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

Leandro Martinez

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The study of the conductivity of electrolyte solutions is important for practical applications and for the understanding of ion mobility. Because of that, undergraduate experiments on ionic conductivity are common practice in first year general chemistry or more advanced physical chemisdegreetry laboratories. Often, the conductivities are measured for solutions prepared for various salts, in a range of concentrations, and the relationship between solution conductivity and concentration is interpreted in terms of the Kohlrausch law. Extrapolation of the molar conductivities to infinite dilution allows the study of the individual ionic conductivities. In practice, the preparation of dilute solutions for these experiments can be cumbersome, because small electrolyte contaminations can dominate the conductivity of the solutions. Additionally, significant amounts of reactants, particularly deionized water, must be used. Here, a simple experimental procedure is proposed to obtain the concentration dependence of ionic conductivities for very dilute (sub-millimolar) electrolyte solutions. The experiment consists in measuring the conductivity of solutions of increasing concentration prepared by dropping the electrolyte solution into a single initial vessel of deionized water. The range of concentrations achieved is one in which the conductivities vary linearly with the concentrations, such that the molar conductivities can be obtained directly without the use of the Kohlrausch equation. The simplicity of the experimental procedure leads the students to obtain very good quality results using minimal amounts of materials. Examples are presented for the conductivities of various strong electrolytes, and for weak acetic acid electrolyte, for which the conductivity is dependent on the degree of dissociation even at very low concentrations

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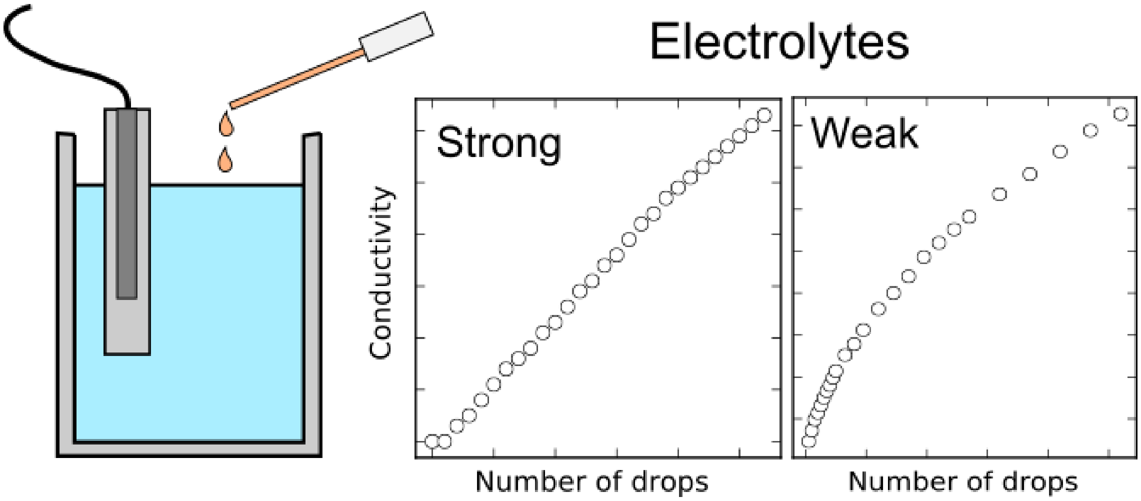
Institute of Chemistry, University of Campinas, Campinas, Sao Paulo 13083-970, Brazil

ABSTRACT

The study of the conductivity of electrolyte solutions is important for practical applications and for the understanding of ion mobility. Because of that, undergraduate experiments on ionic conductivity are common practice in first year general chemistry or more advanced physical chemisdegreetry laboratories. Often, the conductivities are measured for solutions prepared for various salts, in a range of concentrations, and the relationship between solution conductivity and concentration is interpreted in terms of the Kohlrausch law. Extrapolation of the molar conductivities to infinite dilution allows the study of the individual ionic conductivities. In practice, the preparation of dilute solutions for these experiments can be cumbersome, because small electrolyte contaminations can dominate the conductivity of the solutions. Additionally, significant amounts of reactants, particularly deionized water, must be used. Here, a simple experimental procedure is proposed to obtain the concentration dependence of ionic conductivities for very dilute (sub-millimolar) electrolyte solutions. The experiment consists in measuring the conductivity of solutions of increasing concentration prepared by dropping the electrolyte solution into a single initial vessel of deionized water. The range of concentrations achieved is one in which the conductivities vary linearly with the concentrations, such that the molar conductivities can be obtained directly without the use of the Kohlrausch equation. The simplicity of the experimental procedure leads the students to obtain very good quality results using minimal amounts of materials. Examples are presented for the conductivities of various strong electrolytes, and for weak acetic acid electrolyte, for which the conductivity is dependent on the degree of dissociation even at very low concentrations.

