<tr>
<td>0.56-0.67</td>
<td>0.900±0.001</td>
<td>0.1% (0-35°C)</td>
</tr>
</tbody>
</table>
Fused salts

Table F.4  Fractional coefficient for fused slats

<table>
<thead>
<tr>
<th>salt mixture</th>
<th>m (fractional coefficient)</th>
<th>temp. range</th>
<th>viscosity range [cp]</th>
<th>origin of data</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlBr₃(66.7%)-KCl(33.3%)</td>
<td>0.80±0.07</td>
<td>350-440 K</td>
<td>41.6-6.0</td>
<td>tables H4,H.5</td>
</tr>
<tr>
<td>AgBr(69.2%)-KBr(30.8%)</td>
<td>0.58±0.08</td>
<td>630-870 K</td>
<td>4.46-1.79</td>
<td>Janz [24d]</td>
</tr>
<tr>
<td>KNO₃</td>
<td>0.82±0.04</td>
<td>620-750 K</td>
<td>2.80-1.51</td>
<td>quality data[24c]</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.53±0.02</td>
<td>1080-1210 K</td>
<td>1.03-0.79</td>
<td>quality data[24c]</td>
</tr>
</tbody>
</table>

Fig F.2  The fractional law for different ionic solutions [63]. The slopes correlate with ionic size. The results from this work for LiCl are on the same line with the resistivity results for supercooled aqueous LiCl [36] at temperatures below -100°C.
Fig F.3 The fractional law for aqueous LiCl at different concentrations.
Conclusions

We end with the following conclusions:

1) Figures. F.2 - F.4 confirm the “fractional law”, in an adequately large range of viscosities (as in figs. F2-F.3).

2) The “fractional parameter” was found between the values 0.53 to 0.90.

3) In each system the “fractional parameter” is independent of concentration (except for KOH, if the data is reliable it might indicate a unique mechanism of the transport of hydroxide in water).

4) We found empiric formulas for the dependency of conductivity and viscosity on concentration and temperature in systems of simple ionic salts in water. (Some examples are shown in the following page).
III. Interpretations

G. Comparison of shear and conductivity relaxation times

Some questions arise when considering the “fractional law” against other results relating to the comparison of characteristic relaxation times. The corresponding details below lead to some of the conclusions that are made in the next chapters. Let us start with a definition of the two types of relaxation times:

Shear relaxation time is defined according to Maxwell’s visco-elastic theory:
\[ \tau_s = \eta / G_\infty \]  
(G.1)
\( \eta \) is the shear modulus.

Conductivity relaxation time is defined according to electromagnetic theory as:
\[ \tau_\sigma = \rho \varepsilon / 4\pi \]  
[cgs].  
(G.2)

(G.2) is derived as follows. Assuming the density of charge \( q \) changes with time as:
\[ \frac{q}{\tau_\sigma} = -\frac{\partial q}{\partial t} \]  
in the bulk of the solution;  
and using the continuity eq. \[ -\frac{\partial q}{\partial t} = \nabla \cdot j \]
Ohm law: \[ \nabla \cdot j = (1/\rho) \nabla \cdot E \]
and the Poisson eq. \[ \nabla \cdot E = \frac{4\pi q}{\varepsilon} \]
we find:
\[ \frac{\rho}{\tau_\sigma} = \frac{4\pi}{\varepsilon} \]
which is eq. (G.2).

In all ionic systems in the limit of low viscosity \( \tau_s / \tau_\sigma \to 1 \).
The system LiCl-H₂O is remarkable in that the ratio is not much greater than unity at high viscosities, up to the glassy state (defined when viscosity equals 10¹³ P).

In the system Ca(NO₃)₂·8H₂O and also in the fused salt 0.4Ca(NO₃)₂·0.6KNO₃, \( \tau_s / \tau_\sigma \) reaches 10⁴ in the glass transition point, which is a common value.

In Alkali silicate glasses in which the alkali ions can move easily through a glassy network, the ratio \( \tau_s / \tau_\sigma \) reaches around 10¹⁰. The rule that Moynihan et al [35] stated says that \( \tau_s / \tau_\sigma \) at the glass transition point varies in several orders of magnitudes as with the difference in mobility of the two ions. Hence viscosity and resistivity change unequally with temperature, and virtually can not correlate in a fractional power law suggested in eq. (A.1) with \( m = 0.75 \pm 0.1 \). In general a revised “fractional law” should be used where the “fractional parameter” changes according to the size of the ions. The extreme case of Alkali Silicates is excluded from this treatment, that is when some part of the structure arranges in a firm network inside of which a tiny ion can move freely and transport current. It is still pointed out that the ratio \( \tau_s / \tau_\sigma \) stays close to unity in a wide range of viscosities, and indeed the fractional law appears in many ionic systems as was shown in tables F.1-F.4 and in previous works [55],[53].

According to eq. (G.1) the shear relaxation time \( \tau_s \) is determined from viscosity and the shear modulus \( G_\infty \). The real part of the shear modulus is actually measured and the variation of \( G'/G_\infty \) vs. \( \omega \eta / G_\infty \) provides additional parameter that is discussed in chap. I.

![Fig G.1. \( G'/G_\infty \) vs \( \omega \eta / G_\infty \) (\( \beta \) is \( \alpha \) in this text) (picture from [35])](image-url)
H. A model of geometrical barriers

The model of geometrical barriers is suggested to explain the appearance of the fractional law referred by eq. (A.1). The procedure follows the calculations of R.Zwanzig [62] in his model of the rate in a certain chemical reaction, and an extension that was added by N.Eizenberg and J.Klafter [11,12]. An analogy is made here between the concentration in Zwanzig model and the electric field in an ionic liquid model. The electric field relaxes according to the equation:

\[
\frac{dE}{dt} = -K(r) \cdot E
\]

\( r \) - is a random control parameter that describes the width of a gate that forms a bottleneck for the motion of one mobile ion by which the local field can relax. The gate effects the probability of transition by \( r^2 \). A minimum time \( \tau_M \) for the transition of the ion accross an open barrier (from a neutral state to a screening state) is assumed. The rate of field relaxation in a case that \( r \) is pre-defined is:

\[
K = \frac{r^2}{a^2 \tau_M} \quad \text{(related to ion concentration by: } a = N^{-1/3} \).
\]

(H.1)

Transforming to the notations of Zwanzig we define \( k \) and \( \theta \) as:

\[
k \equiv K / r^2 \quad , \quad \theta \equiv < r^2 >
\]

From eq. (H.1) we can make a preliminary estimation (for constant \( r \)) that

\[
k\theta \approx 1 / \tau_o \quad \text{(since } \tau_o \text{ is the relaxation time of the electric field). Using eq. (G.2)}
\]

\[
k\theta \approx 1 / (\rho \cdot 10^{-12} \text{sec/ohm-cm}) \sim 10^8 \div 10^{12} \quad \text{(for aqueous solutions).}
\]

The random parameter \( r \) fluctuates with thermal noise and relaxes as with respect to the viscosity of the liquid according to a Langevin equation. Where \( \lambda = 1 / \tau_o \):

\[
\frac{dr}{dt} = -\lambda r + F(t)
\]

(H.3)

A constraint is imposed on the statistical distribution of the random force \( F \) below. If the fluctuation of the gate is assumed to have an energy of a spring with angular elasticity constant \( Ga^3 \) (\( G \) the shear modulus \( \sim 10^{10} \text{dyn/cm}^2 \)) in a system of one degree of freedom, then by the equipartition theorem:
\[ k_B T = G \cdot a \cdot < r^2 > \]  
\[ (H.4) \]

Therefore I suggest that:
\[ k\theta = A / TG \]  
\[ (H.5) \]

where \( A \) is a constant independent of temperature (if \( 1/\tau_M \propto T^2 \)).

