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Electrolytic conductivity, Debye-Hückel theory, and the Onsager limiting law

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A phenomenological relationship is proposed for electrolytic conductance that works well over a large range of concentration. A comparison of this expression with the Onsager limiting law leads to a modified Debye parameter for ordinary concentrations. The modified Debye parameter thus obtained is consistent with those derived for the primitive model electrolytes. [S1063-651X(97)09903-0]

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I. INTRODUCTION

It has been observed for a long time that electrolytic solutions placed in a measuring cell of either capacitive or inductive type of a radio-frequency circuit interact with the electromagnetic field present there. This interaction changes the oscillation conditions by altering both the oscillation or the resonance frequency and the amplitude of oscillations. The temperature rise in the electrolyte sample can be detected if the power is sufficient [1–3]. Radio-frequency titrations, conductivity, and concentration determinations through radio-frequency interactions have been some practical applications for the method [3–7].

Inductive measuring cells exhibit two different types of interactions with electrolytic solutions, namely, inductive coupling and capacitative coupling. The interaction through capacitative coupling may be eliminated by electrostatic screening [2,3]. Measurements of total conductivity loss factors (x'') and dispersion factors (x') for an inductive measuring cell have been carried out using *RCL* resonant circuits [8–10]. Loss and dispersion factors for capacitative coupling have been expressed in terms of coupling capacitance and solution resistance [8,10]. To get expressions for x'' and x' depending only on solution concentration one has to know how solution resistance and equivalent conductance are related to concentration. The Onsager limiting law for electrolytic conductance gives the latter, but it works only at sufficiently dilute concentrations [11,12].

An empirical relation for the concentration dependence of equivalent conductance is given here that covers a large concentration range and eventually reduces to the Onsager limiting law for sufficiently dilute solutions. Thus x'' and x' can now be expressed as a function of the solution concentration (γ) and the data fitting for x'' is quite good. The proposed function fits the data for equivalent conductance [12,13] almost perfectly.

The Debye parameter κ for the ionic atmosphere has an important role for the electrolytic conductivity [11,12]. Comparing the Onsager limiting law expression with the empirical relation for equivalent conductance, a different parameter, which we call here the ''modified Debye parameter'' κ', can be introduced that seems to correspond to the screening length [14].

The primitive model and the Debye-Hückel theory for electrolytes have been studied intensely and compared with experimental data. Several calculational methods for the primitive models give data that are in agreement with the Debye-Hückel theory and experiment, but they also are restricted to limited concentrations and are accurate only at dilute solutions [14–18]. For all models and theories the concentration dependence of the dielectric constant has not been fully treated [16].

II. EXPERIMENT

The loss and dispersion factors (x'' and x', respectively) due to capacitative coupling have been expressed as

$$x''=\frac{C_s}{C_0}\,\frac{\omega R_s C_s}{1+\omega^2 R_s^2 C_s^2} \tag{1}$$

and

$$x'=\frac{C_s}{C_0}\,\frac{1}{1+\omega^2 R_s^2 C_s^2}, \tag{2}$$

where C_s is the coupling capacitance and R_s is the solution resistance [8,10]. ω is the angular frequency of resonance and C_0 is the resonance capacitance.

The solution resistance is

$$R_s=\frac{1}{\sigma}\,\xi, \tag{3}$$

where σ is the conductivity of the solution (in units of $\Omega^{-1}\,\mathrm{cm}^{-1}$) and ξ is the cell constant for the sample. Conductivity and equivalent conductance (Λ) are related by

$$\sigma=10^{-3}\Lambda\,\gamma, \tag{4}$$

where γ denotes the concentration of the solution (in units of equiv cm^{-3}). The equivalent concentration is defined as moles per cm^3 multiplied by the ionic valence [12]. The solution resistance (R_{sm}) for the maximum loss factor ($x''_{\max}$) can be obtained by differentiating Eq. (1) as

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$$R_{sm} = \frac{1}{\omega C_s}. \tag{5}$$

The cell constant may be determined by using Eqs. (3)–(5) in terms of measurable quantities as

$$\xi = \frac{10^{-3}\Lambda_m \gamma_m}{\omega C_s}, \tag{6}$$

where Λ_m and γ_m denote the equivalent conductance and the solution concentration for $x''_{\max}$.

The solution resistance can now be expressed using Eqs. (3), (4), and (6) in terms of solution and circuit parameters as

$$R_s = \frac{\Lambda_m \gamma_m}{\Lambda \gamma \omega C_s}. \tag{7}$$

Inserting Eq. (7) in Eq. (1), x'' will be

$$x'' = \frac{C_s}{C_0} \frac{\Lambda_m \gamma_m / \Lambda \gamma}{1 + [\Lambda_m \gamma_m / \Lambda \gamma]^2}. \tag{8}$$

Although Eq. (8) shows an explicit dependence of x'' on γ, Λ also varies with solution concentration, though not so rapidly and not known functionally, except for infinite dilution, which is the Onsager limiting law [11,12].