GRAPHICAL ABSTRACT



KEYWORDS

Topics: Conductivity; Domain: Physical Chemistry; Audience: First-Year Undergraduate / General; Upper-Division Undergraduate; Pedagogy: Hands-On Learning / Manipulatives.

The study of the conductivity of electrolyte solutions is important for the development of electrochemical devices,[1,2] for the characterization of the dissociation equilibrium of weak electrolytes,[2–4] and for the fundamental understanding of charge transport by ions.[5] Therefore, experiments in general chemistry and physical chemistry laboratories are widespread in undergraduate chemistry courses, and are subject to many educational developments, from the development of conductivity measuring apparatus to the preparation and study of specific electrolytes.[1,2]

Typically, the conductivity κ of electrolyte solutions is measured for electrolyte solutions with concentrations in the range of 10^{-3} to 10^{-1} mol L^{-1}, as solutions in this range of concentrations can be easily prepared.[2,5,6] The molar conductivity Λ_m ($\Lambda_m = \kappa/c$) of strong electrolyte solutions can be nicely fit by the Kohlrausch equation, [7]

$$\boldsymbol{\Lambda_m = \Lambda_m^\circ - K\sqrt{c}} \tag{1}$$

where Λ_m° is the molar conductivity at infinite dilution and c is the concentration of the solution. The molar conductivity of weak electrolytes, on the other hand, is dependent on the degree of dissociation of the electrolyte. At the limit of very dilute solutions, the Ostwald dilution law is expected to be followed,

$$\boldsymbol{\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^\circ} + \frac{\Lambda_m}{(\Lambda_m^\circ)^2}\frac{C_A}{K_d}} \tag{2}$$

The molar conductivity at infinite dilution can be decomposed into the contributions of each ion,

$$\boldsymbol{\Lambda_m^\circ = \nu^+\lambda^+ + \nu^-\lambda^-} \tag{3}$$

where λ^+ and λ^- are the ionic conductivities of the positive and negative ions, respectively, and ν^+ and ν^- are their stoichiometric coefficients in the salt molecular formula. From the concentration dependence of the molar conductivity of each salt, it is possible to obtain the molar conductivities at infinite dilution through Equation 1. If salts sharing the same ions are studied, it is possible to obtain by solving a linear system of equations the ionic conductivities, which are intrinsic properties of the transport of each ion in the solvent studied.

Currently, portable conductivimeters with μS cm^{-1} sensitivity are accessible to undergraduate laboratories, and are robust enough to be manipulated by students of any level. In principle, this sensitivity would allow the study of electrolyte solutions with concentrations in the micromolar to millimolar range. The difficulty in obtaining good quality conductivity measures is associated mainly to the preparation of the solutions, manipulation, and cleaning of the apparatus, because small contaminants of concentrated solutions of electrolytes can dominate the conductivity measures of more dilute solutions. In the dynamics of an undergraduate laboratory experiment, with limited time available, our experience is that many students fail to obtain conductivity measures which fit the expected equations and the discussion of the results becomes impaired.

Here, a simple experimental procedure is proposed to perform a laboratory experiment on the conductivity of electrolyte solutions at sub-millimolar concentrations. The procedure consists of dropping the electrolyte solution to an initial volume of deionized water. The method saves significant quantities of material and the results obtained are robust and reproducible.

Curriculum context

The strategy was practiced in laboratories of general chemistry and laboratories of physical chemistry taught to students of Engineering and Chemistry of the University of Campinas (UNICAMP).