The fluctuating distribution function \( f(E, r; t) \) should obey **Liouville equation**:
\[ \frac{\partial f}{\partial t} = -\frac{\partial}{\partial E} \{dE \} - \frac{\partial}{\partial r} \{ dr \} \]  
\[ (H.6) \]

and from here we follow step by step the procedure described by Zwanzig [61]:

Substituting the equations for \( E \) and \( r \) in Liouville equation:
\[ \frac{\partial f}{\partial t} = -\hat{L} f - \frac{\partial}{\partial r} \{ F(t) f \} \]  
(*)

\[ \hat{L} \equiv -\frac{\partial}{\partial E} K(r) E - \frac{\partial}{\partial r} \lambda r \]

Solving equation (*) similarly to the way a Langevin equation is solved:
\[ \frac{\partial}{\partial t} \{ e^{i\lambda} f(E, r; t) \} = -e^{i\lambda} \frac{\partial}{\partial r} \{ F(t) f \} \]

\[ f(E, r; t) = e^{-i\lambda} f(E, r; 0) - \int_0^t ds \cdot e^{-i\lambda s} \frac{\partial}{\partial r} \{ F(s) f(E, r; s) \} \]

Substituting the result in the last part of equation (*) (which is used again):
\[ \frac{\partial f}{\partial t} = -\hat{L} f - \frac{\partial}{\partial r} e^{-i\lambda} F(t) f(E, r; 0) + \frac{\partial}{\partial r} \int_0^t ds \{ e^{-i\lambda s} \hat{L} \frac{\partial}{\partial r} F(t) F(s) f(E, r; s) \} \]

and averaging over Gaussian noise:
\[ g(E, r; t) = < f(E, r; t) > \]
\[ < F(t) F(s) f > = < f > + < F(t) > < F(s) f > + < F(s) > < F(t) f > \]
\[ = \delta(t - s) = 2\lambda \theta \delta(t - s) g \]

The last step was made using delta-Gaussian distribution and some factors that will make the amplitude of fluctuation end with \( \theta = < r^2 > \). Substituting the last results and integrating over half the time axis:
\[
\frac{\partial g}{\partial t} = -\dot{L}g + \lambda \theta \frac{\partial^2 g}{\partial r^2}
\]

and we arrive at the **Fokker-Planck** equation of this problem:

\[
\frac{\partial g}{\partial t} = \frac{\partial}{\partial E} [kr^2 E g] + \frac{\partial}{\partial r} [\lambda r g] + \lambda \theta \frac{\partial^2 g}{\partial r^2} \quad (H.7)
\]

The ensemble-averaged-electric-field is:

\[
<E(t)> = \int_0^\infty dr \tilde{E}(r,t), \text{ where:}
\]

\[
\tilde{E}(r,t) \equiv \int_0^\infty dE' \cdot E' \cdot g(E',r,t)
\]

We note that:

\[
\int_0^\infty dE' \cdot E' \cdot \frac{\partial g}{\partial E'} = -2 \int_0^\infty dE' \cdot E' \cdot g = -2\tilde{E}(r,t)
\]

By taking \( \int dE' \cdot E' \) before the two sides of the Fokker-Planck equation we arrive at the **reaction-diffusion** equation \([62,11]\):

\[
\frac{\partial \tilde{E}}{\partial t} = kr^2 \tilde{E} + \lambda \theta \frac{\partial}{\partial r} \left( \frac{\partial \tilde{E}}{\partial r} + \frac{r}{\theta} \tilde{E} \right) \quad (H.8)
\]

The solution of the reaction-diffusion equation (with reflecting boundary condition at \( r=0 \) and initial condition of Gaussian) is integrated to \(< E(t) >\)\([62]\). Expanded in a power series as described in \([62]\), a long time exponential decay is identified as the effective rate of the electric field relaxation:

\[
K_{eff} = \frac{\lambda}{2} \left[ 1 + \frac{4k\theta}{\lambda} \right]^{1/2} - 1 \quad (H.9)
\]

We point out that: \( \frac{1}{\tau_{\sigma}} = K_{eff} \) and \( \frac{1}{\tau_s} = \lambda \) and since \( \tau_s \geq \tau_{\sigma} \) and \( k\theta / \lambda \approx \tau_s / \tau_{\sigma} \) we use the limit of low \( \lambda \) for \( K_{eff} \) and from (H.9):

\[
\frac{1}{\tau_{\sigma}} = \left( \frac{k\theta}{\tau_s} \right)^{1/2} \quad (H.10)
\]

However N.Eizenberg and J.Klafter found an extension to the model that regards a threshold parameter for \( r \) below which \( K(r) \) is zero, defined:

\[
X_L = r_0 / \sqrt{\theta} . \quad (H.11)
\]
\[ K(r) = \begin{cases} 
0 & , r \leq r_0 \\
kr^2 & , r > r_0 
\end{cases} \]

\( r_0 \) is the diameter of the particle that moves across the bottleneck.

The following graph is one result of their numerical analysis study:

![Graph](image)

**Fig H.1.** Results for \( k\theta = 10 \). solid line- eq. H.9, black squares- \( X_L = 0.1 \), squares- \( X_L = 0.25 \), circles- \( X_L = 0.5 \). (picture from [12]).

Given the threshold parameter and order of magnitude of \( k\theta / \lambda \) the fractional parameter \( m \) is found as \( m = -m' \), \( m' \) being the tangent of the plot at the point \( k\theta / \lambda \).

\[
k\theta \tau_{\sigma} = B \left( \frac{1}{k\theta \tau_s} \right)^{-m'} \tag{H.12}
\]

Since we estimated that \( k\theta \approx 10^8 \cdot 10^{12} \) more study is needed for correlating \( X_L \) and \( m' \), but as Eizenberg and Klafter pointed out[12] the value of \(-m'\) is always between the limits 0.5 and 1.

The conclusion from (H.12), (G.2), (H.5) is:

\[
\frac{\varepsilon \rho}{GT} = B \left( \frac{An}{GT} \right)^m , \quad 0.5 \leq m \leq 1 \tag{H.13}
\]

We see that when the dielectric coefficient and shear modulus are constant eq. (H.13) is reduced to eq (A.1).

It can be easily tracked down from the plot that at high fluidity: \( \tau_{\sigma} = 1 / k\theta \), and in fact beyond the point \( \tau_s = 1 / k\theta \) an increase of fluidity does not increase conductivity.
suggests that the rate in an open barrier is indeed independent of viscosity, but this could not be explained from the framework of our mechanical model.

I. Mode Coupling Theory

We present a broader aspect of impedance principally relevant to much higher frequencies than available in our laboratory (such measurements have been made for aqueous LiCl solution). The dielectric coefficient at zero frequency is regarded (which is needed in equation H.13). The description below is based on a collection of papers on the subject, and an original calculation.

The motions of individual atoms (or ions) in glassforming liquids are strongly coupled, more than merely a perturbation to non interacting atoms. For characterization of the system one could speak of a distribution of structural relaxation times $g(\tau)$ and of the time correlation function of (ionic) density fluctuation $\phi(t)$ which is formally stated:

$$\phi(t) = \int_{0}^{\infty} d\tau \ g(\tau) \ \exp\left(-\frac{t}{\tau}\right)$$

(I.1)

Empirically a more definite behavior is found. Roland and Ngai [41] suggest the form:

$$\phi(t) = \begin{cases} 
\exp\left(-\frac{t}{<\tau_{\sigma}>}\right), & t < t_c \\
\exp\left(-\frac{t}{<\tau_{\sigma}>} \right)^{\alpha}, & t > t_c 
\end{cases}$$

(I.2)

The first line is a Debye form and the second is a Kohlrausch-Williams-Watts (KWW) form used already by Moynihan to fit results of aqueous LiCl solutions. Continuity condition implies that $\tau_{\sigma} = \left(t_c^{-1} <\tau_{\sigma}> \right)^{1/\alpha}$ [41], where $t_c$ is the transition between time domains. Debye relaxation usually arises in dipole rotations. However Moynihan pointed out that in aqueous solutions the hydrated cations attract the oxygen in the H-O-H bonds in a way that the dipole directions in the solvent are froze out. We conclude that 1) There are at least two types of resonances in ionic solutions (corresponding to the two parts of $\phi(t)$) 2) A difference in the spectra of impedance is expected between aqueous solutions and other solutions of polar solvents.
This view opens a completely new set of variables for the electric impedance relating to high frequencies (above $10^2$ MHz).

