# Fuoss-Kraus formalism for estimating ionic association degree

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THEORY:

Dissociation is a process in which ionic compound (i.e. salt, complex, etc.) split into smaller parts, like ions (anions, cations) and/or molecules. For simple binary (composed of only one cation and one anion) salt it means, that compound is dividing into anion (A) and cation (C):

$$CA \rightarrow C^+ + A^-$$
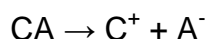
The part of a salt, that can dissociate (the propensity of salt to dissociate), is derived from the dissociation constant (K), which is specific for each compound. Many salts (those consisting of anion of a strong acid and/or cation of a strong base) would dissociate almost completely - the degree of dissociation (α) describes the part of salt that has dissociated. In our case, we will constrain the case to those salts of $\alpha = 1$ (or negligibly close to 1).

Electrolyte is a substance, that is made of ions (anions and cations), where solvent is only surrounding and separating (solvating) the ions.

There are two different ways of ion behavior, depending on a type of solvent. When solvent is polar (has a high dielectric constant – ε), like water ($\varepsilon \approx 80$) or many organic solvents, ions are having low electrostatic attraction, so they exist quite stable in a state of solitarity. In solvent of lower dielectric constant, then ions have electrostatic attraction high enough, so they can associate again (it is independent of the dissociation constant). The easier they associate, the bigger associates can be formed. Associates can be electrically neutral, like an ion pair (CA^0) or be electrically charged. Because of stability issues, associates cannot have too big charge, so the unitary charge is rather the highest one (both positive and negative). For usual cases of organic solvents (with $\varepsilon > 10$) it is assumed, with a negligible inaccuracy, that associates bigger then triplets (associates composed of three ions – CA_2^- or C_2A^+) does not exist. So the usual constituents of typical electrolytes to consider are ions, ion pairs and triplets.

In chemical power sources, such as battery cells, where electrolyte is a part of a cell, it is crucial to have a low concentration of constituents other than ions. Ion pairs are taking free ion's place in electrolyte while not making conductance higher. Ion pairs are immobile in electric field because of neutral charge, so their existence decrease maximum current (current density). Triplets are not only making conductance lower (like ion pairs), but the ion movement which is crucial for a cell (cations moving to the cathode) is reversed by them. When triplet have a negative charge (CA_2^-), it goes to the anode (positive

electrode) pulling with it one cation to the anode, so it decrease maximum current even more than ion pairs existence.

On the other hand, positive charged triplets wouldn't give straight electrical problems in terms of an electrochemical process, but both them and negative charged ones contaminate electrodes with constituents that shouldn't appear there (e.g. pulling a cation into the anode and building it in with anions into the crystalline structure of anode).

To conduct research on electrolytes with low concentration of associates it is necessary to have a research method to estimate their number. The Fuoss-Kraus formalism for estimating ions, pairs and multiplets (triplets) shares within electrolyte in a solvent is one of the most popular among electrochemists. It is because of its simplicity and repeatability of measurements independently of equipment class. Also the big advantage is that this method is used for many years, so it is easy to compare new electrolytes with old ones.

Theoretical basis for the method is a Fuoss-Kraus formalism, introduced in 1933 by Fuoss and co-workers. They were first to logically explain the unexpected drops in conductance in non-polar solvents (solvents with very low dielectric constant) at the very dilute electrolyte concentrations. They also introduced the idea of triplets and the method of deriving their limiting molar conductance. That way, combining mass action equilibrium, interionic forces phenomena (electrostatic attraction – Coulomb forces) and new idea, the formalism was created. The theory was used by Vincent and co-workers in 1986 to develop the method of estimating the ionic association degree and estimating fractions of ions associated in pairs or triplets.
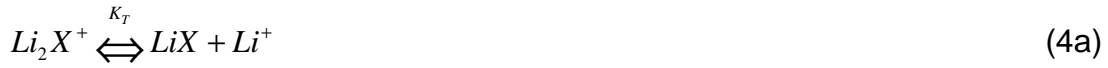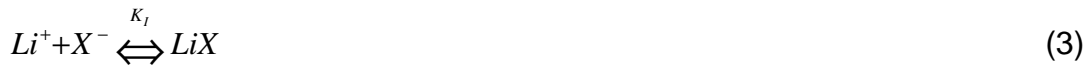
Estimating the association degree of ions in lithium electrolytes

