CONDUCTANCE OF AQUEOUS SOLUTIONS OF BARIUM METABENZENEDISULFONATE

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Add

ABSTRACT

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by David Rablen

The conductance of barium metabenzenedisulfonate in water has been measured in the concentration range 4 x 10^{-4} to 6 x 10^{-2} normal. The phoreogram is slightly catabatic. The data were successfully fitted up to about 2 x 10^{-3} normal using the Fuoss-Onsager theory (without ionic association), including extended terms of the electrophoretic effect, and the Einstein viscosity correction for the metabenzenedisulfonate ion. In the light of the behavior of 1-1 electrolytes in water, this seems to be a reasonable range of applicability of the extended theory to a 2-2 salt.

CONDUCTANCE OF AQUEOUS SOLUTIONS OF BARIUM METABENZENEDISULFONATE

By

David Rablen

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INTRODUCTION

Electrolytic solutions conduct in the presence of an electrical field because of the existence in the solution of electrically charged ions. The results of resistance measurements of electrolytic solutions have shown that the equivalent conductance increases with increasing dilution. In 1887 Arrhenius (1) first attempted to explain this behavior by assuming that the change in conductance with concentration was entirely due to the change in the number of free ions present. While the behavior of weakly conducting systems tended to substantiate this idea, strongly conducting systems could not be adequately explained. This anomalous behavior of strong electrolytes led to the rejection of the Arrhenius incomplete dissociation hypothesis and adoption of the modern view that strong electrolytes are completely dissociated and that the coulombic forces which exist between the ions must play the dominant role in determining the properties of electrolytic solutions. Although in the first two decades of the present century attempts were made to develop an interionic attraction theory, it was not until 1923 that a statistical electrostatic theory of dilute solutions was formulated by Debye and Hückel (2). By assuming complete dissociation and attributing all deviation from ideality to interionic forces, they were able to successfully derive the limiting law for the activity coefficients of strong electrolytes.

In 1927, using the results of the interionic attraction theory and fundamental concepts of hydrodynamics, Onsager derived the limiting law of electrolytic conductance (3). This theory predicts the limiting slope of the observed conductance curve as a function of the charge type of the electrolyte and solvent properties. A recent extension by Onsager and Fuoss (4, 5, 6) provides a theoretical expression for conductance which is applicable to higher concentrations (up to approximately 0.01 normal for 1-1 electrolytes). This extension, involving the inclusion of finite ionic size and a more complete mathematical treatment, was developed for symmetrical electrolytes only. The conductance behavior of a number of 1-1 electrolytes is in good agreement with the extended theory. Since this theory is also capable of handling 2-2 electrolytes, an attempt was made by Dye and co-workers (7) to apply the Fuoss-Onsager theory and higher terms of the electrophoretic effect (8) to explain the conductance behavior of zinc sulfate. The anomalous results obtained prompted a search for a strong 2-2 electrolyte which would be free of the complications of ionic association and hydrolysis. The electrolyte barium metabenzenedisulfonate seemed to fit these requirements. The purpose of this research was to determine the conductance of this salt and establish the applicability of the extended theory to 2-2 electrolytes.

THEORY

A. Introduction

When subjected to a directed electrical field, under conditions of normal field strength and frequency, electrolyte solutions obey Ohm's Law, $E = I\,R$, where E is the potential applied across the solution, I the current, and R the resistance of the solution. Since for a homogeneous conductor of length l and cross sectional area A, $R = \rho / A$, the specific resistance ρ can be determined from l, A, and the measured resistance R. The specific conductance L is given by $1/\rho$. For electrolytic solutions it is convenient to define the equivalent conductance Λ as the specific conductance divided by the stoichiometric concentration in equivalents per liter times one thousand: $\Lambda = 1000\ L/c$. The equivalent conductance may also be written as

$$\Lambda = \sum_i \lambda_i \qquad (1)$$

since it is made up of the sum of the contributions of all the ions. For a completely dissociated electrolyte the individual ion conductance λ_i may be related to u_i, the ionic mobility or velocity per unit gradient of potential, by the equation

$$\lambda_i = F\ u_i \quad . \quad (2)$$

Equivalent conductances computed from stoichiometric concentrations and measured resistances are found to decrease with increasing concentration. From equations (1) and (2) it is evident that this change is due to the concentration dependence of the ionic mobilities. By suitable extrapolation of conductance data, Λ^0, the limiting value of equivalent conductance at infinite dilution can be determined. Experimentally resolving $\underline{\Lambda}^0$ into the cation and anion contributions, $\underline{\lambda^0{+}}$ and $\underline{\lambda^0{-}}$, requires measurement of the transference number defined by

$$t_i \equiv \frac{u_i}{\sum\limits_i u_i} = \frac{\lambda_i}{\sum\limits_i \lambda_i} . \qquad (3)$$

By extrapolation t_i^0 can also be obtained which with $\underline{\Lambda}^0$ serves to evaluate the individual ionic conductances at infinite dilution. They are characteristic of the ion and solvent, depending largely upon the size and the extent of solvation, and the solvent viscosity. In the development of the theory of electrolytic conductance the limiting conductances are treated as empirical constants, the primary aim being to account for the difference between the limiting values and those at non-zero concentrations as a function of the properties of the ions, the solvent, and particularly the concentration.

The theory of the conductance of dilute electrolytic solutions is long and complicated: for that reason the discussion presented here will be largely qualitative with theoretical results stated rather than mathematically developed in detail.