A Dielectric modulus is defined:

$$M_e = \frac{1}{\varepsilon^*} = \frac{1}{-i4\pi\sigma^*(\omega)/\omega} \quad [\text{cgs}]$$ (1.3)

An appropriate empiric formula for the dielectric coefficient is the Cole-Davidson [29] formula:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{(1 + i\omega\tau_\sigma)^\alpha} - i4\pi\frac{\sigma_0}{\omega}$$ (I.4)

($\sigma_0$ is the DC conductivity, * - marks a complex amplitude)

At high frequencies (certainly above $1/\tau_\sigma$) the third term (of D.C conductivity) does not play any part in the impedance.

It is now thought that $M_e$ is related to density correlation by:

$$M_e = M_\infty (1 + \int_0^\infty e^{-i\omega t} \frac{d\phi}{dt} dt)$$ (I.5)

$\phi(t)$ is the electric field relaxation function, with the form as shown above. A former suggestion by Williams and Watts [58] stated:

$$\frac{\varepsilon^* - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = \int_0^\infty e^{-i\omega t} \frac{d\phi}{dt} dt$$, and then by numerical calculations it was shown that for frequencies above the maximum peak in $\varepsilon''$ (the imaginary part of $\varepsilon^*$) the useful Hamon approximation is valid, which states that:

$$\frac{\varepsilon''_{\text{Hamon}}}{\varepsilon_0 - \varepsilon_\infty} = \frac{d\phi/dt}{\omega} \bigg|_{t=0.63/\omega}$$ (I.6)

For example with KWW relaxation function and $\omega >> 1/\tau_\sigma$:

$$\varepsilon''_{\text{Hamon}} \approx \frac{(\varepsilon_0 - \varepsilon_\infty)}{(\omega\tau_\sigma)^\alpha}$$ (I.7)

Hasz et al [19] noticed that the $\alpha$ parameter when fits to empiric results ($0 < \alpha < 1$) varies according to a pattern: It is a constant below the glass temperature transition and decrease above that point (in CKN melt and CLAP glass).
Halalay et al. [15] showed that in LiCl solution a scaling is found in (at least) two of its kinetic properties: the compressibility and dielectric modulus. A graph of \( \log(M'') \) (the imaginary part of the modulus) vs. \( \log(\omega / \omega_0) \) reduces the results at different temperatures to a single plot by choosing arbitrary \( \omega_0 \) (see below).

---

**Fig 1.1** Reduced plot of electric modulus for H2O/LiCl 13% (picture from [15]).

**Fig 1.2** The \( \alpha \) and \( \beta \) relaxation peaks (demonstration).
At higher frequencies we see another time zone (above 10^5 Mhz in aqueous solutions at room temperature, or above 10^3 Mhz in the glassy state). The short times behavior is marked with the β type of relaxation and it concerns with the process of escape of a particle from a “cage” of local minimum in energy [3]. In this range of times Roland and Ngai used the Debye form of \( \phi(t) \). In the long times behavior the KWW form of \( \phi(t) \) is well established. It is marked as the α type relaxation and it is a process of mid range diffusion or rearrangements involved in an interdependent motion of particles.

Mode-coupling-Theory predicts a connection between the relaxation peaks (or “resonances”). Using the notation in fig I.2 (\( a, b \): are the power coefficients) the relation is between the following gamma functions:

\[
\frac{\Gamma^2(1-a)}{\Gamma(1-2a)} = \frac{\Gamma^2(1+b)}{\Gamma(1+2b)}
\]

(I.8)

In a limited range of (high) temperatures: \( 1/\omega_0 - T - T_c \gamma \), \( T_c \) is somewhat higher than the glass transition), \( \gamma = (1/2a) + (1/2b) \).

Hasz et al reported [20] that they assessed \( \alpha \) from the width of the plot of \( \log(M''') \) vs \( \log(\omega / \omega_0) \). Their results for ZrF4 glasses confirm a law established by Angell of a linear relation between KWW parameter \( \alpha \) and the ratio of shear and conductivity relaxation times at the glass transition, as follows:

\[
\alpha = 0.85 \pm 0.05 - (0.025 \pm 0.005) \log_{10} \frac{\tau_\sigma}{\tau_g}
\]

(I.9)

However it is believed to suit only fused ionic salts, this rule fails in the case of aqueous LiCl solutions.

Based on Cole-Davidson formula - eq. (I.4), a calculation is offered which predicts the imaginary part of the dielectric modulus for \( \omega \tau_\sigma >> 1 \) (for details see the end of this chapter).

\[
\text{Im}\{M\}_{\omega \tau_\sigma >> 1} \approx \frac{\Delta \varepsilon \cdot \omega \tau_\sigma}{\left[ (\omega \tau_\sigma)^a + \Delta \varepsilon^2 / (\omega \tau_\sigma)^a \right] / \cos(\arctan(\omega \tau_\sigma)) + 2 \Delta \varepsilon}
\]

(I.10)

\( \Delta \varepsilon \equiv \varepsilon_0 - \varepsilon_\infty \) (and assuming \( \varepsilon_\infty \approx 1 \)).
To advance further we make numerical calculations. The slope (-b) near the α -peak was calculated according to eq. (I.10) with different values of α and ∆ε and it appeared that a rule can be stated, that:

\[ b \approx \alpha \quad \text{(nearly without depending on } \Delta \varepsilon) \quad \text{(I.11)} \]

([−b] is the slope of log [dielectric modulus] vs. log [frequency] in the range of frequencies \(10 \cdot \omega_\alpha\) to \(10^4 \cdot \omega_\alpha\), where \(\omega_\alpha\) is the point of the α -peak). For example the empiric value \(b=0.28\) for LiCl-H₂O corresponds to the value \(\alpha \approx 0.3\) where in fig G.1 appeared \(\alpha \approx 0.4\). On this theoretical basis when \(\alpha\) depends on temperature as in Angell’s rule \(b\) should depend on temperature in the same manner. The scaling that was found by Halalay (in fig I.1) is unique for LiCl aqueous solution, and not expected to hold for the glassformers that fit eq. (I.9).

The frequency point of the α -peak (\(\omega_\alpha\)) depends on \(\Delta \varepsilon\) according to eq. (I.10). By numerical calculation eq. (I.12) is determined, and can be used to estimate (within 10%) the value of \(\Delta \varepsilon\):

\[ \Delta \varepsilon_{\omega} = c_{(\alpha)} \cdot \frac{\log_{10} \omega_\alpha \tau_\sigma - 2.2}{\log_{10} \omega_{\alpha(\max)} \tau_\sigma - 2.2} \quad \text{(I.12)} \]

The coefficients appear in table I.1.