First-year undergraduate students of Mechanical Engineering were introduced to the concept of ionic conductivity in the context of understanding electrolytic cells and ionic current. The experiment was performed in the “QG100 – Chemistry” course of the University of Campinas, which consists in a 2 hour lecture coupled to a 2 hour laboratory practice. In this case, the laboratory practice was performed by a group of about 70 students which formed groups of 3 students. Each group was responsible for conducting conductivity measures for a two different electrolytes. In this case, the outcome was that the students were able to probe and discuss qualitatively the differences in ionic conductivities of different cations and anions, by comparing the results with the ones of other groups.

The same experimental strategy was used in the “QF632 – Experimental Physical Chemistry I” course of the Institute of Chemistry of the University of Campinas, which is taught to second year undergraduates of the Chemistry course. Each practice consists of a two-hour lecture followed by a four-hour practice. The experiment was performed by groups of 3 students, formed from classes of about 30 students. In this case, given the greater student training and increased laboratory time, the groups performed the conductivity measures for several (up to four) electrolytes, including a weak electrolyte for every group. The students were then guided through the construction of Ostwald dilution plots and the discussion on degrees of dissociation, conductivities, and ionic transport mechanisms.

In both cases, the quality of the results obtained on the conductivity measures was similar to that presented in this article. Since in the range of concentrations probed the conductivity of strong electrolytes is linear with concentration, the possibility of decomposing the salt conductivity in individual ionic conductivities can be discussed without appealing to ionic interactions and deviations from ideality. Therefore, the students can readily associate the different salt conductivities with the transport velocities of the ions in solution. These velocities can be discussed qualitatively or quantitatively, depending on student background and lecture time.

EXPERIMENTAL PROCEDURE

In brief, the procedure consists on measuring the conductivity of solutions of electrolytes with increasing concentration, which are prepared simply by dropping the stock electrolyte solution into a sample of initially deionized water of known volume. The volume of the drop was determined previously by weighing samples of 20 drops and averaging. The conductivity was measured after each drop addition, after a proper stabilization time. All the measurements were performed with solutions thermalized at the desired temperature (298K) by coupling to a thermal bath, as shown in Figure 1. Additional experimental details, involving the careful cleaning and calibration of the conductivimeter are similar to other procedures proposed for the study of electrolyte conductivities in general chemistry and physical chemistry undergraduate laboratories, and are described in the Supplementary Information.[2,5]

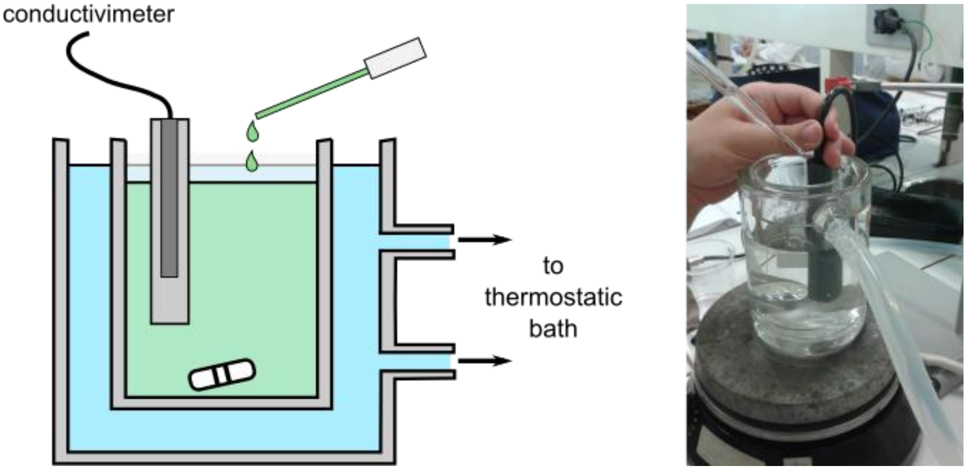


Figure 1. Experimental arrangement for conductivity measurements. The conductivimeter is placed inside a thermalized vessel containing deionized water. Drops of an electrolyte solution are added to the system under constant stirring. The conductivity is measured after the addition of each drop, after a proper delay for the homogenization of the solution and stabilization of the measured conductivity.