B. Interionic Attraction Theory

The modern theory of electrolytic conductance is based on the interionic attraction theory formulated by Debye and Hückel (2) in a treatment of the equilibrium properties of electrolytic solutions. Debye and Hückel assumed that the solute of an electrolytic solution consists entirely of ions which may be treated as a dilute solution of point charges or charged spheres in a structureless medium of uniform dielectric constant. These assumptions allow the application of Poisson's equation of electrostatic theory:

$$\Delta\Psi = \frac{-4\pi}{D} \rho \qquad (4)$$

where D is the dielectric constant of the solvent, Ψ the electrostatic potential, and ρ the charge density at the point considered. Due to the complexity of an electrolytic solution the theoretical approach is necessarily statistical, the function of interest being the time average potential with respect to a given type of ion, say a j-type, chosen as origin. The calculation of Ψ_j using Poisson's equation requires that the time average charge density, hence the time average ionic distribution about the j-ion be known. The dependence of the distribution upon position is due to the mutual attractive forces between oppositely charged ions and mutual repulsive forces between like charges. The distribution is assumed to be given by the Boltzmann equation

$$n_{ji}(r) = n_i \exp - e_i \Psi_j(r) /kT \qquad (5)$$

where the quantities in the equation are defined as:

n_{ji} is the local concentration of i-ions about a j-ion;

n_i is the bulk concentration of i-ions;

e_i is the charge on an i-ion;

$\Psi_j(r)$ is the electrostatic potential at a distance r from a j-ion due to the presence of the j-ion and the ions assembled about it;

k is the Boltzmann constant;

T is the absolute temperature.

The charge density is then given by

$$\rho_j = \sum_i e_i n_i \exp [-e_i \Psi_j /kT] . \qquad (6)$$

Substitution of this expression for charge density in Poisson's equation yields a non-linear differential equation for which no general solution is known and which implies a contradiction of the linear superposition of fields principle. However, by restricting the results to dilute solution where $e_i \psi_j \ll kT$, the exponential can be expanded and terms quadratic and higher neglected. A linear differential equation results which when integrated using boundary conditions which consider the ions as hard spheres yields

$$\psi_j = \left(\frac{e_j}{Dr}\right)\left(e^{-\kappa r}\right)\left(\frac{e^{\kappa a}}{1+\kappa a}\right) \qquad (7)$$

for the potential. The quantities in the equation are defined as:

r is the distance from the j-ion;

e_j is the charge on the j-ion;

D is the dielectric constant of the medium (solvent);

a is the mean distance of closest approach of the ions;

$$\kappa^2 = \frac{4\pi e^2 N}{DkT\ 10^3} \sum_i c_i z_i^2, \qquad (8)$$

where

e is the electronic charge;

z_i is the valence of an i-ion;

c_i is the equivalent concentration of the i-ions;

N is Avogadro's number.

The potential has been written as the product of three factors. The first is the potential due to an isolated j-ion at the origin, the second factor represents the electrostatic screening which arises between two ions due to the presence of the other ions in the system, and the third factor gives the effect of finite ionic size.

According to the interionic attraction theory picture the compensating charge of a reference ion of charge $\underline{+e}$ is a spherically symmetrical, continuous distribution of total charge $\underline{-e}$ which is called the ion atmosphere. The radial charge density can be shown to have a maximum at $1/\kappa$ which is considered to be the mean diameter of the atmosphere and is of the order of magnitude of molecular dimensions. This preponderance of opposite charge "up close" is a natural consequence of the coulombic attractions between unlike charges and repulsions between like charges.

Using the above expression for $\underline{\psi_j}$ and assuming all non-ideality could be attributed to interionic forces, Debye and Hückel successfully predicted the limiting law for the activity coefficients of strong electrolytes.

C. Onsager Theory of Conductance

Upon the basis of their interionic attraction theory Debye and Hückel (2) deduced a simple theory of electrolytic conductance which was not completely satisfactory. The necessary refinements of the Dubye-Hückel treatment were made by Onsager (3) who first successfully derived the limiting law for electrolytic conductance.

At equilibrium the average ionic velocities are zero. The application of a directed external field initiates ionic motion parallel to its direction. At infinite dilution the only forces exerted on an ion are the external field and the frictional resistance of the solvent. The equation of motion is then simply

$$v_i = Xe_iu_i^0 \qquad (9)$$

where

$\underline{v_i}$ is the velocity relative to an external observer;

$\underline{X}$ is the external electric field;

$\underline{e_i}$ is the ionic charge,

$\underline{u_i^0}$ is the limiting ionic mobility, the reciprocal of which is the ionic coefficient of friction.

At non-zero concentrations the ions influence the motion of each other because they are coupled through their electrostatic fields. A retarding effect arises in the following way. When an electric field is applied a given reference ion starts to move. If the ions of its atmosphere were able to immediately redistribute themselves, the spherical symmetry of the equilibrium state would be retained. However, due to the non-zero coefficients of friction of the ions, the atmosphere lags behind the central ion giving rise to an asymmetry in the distribution. In effect there is more opposite charge behind the reference ion than in front. As a result a local field exists about the central ion which opposes the external field which produces it. As a consequence the force felt by the reference ion is less than that for the isolated ion and the ionic velocity is necessarily decreased. Due to its connection with the finite time required for a perturbed state to decay to an equilibrium state, this effect is referred to as the relaxation field. The non-equilibrium potential may be expressed as the sum of the equilibrium value calculated by Debye and Hückel, and a small perturbation term ψ_j:

$$\Psi_j = \Psi_j^0 + \Psi_j' \qquad (10)$$

The problem is to calculate $\underline{\psi_j'}$, the gradient of which gives the magnitude of the relaxation field. This is a more difficult task than the equilibrium problem because the local concentrations about a reference ion are a function of direction as well as distance. Essential to the formulation of the solution are the symmetrical distribution functions

$$f_{ji}\ (\bar{r}_{12}) = n_j\, n_{ji} = n_i\, n_{ij}\ (\bar{r}_{21}) = f_{ij}\ (\bar{r}_{21}) \qquad (11)$$

where n_j is the average concentration of j type ions, and n_{ji} is the local concentration of i type ions located by a vector $\bar{r}_{21}$ with respect to a j ion as origin. The quantity f_{ji} $(\bar{r}_{12})$ is proportional through $1/V$ to the total number of i ions in the atmosphere of j ions. These distribution functions satisfy the conservation condition

$$\nabla_1 \cdot f_{ij}\ \bar{v}_{ij} + \nabla_2 \cdot f_{ji}\ \bar{v}_{ji} = 0 \qquad (12)$$

which is the equation of continuity for ion flow. In the equation $\bar{v}_{ij}$ is the time average velocity of a j ion located at $\bar{r}_{12}$. The distribution functions can be related to the potentials through the Poisson equation. Once the internal forces in the equations of motion for the ions have been expressed in terms of the unknown potentials, the equation of continuity and the Poisson equation constitute the system of equations necessary for the evaluation of Ψ'.

A fourth order non-homogeneous differential equation is obtained for Ψ'_j which in the original treatment was greatly simplified by neglecting all terms of higher order than first in the ionic charge. The differential equation was then integrated subject to boundary conditions for point charges. Onsager's final result for the relaxation field is

$$\left(\frac{-\partial \Psi'}{\partial x}\right)_{r=0} = \Delta\ X_0 = \frac{X\, e_i e_j\, q^2 \kappa}{3\ DkT(1+q)} \qquad (13)$$

where $q = 1/2$ for symmetrical electrolytes. The "corrected" field at the reference ion is then

$$X + \Delta X_0 = X\left(1 + \frac{e_j e_i \kappa}{18DkT}\right). \qquad (14)$$

When an ion moves in an electrical field it pushes solvent away, directly in front, and also drags it along, from behind. Oppositely charged ions move in opposite directions. As a consequence a given reference ion finds itself swimming upstream in a counter current of solvent produced by its oppositely charged atmosphere. This is called the electrophoretic effect and obviously leads to a decrease in the ionic velocity relative to an external observer. The magnitude, Δv_j, of the solvent counter velocity can be calculated in the following manner. If the ion atmosphere about a reference ion of charge e_j is represented as a spherical shell of radius $1/\kappa$ with the charge $-e_j$ uniformly distributed over its surface, it will be subjected to force $-Xe_j$. The velocity of this sphere can then be calculated by applying Stoke's law of hydrodynamics, $F = v/6\pi\eta r$ which is the equation of motion for a sphere of radius r traveling in a hydrodynamic continuum of viscosity η. The counter current velocity is given by

$$\Delta v_j = \frac{-Xe_j\kappa}{6\pi\eta} \quad . \qquad (15)$$

This is the limiting form of

$$\Delta v_j = \left(\frac{-Xe_j}{6\pi\eta}\right)\left(\frac{\kappa}{1+\kappa a}\right) \quad , \qquad (16)$$

the electrophoretic effect obtained by more rigorous methods (3). Combining the two retarding effects, the velocity of an ion may be written

$$v_j = \Delta v_j + e_jX\left(1 + \frac{\Delta X_0}{X}\right)u_j^0$$

$$= -\frac{Xe_j\kappa}{6\pi\eta} + e_jX\left(1 + \frac{+e_je_i}{18\,DkT}\right)u_j^0 \qquad (17)$$

or in terms of equivalent conductance

$$\Lambda = \Lambda^0 - (\alpha\Lambda^0 + \beta)\,c^{1/2} \qquad (18)$$

which is the Onsager limiting law for electrolytic conductance. The constants $\underline{\alpha}$ and $\underline{\beta}$ are completely determined by the absolute temperature, the dielectric constant, and viscosity of the solvent, the valency type of the electrolyte, and universal constants. The only arbitrary constant is $\underline{\Lambda^0}$. The Onsager limiting law has been extensively tested by precise experimental data and has been shown to be the exact expression for the tangent to the conductance curve for many systems.

D. Extension of Onsager's Theory

1. Higher terms of the electrophoretic effect--In the original calculation of the electrophoretic correction by Onsager (3), the exponential distribution function was approximated by expansion and retension of only the linear term. Dye and Spedding (8) have pointed out that it is invalid to neglect the higher terms for ions of high charge even at quite low concentrations. In their treatment they have evaluated the integrals approximated by Onsager by retaining the complete exponential. The integrals have now been evaluated by numerical methods using a high speed digital computer for a range of concentrations, charge types, and ion sizes (9).

2. Fuoss-Onsager Theory--An extension by Fuoss and Onsager (4, 5, 6) involves both an improvement in the model and the mathematical approximations used in the calculation of the relaxation field. In expanding the equation of continuity, all terms were retained except those quadratic in field which by hypothesis were negligible. This gave rise to five higher order terms in the differential equation which had been neglected in the original derivation of the relaxation field by Onsager. As a first approximation only the terms originally retained were used but subject to boundary conditions for spherical ions of radius $\underline{a}$ instead of for point charges.