**Table I.1. Coefficients for formula I.12 for the dielectric coefficient at zero freq.**

<table>
<thead>
<tr>
<th>α</th>
<th>(k_{(\alpha)})</th>
<th>(\omega_{\alpha(\max)})</th>
<th>(c_{(\alpha)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>3.6</td>
<td>7.0</td>
<td>0.26</td>
</tr>
<tr>
<td>0.4</td>
<td>3.4</td>
<td>5.6</td>
<td>0.16</td>
</tr>
<tr>
<td>0.5</td>
<td>2.9</td>
<td>4.4</td>
<td>0.11</td>
</tr>
<tr>
<td>0.6</td>
<td>2.0</td>
<td>3.6</td>
<td>0.048</td>
</tr>
</tbody>
</table>

**Obtaining eq. I.10 from eq. I.4**
A remark: \((1 + i \omega \tau)^a = [1 + (\omega \tau)^2]^{a/2} e^{i \arctan(\omega \tau)}\)
and: \(e_\omega = 1\)

\[ \text{Im}\left\{ \frac{1}{1 + \frac{\Delta \varepsilon}{(1 + i \omega \tau)^a}} \right\} = ? \]

\[ = \text{Im}\left\{ \frac{1}{1 + \frac{\Delta \varepsilon}{[1 + (\omega \tau)^2]^{a/2}} e^{-i \arctan(\omega \tau)}} \right\} \]

\[ = \text{Im}\left\{ \frac{1 + \frac{\Delta \varepsilon}{[1 + (\omega \tau)^2]^{a/2}} e^{i \arctan(\omega \tau)}}{1 + \frac{\Delta \varepsilon^2}{[1 + (\omega \tau)^2]^{a/2}} + \frac{2 \Delta \varepsilon}{[1 + (\omega \tau)^2]^{a/2}} \cos[\arctan(\omega \tau)]} \right\} \]

\[ = \frac{\Delta \varepsilon}{[1 + (\omega \tau)^2]^{a/2}} \sin[\arctan(\omega \tau)] \]

\[ \approx \frac{\Delta \varepsilon}{(\omega \tau)^a} \sin[\arctan(\omega \tau)] \]

\[ = \frac{\Delta \varepsilon (\omega \tau)}{[1 + \frac{\Delta \varepsilon^2}{(\omega \tau)^{2a}}] \frac{1}{\cos[\arctan(\omega \tau)]} + \frac{2 \Delta \varepsilon}{(\omega \tau)^a}} \]

\[ = \frac{\Delta \varepsilon (\omega \tau)}{[(\omega \tau)^a + \frac{\Delta \varepsilon^2}{(\omega \tau)^{2a}}] \frac{1}{\cos[\arctan(\omega \tau)]} + 2 \Delta \varepsilon} \]
J. Microscopic objects and Einstein’s relation

This unit is intended to trace the roots of the decoupling between conductivity and diffusion by using formal definitions of these variables in liquid theory. We show that viscosity has entirely independent formal definition, it is related to the other kinetic properties through correlation functions.

Simple Liquids Theory

The theory of liquids [18] predicts the values of kinetic properties from density and current correlation functions. The analysis is built in the reciprocal space which is consequently taking a summation over the coordinates of \( N \) particles (as many as the edge becomes neglected):

\[
\begin{align*}
n_k(t) &= \int n(r,t) \exp(-ik \cdot r) dr = \sum_{i=1}^{N} \exp(-ik \cdot r_i(t)) \\
j_k(t) &= \sum_{i=1}^{N} u_i(t) \exp(-ik \cdot r_i(t))
\end{align*}
\]

\((u_i \text{ the velocity and } r_i \text{ the coordinate of the } i \text{ particle}).

A system of axes is chosen such that \( z \) is in the direction of \( k \) (of one fourier component). The longitudinal and transverse correlation functions are defined for an isotropic fluid as follows:

\[
\begin{align*}
C_l(k,t) &\equiv \frac{1}{N} <\hat{n}_k(t)\hat{n}_{-k}> k^2 <j^z_k(t)j^z_{-k}> \\
C_t(k,t) &\equiv k^2 <j^x_k(t)j^x_{-k}>
\end{align*}
\]

The longitudinal correlation function is related to the dynamic structure factor:

\[
S(k,\omega) = \omega^{-2} C_l(k,\omega) = \omega^{-2} (1/2\pi) \int_{-\infty}^{\infty} C_l(k,t) \exp(i\omega t) dt
\]

which is extracted from neutron scattering cross section:

\[
\frac{d^2\sigma}{d\Omega d\omega} = b^2 N S(k,\omega)
\]
(assuming coherent scattering, i.e. the same scattering potential for each particle).

Using the diffusion equation and hydrodynamic theory it follows respectively [18]:

\[
\frac{\partial}{\partial t} n_k(t) = -D k^2 n_k(t) \quad (J.7)
\]

\[
\frac{\partial}{\partial t} j^z_k(t) = -\nu k^2 j^z_k(t) \quad (J.8)
\]

(\(D\) is diffusion coefficient, \(\nu\) is kinematic viscosity).

Therefore:

\[
C_i(k,t) = C_i(k,0) \exp(-D k^2 t) \quad (J.9)
\]

\[
C_i(k,t) = C_i(k,0) \exp(-\nu k^2 t) \quad (J.10)
\]

which is an impressive point since \(D\) and \(\nu\) are usually in reciprocal relation to each other, and for water at room temperature \(\nu\) is ap. 100 times larger than \(D\).

A note should be added that using the equipartition theorem for one mass classical particles it is found that:

\[
C_i(k,0) = C_i(k,0) = k^2 (k_B T / M) .
\]

In a picture of one type classical particles and by the solutions above it follows:

\[
\nu = \frac{\pi M}{k_B T} \lim_{\omega \to 0} \lim_{k \to 0} \omega^2 C_i(k,\omega) \quad (J.11)
\]

and using Euler equation in the form \(\dot{j}^z_k(t) + (ik / M)\sigma^{zz}_k(t) = 0\) and Green-Kubo equation:

\[
\lim_{t \to \infty} \frac{1}{2t} \int_0^\infty <A(t) - A(0)> dt = \frac{1}{2} \int_0^\infty \dot{A}(t) \dot{A} > dt
\]

(J.12)

it has been shown that viscosity takes the from:

\[
\eta = \frac{n / N}{k_B T} \lim_{t \to \infty} \frac{1}{2t} <[A(t) - A(0)]^2 > \quad (J.13)
\]

\[
A(t) \equiv M \sum_{i=1}^N u_{ii}(t) r_{ei(t)} \quad (\text{In center of momentum axes frame.}) \quad (J.14)
\]

which is the form used in computer simulations.
**Linear Response Theory and the grounds for Einstein’s relation**

The procedure begins with a linear perturbation to a hamiltonian in the equilibrium state. A classical hamiltonian is preferred as a convenient tool to get meaningful results.

The perturbation hamiltonian:

\[ H' = F(r,t) \cdot A \]

is found as a product of a field and dynamic variable \( A \). The response to the force is found in a second dynamic variable \( B \):

\[ \phi_{BA}(t) = \int_0^t \phi_{BA}(t-s)F(r,s)ds \quad (J.15) \]

\[ \phi_{BA}(t) = -\int \sum_{i=1}^N \left( \frac{\partial A}{\partial r_i} \frac{\partial f_0^{(N)}}{\partial p_i} - \frac{\partial A}{\partial p_i} \frac{\partial f_0^{(N)}}{\partial r_i} \right)B(t)dr dp \quad (J.16) \]

The expression in parentheses is identified as the Poisson bracket \( \{A, f_0^{(N)}\} \).

The next step, which is usually taken without notice, is valid only by assuming the equipartition theorem is applicable, i.e. that \( f_0^{(N)} \sim \exp\left(\sum_i -H(p_i) / k_B T\right) \), thus:

\[ \{A, f_0^{(N)}\} = -\frac{1}{k_B T} \{A, H_0\}, f_0^{(N)} = -\frac{1}{k_B T} \dot{A}f_0^{(N)} \quad (J.17) \]

and then:

\[ \phi_{BA}(t) = \frac{1}{k_B T} <B(t) \dot{A}> \quad (J.18) \]

It is quite likely that the equipartition theorem can not be used in systems of atomic sized particles in viscous liquids (interaction depends on their place not as brownian particles). It is shown below how it is built into Einstein’s relation.