Dependence of equivalent conductance on concentration

A general expression for equivalent conductance in terms of solution concentration should represent Λ in a wide range of concentration and reduce to the Onsager limiting law for high dilutions. The phenomenological relation

$$\Lambda = \Lambda_0 (1+y)^m \tag{9}$$

is proposed here to fulfill the requirements stated above; here $y = (\gamma/\gamma_r)^{1/2}$, $m = \text{const}$, and γ_r is a reference concentration, Λ_0 being the equivalent conductance at infinite dilution.

Inserting Eq. (9) in Eq. (8), x'' is fully expressed in terms of γ as

$$x'' = k_1 \frac{(1+k^{1/2})^{-m} k [1+(b\gamma)^{1/2}]^{-m} (b\gamma)}{(1+k^{1/2})^{-2m} (b\gamma)^2 + k^2 [1+(b\gamma)^{1/2}]^{-2m}}, \tag{10}$$

where $k_1 = C_s/C_0$, $b = 1/\gamma_r$, and $k = \gamma_m/\gamma_r$. Data fitting with Eq. (10) for HCl solutions is shown in Fig. 1. The fitting parameters are $m = -0.127$ and $\gamma_r = 0.109$ mole/liter. The parameter m evaluated in an alternative way by using Eq. (17) gives $m = -0.081$, which is comparable with the former value within a limit of about 36%. Data for x'' denote the sum of the capacitative and inductive losses and the function in Eq. (10) represents the capacitative loss only [9,10]. For high concentrations the inductive coupling becomes dominant and eddy losses dominate in that region, and for the points where inductive coupling is dominant the fit is poor.

Equation (9) is an empirical relation and represents equivalent conductance data in a wide concentration range almost as perfectly as Fig. 2 depicts and it reduces to the Onsager limiting law for sufficiently dilute solutions. Equation (9) is the main relation in this work. m and γ_r can be determined for an electrolyte solution by fitting conductance data with this equation. Equivalent conductance data for KCl solutions [12,13] fitted with Eq. (9) are shown in Fig. 2, the fitting parameters being $m = -0.187$ and $\gamma_r = 0.066$ mole/liter.

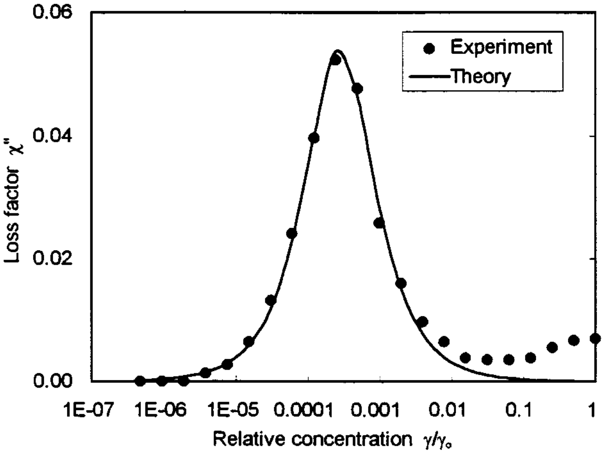

FIG. 1. Concentration dependence of the capacitative loss factor, $\gamma_0 = 6$ mole/liter. Equation (10) was used as the theoretical curve. The experimental data were obtained as described in Refs. [9,10]. The fitting parameters are $m = -0.127$ and $\gamma_r = 0.109$ mole/liter. Data for inductive loss factors are dominant for high concentrations as the right-hand side of the figure shows.

III. EMPIRICAL RELATION FOR EQUIVALENT CONDUCTANCE AND THE ONSAGER LIMITING LAW

The Onsager limiting law for electrolytic conductance given as [12]

$$\Lambda = \Lambda_0 - \frac{|z_1 z_2| e^2}{3\varepsilon kT} \frac{\Lambda_0 q \kappa}{1+q^{1/2}} - \frac{F^2}{6\pi\eta N} (|z_1| + |z_2|) \kappa \tag{11}$$

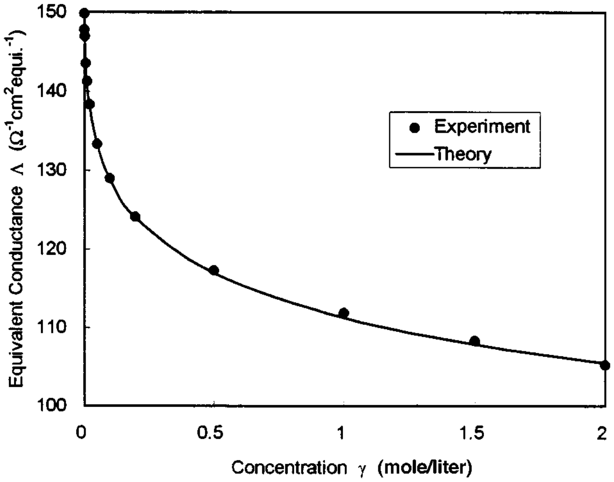

FIG. 2. Dependence of equivalent conductance on the solution concentration for KCl. Equation (9) was used as the theoretical curve and the experimental data were taken from Refs. [12,13]. The fitting parameters are $m = -0.187$ and $\gamma_r = 0.066$ mole/liter.

