Supplementary Information for:

Measuring the conductivity of very dilute electrolyte solutions, drop by drop

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DETAILED EXPERIMENTAL PROCEDURE

The experimental procedure for measuring the conductivity of the electrolyte solutions requires the calibration, washing and preparation of the vessel containing a precisely determined volume of deionized water, as follows:

1. Carefully wash the potentiometric cell of the conductivimeter with deionized water, until the conductivity measured in a sample of deionized water is at most 5 μS.

2. Calibrate the conductivimeter by measuring the conductivity of a solution of KCl 0,0100 mol L^{-1}. Adjusting or compute the cell constant of the conductivimeter such that the conductivity of this solution corresponds to that of KCl at the desired temperature (κ=1.4088 × 10^{-3} at 298K for KCl 0,0100 mol L^{-1}). After calibration, wash all the materials again until the conductivity of deionized water falls again below 5 μS.

3. For each electrolyte of interest (usually NaCl, HCl, KCl, NaAc, HAc, etc.): Solutions of these electrolytes of concentrations of about 0.05 mol L^{-1} should be prepared with the highest precision possible. These solutions can be already available or prepared by the students, depending on the time availability.

4. Estimate the volume of the drop of the electrolyte solution: Weight the volume of 20 drops of the electrolyte solution, and estimate the volume of a single drop from the density of the solution used. Repeat the procedure 5 times to estimate the error in the drop volume estimate (see Results and Data Analysis).

5. Add deionized exactly about 150 mL of deionized water to the vessel where the conductivity measures will be performed. Determine with the greatest precision

possible the initial amount of water, either by a precise volumetric determination or by weighing. Thermalize the system and place the conductivimeter inside to perform conductivity measures. Turn on gentle magnetic stirring.

6. Add a single drop of the electrolyte solution to the deionized water, as shown in Figure 1. The solution must be kept under constant magnetic stirring. Wait for the stabilization of the conductivity and annotate.

7. Repeat step 6 until about 50 to 100 drops are added. The number of drops added at each step can be increased as the student notes that a single drop does not promote a measurable change in conductivity.

LABORATORY ORGANIZATION AND DATA SHARING

Depending on the time availability and undergraduate level of the students the experiment can be organized in different forms. Some suggestions follow:

1. *In a two-hour laboratory experiment (General Chemistry, first-year undergraduate):* The stock solutions of all electrolytes should be already available in advance. Each student group is responsible for determining the conductivity as a function of the concentration for one electrolyte, three times, and the data is shared among all students for the different properties of the electrolytes to be compared.

2. *In a four-hour laboratory experiment (Physical Chemistry - advanced undergraduate):* The KCl solution for calibrating the conductivimeter should be prepared in advance. The solutions of the other electrolytes might be prepared by the students. Alternatively, each student or group of students might obtain the conductivity curves for multiple electrolytes. The data obtained can be shared among students to discuss sources of error. A third alternative is to study the temperature-dependence of the conductivity, in which case each group might be responsible for a single electrolyte.

DATA ANALYSIS

The students are requested to analyze the data according to the following procedure:

1. Use a spreadsheet to compute the total volume of the solutions after the addition of the electrolyte solutions, drop by drop. Using the concentration of the added solution and the initial volume of water, determine the concentration of the electrolyte following each addition.

2. Plot the conductivity measured as a function of the concentration of the electrolyte.

    a. For strong electrolytes: Obtain a linear fit of the plot, and from the slope obtain the molar conductivity.

    b. For weak electrolytes: Compute the molar conductivity at each concentration, and plot the inverse of the molar conductivity as a function of the molar conductivity times the concentration, according to the Ostwald dilution law. From the intercept at the slope obtain the molar conductivity at infinite dilution and the dissociation constant of the electrolyte.

3. From the molar conductivities at infinite dilution obtained, compute the limiting ionic conductivities of each ion. Use the limiting ionic conductivity of one of the ions obtained in the literature to successively obtain other values. For example, if HCl and NaCl molar conductivities were obtained, use the literature value of the ionic conductivity of H^+ to obtain that of Chloride and, then, that of Sodium ion.

4. Additional analysis to performed in a physical-chemistry course: Compute the transport velocity of all ions relatively to that of H^+ (the rate of the velocities is the rate of the limiting ionic conductivities[1]). Discuss why the velocity of the hydronium is particularly greater than all others.

5. Compare the molar conductivities at infinite dilution, limiting ionic conductivities, and dissociation constants, with literature values. Discuss sources of errors.

UNITS ANALYSIS

Units are a major source of confusion in the interpretation of the data of this experiment. The conductivimeter is set to show conductivities in µS cm^{-1}. The concentrations are most adequately plot in mmol L^{-1}, as presented in Figures 2 and 3 of the main manuscript.

The slope of the strong electrolyte solution linear fit has, therefore, units of

$$(µS\ cm^{-1})/(mmol\ L^{-1}).$$

These units are equivalent to S cm^2 mol^{-1}, which are usual units in which limiting ionic conductivities are presented.[1]

For weak electrolytes, using the same units, the plot of the inverse of the molar conductivity as a function of the conductivity times the concentration, must also be analyzed with care. The inverse of the molar conductivity will have units of [(µS cm^{-1})/(mmol L^{-1})]$^{-1}$, or

$$µS^{-1}\ cm\ mmol\ L^{-1}$$

which are equivalent to S^{-1} cm^{-2} mol. The plot in Figure 3D of the manuscript was drawn multiplying the obtained values of the y-axis by 10^3, such that the units are S^{-1} cm^{-2} mmol. As such, the inverse of the intercept of the plot will have units of S cm^2 mmol^{-1}. In Figure 3D, the intercept value is 2.966, with an inverse of 0.337 S cm^2 mmol^{-1}, or 337 S cm^2 mol^{-1}, which are the most common units for molar conductivities.

The slope of the linear fit of Figure 3D has units, therefore, of

$$(S^{-1}\ cm^{-2}\ mmol)/(µS\ cm^{-1}).$$

The goal is to obtain, from the slope, the dissociation constant, using

$$K_d = 1/[(\Lambda_m^\circ)^2 \times Slope].$$

With the units used to build the plot in Figure 3D, K_d results to have units of

$$1/\ [\ (S\ cm^2\ mmol^{-1})^2 \times (S^{-1}\ cm^{-2}\ mmol)/(µS\ cm^{-1})]$$

careful rearrangement leads to the equivalent units

$$10^{-6}\ mol\ L^{-1}.$$

The numerical value of K_d obtained directly from the plot is, then, 23×10^{-6} mol L^{-1}, or 2.3×10^{-5} mol L^{-1}, to be compared with the literature value.[2]

REFERENCES

(1) ATKINS, P.; DE PAULA, J. *PHYSICAL CHEMISTRY*; W. H. FREEMAN, 2009.
(2) COHN, E. J.; HEYROTH, F. F.; MENKIN, M. F. THE DISSOCIATION CONSTANT OF ACETIC