These boundary conditions are: the field must vanish at infinity; the potential and field must be continuous at r = a; the ions are impenetrable. The last condition was fitted by requiring that the radial components of the relative velocity of any two ions vanish at contact (r = a). The first order solution was then substituted into the higher order terms in the differential equation for Ψ' which was then resolved as a perturbation problem.

The resulting relative relaxation field can be written symbolically as

$$\frac{-\Delta X}{X} = \left(\alpha\, c^{1/2}\right)\left(1 - \Delta_1 + \Delta_2 + \frac{\Delta X_v}{X}\right) \qquad (19)$$

in which

$\alpha\, c^{1/2}$ is the limiting value of the relaxation term for point charges;

Δ_1 involves terms which allow for finite ion size;

Δ_2 includes all the effects of the perturbations in the relaxation field except those due to ΔX_v, a hydrodynamic term which is more conveniently combined with the electrophoresis term in the conductance equation.

Another effect which causes conductance to change with concentration was pointed out by Onsager (10). Mutual attractive forces naturally lead to cation-anion collisions. As previously mentioned, in the presence of an external field the distribution of anions about a reference cation is asymmetric with an excess of anions behind it. As a result the cation will be struck more often from behind giving it a component of velocity in its normal direction of motion. The virtual force ΔP_j on the reference ion due to this effect is calculated by integrating the directed component of the local osmotic pressure over the surface of the ion. The solution is of the form

$$\Delta P_j = X e_j c\, f(D, T, a) \quad . \qquad (20)$$

The conductance equation including all of the above mentioned effects may be written

$$\Lambda = \left(\Lambda^0 - \frac{\beta c^{1/2}}{1+ a}\right)\left(1 + \frac{\Delta X}{X} + \frac{\Delta P}{X}\right). \quad (21)$$

The expansion of this product, dropping all terms of order $c^{3/2}$ and higher is

$$\Lambda = \Lambda^0 - (a\Lambda^0 + \beta)c^{1/2} + Ec\log c + Jc \quad (22)$$

in which

$(a\Lambda^0 + \beta)$ is the limiting law coefficient;

J is an explicit function of a, Λ^0, and the properties of the solvent;

E is independent of a, depending only on Λ^0 and the properties of the solvent.

The two parameters Λ^0 and a must be evaluated from the experimental data.

When the ions are large compared to solvent molecules their influence on the viscosity of the solvent must be considered. This is taken into account by including Einstein's viscosity equation

$$\eta = \eta_0 \left(1 + \frac{5}{2}\varphi\right) \quad (23)$$

where η is the viscosity of a solution in which a volume fraction, φ, of solute molecules is present in a solvent of viscosity η_0. This leads to another linear term in the conductance equation and includes another parameter, the hydrodynamic radius, which must be evaluated from experimental data.

The results of the Fuoss-Onsager theory are limited to symmetrical electrolytes and to concentrations less than about .01 normal. This extension of the relaxation field offers a ready explanation of the anabatic phoreograms exhibited by electrolytes such as the alkali halides.

EXPERIMENTAL

A. Preparation of barium m-benzenedisulfonate dihydrate

Barium m-benzenedisulfonate was prepared by the neutralization of an aqueous solution of m-benzenedisulfonic acid with barium hydroxide. Due to the presence of sulfuric acid in the technical grade m-benzenedisulfonic acid employed, a precipitate of barium sulfate formed which was removed by filtration. The resulting solution was concentrated by evaporation and the barium m-benzenedisulfonate precipitated by addition of ethanol. Five to six recrystallizations were carried out from conductivity water and ethanol. The salt obtained in this manner was hydrated to an unknown extent.

In order to calculate stock solution molalities it was necessary to prepare a form of the salt suitable for weighing. The possibility of preparing a stable hydrate was explored. A two gram sample was dried in a desiccator over phosphorous pentoxide after which it was transferred to a second desiccator containing a 100 milliliter beaker of saturated solution of the salt. Successive weighings showed that the sample weight initially increased but reached a constant value after a few hours. When this sample was again placed in the "drying desiccator" a weight loss occurred. When the drying agent was replaced with the saturated solution the initial constant weight was again attained, which furnished convincing evidence that a stable hydrate had been prepared. The results of a Fischer titration and a hydrogen analysis established that the salt in equilibrium with the saturated solution was the dihydrate.

All stock solutions were prepared from barium m-benzenedisulfonate treated in a similar manner. The molalities of the stock solutions were calculated directly from the weight of salt and water used.

TABLE I. Composition of Barium *m*-Benzenedisulfonate Hydrate

Hydrogen analysis (percent by weight):

found	theoretical (dihydrate)
1.91%	1.97%
1.94%	

Fischer Titration:

1.85 moles water per mole of salt
1.92

B. Preparation of Conductivity Water

The distillation of an alkaline permanganate solution of demineralized water yielded water reasonably free of contaminants except for atmospheric carbon dioxide. This water was then transferred to a second distilling flask and redistilled in a stream of nitrogen. The nitrogen was purified before entering the distillation system by passage through gas-washing towers containing concentrated sulfuric acid and an aqueous solution of potassium hydroxide. The conductivity water prepared in this way had a specific conductance of about 0.6×10^{-6} ohm^{-1} cm^{-1}.

C. Apparatus

1. Bridge--The resistance measurements were made using a modification of the Jones bridge described by Thompson and Rogers (11). It consisted of an audio frequency oscillator, an amplifier, and a cathode ray tube null point detector. The apparatus permitted resistance readings to be made at five frequencies over the range 400 to 5,000 cps. and gave results reproducible to ± .01%.