In the case of a simple liquid it is shown how Einstein’s relation (A.3) is derived. The substitution is:

- \( z \rightarrow A \) for location of a particle in direction of a force \( F \rightarrow F(r,t > 0) \).
- \( u_x \rightarrow B \) for velocity of a particle. And using eqs. (J.18) and (J.15) we derive:

\[ <\Delta u_x>_{(t)} = \int_0^t \frac{1}{k_B T} F <u_x(t)u_x> dt' \quad (J.19) \]

The mobility of a particle, hence:
\[ \mu = \lim_{t \to \infty} \frac{\Delta u_x > (t)}{F} = \frac{1}{k_B T} \int_0^\infty < u_x(t) u_x > dt' = \frac{D}{k_B T} \] (J.20)

Of course the last step needs an explanation. The diffusion coefficient \( D \) has another definition not reviewed above which is actually based on a solution of the diffusion equation in a certain initializing condition: the case that the initial location of a particle is known. Applying Green-Kubo formula (J.12) leads to the fact that \( D \) is related to the correlation function of velocity, and assuming isotropic liquid:

\[
D = \lim_{t \to \infty} \frac{1}{6t} < [r(t) - r(0)]^2 > = \int_0^\infty \frac{1}{3} < u(t') \cdot u > dt' = \int_0^\infty < u_x(t') \cdot u_x > dt' \] (J.21)

In ionic solutions eq (J.21) holds, but this time we are interested in the effect of an electric field \( E(t) \to F(r,t) \) on the current \( j_i \to B \). The perturbation hamiltonian is identified as:

\[
H = -\sum_{i=1}^{N} z_i e r_i E(t)
\]

\[
\sum_{i=1}^{N} z_i e r_i \to A
\]

(\( z_i \) is the ionicity, \( r_i \) the location of ion \( i \) on axis \( x||E \))

The result of substitution:

\[
< \Delta j_x (t) > = \int_0^t \frac{1}{k_B T} E(t') \sum_{i=1}^{N} < j_x (t') \dot{r}_i > z_i e dt'
\] (J.22)

For an AC field and 1:1 electrolye the conductivity is:

\[
\sigma(\omega) = \frac{ne^2}{k_B T} \int_0^\infty < j_x (t') j_x > \exp(i \omega t) dt' \] (J.23)

Since the correlation function decays after a characteristic time \( \tau_\sigma \) it appears from eq. (J.23) that for frequencies \( \omega << 1/ \tau_\sigma \):

\[
\sigma(\omega) = \frac{ne^2}{k_B T} D
\] (J.24)

However it should be remembered that eqs. (J.19) to (J.24) can be valid only based on the equipartition theorem. Hence the breakdown of this theorem in viscous ionic solutions may explain both the decoupling between diffusion and conductivity that was shown in chapter B, and the breakdown of Einstein’s relation.
**K. Dilute ionic solutions (supplement)**

For dilute solutions theory meets experiment. Some successful relations are detailed below for the sake of integration of previous works that were written 20-50 years ago with this work. The units used are in cgs, except for the units of equivalent conductivity which are traditionally in cm²/Ω mol. The concentration \( c \) is in mol/cm³. Mixed units are common in this field and usually omitted from the text. Formulas in [cgs] are put in a “convenient” form [38,13] by multiplying the conductivity as in \( 1/\Omega \cdot \text{cm} \) by 300 (volt to statvolt) and changing in one place \( N_A \times e \) in [cgs] to Faraday number in [mks]:

\[
N_A \times 1.6 \cdot 10^{-19} \text{coulomb} = 96500.
\]

We shall specify each time “convenient” variables are used (where equivalent conductivity is substituted in cm²/Ω mol but other variables are substituted in [cgs]). For dimensionality analysis we note that \( 1 \Omega = 1.113 \cdot 10^{-12} \text{cm}^2\text{sec} \).

**Falkenhagen-Vernon formula [38]**

Formula (K.1) based on the theory of Falkenhagen resembles a part of the empiric Jones-Dole formula. It is applicable up to a concentrations of 0.1 molar.

\[
\frac{\eta}{\eta_{\text{solvent}}} = 1 + s(\eta)\sqrt{c} \quad \text{(K.1)}
\]

\[
S(\eta) = \frac{0.2561 \cdot f_1}{\eta_{\text{solvent}} (eT)^{1/2}} \frac{\Lambda_0}{\lambda_+^0 \lambda_-^0} [1 - 0.6863 (\frac{\lambda_+^0 - \lambda_-^0}{\Lambda_0})^2]\]

\[
f_1 = \left(\frac{z_+ + z_-}{2}\right) \left(\frac{\nu_+ + \nu_-}{2}\right) |z_+ z_-|^{1/2}
\]

The symbols \( \lambda_+^0, \lambda_-^0 \) denote the equivalent conductivity \( (\sigma_i/c) \) of each ionic specie, and upper zero denotes the limit at infinite dilution: \( \Lambda_0 \equiv \lambda_+^0 + \lambda_-^0 \).
**Harned-Owen formula [38]**

The formula (K.2) is based on Debye-Hückle’s and Onsager’s theories and describes the limiting slope of equivalent conductivity versus concentration.

\[
\Lambda = \Lambda_0 - s(\Lambda) \sqrt{c} \tag{K.2}
\]

\[
s(\Lambda) = \Lambda_0 \frac{2.786 \cdot 10^6}{(\varepsilon T)^{3/2}} \frac{q^*}{1 + q^* f_2}
\]

\[
q^* = \frac{|z_+ z_-| (\Lambda^0_+ + \Lambda^0_-)}{(z_+ + z_-) (|z_+| \Lambda^0_+ + z_+ \Lambda^0_-)}
\]

\[
f_2 = |z_+ z_-|^{3/2} [(\nu_+ + \nu_-)/2]^{1/2}
\]

**Fuoss’ parametric equation (1978) [13]**

Fuoss equations have been used for the last three decades to interpret conductivity results for ionic solutions (recently see [22]). It is based on Debye-Hückle and the ideas of Onsager of the relaxation field effect (in the form \( \Delta \Lambda_{RX} = (\Delta E/E) \Lambda_0 \)) and the electrophoretic effect (originally in the form \( \Delta \Lambda_{EL} \sim \sqrt{c/\eta} \)). Fuoss’ 1978 model (K.3) includes a consideration of different classes of ionic pairing:

1. Active pairs which are free ions.
2. Virtual pairs which are paired by electrostatic force and correspond to Poisson-Boltzmann equation.
3. Dipolar pairs which never dissociate.

Virtual pairs and Dipolar pairs compose the group of diffusion pairs. In the equations below \( \gamma \) denotes the relative part of diffusion-paired ions in the sum of all ions, and \( \alpha \) denotes the part of dipolar pairs in the diffusion-pairs group.

The equation is defined only in a limited range of concentrations in view of one of Fuoss’ earlier papers (where he found a concentration point of transition from pairing ionic interaction to multiple body interaction to be around 1 molar).

The dependency on concentration is described in terms of a dimensionless variable \( t \):

\[
t = \kappa \sqrt{\nu} .
\]
κ is the reciprocal Debye length and changes as \( \propto \sqrt[2]{c} \).