Lithium cells are the most popular in battery industry these days. As an element of the most promising power source, lithium electrolyte will be taken for this very exercise as an example of use of this research method:

Concept of the method starts with the equilibria as follows:

$$LiX \Leftrightarrow Li^+ + X^- \tag{1}$$

$$LiX \Leftrightarrow \tfrac{1}{3} Li_2 X^+ + \tfrac{1}{3} LiX_2^- \tag{2}$$

where it is introduced the idea of the hypothetical electrolyte $Li_2X^+LiX_2^-$, which of course is the same as LiX, but is necessary for the next steps. First, we define constants K_I and K_T (indexes I, P and T stand for Ion, Pair and Triplet, respectively):

$$Li^+ + X^- \overset{K_I}{\Longleftrightarrow} LiX \tag{3}$$

$$Li_2 X^+ \overset{K_T}{\Longleftrightarrow} LiX + Li^+ \tag{4a}$$

$$LiX_2^- \overset{K_T}{\Longleftrightarrow} LiX + X^- \tag{4b}$$

and then we define α_I and α_T as the fractions of electrolyte existing as a solitary ions and triplets, respectively. Then:

$$K_I = \frac{1 - \alpha_I}{\alpha_I^2 c} \tag{5}$$

which after transformation gives

$$\alpha_I = \frac{-1 + \sqrt{1 + 4K_I c}}{2K_I c} \tag{6}$$

$$K_T = \frac{\alpha_T}{\alpha_I c (1 - \alpha_I - 3\alpha_T)} \tag{7}$$

which after transformation gives

$$\alpha_T = \frac{K_T \alpha_I (1 - \alpha_I) c}{1 + 3K_T \alpha_I c} \tag{8}$$

That all makes:

$$c_{Li^+} = c_{X^-} = \alpha_I c \tag{9a}$$

$$c_{Li_2 X^+} = c_{LiX_2^-} = \alpha_T c \tag{9b}$$

$$c_{LiX} = \alpha_P c = (1 - \alpha_I - 3\alpha_T) c \tag{9c}$$

while apparently:

$$\alpha_P = 1 - \alpha_I - 3\alpha_T \tag{9d}$$

We describe total conductance as:

$$\Lambda = \alpha_I \Lambda_0^I + \alpha_T \Lambda_0^T \tag{10}$$

where we define Λ_0 as a limiting molar conductance, which is a conductance measured in an infinitely diluted electrolyte.

Then, when α_I and α_T are small, equation (10) with substitution from equation (6) and equation (8) simplifies to:

$$\Lambda\sqrt{c} = \frac{\Lambda_0^I}{\sqrt{K_I}} + \frac{\Lambda_0^T K_T c}{\sqrt{K_I}} \tag{11}$$

which for a plot of $\Lambda\sqrt{c} = f(c)$ should give a linear plot (for concentrations small enough – near to the infinite dilution). From that plot (linear, $y = ax + b$ regression type) we can experimentally determine K_I and K_T (now coming back the way to obtain α_I, α_P and α_T). If we define, following the regression type:

$$\Lambda\sqrt{c} = \frac{\Lambda_0^I}{\sqrt{K_I}} + \frac{\Lambda_0^T K_T c}{\sqrt{K_I}} \Rightarrow \Lambda\sqrt{c} = b + ac \tag{12}$$

$$b = \frac{\Lambda_0^I}{\sqrt{K_I}} \tag{12a}$$

$$a = \frac{\Lambda_0^T K_T}{\sqrt{K_I}} \tag{12b}$$

then we will obtain:

$$K_I = \left(\frac{\Lambda_0^I}{b}\right)^2 \tag{13}$$

$$K_T = \frac{a\sqrt{K_I}}{\Lambda_0^T} \tag{14}$$

which will be possible to calculate, if we define the relation between limiting molar conductance Λ_0 and limiting molar conductances of free ions and triplets – Λ_0^I and Λ_0^T. These is usually assumed as a

$$\frac{\Lambda_0^T}{\Lambda_0^I} = \frac{2}{3} \tag{15}$$

And thus, while now all necessary data are obtained, one can calculate α_I, α_P and α_T from equations (6), (8) and (9d).

4

CARRYING OUT THE EXERCISE

The exercise consists of three parts:

1. Theoretical introduction and samples preparation;
2. Conductance measurements;
3. Calculations.

Preparation of the samples

Salt used in the exercise is $LiClO_4$, as a typical lithium electrolyte.

Solvent used in exercise is PC – Propylene Carbonate ($\varepsilon = 64.9$ at 20°C), which is commonly used as a solvent (usually mixed with other solvents) in commercially available cells.

Students should prepare about 6-7 samples (volume of few milliliters) of $LiClO_4$ in PC (1 M, 0.1 M, 0.01 M, 0.005 M, 0.001 M, 0.0005 M, 0.0001 M). The concentrations should be very low, because samples will be used for estimating the limiting molar conductance.

Each next sample (starting with the biggest concentration) should be prepared by diluting a part of the previous, as for obtaining precise concentrations.

Such electrolytes will be used to soak polypropylene separator (small circle cut out of separator sheet) with it. Then, soaked separator will be packed into the two-electrode cell (with blocking electrodes) as an electrolyte.

Conductance measurements

Conductance will be measured with the impedance spectroscopy measurement on Atlas FRA (Frequency Response Analyzer) system. For this exercise, no special processes will happen in a sample, because of blocking electrodes (not interfering with the electrolyte) used for measurement. Thus we will get an impedance of the sample as a resistance (real part of impedance) of it, and the geometrical capacity (imaginary part of impedance) of the sample (as if it was a large capacitor, not usable for exercise in any way).

For conductance measurement the amplitude of the ac signal should be set to 10 mV. Frequency range should be set between 100 kHz and 10 Hz (using logarithmic distribution of frequencies, four points for a decade).

Calculations

After collecting resistance (R) of the electrolyte at the certain concentrations, one should calculate a molar conductivity from it. To get it, the width (l) and surface (S) of the soaked, pressed separator is needed to obtain a value of the so-called cell constant (k). Then, the resistance is the inverse of the conductivity (κ), and so:

$$\Lambda = \frac{1000\kappa}{c} = \frac{1000k}{Rc} = \frac{l}{10\ SRc} \qquad (16)$$

where: Λ / S·cm^2·mol^{-1}

S / cm^2, l / µm, R / Ω, c / mol·dm^{-3}

k / cm^{-1}, κ / S·cm^{-1}

This values will be used to make the $\Lambda\sqrt{c} = f(c)$ plot, where the linear part will be of the interest. Regression made on the linear fragment will give the a and b coefficients from equation (12) for use in equations (13) and (14).

The limiting conductance (Λ_0) can be calculated fitting the plot of $\Lambda = f(c)$ with the Onsager equation:

$$\Lambda = \Lambda_0 - S\sqrt{c} + E \cdot c \cdot \log(c) + J \cdot c \qquad (17)$$

Calculation of the limiting conductance will be made by fitting with GnuPlot application (S, E, J and Λ_0 are the fitting variables).

Then the calculation of the α_I, α_P and α_T will be possible. It is also advisable to use obtained constants to calculate fractions of electrolyte for different concentrations to plot those values over the broad range of concentrations and to see the changes trends.

AFTERWORD:

Because of used model, the results are quite virtual. Firstly, basing on the specific model (with its limitations and idealistic assumptions), not on the direct calculation on empiric physical data, have to influence the result. Secondly, the differences between viscosities at different concentrations are one of the additional problems.

The disadvantage of the Fuoss-Kraus formalism is that it is only an electrochemical tool. To distinguish forms of ion bonding it has to be supported with other types of the measurements. That is why this very exercise is thematically connected with the IR/Raman exercise, where students can learn other way of estimating the constituents fractions in electrolytes.