HAZARDS

The solutions used are usually very dilute and do not have significant hazard. Leftover solutions can be disposed down the drain.

RESULTS AND DATA ANALYSIS

Drop volume and error

The drop volume was estimated by measuring the mass of 20 drops and averaging for a single drop. The densities of the solutions were considered to be the same of that of water at the same temperature. Alternatively, they could be determined by the students. Five estimates of the drop volume were obtained to compute an average, using each electrolyte solution studied.

A typical drop volume was of about 0.05 mL. The initial volume of water was proposed to be of 150 mL, such that the addition of 100 drops represented less than 4% of the total volume of the solution. The students used a spreadsheet to compute the total volume of the solution after the addition of each drop for computing the concentrations. At the same time, the error associated with ignoring the volume of the solution added was discussed: If the electrolyte solution has a concentration of 0.05 mol L^{-1}, the concentration of the solution after the addition of the first drop is ~1.7×10^{-5} mol L^{-1}. After the addition of 100 drops, the concentration rises to ~1.7×10^{-3} mol L^{-1}. Thus, most of the experiment was performed in the sub-millimolar concentration range.

As an advanced topic, the teacher might want to discuss how to estimate the variation in the volume of a single drop from the standard deviation of the means measured. Indeed, each volume estimate was obtained by averaging the volume of 20 drops. Therefore, the standard deviation obtained between the estimates was the *standard deviation of a mean*. The standard deviation of individual estimates (SD) is related to the standard deviation of the mean ($SD_{\bar{x}}$) through $SD = SD_{\bar{x}}\sqrt{N}$, where N is the number of samples used to compute the mean.[8] A typical result was to obtain a standard deviation of the mean of the weights of 20 drops of 1-2%, such that the variation in the volume of a single drop was of the order of 4-8%. The volume, and thus the concentration, error after the addition of N drops was estimated as the standard error of the mean of N drops, and was of the order of (4-8)/$\sqrt{N}$%. The greatest error in the concentration estimate is associated to the addition of the first drop, and was reasonably estimated to be below 10%, not compromising overall quality of the results.

Strong electrolytes

The molar conductivity of strong electrolytes is expected to follow the Kohlrausch law (Equation 1). For sufficiently dilute solutions, however, $\Lambda_m^\circ \gg K\sqrt{c}$, and thus the molar conductivity is expected to be approximately constant and equal to the molar conductivity at infinite dilution ($\Lambda_m \approx \Lambda_m^\circ$). In other words, since $\kappa = \Lambda_m c$, if one plots the conductivity κ as a function of the concentration, a linear correlation with slope Λ_m° is expected.

In Figure 2 we display the results obtained by students at the regular course "QF632 - Experimental Physical Chemistry – I" of the Institute of Chemistry of the University of Campinas (UNICAMP), for strong electrolytes. The range of concentrations achieved was within 10^{-5} and 0.5×10^{-3} mol L^{-1} for the addition of up to 100 drops of 0.05 mol L^{-1} electrolyte solutions into initial deionized water volumes varying between 150 and 250 mL, depending on the student's solution preparation details. All experiments were performed at 298K, within the precision of the thermostatic bath available. We plot here the conductivity as a function of the number of drops added or concentrations, up to 0.5×10^{-3} mol L^{-1}. In this range of concentrations, the linearity of the conductivity with the concentration is clear, as shown in Figure 2, and suggests that the approximation that $\Lambda_m^\circ \gg K\sqrt{c}$ can be used. The data obtained can be fit by linear equations with correlation coefficients greater than 0.997 in all cases. The slopes provide directly the molar conductivity in this range of concentrations, which is constant and expected to be a good approximation of the molar conductivity at infinite dilution.