\( \bar{r} \) is a fitting parameter of the minimum distance between opposite charge ions.

\[
\Lambda = [1 - \alpha(1 - \gamma)][\Lambda_o(1 + RX) + EL] \quad \text{(K.3)}
\]

where:

\[
RX = (\beta\kappa / 6)(1+q)(1+t)(1+qt) + \beta^2 \kappa^2 [(\ln t) / 12 + FH2 + (\beta\kappa)FH3] + DXV
\]

\[
EL = -\phi \gamma ^{1/2} [1 / (t + 1) + \beta\kappa(0.125\ln t + 0.5H1)]
\]

\[
DXV = (\phi \gamma ^{1/2} \beta\kappa / 8\Lambda_o)(0.5H2 - \ln t)
\]

\[
H1 = 0.19295 - 0.18508 t - 0.32106 t^2 + 0.40243 t^3 , \quad 0 < t \leq 0.4
\]

\[
0.20742 - 0.31145 t + 0.06461 t^2 , \quad 0.4 < t \leq 0.8
\]

\[
H2 = -2.6851 + 18.438 t - 35.735 t^2 + 28.476 t^3 , \quad 0 < t \leq 0.3
\]

\[
-2.0722 + 12.452 t - 15.804 t^2 + 6.0045 t^3 , \quad 0.3 < t \leq 0.6
\]

\[
-1.0425 + 6.9012 t - 5.812 t^2 , \quad 0.6 < t \leq 0.8
\]

\[
FH2 = 0.13842 - 0.25289 t + 0.16281 t^2 - 0.044868 t^3 , \quad 0 < t \leq 0.4
\]

\[
0.20758 - 0.32739 t + 0.14034 t^2 - 0.041583 t^3 , \quad 0.4 < t \leq 0.8
\]

\[
FH3 = 0.0084869 - 0.029776 t + 0.045001 t^2 - 0.026344 t^3 , \quad 0 < t \leq 0.4
\]

\[
0.007047 - 0.017767 t + 0.018269 t^2 - 0.006868 t^3 , \quad 0.4 < t \leq 0.8
\]

and:

\[
\phi = \frac{1.6390 \cdot 10^{-10} \kappa}{\eta \ c^{1/2}} \quad \text{[convenient units] (} \Lambda \text{ in cm}^2 / \Omega \text{ mol)}
\]

\[
\phi = \frac{N_A e^2 \kappa}{3\eta \ c^{1/2}} \quad \text{[cgs] (} \Lambda \text{ in [cgs] units)}
\]

\[
\beta = e^2 / \varepsilon k_b T = 1.6710 \cdot 10^{-3} / \varepsilon T
\]

\[
q = 1 / \sqrt{2}
\]

\[
\kappa = \left[ \frac{4\pi e^2 N_A}{\varepsilon k_b T} \gamma c \left( z^2 \nu^2 + z^2 \nu^2 \right) \right]^{1/2} = 1.1246 \cdot 10^{11} \cdot \left[ \frac{\gamma (z^2 \nu^2 + z^2 \nu^2)}{\varepsilon T} \right]^{1/2} \sqrt{c}
\]

Fuoss’ calculations are based on a linearized Poisson-Boltzmann equation which, regarding the size of an ion, is not always justified: The solution of the linear Poisson-
Boltzmann equation in case of 1:1 electrolyte with the conditions 
\[ \frac{\partial \psi}{\partial r} \rightarrow 0, \quad \psi \rightarrow 0 \]  is the Debye-Huckel potential:

\[ \psi(r) = \frac{ze}{\varepsilon} \frac{\exp(\kappa \tilde{r}) - \exp(\kappa r)}{1 + \kappa \tilde{r}} r, \quad \kappa = \frac{8\pi e^2 c N_A}{\varepsilon k_B T} \quad [\text{cgs}] \]

(\tilde{r} is the sum of two ionic radii). Then this approximated result is justified only if the following expression is much lower than \(1/z\):

\[ \frac{e \psi}{k_B T} = \frac{e^2}{k_B T \varepsilon (1 + \kappa \tilde{r}) \tilde{r}} \approx \frac{(4.8 \times 10^{-10})_{\text{esu}}^2}{4 \times 10^{-14}_\text{esu} \cdot 70 \cdot 5 \times 10^{-8}_\text{cm} (1 + \kappa \tilde{r})} \approx \frac{1.7}{(1 + \kappa \tilde{r})} \]

which is valid when the concentration is much higher than 0.15 molar. There are arguments, that the approximation is still true in most of the range around the ion and therefore, Debye-Huckel theory is valid for all ionic-sized particles.

It is remarked that Fuoss’ equations have been tested only at room temperature and are not expected to hold at low temperatures. That is since the correlation length in dilute solutions increases many times with lowering of temperature, and at the result degrees of freedom are lost (also not all interactions are electrostatic).

**Activity coefficient**

**Nernst equation**

The activity coefficient is somewhat an enforced entity that enters into the Nernst equation (K.4) because in dilute solutions the activity coefficient \(\gamma_{\pm}\) can be replaced by a constant and a simple empiric law is revealed. Nevertheless the activity coefficient dependency on concentration provides a valuable information about the ionic system. At infinite dilution the value for completely soluble salts is \(\gamma_{\pm} = 1\), but usually \(\gamma_{\pm 0}\) is less than 1 [CRC] and can be identified as the \(\gamma\) parameter in Fuoss’ equations.

The Nernst equation shows the effect of concentration on the electric potential of an electrode in open circuit (conventionally relative to a normal hydrogen electrode). For the reaction \(X^{z_e} \rightarrow X^{z_p}\)
The reversible potential is related to the free energy per mole ions, that is the electrochemical potential $\mu_e$, by:

$$
\mu_e = \mu_0 - eN_A \Phi_{rev} \\
= \mu_0 - \frac{RT}{(z_p - z_R) N_A e} \ln \left( \frac{\gamma_p m_p}{\gamma_R m_R} \right)
$$

(K.4)

where $m_R, m_p$ are the molal concentration of an ionic reactant and product (for a metal or a gas at one atmosphere $m = 1, z = 0$).

**Vapor pressure**

The activity coefficient can be found in measurements of the freezing point (or boiling point) temperature and in vapor pressure measurements. The latter is more common and is explained as follows:

We are treating a system of three components in equilibrium: the salt, the water, and the water vapor. The latter is almost an ideal gas. Designating $\alpha$ for some correction of the ideal gas equation:

$$
V = \frac{RT}{P} - \alpha
$$

(where $P$ is the pressure) and since the pressure effect is expressed in

$$
\Delta \mu_0 = \Delta P \cdot V = RT \Delta \ln(a_w)
$$

where $a_w$ is the activity of water in the solution (since it is proportional to the activity of water vapor), then:

$$
\frac{d \ln(a_w)}{dP} = \frac{1}{P} - \frac{\alpha}{RT}
$$

and thus:

$$
\ln(a_w) = \ln \left( \frac{P}{P_0} \right) - \int_{P_0}^{P} \frac{\alpha dP}{RT}
$$

(K.6)

However the second term in the right wing is negligible (below 0.1%) and it is excluded. Hence the activity of water is related to the vapor pressure of the solution $P$ and to the vapor pressure of a pure solvent (water) $P_0$ by:

$$
a_w \approx \frac{P}{P_0} \quad \text{(for exothermic<1, for endothermic>1, by eq. (K.13))}
$$

(K.7)

The water is in equilibrium with the ions and so we can use the Gibbs-Duam equation:
\[ \sum n_i dG_i = 0 \], and we arrive at:
\[ d \ln \gamma_\pm m_{salt} = - \frac{(1000/18)}{(\nu_+ + \nu_-) m_{salt}} d \ln(a_w) \]  
(K.8)

\( m_{salt} \) molality concentration in mol/kg).

The procedure to extract the average activity coefficient of the salt \( \gamma_\pm \), defined in the glossary) from the water activity involves expansion of \( \ln a_w \) in power series of \( m_{salt} \) and neglecting the first order term. It was shown to agree with the results from reversible potential measurements [40].