2. Bath--A constant temperature bath was used for all conductance measurements. It consisted of a 12 inch diameter by 18 inch Pyrex glass

cylinder filled with oil which was circulated with a centrifuge pump. The temperature of the bath was determined using a platinum resistance thermometer and was maintained at 25 ± .01°C. by means of a thermoregulator and a heat lamp.

3. Conductivity Cells--For high concentration conductance measurements, a Leeds and Northrup type B conductivity cell was used. The "low cell" employed was similar to the erlenmeyer type used by Kraus and co-workers (12). It consisted of a Leeds and Northrup type A cell which was sealed to a 500 milliliter flask fitted with a standard taper cap. The flask had two stopcocks, one mounted on a side arm and the other on the cap. This arrangement permitted the introduction of conductivity water under nitrogen pressure and for a flow of nitrogen over the solution when additions of stock solution were made.

D. Procedure

1. Low Cell--Before a run, the cell was cleaned with hot fuming nitric acid, rinsed, and allowed to soak overnight filled with conductivity water. After drying the cell in an oven the cap was lubricated, inserted, and the cell was weighed. About 300 grams of conductivity water was transferred into the cell under nitrogen pressure. The filled cell was then reweighed to determine the weight of water. For these weighings a torsion balance, accurate to ± .05 gram, was employed. The cell was placed in the oil bath for one-half hour before resistance readings were taken. A reading was recorded when mixing gave results reproducible to ± .01%. Due to the high resistance of the conductivity water, a 20,000 ohm shunt was used in parallel with the cell. From the resistance readings of the shunt and the parallel combination, the conductance of the water was computed. This solvent conductance measurement was necessary in order that the total conductance could be corrected for the contribution of the solvent.

Using a weight buret, successive small portions of stock solution were added to the cell, the additions being made with wet nitrogen flowing through the cell. After each addition the solution was thoroughly mixed and resistances were recorded when reproducible to ± .01%.

2. High Cell--The stock solution and appropriate weight dilutions were measured directly in the high cell. In each case the cell was rinsed with several portions of solution before a resistance measurement was made. The cell was then emptied, re-rinsed, and a second check determination made.

3. Cell Constants--The cell constants were determined using potassium chloride solutions in a manner identical to that used for the sample solutions. The stock solution was prepared from conductivity water and salt which had been recrystallized twice from boiling conductivity water and then fused in platinum under nitrogen.

4. Density Measurements--Densities of several solutions of barium m-benzenedisulfonate were measured to be used in converting molality data to molarity. They were determined at 25°C. using a fifty milliliter pycnometer which was previously calibrated with water. The densities are expressed by the equation

$$\rho = 0.9971 + 0.252\ m$$

where m is the molality.

E. Reagents

The following is a list of the reagents used in this work:

Barium hydroxide, $Ba(OH)_2$
    "Baker's Analyzed" Reagent
    Fischer Scientific, C. P.. Reagent

Metabenzenedisulfonic acid, $C_6H_6S_2O_6$, Technical,
    Eastman Organic Chemicals
    Matheson, Coleman and Bell

Potassium chloride, KCL,
    Baker's Analyzed" Reagent

Ethanol, C. P.

RESULTS AND DISCUSSION

The following relationships were used to calculate the equivalent conductances of the solutions from the measured quantities:

$$c = \left(\frac{w f_m \, 10^3}{w f_w + W} \right) \left(\frac{2 \rho}{1 + mM/10^3} \right) \qquad (24)$$

$$L = k \left(\frac{1}{R} - \frac{X_g}{R_g} - \frac{X_e L_e}{k} \right) \qquad (25)$$

$$\Lambda = \frac{L \, 10^3}{c} \qquad (26)$$

in which

c is the normality of the solution;

w is the sum of the weight increments of stock solution added;

ρ is the density of the solution;

f_w is the weight of water per gram of stock solution;

f_m is the number of formula weights of solute per gram of stock solution;

W is the weight of "good" conductivity water;

m is the molality of the solution;

M is the formula weight of the solute;

L is the specific conductance of the solute;

k is the cell constant;

R is the resistance of the solution;

R_g is the resistance of the "good" water;

X_g is the weight fraction of "good" water;

X_e is the weight fraction of equilibrium water;

L_e is the specific conductance of the equilibrium water.

Some comment regarding the form of equation (25) is in order. The total measured specific conductance (k/R) is that due to the solute and the solvent. The assumption was made that the solvent conductance is just superimposed on that of the solute. The solute conductance is then simply the total conductance minus the conductance of the water which was measured previous to addition of solute. To take into account the presence of two "kinds" of water, "good" water and equilibrium water, the assumption was made that the two kinds of water contribute proportionally as their weight fractions (mole fractions). The conductance of the "good" water (0.6×10^{-6} ohm^{-1} cm^{-1}) was measured directly in the conductance cell before commencing with stock solution additions. The specific conductance of the equilibrium water (1.2×10^{-6} ohm^{-1} cm^{-1}) used in the preparation of the stock solution was calculated from a resistance measurement made in a different cell. Using equation (25) the solute specific conductance was then calculated.

The advantage of the procedure used lies in the fact that even after several stock solution additions have been made $\underline{X}_g >> \underline{X}_e$, keeping the solvent conductance essentially that of the "good" water. In this way the solvent correction to be applied to the total conductance is kept small. Were equilibrium water to be used for dilution purposes, the solvent correction would be an uncomfortably large percentage of the total conductance. It would be impractical to prepare the stock solution with better than equilibrium water in the interest of further minimizing the solvent correction because elaborate precautions would be necessary to avoid exposing it to the atmosphere. For highly conducting solutions the specific conductance of the solute is sufficiently large that the solvent effects are almost negligible and the use of equilibrium water for dilution purposes is permissible.