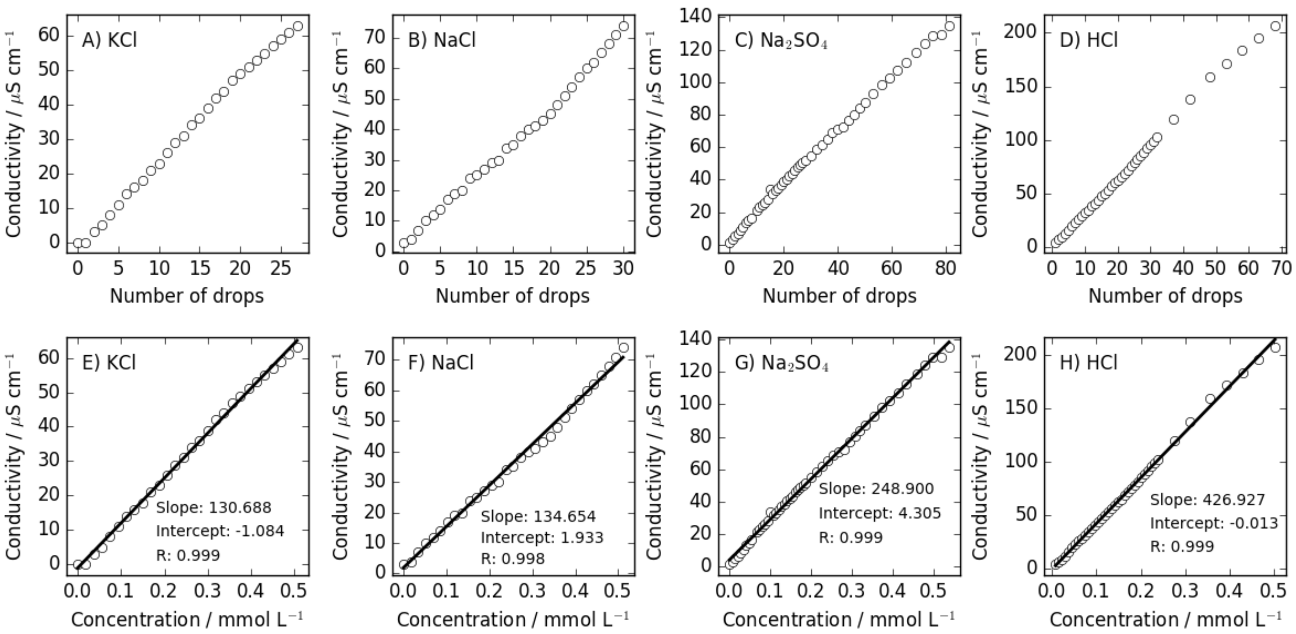


Figure 2. Conductivity as a function of the number of drops of electrolyte solution added or concentrations, for strong electrolytes. At the sub-millimolar range of concentrations probed, the conductivity is clearly linearly dependent on the concentration, and the molar conductivities at infinite dilutions can be obtained directly from the slopes of the linear fits.

Table 1 displays the molar conductivities at infinite dilution obtained from the linear fits of Figure 2 and the expected results from the literature. The greatest absolute error in this set is observed for KCl and is of 12.6% of the tabulated value. It is not possible to attribute the imprecision of the obtained data to the conductivity measures, as the remarkable linearity of the plots in Figure 1 indicate that no random error was associated with the estimate of the slopes. The errors are, therefore, systematic for each experiment, and can be attributed to the preparation of the solutions, or the improper control of temperature or calibration of the conductivimeter. For example, a 1°C error in temperature is associated to a conductivity variation of ~3% for NaCl.[3] These errors are acceptable for an undergraduate laboratory experiment and are similar to those obtained using more concentrated solutions and the use of the Kohlrausch equation, as reported by Eslek and Tulpar.[5]

Table 1. Molar conductivities at infinite dilution in S cm^2 mol^{-1} obtained by students for strong electrolyte solutions, compared to expected values from the literature, according to the data shown in Figure 1.