can be expressed for 1-1 electrolytes in a compact form as

$$\Lambda = \Lambda_0(1 - \kappa d), \tag{12}$$

where κ is the Debye parameter, and is expressed as

$$\kappa = \left(\frac{8\pi e^2 N \gamma}{\varepsilon k T} \right)^{1/2}, \tag{13}$$

and d is a constant having dimension of length and is expressed as

$$d = \frac{e^2 a}{3\varepsilon k T} + \frac{F^2}{3\pi \eta N \Lambda_0}, \tag{14}$$

where all quantities on the right-hand side are constants [11,12]: e is the electronic charge, ε the dielectric constant of the solvent ($4\pi\varepsilon_0\varepsilon_r$ in SI units), k Boltzmann's constant, T the absolute temperature in Kelvin, F Faraday's constant, η the viscosity coefficient of the solvent, N Avogadro's number, and Λ_0 equivalent conductance at infinite dilution. a is a constant depending on ionic parameters defined as $a = q/(1+\sqrt{q})$ and q is defined as

$$q = \frac{|z_1||z_2|(\lambda_1^0 + \lambda_2^0)}{(|z_1| + |z_2|)(|z_2|\lambda_1^0 + |z_1|\lambda_2^0)}, \tag{15}$$

where z denotes ionic valence and λ^0 denotes limiting ionic equivalent conductance [12]. Equation (14) gives $d = 0.82$ Å for KCl and $d = 0.74$ Å for HCl. These values agree with the ionic diameters given in Ref. [12].

The empirical relation for equivalent conductance, Eq. (9), opened in series will be

$$\Lambda = \Lambda_0\{1 + my[1 + (m-1)y/2! + (m-1)(m-2)y^2/3! + \cdots]\}, \tag{16}$$

which will reduce to the Onsager relation for $\gamma \ll \gamma_r$. Comparing with Onsager's equation, m is determined as

$$m = -\kappa_r d, \tag{17}$$

where κ_r refers to the Debye parameter for the reference concentration. Inserting the value for m in Eq. (16), the equivalent conductance becomes

$$\Lambda = \Lambda_0\{1 - \kappa d[1 + (m-1)y/2! + (m-1)(m-2)y^2/3! + \cdots]\} \tag{18}$$

for all concentrations. This equation may be put in the form

$$\Lambda = \Lambda_0(1 - \kappa' d), \tag{19}$$

which has the same structure as Onsager's, Eq. (12), where κ' is defined as

$$\kappa' \equiv \kappa[1 + (m-1)y/2! + (m-1)(m-2)y^2/3! + \cdots] \tag{20}$$

and will be called the modified Debye parameter in analogy with the Debye parameter.

The modified Debye parameter κ', defined by Eq. (20), can be put in a compact form for the whole concentration range as

$$\kappa' = \kappa\{[f(y) - 1]/my\}, \tag{21}$$

where $f(y) = (1+y)^m$, or

$$\kappa' = \frac{1}{d}[1 - (1 + \kappa/\kappa_r)^{-\kappa_r d}]. \tag{22}$$

κ' reduces to κ for highly diluted solutions. For sufficiently dilute solutions κ' can be expressed as

$$\kappa' = \kappa \Bigg/ \left[1 + (\kappa d)(1 - 1/m) - \frac{(\kappa d)^2}{3}(1 - 1/m)(1 - 2/m) + \frac{(\kappa d)^3}{12}(1 - 1/m)(1 - 2/m)(1 - 3/m) \right]^{1/2}. \tag{23}$$

This expression is similar to the one obtained for primitive model electrolytes [14].

IV. RESULTS AND DISCUSSION

Equivalent conductance data for electrolytic solutions have been expressed by a phenomenological relation in a wide range of concentration, Eq. (9). For sufficiently dilute solutions, this relation converges to the Onsager limiting law Eq. (12) and the phenomenological power m was determined as $m = -\kappa_r d$, where κ_r is the Debye parameter for the reference concentration and d corresponds to the ionic diameter mentioned in previous works [12,14].

Equation (9) can be put in the form of the Onsager limiting law but with the modified Debye parameter κ' defined by Eq. (20) replacing the usual Debye parameter κ. The modified parameter reduces to the usual one for sufficient dilution. An expression of the modified parameter κ' for dilute solutions, Eq. (23), is similar to that derived for the primitive model electrolytes [14]. The decay length ($1/\kappa'$) is an important parameter in describing physical and chemical properties of electrolyte solutions such as conductivity and osmotic and activity coefficients.

The ionic charge for the central ion and the decay length given by theoretical treatments based on ionic correlations differ from the bare ionic charge and the Debye length. The decay length depends on the effective ionic charge, which reduces to the bare ionic charge for sufficient dilution. Then the decay length also becomes the Debye length [14,16].

It is now expected that Eq. (22), a phenomenological relation for the modified Debye parameter in terms of ionic and solution parameters, can be derived from purely theoretical considerations. A self-consistent theory to explain the behavior of electrolytes for the whole concentration range is still awaited [19].

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