To calculate the cell constants from resistance measurements of standard potassium chloride solutions the equations given above were used with the modification that equation (25) was used to evaluate $\underline{k}$.

Values of Λ_{KCl} (13) used to evaluate L were calculated from the empirical equation

$$\Lambda_{KCl} = 149.87 - 93.985\, c^{1/2} + 31.8\, c \log c + 144\, c\ . \qquad (27)$$

Since the second correction term in equation (25) involves the unknown cell constant, a preliminary conductance L' is calculated assuming $X_g = 1$, then L is recomputed from the equation

$$L = L' + X_e \left(\frac{1}{R_g} - \frac{L_e}{k} \right) \quad . \qquad (28)$$

The conductance results are given in Table II and are divided into two series, *A* and *B*. In both series the measurements up to 4 x 10^{-3} normal were made using the same low cell of constant about one. In series *A* the higher concentrations were measured using a "type B" cell of constant about 30 while in series *B* a cell of constant about 10 was employed. In the low concentration region, the data of series *A* were obtained in two runs and those of series *B* were obtained in one. Both series have good internal precision but the conductances for the *B* series are about two parts per thousand lower than those for series *A* and is the reason for the division of the results into two series. The reason for this discrepancy is not known. The internal consistency of the high and low ends of each series which were obtained from measurements with different stock solutions rules out mistakes in the preparation of the stock solution as a cause. The cell constants were determined for each series so that discrepancies cannot be attributed to an undetected change in the cell constant. The most significant fact is that the stock solution for the two series were prepared from different batches of salt. Perhaps impurities such as barium benzenesulfonate in one or both caused the observed discrepancy. The measurements of series *B* were used for the comparison of experiment and theory and are shown in Figure I. It is to be noted that the small discrepancy will affect the value of Λ^0, but not the theoretical interpretation of the conductance. Included in Figure I is the Onsager limiting law slope, $\alpha\Lambda^0 + \beta$, calculated using values of α and β taken from Harned and Owen (14). The limiting equivalent conductance Λ^0 was obtained from the data using the extended theory. The phoreogram is slightly catabatic. Besides the limiting law, several other theoretical

TABLE II. Conductance Results

Equivalent Conductance	Normality x 10^4
Series A	
117.44	2.6586
116.43	3.6537
115.72	4.4667
115.05	4.7605
114.47	5.5919
114.10	6.3245
113.69	6.9629
113.32	7.6821
112.91	8.3110
112.51	9.0241
111.91	9.2072
111.04	10.5902
94.62	82.545
93.84	89.225
88.53	145.80
85.30	207.56
80.12	346.31
76.68	431.35
76.49	503.68
Series B	
115.67	3.9055
113.09	6.9297
112.23	8.1790
110.98	9.9556
110.00	11.699
108.39	14.940
106.39	19.694
104.61	25.122
101.29	37.535
93.73	78.541
90.65	112.32
87.66	152.82
86.94	165.79
82.43	250.51