Electrolyte	Experimental	Expected	Error
KCl	131	149.8	-12.6%
NaCl	135	126.4	+6.8%
Na_2SO_4	249	260.2	-4.3%
HCl	427	426.0	+0.2%

Weak electrolytes

The use of the drop by drop strategy was also use for the study of the conductivity of acetic acid (HAc). At the range of concentrations achieved by the present experimental procedure, the degree of dissociation of HAc varies between 0.8 and 0.1, as shown in Figure 3A. The degree of dissociation is computed from

$$K_d = \frac{\alpha^2 C_A}{1-\alpha}$$

where C_A is the analytical concentration, and K_d = 1.75×10^{-5}, which is the expected value for T=298K.[9] Because of the range of dissociation degrees probed, the conductivity varies non-linearly with the concentration of the acid. Figures 3B and 3C show the conductivities obtained by students as a function of the number of drops added to the solution and as a function of the concentration of the acid. Clearly, the conductivity increases less than linearly with concentration, because of the decreasing degree of dissociation.

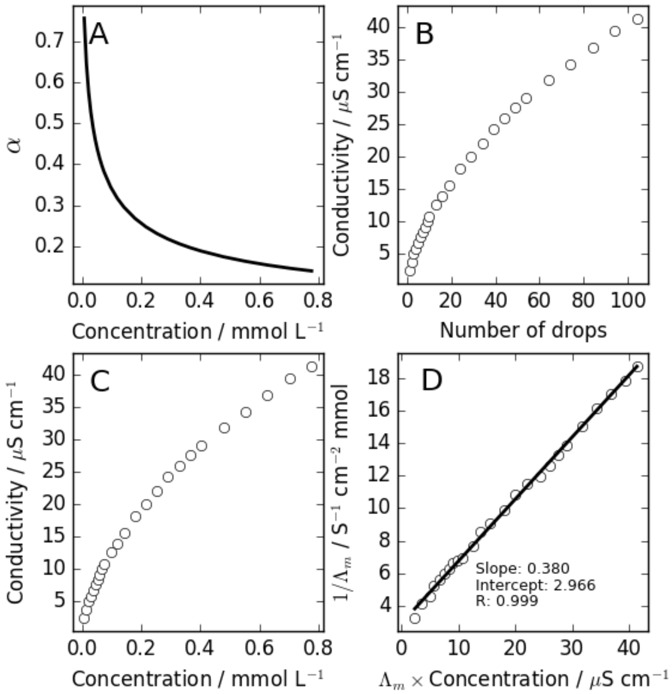


Figure 3. Study of the conductivity of weak electrolyte solutions: acetic acid as an example. (A) Degree of dissociation, α, as a function of the concentration in the range of concentrations probed by the dropping procedure. (B) Conductivity as a function of the number of drops added. (C) Conductivity as a function of the concentration of the solution. (D) Inverse of the molar conductivity as a function of the molar conductivity times the concentration, which corresponds to the Ostwald dilution law plot. From the intercept and slope of the linear fit it is possible to obtain the limiting molar conductivity and the dissociation constant of the electrolyte.

The analysis of the conductivity of weak electrolytes, taking into account the degree of dissociation, was performed with Ostwald dilution law (Equation 2). A plot of the inverse of the molar conductivity as a function of the product between the molar conductivity and the concentration is expected to be linear, with intercept $1/\Lambda_m^\circ$ and slope $1/[(\Lambda_m^\circ)^2 K_d]$. From the intercept the molar conductivity at infinite dilution was computed, and from that the dissociation constant using the slope of the linear fit.

Figure 3D shows results obtained by students for the application of the Ostwald dilution law to the conductivity measures of acetic acid. The linearity of the plot is clear, and the intercept and the slope of the plots can be used to compute the limiting molar conductivity and dissociation constant of the acid. Table 2 shows the final results obtained. The limiting molar conductivity was obtained within

14% of the expected value, and the dissociation constant was obtained with a 24% error, nicely within the expected order of magnitude.

Table 2. Molar conductivity at infinite dilution and dissociation constant obtained for acetic acid from the application of Ostwald dilution law to the data presented in Figure 3.

	Experimental	Expected	Error
Λ_m° / S cm^2 mol^{-1}	337	390.7	-13.7%
K_d	2.3×10^{-5}	1.75×10^{-5}	+23.9%

SUMMARY

In this article, we suggest a simple method to prepare solutions of very low (sub-millimolar) concentration, to be used in the study of conductivity of electrolyte solutions in general chemistry or physical chemistry undergraduate laboratories. The method consists in preparing solutions with increasing concentration by dropping the electrolyte solution into an initial sample of deionized water. The procedure saves material and is robust in the sense that the manipulation of the solutions is minimal, such that the students frequently obtain satisfactory results. The range of concentrations obtained is such that the limiting molar conductivities of strong electrolytes can be obtained with good accuracy without the use of Kohlrausch law, directly from the molar conductivity of the solutions, which is essentially constant at the concentration ranges sampled. The method can be used also to study the dissociation equilibrium of weak electrolytes by means of the Ostwald dilution law. The method was satisfactorily used in first-year General Chemistry and second-year Physical Chemistry laboratories.

ASSOCIATED CONTENT

Supporting Information

Supporting Information is available: Hazards, Detailed Experimental Procedure, Laboratory Organization and Data Sharing, Data Analysis; Units Analysis.

AUTHOR INFORMATION

Corresponding Author

*E-mail: leandro@iqm.unicamp.br

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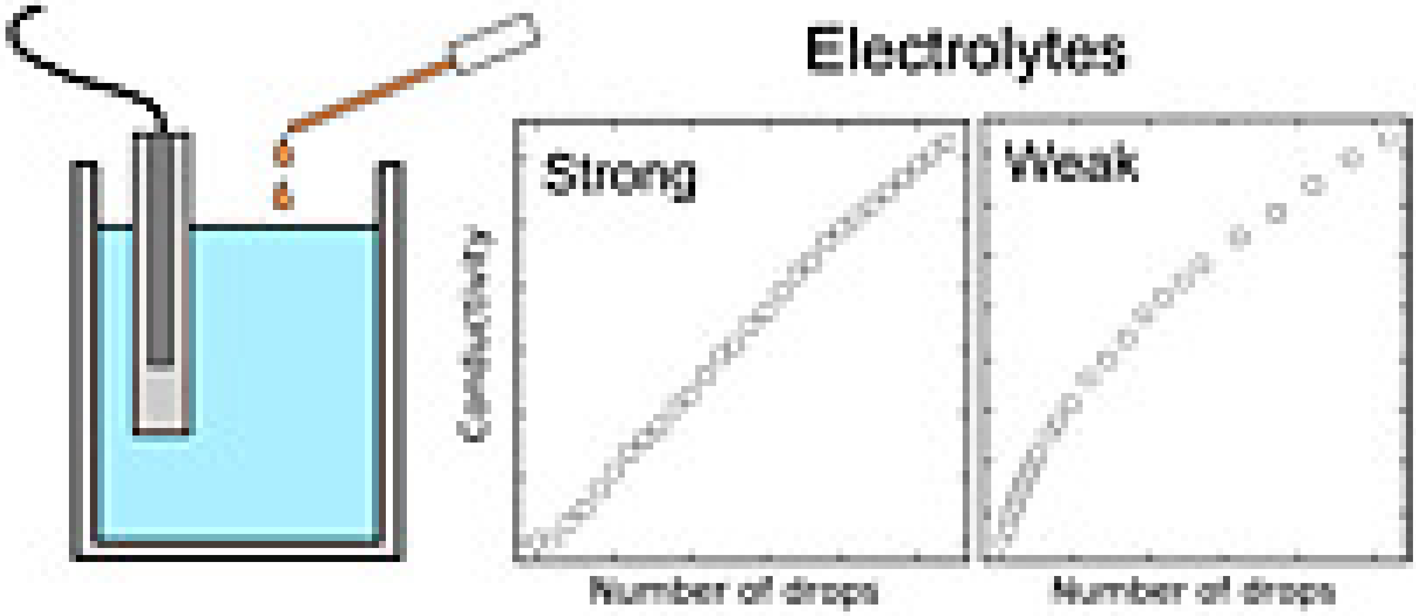
Electrolytes
Strong
Weak
Conductivity
Number of drops
Number of drops

Supplementary Information for:

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Institute of Chemistry, University of Campinas, Campinas, São Paulo 13083-970, Brazil

leandro@iqm.unicamp.br

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 × (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]

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