**Freezing point**

The freezing point temperature can be used to estimate the activity of water \( (a_w) \) in dilute solutions, and it is done by the following principles:

The idea is that the activity of the solid solution equals the activity of pure water ice \( (a_w^0) \) at the freezing temperature of the solution:
\[ \ln(a_w^0|_{T_w}) = \ln(a_s|_{T_w}) \]  
(K.9)

The activity of water in a solution \( (a_w) \) is quite different than the activity of water as a pure solvent \( (a_w^0) \): The former is constant for temperature down to the freezing point but the latter decreases just below 0°C. Therefore:
\[ \ln(a_w|_{T_w}) = \ln(a_w^0|_{T_w}) = \ln(a_w^0|_{T_w}) \]  
(K.10)

The key parameter of this dependency is the latent heat or the change in the enthalpy \( \Delta H_0 \) of the system during melting (per mole molecules of solvent) as shown below:
\[ \Delta \mu_0 = \Delta H_0 + T \Delta S_0 = \Delta H_0 + T \left( \frac{\partial \Delta \mu_0}{\partial T} \right)_p \]  
(K.11)

\[ \left( \frac{\partial \ln a_w^0}{\partial T} \right)_p = \left( \frac{\partial (\Delta \mu_0 / RT)}{\partial T} \right)_p = \frac{-\Delta H_0}{RT^2} \]  
(K.12)

(K.12) is named the Van’t Hoff equation.
using (K.9) (K.10) (K.12) and assuming the change in the freezing point is small 
\( \Delta T_m << T_m^* \) we find:

\[
\ln \left( a_w^{(\varphi - c)} \right) = \int_{273^\circ K}^{273^\circ K + T_m} \frac{-\Delta H_2}{RT^2} dT \approx \frac{-\Delta T_m \Delta H_0}{RT_m^2} = \frac{|\Delta T_m| \Delta H_0}{RT_m^2}
\]  
(K.13)

This equation has been examined and confirmed experimentally [38]. It is interesting to note that comparing to [K.7] we see that for an exothermic reaction of melting \( \Delta H_0 < 0 \) the product solution has lower vapor pressure.

**Diffusion coefficient**

Accurate and systematic results of activity coefficients are available for many aqueous ionic solutions in different concentrations [CRC]. Therefore it is pleasing to know that there is a way to extract from them the values of **diffusion** coefficients.

We step back to the original definition of the diffusion coefficient, superseding the form that was written in [A.4] by:

\[
\mu_{\text{salt}} = -D \nabla m_{\text{salt}}
\]  
(K.14)

\( m_{\text{salt}} \) - molality concentration, \( u \) - velocity). Also:

\[
\mu_{\text{salt}} = -Q \nabla \mu_{\pm}, \quad \mu_{\pm} = \frac{(v_+ \mu_+ + v_- \mu_-)}{v_+ + v_-}
\]  
(K.15)

Therefore:

\[
D = (-\frac{\partial \mu_{\pm}}{\partial m_{\text{salt}}} ) Q
\]  
(K.16)

and by using \( \Delta \mu_{\pm} = RT \ln(m_{\text{salt}} \gamma_{\pm}) \) ([K.4] + [K.5]) the result is:

\[
D = \frac{RT}{m_{\text{salt}}}[1 + m_{\text{salt}} \frac{\partial \ln(\gamma_{\pm})}{\partial m_{\text{salt}}} ] \cdot Q
\]  
(K.17)

A semi-empiric equation of Hall, Wishaw and Stokes [40] adopts this form and use fitting parameters that are valid up to 1 molar solutions (for 1:1 electrolyte):

\[
D = [D^0 + \Delta_1 + \Delta_2][1 + 0.036m_{\text{salt}}(\frac{D_{H \alpha}}{D^0} - n_H) \frac{\eta_{H \alpha, O}}{\eta}][1 + m_{\text{salt}} \frac{\partial \ln(\gamma_{\pm})}{\partial m_{\text{salt}}} ]
\]  
(K.18)

\[
D^0 \equiv \frac{RT}{N_\alpha \alpha \eta_{H \alpha, O}} \quad (4\pi < \alpha < 6\pi)
\]
where $D_{H_2O}$ is the self diffusion of water, and $n_H$ is the hydration number (number of water molecules hydrated to a positive ion).
Summary

Measurements of electric impedance were performed in two glassforming ionic liquids, resistivity was extracted according to the real part of impedance at a typical point. The results for AlBr3/KCl can be compared to previous results of Gorenbein [24-b], our results are more expanded in temperature range. Our results for aqueous LiCl (at stable condition) fit in one line with the results of Moynihan [36] at temperatures below (minus)-100°C (in supercooled condition), plotted in log-log graph for resistivity vs. viscosity (fig. F.2).

Data on low temperature measurements of resistivity and viscosity in aqueous solutions was searched by the indices of the Chemical Abstract in the years 1910-1998 and ended with additional data on KOH (and partially on KCl). Data on temperature and concentration dependence of resistivity and viscosity was tried into different formulas in the literature, and the conclusion was that for a wide range of concentrations and temperatures the following formulas are valid:

\[
T \frac{\sigma}{c} = B_1(T) - A_1(T) \cdot \sqrt{c} \tag{F.6}
\]

\[
T \frac{e^{-c/\epsilon_0}}{\eta(T)} = B_2(T) - A_2(T) \cdot \sqrt{c} \tag{F.7}
\]

The parameters change with temperature according to a VTF law:

\[
A_1, A_2, B_1, B_2 \sim \exp[-E_{i=1,2,3,4} / (T - T_0)]
\]

with \(T_0 = -130°C\) the glass transition temperature of “Naive water” (water without an instability point at -45°C as in hyperquenched and vapor-deposited water [31,45,46]). The formulas were used to extrapolate viscosity of aqueous LiCl. We also noticed that the maximal conductivity point is usually not at saturation.

Resistivity and viscosity results were compared in several ionic solutions and the “fractional law” (A.1) was confirmed in a wide range of systems and concentrations, as was shown in previous works [55,56]. The “fractional parameter” was found not to depend on concentration but on the solute itself (except perhaps in KOH). This suggests
that the “fractional parameter” depends exclusively on the size of the ion and its atmosphere. However the “fractional” relation between resistivity and viscosity is not a complete relation and the proportion between the two sides of eq. (A.1) is concentration dependent. The general behavior is summarized in eqs (F.6) and (F.7) but there are 8 parameters to be fitted to each solution and only 2 equations follows from eq. (A.1).

A model was developed which results with the “fractional law” when the shear modulus is not changing much over temperature. According to the model:

$$\frac{\varepsilon \rho}{GT} = B\left(\frac{A\eta}{GT}\right)^m, \quad 0.5 \leq m \leq 1$$

(H.13)

$m$ is expected to increase with the ionic size relative to the average opening of the gates (the threshold parameter eq. H.11, fig. H.1) and this was preliminarily confirmed by the experiments (fig. F.2, hydrated ion of Li is larger than K ion in molten salt, Ca and Na ions are even smaller). It is hoped that in eq. (H.13) $A, B$ are not concentration dependent and thus a mapping between resistivity and viscosity is established. In order to establish a new theory of resistivity in ionic solution the next scope should be on measurements of the shear modulus and its dependency on temperature and concentration.

In other works impedance measurements at extremely high frequencies yielded a parameter $b$, and a temperature dependent KWW parameter $\alpha$ (which is constant and maximal below the glass transition temperature). It was found here by numerical calculation that for $\alpha \geq 0.3 \ b \approx \alpha$. Assuming the Cole-Davidson form is correct, then $b$ is not a constant of the solution as was suggested by Halalay. On the basis of that calculation the dielectric coefficient at zero frequency depends on the frequency point of the $\alpha$-peak $\omega_\alpha$ according to:

$$\Delta \varepsilon_{\alpha(\omega)} = c(\alpha) \cdot \frac{\log_{10} \omega_\alpha \tau_\sigma - 2.2}{\log_{10} \omega_{\alpha(max)} \tau_\sigma - 2.2}$$

(I.12)

The result $\varepsilon \approx 1 + \Delta \varepsilon$ can be fitted to equation (H.13).

Aqueous LiCl has been investigated before in relation to the study of glasses [8]. Today some new ionic Fluorine-based glasses (used in the industry of fiber-optics [20]) are found of which viscosity decouples from electric resistivity and the fractional law (A.1)
becomes inapplicable. It is offered to test the shear modulus, via acoustic measurements, in order to understand this anomaly.

A practical tool for studying viscosity via impedance measurements can be provided if a mapping is established between the two kinetic properties, parametrized only by the size of the ions. The new experimental evidence that the “fractional law” is valid in dilute solutions leads to a possibility to dissolve a small amount of ionic salt in non-conducting liquids and apply the tool to study viscosity.