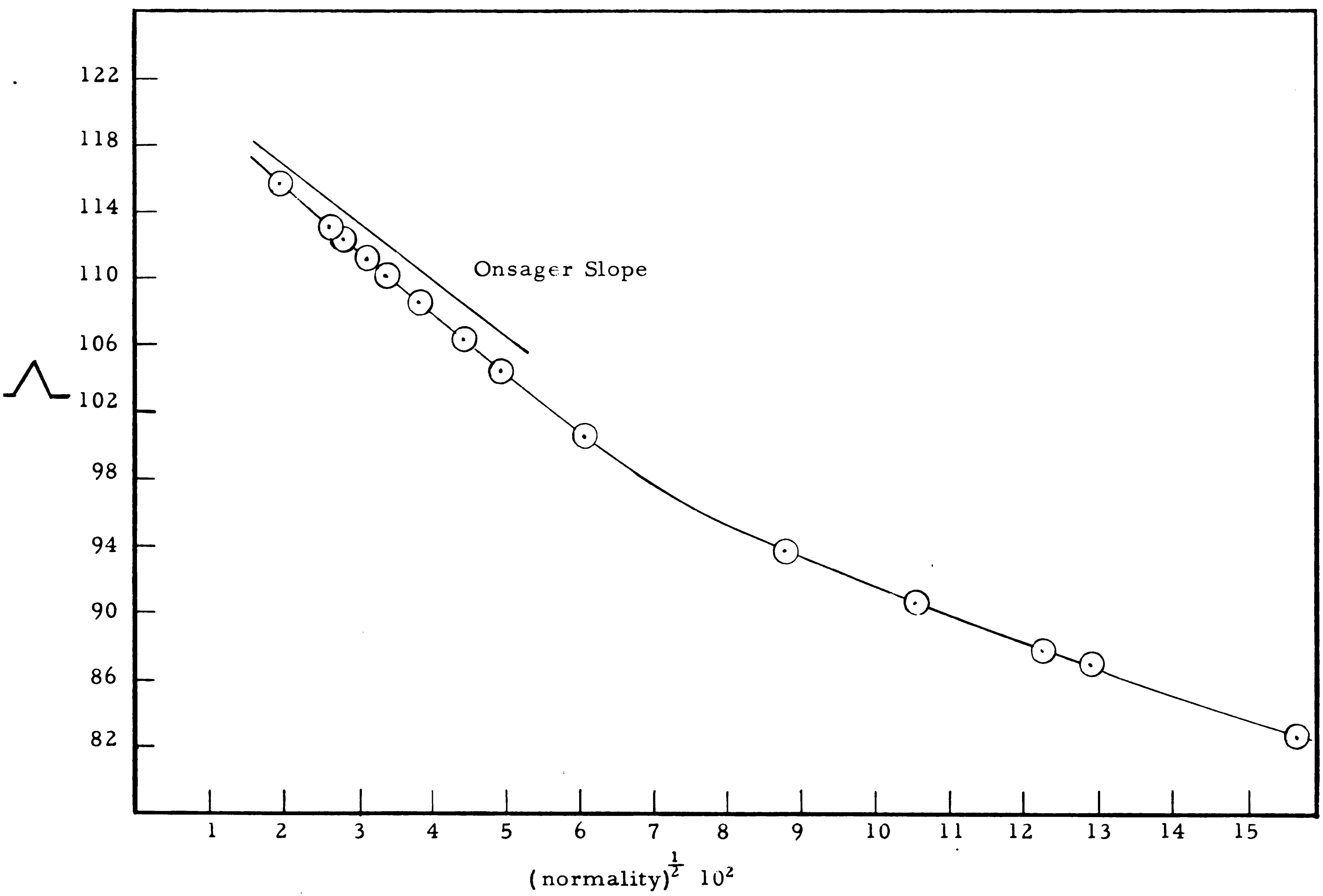

Figure I. Phoreogram of barium m- benzenedisulfonate.

conductance equations are available with which to compare the experimental data. The possible combinations are the Fuoss-Onsager theory, the Fuoss-Onsager theory including higher order electrophoretic terms, and either of these two including the Einstein viscosity correction for one or both ions; also, ionic association might be considered.

Fitting the theory with the inclusion of ion-pairing involves four adjustable parameters:

$\underline{\Lambda^0}$,	the equivalent conductance at infinite dilution;
$\underline{\mathring{a}}$	the distance of closest approach to the ions;
$\underline{R}$	the ionic hydrodynamic radius; and
$\underline{K_A}$	an association constant.

In all attempts to fit the data the assumption of ionic association was excluded. Without $\underline{K_A}$, the number of adjustable parameters drops to three. While $\underline{\mathring{a}}$ and $\underline{R}$ are independent of $\underline{\Lambda^0}$, $\underline{R}$ ought to be of "reasonable" size, comparable in magnitude to $\underline{\mathring{a}}$. The model of Fuoss (6) makes the assumption $\underline{R = \mathring{a}}$. Using this assumption the number of adjustable parameters reduces to only two. Although a reliable value of $\lambda^0_{Ba^{++}}$ is available, none is available for the metabenzenedisulfonate ion. If it were, $\underline{\Lambda^0}$ for barium metabenzenedisulfonate could be computed and the only adjustable parameter would be $\underline{\mathring{a}}$.

Several attempts to fit data were made in the following manner: A preliminary value of $\Lambda^0 = 123.20$ ohm^{-1} cm^2 equiv.$^{-1}$ was obtained by a graphical extrapolation of the phoreogram to zero concentration. Using the program of Karl (9), values of $[\,1 + \frac{\Delta X}{X} + \frac{\Delta P}{X}\,]$ and $\Delta\Lambda_E$ (the electrophoretic correction including higher order terms) were then computed for several concentrations and values of $\mathring{a}$ and Λ^0. From these quantities $\underline{\Lambda'}$s were calculated using equation (21) with the modification that $\underline{\Delta\Lambda_E}$ replaced $\beta c^{1/2}/1 + \kappa a$ when the higher order electrophoretic terms were included. $\underline{\Lambda_\eta}$, the conductance corrected for the viscosity effect of the metabenzenedisulfonate ion, was computed from the relation

$$\Lambda \eta = \Lambda/(1+\tfrac{5}{2}\varphi) \qquad (27)$$

where

$$\varphi = \frac{\frac{4}{3}\pi R^3 N c/2}{1000} \qquad (28)$$

Since the differences between the experimental data and the theoretical expressions are almost invisible on a direct graph of Λ versus $c^{1/2}$, a more sensitive plot was made as shown in Figure II to demonstrate the fit of the theory to experiment. The function shown is $\Lambda^{0'} - \Lambda^0$ where

$$\Lambda^{0'} = \Lambda \text{ (experimental or theoretical)} + (\alpha\Lambda^0 + \beta)\, c^{1/2}$$

which is the difference between Λ and the values predicted by the limiting law. The data is best fit using $\Lambda^0 = 123.30$ $\text{ohm}^{-1}\text{cm}^2$ equivalent^{-1}, and *å* = 6.5 Å. This combination fits up to 1.8×10^{-3} normal, after which systematic deviations occur.

Two of the less successful attempts at fitting, curves *B* and *E*, illustrate the effect of changes in *å* on the predicted conductance. All the curves in Figure II were made assuming $\Lambda^0 = 123.30$. The major effect of changing Λ^0 is a slight displacement of the conductance curve rather than a change in its shape. The Einstein viscosity effect is not very large, for this case, decreasing the equivalent conductance at 10^{-4} normal by only about one part in ten thousand and at 5×10^{-3} normal by four parts in one thousand. All the curves in Figure II include the viscosity correction, which is made only for the metabenzenedisulfonate ion, and assumes *R* = *å*.

Curve A shows that the Fuoss-Onsager theory without ion-pairing predicts conductances which are too high for any reasonable value of *å*.

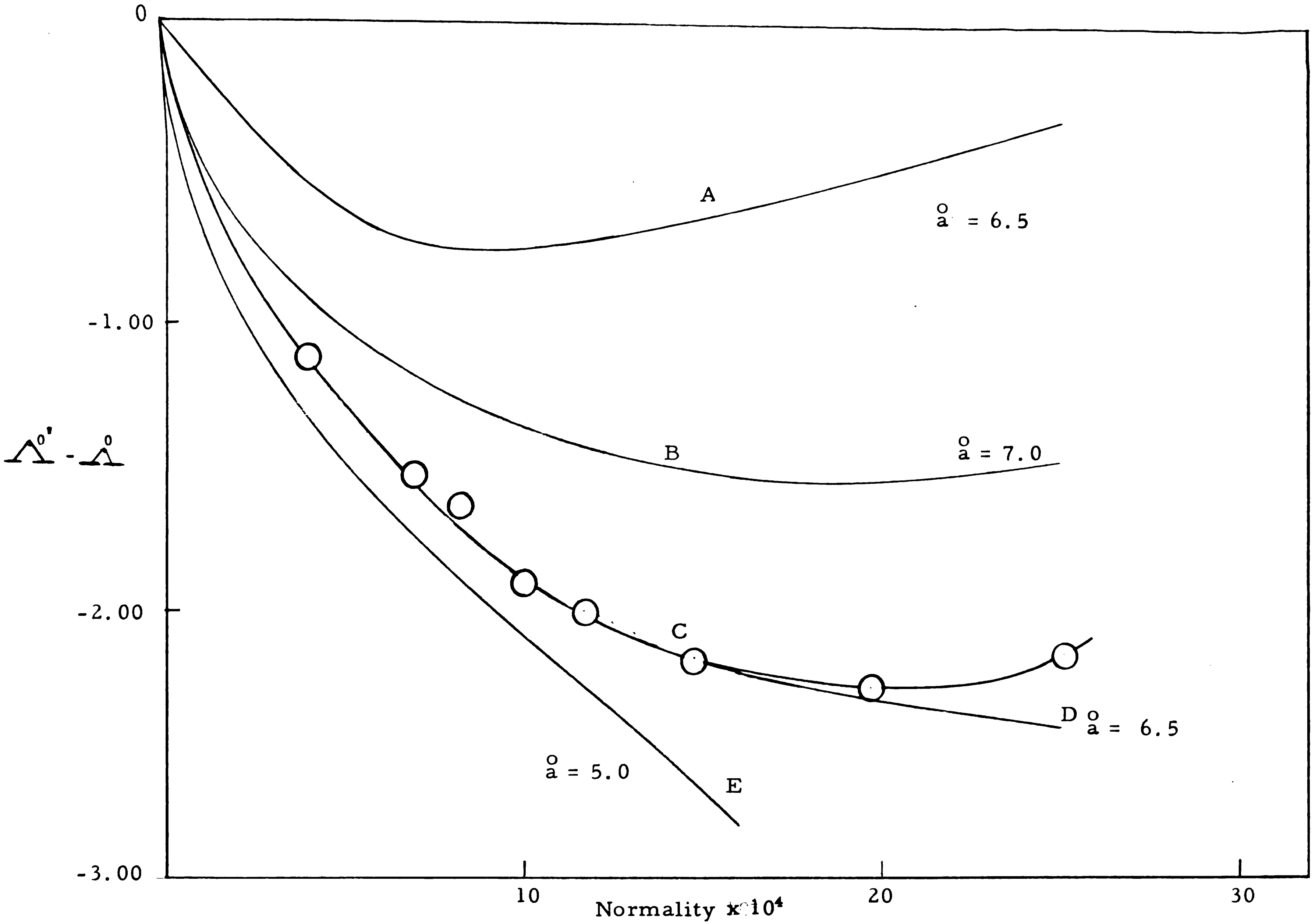

Figure II. Deviations of the experimental data and several theoretical expressions from the Limiting Law.

Only by using an unlikely $\overset{0}{\underline{a}}$ of less than $3\overset{0}{A}$ could this conductance equation be made to come close to fitting the experimental data.

While curve D fits the data very well it is probably not unique; the data could no doubt have been fit as well without the viscosity term by using a lower $\overset{0}{\underline{a}}$ or by including the viscosity correction for both ions and using a slightly larger $\overset{0}{\underline{a}}$. All this means is that the presence of the viscosity effect is not proven by these data, but, on the other hand this theoretically predicted effect is certainly compatible with the data. The concentration at which the theory breaks down seems reasonable, as one would expect systematic deviations to begin to occur at about 2.5×10^{-3} normal, or one-fourth the concentration at which the theory breaks down for 1-1 electrolytes.

The value of $\underline{\Lambda}^{0}$ obtained in this research combined with the value of $\lambda^{0}_{Ba^{++}}$ given in Robinson and Stokes (15) yields 59.67 $ohm^{-1}cm^{2}$ $equivalent^{-1}$ for the metabenzenedisulfonate ion.

The results of this work show that the 2-2 electrolyte barium metabenzenedisulfonate gave the expected strong electrolyte behavior and that the extended theory can successfully analyze the data to a reasonably high concentration without assuming ionic association. Only after this and other 2-2 electrolytes have been studied in water and mixtures such as dioxane-water, can the general applicability of the extended theory to 2-2 electrolytes be determined.

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