In June 1998 two samples from the Dead-Sea water were taken of the north and south lakes (the latter is higher in concentration) and resistivity was extracted from impedance measurements. The results were closer than expected: 5.28 ohm·cm (north) and 5.33 ohm·cm (south) at 25°C. Referring eq. (F.6) and typical results such close values are found either in solutions of negligible difference in concentration, or around the maximum of conductivity. The second possibility is correct and therefore the concentration of maximal conductivity for this solution lies between the concentrations of the two lakes.

A theory of resistivity in ionic solutions may find other applications such as in optimization of electrolytic batteries, engineering of solar heat reservoirs in sea waters, probing body liquids in medicine, probing magma properties, evaluation of the heat exchange in melting of icebergs in sea waters, etc.
A study of viscosity of aqueous solutions of copper sulphate and zinc sulphate.


Glassforming liquids with microscopic to macroscopic two-state complexity
(classification of types glassforming liquids: H-bonds - microscopic, long organic
molecules- mesoscopic, first order transition - macroscopic)

Contrasting effect of tetrahedral and octahedral complexing of trivalent cations on binary
molten salt solution transport properties. (e. conductivity and fluidity for α-
picHCl+FeCl3/CrCl3 at 300-500 deg in different concentrations)

Glass-forming composition regions and glass transition temperatures for aqueous
electrolyte solutions (phase diagrams for salt-water system: nitrates and chlorides).

Heat capacity changes in glass-forming aqueous solutions and glass transition in vitreous
water. (stating the idea of using aqueous solutions to test the glass transition of water,
and refering to an experiment with pure water ice ASW vapor deposited that reveals the
same temp transition).

Comparison of a primitive model perturbation theory with experimental data of simple
electolytes (formula to calculate activity coeff γ± and fitting parameters for the average
diameter of the ions for salts Li/K/Cs-Cl/Br/I)

[8] P. Chieux: The study of aqueous ionic glasses, (The physics and chemistry of aqueous
(Phase diagrams for LiCl.)

High-precision viscosity measurements (Jones-Dole coefficient for some salts)

(Bottlenecks as energy barriers or geometry barriers. Zwanzig model is applied to calculate fractional power law between rate of a process and viscosity of the liquid: in some cases it is 0.5-1. Applying the equipartition theorem leads to values that exceeds their tested values)


Molecular motion under stochastic gating.


Paired ions: Dipolar pairs as subset of diffusion pairs (summary of models, classification of ionic pairs, and numerical details of Fuoss’ conductance equation in the appendix)


Time-resolved measurements of scaling behavior in LiCl/H2O near the liquid-glass transition. (relating to MCT constants)


Liquid-glass transition in LiCl/H2O (graph from p.3569. p.3566: α-relaxation is typically the action of interdependence of nearby particles motions that effects long-distance diffusion, and β-relaxation is the action of caging a localized particle).


The temperature dependence of the viscosity of supercooled water.


Electrical relaxation in a CdF2-LiF-AIF3-PbF2 glass and melt. (KWW parameter dependence on temperature, electric modulus is related to the correlation function).


Physical properties of ZrF4-based glass-forming melts and glasses. (KWW parameter by width assesment of electric modulus, the linear relation between the parameter and τ ratio at Tg).


Applicability of Fuoss’s conductance equation to dilute electrolytic solutions in aqueous, nonaqueous, and aquo-organic mixtures. (for many salts)


Extension of the Falkenhausen-Leist-Kelbg equiation to the electrical conductance of concentrated aqueous electrolytes.
d- (1977).
Ion-solvent interaction and the viscosity of strong-electrolyte solutions (the model for increased fluidity in some solutions and how Jones-Dole coefficients relate to ionic interactions and long range structure breaking).
Pressure coefficients of conductance and glass transition temperatures in concentrated aqueous LiCl,LiI,AlCl3 solutions. (glass transition rise slowly with pressure 3deg/kbar, Tg~134°C , the 3 salt solutions are glassforming)
Transport properties of a dense fluid of hard spheres. (some part of the formulas should alter regarding to liquids but the products of diffusion-viscosity or thermal conductivity - viscosity are expected to hold for any fluid that consists of hard sphere particles with maxwellian distribution. Hence rejecting these results follows rejecting the picture of brownian ionic particles)
(Tables for KOH).
Glass liquid transition and devitrification of LiCl-11H2O solution and of hyperquenched and vapor-deposited water.
Concentrated salt solutions. I. Activity coefficients (NaSCN,NaI,NaClO4).
Concentrated salt solutions. II. Viscosity and Density (NaSCN,NaI,NaClO4).
Concentrated salt solutions. III. Electrical Conductance (NaSCN,NaI,NaClO4).
(good source for NaSCN in 25 deg for whole range of concentrations).
Comparison of shear and conductivity relaxation times for concentrated lithium chloride solutions. (the source for viscosity at low temp for 14.8%, 16.58%, 18.2%, and for the shear modulus of aqueous LiCl).

Conductivity and dielectric relaxation in concentrated aqueous lithium chloride solutions (supplement our measurements with lower temperature ones).

(Justification for Debye-Huckel model in light of linear approx of Poisson-Boltsman equation even though the approximation fails in the near neighborhood of the ion.)

The water activity of lithium chloride... (from vapor pressure).

(methods of diffusion measurements)

The anomalous Debye-Waller factor and the fragility of glasses. (defining fragility as the degree of departure of viscosity from Arrhenius law, it is connected with Debye-Waller factor)

The viscosity of concentrated aqueous solutions of strong electrolytes (source for viscosity vs.concentration at 25 deg for many salts. Partly for LiCl).

Evaluation of velocity correlation coefficient from experimental transport data in electrolytic systems. (generalized conductivity and diffusion).

The vapor pressure of aqueos solutions of sulfuric acid (comparision of activity coef by e.m.f and by vapor pressure up to 6m, in agreement)

Conductivity of supercooled aqueous Potassium Chloride solutions to -27°C and 50 MPa (What happens to dilute solutions that are not glassforming. The instability of water at -45°C effects with a power law divergence in resistivity, compressibility, viscosity, reciprocal self diffusion. explained in long range denisty-density correlation.)
Isothermal compressibility of supercooled water and evidence for a thermodynamic singularity at -45°C. (Table 1 summarizes the power law of different properties of water. Suggest that the divergence point is the temperature limit of supercooling stability, where nucleation must start whatever the rate of cooling is)

The diffusion coefficients of eight uni-univalent electrolytes (diaphragm)


Changes in Density, Viscosity, and Electrical Conductivity of Solutions of Alkali Metal Salts. (sigma vs. sqrtC, eta=a+b*eta0)

Electrical conductance of concentrated solutions of zinc sulphate.

Electrical conductance of concentrated solutions of strong electrolytes.

Power-law behavior in the viscosity of supercooled liquids. (Cites data on many pure liquids that are believed to show the divergence point of density-density correlation at supercooling, and also it is shown that this temperature point is lowered by mixing with viscosity-increasing salt).

Breakdown of the Stokes-Einstein relation in supercooled liquids. (Translational diffusion “decouple” from that relation because the motion passes through different domains.)


The fractional Stokes-Einstein law and Ionic transport in liquids.

(Source for accurate data on sea-water in different concentration/salinity and temperatures).

Viscosity and density of aqueous solutions of LiBr, LiCl, ZnBr2, CaCl2 and LiNO3.
Variation of the diffusion coefficients of electrolytes (diffusion×viscosity vs activity of water law. Does not fit recent data from CRC).

Rate processes with dynamical disorder. (in Appendix: derivation of Fokker-Planck eq from Liouville eq).

Dynamical disorder: Passage through a fluctuating bottleneck. (solution of the reaction-diffusion equation and long times effective rate).


File references: