CONDUCTANCE AND TRANSFERENCE NUMBERS OF AQUEOUS SOLUTIONS OF SODIUM METABENZENEDISULFONATE

Thesis for the Degree of M. S.
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Hossein Pazandeh
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CONDUCTANCE AND TRANSFERENCE NUMBERS OF AQUEOUS SOLUTIONS OF SODIUM METABENZENEDISULFONATE

By

HOSSEIN PAZANDEH

AN ABSTRACT

Submitted to the College of Science and Arts
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Department of Chemistry

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ABSTRACT

Recent theoretical developments have prompted an investigation of the behavior of strong 2-2 electrolytesin water. Certain anomalies which appeared using zinc sulfate, resulted in a search for another 2-2 electrolyte which would not undergo hydrolysis and whose ions would not be capable of forming covalent bonds with the solvent or with oppositely charged ions. The strong electrolyte, barium metabenzenedisulfonate seemed to fit these requirements. In order to aid in the theoretical treatment, an independent value of the limiting equivalent conductance of the metabenzenedisulfonate ion was needed. This thesis describes the measurement of the conductance of sodium metabenzenedisulfonate. The value of $\lambda^{\underline{o}}$ obtained is 59.66 ohm^{-1} equiv.$^{-1}$ cm^{2}.

It was found that in dilute solutions, the conductance data fit the limiting slope predicted by the Onsager equation. At higher concentrations, the deviations were in the proper direction, and had the correct magnitude to be described by higher order terms of the electrophoretic equation.

In view of recent deviations of some 1-2 and 2-1 electrolytes from the Onsager equation in dilute solutions, it would be of interest to determine the effect of cation size on the conductance. This measurement on sodium metabenzenedisulfonate is one step in this series.

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I. INTRODUCTION

Ever since Arrhenius(1) in 1883, from studies of the conductances of aqueous solutions of acids, postulated that an electrolyte solution contains free ions, solutions of these ions have been studied extensively. Kohlrausch in studying the conductances of such solutions noticed that oxygen and hydrogen which tend to be absorbed at the surface of the electrodes can be dissolved when the polarity is reversed. This led him to apply an alternating potential when making conductance measurements. As the adsorption is also affected by the surface area, he coated the platinum with platinum black. Kohlrausch(2), who also emphasized the importance of good temperature control, made quite precise measurements; his data on potassium chloride in water are still valid. Since specific conductance of the solution refers to that of one cubic centimeter, it is necessary to measure the cell constant $\frac{d}{A}$. (The area of electrodes is A and the distance which separates the electrodes is d.)

In 1923 Parker(3) observed that the cell "constants" are apparently not really constant, but vary with the resistance being measured. Shedlovsky, Jones, and Bollinger(4), showed that this effect is due to the capacitance of the cell, and designed new types of cells which minimized the effect. Jones and his co-workers, with some refinements in the technique, *i.e.*, using an oil bath, a special bridge and a sensitive amplifier with a telephone headset for detection, were able to get results of high precision (0.02%).

Any modern theory of conductivity must be concerned with the concept of the interaction between thermal motion of the ions and their electrical attractions and repulsions. Using the results of Debye-Huckel(5) theory of ionic interaction (1923), Onsager(6) (1929) was able to calculate from solvent properties the limiting behavior of 1-1 electrolytes, alkaline earth halides (2-1) and rare earth halides (3-1). The disagreement of the conductance of 1-4 and 2-2 electrolytes from this theory was attributed to ion-pair formation. In a study of theoretical and experimental behavior of $ZnSO_4$ by J. L. Dye and co-workers(7), it was desired to measure $\lambda^{\circ}_{Zn^{++}}$ from data on $Zn(ClO_4)_2$. These workers found a large deviation from the Onsager equation even in dilute solution. Probably hydroysis effects or covalent tendencies of Zn^{++} are responsible. In the case of $K_2Pt(CN)_4$ for which similar deviation are observed(8), the spatial configuration (square coplanar) could allow attachment of water molecules in the octahedral positions. The observed deviations prompted a search for another 2-1 or 1-2 electrolyte for which hydrolysis could be definitely ruled out and for which the formation of covalent bonds was unlikely.

The purpose of this study of sodium metabenzenedisulfonate,

Na_2m $\varphi(SO_3)_2$, is a basic step in the interpretation of 2-2 electrolyte behavior. This involves the study of Ba m $\varphi(SO_3)_2$: which has already been begun$^{(9)}$. The measurements on Na_2 m-$\varphi(SO_3)_2$ were done to evaluate λ°_- for m-$\varphi(SO_3)_2$.

In addition it would be desirable to study the effect of cation type on the conductivity. Some other metabenzenedisulfonates such as Li_2 m-$\varphi(SO_3)_2$, $[N(CH_3)_4]_2$ m-$\varphi(SO_3)_2$ and $[N(Bu)_4]_2$ m-$\varphi(SO_3)_2$ will be studied to determine the effect of cation size on the conductance. Such an effect has been recently found to be very significant for 4-1 electrolytes$^{(10)}$.

The observation by Daniel$^{(11)}$ of electroanalysis in a three compartment cell showed that positive and negative ions do not carry equal amounts of electricity. In other words, different ions have different ease of movement under the influence of an electrical field. This is contrary to the earlier idea of Arrhenius who erroneously ascribed the decrease of equivalent conductance to a decrease in the number of free ions and assumed the mobilities to be constant.

Ionic conductivity and transference number are internally related by the equation $t_+ = \frac{\lambda_+}{\Lambda}$ and $t_- = \frac{\lambda_-}{\Lambda}$, where t_+ and t_- are transference numbers, λ_+ and λ_- are the ionic conductances of cation and anion respectively, and Λ is the equivalent conductance.

Three types of experimental methods of determination of transference number have been employed:

(1) The Hittorf method of experiment, which was frequently used in the past, requires accurate analytical work and is quite time consuming.

(2) The e.m.f method, involving measurements of cells with and without transference, requires electrodes reversible to both ions, and even then is of limited accuracy.

(3) The moving boundary method, with which these experiments are concerned, involves the observation of the velocity of a boundary between two solutions. This method is relatively rapid and provides the best accuracy attainable at present.

In addition, transference numbers afford an independent experimental test of theory. It happens that transference numbers of unsymmetrical electrolytes are more sensitive to deviation from Onsager theory than are conductances(12).

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II. THEORY

A. Debye-Huckel Theory of Ion-Interaction

It has been shown that the Debye-Huckel limiting law gives theoretical predictions which fit experiment at very low concentrations. However the theory is not valid at high concentrations.

Debye and Huckel made some assumptions in developing the theory, which in most cases are not valid at high concentrations. These assumptions are the following:

1. Ions behave as hard non-polarizable spheres. This assumption gives to each electrolyte a mean distance of closest approach. Ions are assumed unable to penetrate within this distance and the charges are assumed to be spherically distributed over the ions. It is expected that this assumption will be invalid for large ions whose charge distribution is somewhat distorted.

2. The solution is assumed to have a uniform dielectric constant - actually solvent molecules are about the same size as ions and the assumption of uniform dielectric constant cannot be valid if a few solvent molecules are on the average between each pair of ions. The dielectric constant of the bound water is not the same as that of free water in the pure state. Furthermore the work of Hasted,

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Ritson and Collie(13) shows that the dielectric constant of a solution is less than that of the pure solvent.

3. The time-average charge distribution can replace the instantaneous distributions.

In using the time-average distribution of ions in the Poisson equation, instantaneous interaction forces were ignored. These forces give rise to the so called "fluctuation term", whose magnitude has been the subject of much study over the years. A semi-empirical treatment by Bjerrum(14), Fuoss, and Kraus(15) took care of this situation reasonably well for symmetrical electrolytes through the introduction of the ion-pair concept. This does not completely explain the behavior of unsymmetrical electrolytes however. Recent advances using statistical mechanics by Mayer and Poirier(16), Kirkwood(17) and Meeron(18), have sought the answer to this problem.

The interaction between two ions of given charge depends upon the sign, structure and polarizability of the ions, and also on the size, structure, dipole moment, and polarizability of the solvent molecules with which the ions likewise interact. As the interaction between ion and solvent increases, the ion-ion interaction decreases and when ion-solvent interaction decreases, ion-ion interaction increases and ion-pairs will form. For weak ion-solvent interaction there is a likelihood of the formation of ion-triples and higher clusters.

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4. Solutions are dilute--the theory of Debye and Huckel accounts satisfactorily for the behavior of normal 1-1 salts, such as KCl, in aqueous solution up to concentrations of about 0.01 M. Above this concentration both the physical and the mathematical approximations break down.

The essential feature of Debye-Huckel theory is the calculation of electrostatic potential ψ at a point in the solution in terms of concentrations and charges of the ions and the properties of the solvent. This is achieved by the device of combining the Poisson equation of electrostatic theory with a statistical mechanical distribution formula. The result for the potential ψ_j is given by:

$$\psi_j = \frac{-Z_j e}{} \cdot \frac{\kappa a}{1+\kappa a} \cdot \frac{e^{-\kappa a}}{r}$$

Where is the electrical charge on the central j-ion, "a" represents the limit within which no other ion can approach the central ion and

$$\kappa = \left[\frac{4\pi e^2 \sum_i n_i Z_i^2}{kT}\right]^{\frac{1}{2}}$$

Onsager$^{(19)}$ has shown that the correct time-average ionic distribution function is given by the equation

$$r_{ji} = n_i \exp\left(-\frac{W_{ji}}{kT}\right)$$

Where W_{ji} represents the time-average energy to charge the i-ion at a distance of r from j-ion, less the time average **energy**

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required to charge the i-ion at an infinite distance from the j-ion, (but still remaining in solution). The corresponding value of Wji from the equation of Debye and Huckel is $W_{ji} \cong e_i \psi_j$.

B. Onsager Theory of Conductance

The Debye-Huckel theory, in its general form, accounted satisfactorily for the thermodynamic properties of dilute solutions. A simple conductance treatment of dilute solutions by Debye-Huckel was not completely satisfactory. However, the necessary refinements were given by Onsager$^{(6)}$, who studied the theory of conductance and diffusion in electrolyte solutions. Onsager developed a theory considering the quantitative aspects of the conductance problem which gives the individual ionic conductivity of dilute solutions as a function of concentration. At the same time the results are applicable to the change of transference number with concentration.

The motion of an ion under an external field is complicated by two effects arising from interionic forces; the relaxation and the electrophoretic effect. Each of these acts as a drag operating between oppositely charged ions moving in opposite directions.

1) The time of relaxation effect - Onsager in the calculation of retardation by the time of relaxation effect used the equation of motion and the equations of continuity to

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set up an expression for the asymmetry of the ionic atmosphere. This treatment involves the use of expressions for frictional forces and ionic interaction and results in a complex differential equation. Approximate solution of the differential equation gives a retarding force which is proportional to the square root of the concentration and to the mobility of the ion in question. The expression also includes the dielectric constant of the solvent and the temperature.

2.) The electrophoretic effect - Another electrostatic action which lowers the mobility of the ion is the electrophoretic effect. The ions comprising the atmosphere around the central ion are moving themselves in the opposite direction. As these ions are usualy solvated they tend to carry with them their associated solvent molecules, so that there is a net flow of solvent in a direction opposite to the motion of the central ion, which is thus forced to "swim upstream" against this current. The electrophoretic effect normally makes the larger contribution to the conductance. The basic expression used in the treatment of the electrophoretic effect is Stokes' Law of the velocity of a sphere moving through a viscous medium. It is also assumed that a steady state is quickly reached in which momentum is transferred from the ions to the solvent and vice-versa.

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According to the Onsager theory, the conductance of an electrolyte is given by the equation:

$$\Lambda = \Lambda_0 - (\alpha \Lambda_0 + \beta) c^{\frac{1}{2}}$$

where α and β are constants depending on the dielectric constant, temperature, and viscosity, and Λ_0 is the limiting conductance. This equation is a limiting form. If Λ is plotted versus $c^{\frac{1}{2}}$, then in dilute solutions the points approach a straight line whose slope is equal to $\alpha \Lambda_0 + \beta$. For salts of a given charge type, the slopes differ little, but the magnitude of the slope increases markedly as the number of unit charges on the ions increases. Onsager's equation is very useful as a limiting form for purposes of extrapolation.

C. Extensions of Onsager's Theory

1. Fuoss-Onsager Theory - Recently Fuoss and Onsager(20) re-examined the equations of continuity and the boundary condition of the differential equation and included higher order terms than before as well as the idea of a finite ionic diameter. These workers obtained a new expression for the relaxation field. The resulting equation for conductance has the form

$$\Lambda = \Lambda_0 - (\alpha \Lambda_0 + \beta) c^{\frac{1}{2}} + Dc \ln c + (J_1 c + J_2 c^{3/2})(1 - c^{\frac{1}{2}})$$

where the terms higher than $c^{3/2}$ are neglected. The terms

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J_1 and J_2 are explicit functions of ionic size, Λ_0 and some solvent properties; D is independent of ionic size. This equation was derived only for symmetrical electrolytes. Tests of this equation in solvents of various dielectric constants give consistent results for the ionic size and reasonable values of the association constant.(12).

2. Higher terms of the electrophoretic effect - Extension of Onsager's theory by Dye and Spedding involved the inclusion of higher-order terms in the distribution function used in the electrophoretic effect. This treatment gave satisfactory agreement for both conductances and transference numbers of alkaline earth and rare earth halides. Recently, the integrals have been evaluated by numerical methods using machine calculations(21) for a variety of charge types, ion sizes, and concentrations.

D. Deviations from All Theories

1. Solvent structure - The ions in solution are subject to strong electrical fields due to solvent molecules. The intensity of this field depends on the value of the dipole moment of the solvent molecules. In considering this interaction the smaller the molecules of solute, the greater is the force of interaction with the solvent. In general the results of solvent-ion interaction will manifest themselves in three different ways: effect on the motion of ions; solvation properties; and interaction of ions with each other.

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2. High concentrations - In experimental work on 1-1 electrolytes up to concentrations of 0.01 normal, the limiting law of Onsager can be applied. Beyond this concentration many varied and complex effects come into play which cannot be quantitatively predicted. For example, the viscosity of the solutions is altered, and as the concentration increases, a quasi-lattice forms and certainly in very concentrated solution the ionic distribution must alternate as in a crystal.

3. Unsymmetrical electrolytes - Unsymmetrical electrolytes are complicated by the fact that the theory of Fuoss and Onsager(22) is applicable only to the symmetrical type. Further complications arise from the fact that any ion-pair which might form still carries a net charge and this species has an unknown mobility.

III. EXPERIMENTAL

A. Purification and Preparation

Since pure $Na_2\ m-\varphi(SO_3)_2$ was not available, and because of uncertainties in weighing due to hydration of the salt, the stock solutions were prepared as follows:

Benzenedisulphonic acid was neutralized with barium hydroxide according to $H_2\ m-\varphi(SO_2)_3 + Ba(OH)_2 \longrightarrow Ba\ m-\varphi(SO_3)_2 + H_2O$, and the end-point was checked with pH paper indicator. After purification, a solution of known concentration of $Ba\ m-\varphi(SO_3)_2$ and also a solution of Na_2SO_4 was metathesized. After removal of barium sulfate by filtration, the solution was weighed and its molality calculated. Other solutions were prepared from the stock by weight and stored in Pyrex brand flasks with rubber caps to prevent loss by evaporation.

1. Barium metabenzenedisulfonate - The crude $Ba\ m-\varphi(SO_3)_2$ obtained from neutralization was dissolved in a small amount of conductance water and recrystallized with ethyl alcohol five or six times.

2. Sodium sulfate - Analytical reagent grade sodium sulfate which might still contain some sodium hydrogen sulfate and moisture was heated for three hours at 500° C., cooled in a dessicator and used to prepare stock solutions.

These solutions were analyzed for sulfate by barium sulfate precipitation.

3. Water - Preparation of a good conductivity water free from CO_2 and other impurities which may contaminate the water is of great importance. To provide a good water for the experimental work of this thesis, the following essential points have been observed:

a. The distillation flasks and columns were thoroughly washed with cleaning solution and soaked in good water for a period of time before using.

b. For the purpose of preparation of water free from organic substances and contaminant gases, a two-step distillation was performed. First demineralized water was distilled from an alkaline permanganate solution to remove organic materials by oxidation. Secondly, the water thus produced was introduced into a separate distillation flask, and distilled under a stream of nitrogen. Before the nitrogen was introduced into this system, it was purified by passage through gas-washing towers containing H_2SO_4, KOH solution and water containing phenolphthalein respectively.

The average conductivity of the water used was 0.37 x 10^{-6}. $ohm^{-1} cm^{-1}$

B. <u>Conductance Measurement</u>

The apparatus used for measurement of conductivity is described below:

1. Bridge - The bridge used is a modification of the Jones bridge described by Rogers and Thompson(23). It consisted of an audio frequency oscilator, an amplifier and a cathode ray tube. This bridge allows the use of frequencies of 400, 600, 1000, and 4000 cps. The balance point can be reproduced to ± 0.101%. The resistance showed a slight frequency dependence which was corrected to infite frequency in the usual fashion. For high resistance a 20,000 ohm shunt was used in parallel with the cell.

2. Oil Bath - An oil bath was used instead of a water bath in order to decrease the capacitance effect. Temperature control to ± 0.01° C. was obtained using a mercury thermoregulator to control a heat lamp. The bath was stirred with a Gorman - Rupp centrifugal pump and temperature gradients within the bath were less than .02° C.

3. Conductance Cell - The conductance cells for low concentrations were constructed from Leeds and Northrup Type A cells. A 500 ml. Erlenmeyer flask was attached to the electrode chamber. This makes thorough mixing of the solution possible. The platinum electrodes were lightly platinized before using (ca. 40 sec. at 40 ma.). The steps involved in a typical conductivity run are:

a.) Water transfer and measurement - Before introducing the water into the cell, it was cleaned with hot, fuming nitric acid and rinsed 15-20 times with water and finally allowed to stand overnight filled with conductance water. After drying the cell, the stopcock and standard taper cap were lubricated with Apiezon "N" grease and the cell was weighed. Water from the final distillation under nitrogen was transferred into the cell under nitrogen pressure. Before introducing any water, the trapped air inside the cell was swept out with nitrogen for 15 minutes. Only about 300 ml. or less of water was used so that efficient mixing could be obtained. After completion of the transfer, the cell and water were weighed to ± 0.01 g.

b. Measurement of water conductance. - The cell with water was placed into the oil bath for at least 1/2 hour before measuring the resistance. Due to the high resistance of water, it was necessary to measure the resistance in parallel with a 20,000 ohm shunt. The cell was removed and the contents mixed gently until reproducible resistance readings were obtained.

c. Addition of a solute - A weight burette containing stock solution was used to introduce solution into the water which was previously weighed and whose conductance was measured. By knowing the weight of the burette before and after addition the amount of solute introduced into the cell could be obtained. The addition was made with nitrogen flowing through the cell. Care was exercised in introducing the solute into the cell, to make sure that the drops fell directly into the bulk of the liquid.

d. Measurement of resistance - The resistance measurement was carried out as for the water except that the shunt was not necessary. If the room temperature was lower than the bath, some condensation appeared on the cap and neck of the cell. It was then necessary to heat the portion of the cell above the bath with a heat lamp.

e. For measurement of high concentrations (.007 N.), a Leeds and Northrup type B cell was used. Solutions made from the stock were prepared in Pyrex flasks and measured directly. The water used in this preparation was separately stored and its conductance measured.

C. Transference Numbers

Transference numbers were measured by the moving boundary method using visual observation of the boundary. This detection is based upon the difference of refractive indices between the leading solution and the indicator solution. The instruments used in this experiment are:

1. Cell - The cell consists of anode and cathode compartments and a U tube with a calibrated pipette forming one of the arms. The cathode and anode compartments are separated by two hollow stopcocks which allow measurement of either rising or falling boundaries. When the stopcock between the leading and indicator solutions is opened and an adjusted potential is applied, the boundary will form and begin to move through the calibrated tube. The rate of

motion of the boundary is observed visually. The anode is made of a chemically pure cadmium plug and the cathode is a silver-silver chloride electrode made from silver sheet.

2. Current Control Apparatus - Current for the measurement was supplied by an electronic constant-current device described by Spedding, Porter, and Wright(24) and modified by Dye. The current through the cell was also passed through a standard 100 ohm resistor and the emf developed was measured with a Leeds and Northrup Type K potentiometer. The unbalance from the potentiometer was fed to a Brown "Electronik" amplifier which was used to drive a synchronous motor attached to the control Helipot" of the constant-current circuit. The current could be maintained constant at 0.5 to 10 ma to ± 0.05%.

3. Light and Telescope - The position of the boundary was detected by means of a narrow slit of light passed through the transference tube from the back side with a telescope focused on the tube from the front.

4. Stopwatch - The time required for the boundary to pass between the gaps that were marked on the pipette was measured with stopwatches which had been calibrated against the standard WWV signal.

IV. RESULTS AND DISCUSSION

A. Results

The analyses of solutions used are given in Table I. The conductance results are given in Table II and are shown graphically in Figures 1 and 2. Figure 2 is a graph of Λ_0' versus the square root of normality, where

$$\Lambda_0' = \Lambda + (\alpha \Lambda_0 + \beta)\sqrt{C}$$

The values of α and β used were taken from Harned and Owen(25) and are

$$\alpha = \frac{\alpha^*}{\sqrt{2}} = 0.5227 \qquad \alpha^* = 0.2289\,\omega' Q$$

and

$$\beta = \frac{\beta^*}{\sqrt{2}} = 110.59 \qquad \beta^* = 60.19\,\omega^*$$

Table III gives the data used for determination of the cell constant. For the equivalent conductance of KCl, the equation

$$\Lambda = \Lambda_0 - S_\lambda\sqrt{C} + AC\log C + BC$$

was used.

The transference cell was checked a number of times using KCl solution. The values obtained for T_+ agreed with the literature values to within 0.1%.

Five runs were made with Ba-m$\varphi(SO_3)_2$ solution which were combined with earlier data of Dye and Gordon$^{(26)}$. The combined results are given in Table IV and shown in Figure 3. The limiting value of T_+, denoted by T_+^o is of particular interest since it fixes a value of λ^o_- for m-$\varphi(SO_3)_2^=$ which can be compared with conductance results. $T_+^o = 0.5118$ and this gives with $\lambda^o_{Ba^{++}} = 63.6$ a value of $\lambda^o_- = 60.70$

Three attempts were made to measure the transference number of sodium metabenzenedisulfonate without success. Only for the most concentrated solution could a boundary be seen and even for this case it was too faint to follow. This could be caused by close values of the refractive index of the leading and following solutions or by the presence of a slight excess of Ba^{++} or $SO_4^=$ ions. This will need further investigation.

The value of Λ^o obtained in this work is 109.76 ohm^{-1} $equiv^{-1}$ cm^2. Using

$\lambda^o_+ = 50.10\ ohm^{-1}\ equiv^{-1}\ cm^2$ for Na^+ gives

$\lambda^o_- = 59.66\ ohm^{-1}\ equiv^{-1}\ cm^2$ for m- $(SO_3)_2$

This is to be compared with the value of $\lambda^o_- = 60.7$ obtained from transference measurements on the barium salt.

Application of the extended electrophoretic calculations of Dye and Spedding gives an å value of about 7

Angstroms. This is to be considered tentative, however since transference numbers are also needed for this calculation.

B. Discussion of Errors

Errors due to actual measurement of resistance were certainly negligible. This is evident in repeat runs of conductivity using the high cell. Repeat measurements differed by not more than ± 0.02%.

Different analysis for the stock solutions used to make the final solution agreed with each other to within ± 0.1% and the metathized solution was checked for extra ion of each reactant. Nevertheless, the solution certainly contained some extra Ba^{++} and $SO_4^{=}$ because of the solubility of $BaSO_4$. This should not have made an appreciable error in conductance, however, pH measurements showed that the acidity of the $Ba\ m\text{-}\phi\ (SO_3)_2$ stock solution after several months standing was essentially unchanged from that of the water used. Check determinations of the conductance showed no change during this period. This indicates no decomposition or evaporation of the solution. As the graph of conductance *versus* the square root of concentration shows, at concentrations below about 0.005 N the changes in conductance are in accordance with Onsager's theory. At higher concentrations where the theory mathematically breaks down, systematic deviations set in. At least some of these deviations can be attributed to higher terms in the electrophoretic equation.

It will be interesting to see whether other salts of $m\text{-}\phi(SO_3)_2^{=}$ with univalent cations also give agreement with theory or whether a pronounced ion-size effect occurs.

TABLE I

ANALYSIS OF STOCK SOLUTION AND METATHESIS CALCULATIONS

Ba m - $\varphi(SO_3)_2$	Experimental Run		
	No. 1	No. 2	No. 3
Weight of solution	5.7453	5.1146	5.2341
Weight of $BaSO_4$	0.2699	0.2400	0.2455
Molality (calculated)	0.2176	0.2173	0.2172
<u>Na_2SO_4</u>			
Weight of solution	5.6061	5.3[illegible]	5.[illegible]301
Weight of $BaSO_4$	0.5563	0.5152	0.5451
Molality (calculated)	0.4353	0.4355	0.4366

Metathesis - 603.20 g. Ba m $\varphi(SO_3)_2$ stock = 0.245 equivalent of m-$\varphi(SO_3)_2^{=}$

299.52 g. Na_2SO_4 stock = 0.246 equivalent of Na_2SO_4

0.0[illegible]2[illegible]7 = molality of final solution

TABLE II

CONDUCTANCE RESULTS

Series 1 - Cell E-3; constant = 1.0267

H_2O conductance = 0.348 x 10^{-6} $cm^{-1}.ohm^{-1}$.

Initial weight of water = 305.49

Molality of stock = 0.042573

(at 25° C)

g. Stock	Molality of solution x 10^4	Normality of solution x 10^4	R_∞	Λ	Λ_0'
1.0635	1.4665	2.9243	32477.6	106.32	109.80
1.7953	2.4583	4.9021	19730.0	106.12	109.84
2.8191	3.8475	7.6723	12773.5	105.23	109.83
3.9156	5.3254	10.6193	9315.0	104.43	109.90
5.1654	6.9972	13.9530	7137.0	103.32	110.09

TABLE II

CONDUCTANCE RESULTS

Series 2 - Cell E-3; constant = 1.0367

H_2O Conductance = 0.37 x 10^{-6} ohm^{-1} cm^{-1}

Initial weight of water = 296.62

Molality of stock = 0.042578

(at 25° C)

g. Stock	Molality of solution x 10^4	Normality of solution x 10^4	R_∞	Λ	Λ_0'
3.0341	4.2609	8.4966	11567	105.05	109.94
4.4950	6.2814	12.5257	7925	104.14	110.03
5.9471	8.2722	16.4955	6067	103.36	110.13
8.3291	11.4943	22.9206	4406.6	102.43	110.52
10.3403	14.1786	28.2734	3600.1	101.72	110.65
12.5237	17.0531	34.0054	3014	101.04	110.84
14.1504	19.1673	38.2223	2693.7	100.59	110.97
16.2604	21.8797	43.6300	2370.1	100.17	111.26
21.2936	28.2031	56.2395	1857.0	99.20	111.79

TABLE II

CONDUCTANCE RESULTS

Series 3 - Cell E-1; constant = 29.19
(at 25° C)

g. Stock	g. Solution	Molality of Solution	Density	Normality	Λ
197.58	398.80	0.02097	1.0004	0.04172	86.8
275.7	414.32	0.02822	1.0015	0.05626	84.46
stock	stock	0.042578	1.0039	0.08447	81.45

TABLE III

CELL CONSTANT DETERMINATION

Low Cell - B-1

Molality of stock = 0.04918

H_2O Conductance = 0.83 x 10^{-6} ohm^{-1} cm^{-1}
(at 25° C)

g. stock	Molality of solution x 10^4	Normality of solution x 10^4	R_∞	Λ	k
1.6776	2.6820	2.6741	25543	148.34	-
2.5520	4.0681	4.0562	17040	148.00	1.0370
3.5499	5.6409	5.6244	12363	147.66	1.0370
4.4348	7.1050	7.0842	9349.3	147.40	1.0366
5.5271	8.7270	8.7014	8043.3	147.15	1.0366
6.8912	10.833	10.801	6499.4	146.88	1.0362
8.2473	12.909	12.871	5472.0	146.57	1.0368

TABLE IV

TRANSFERENCE NUMBER OF Ba m-$\Phi(SO_3)_2$
(at 25° C)

C^*	$\sqrt{C^*}$	T_+
0.02036	.1426	0.5128
0.04100	.2025	0.5137
0.06102	.2470	0.5142
0.06102	.2470	0.5146
0.06494	0.2546	0.5143
0.10906	0.3302	0.5144
0.10906	0.3302	0.5142
0.10906	0.3302	0.5147

$T_+^\circ = .5118$ $T_-^\circ = .4882$

$\lambda^\circ_{++} = 63.6$ $\lambda^\circ_- = 60.7$

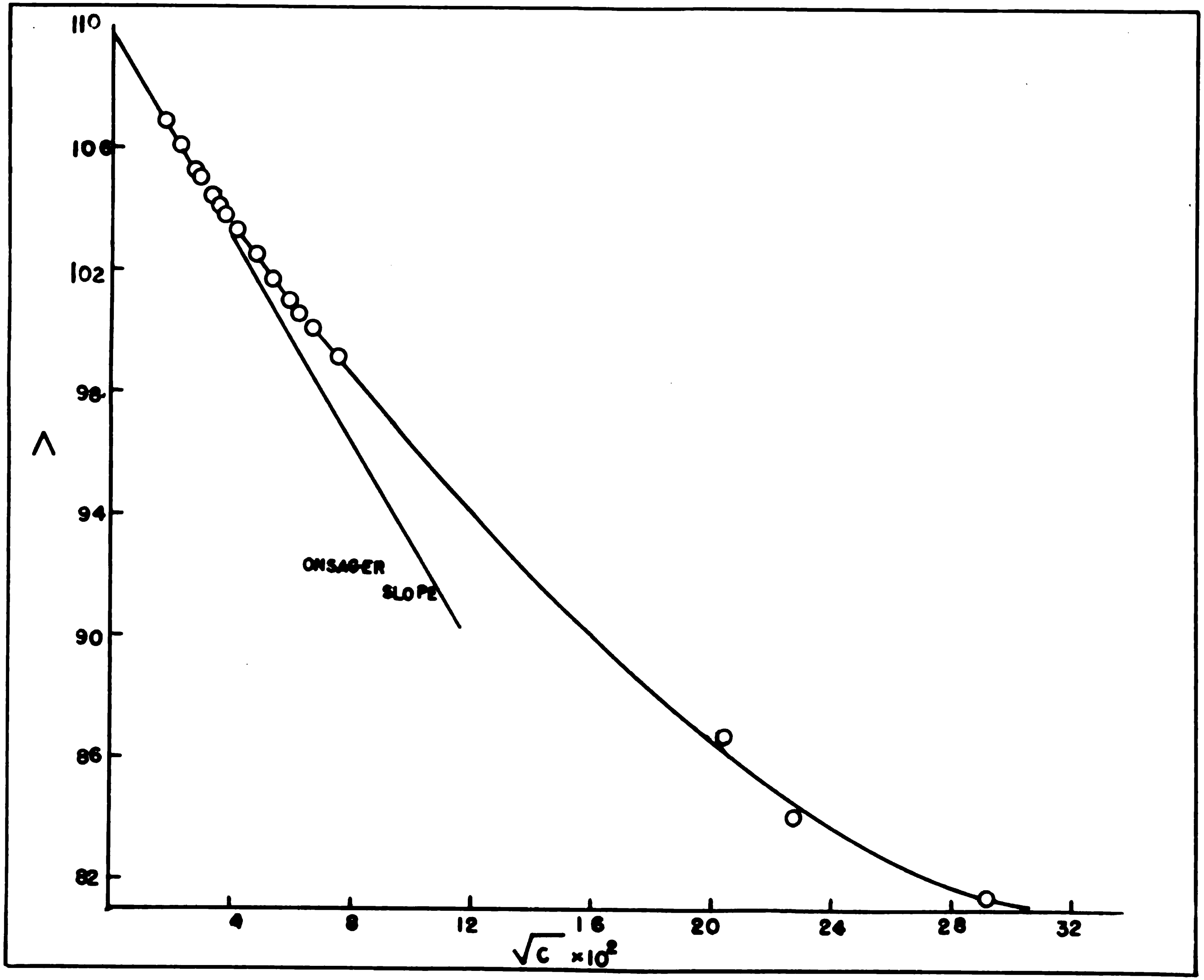

Figure 1. Conductance of sodium metabenzenedisulfonate versus square root of concentration.

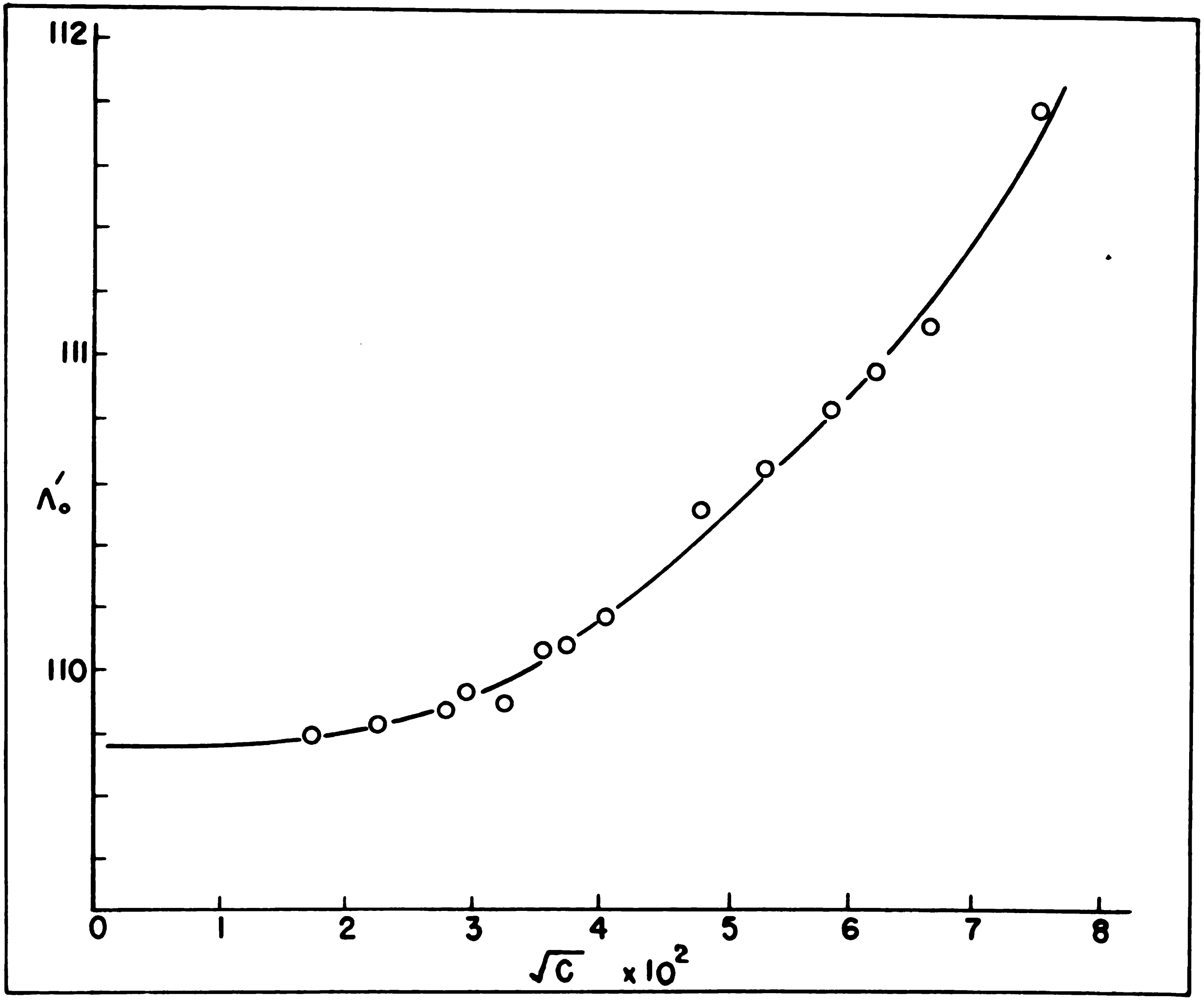

Figure 2. Deviation from the Onsager theory of conductance.

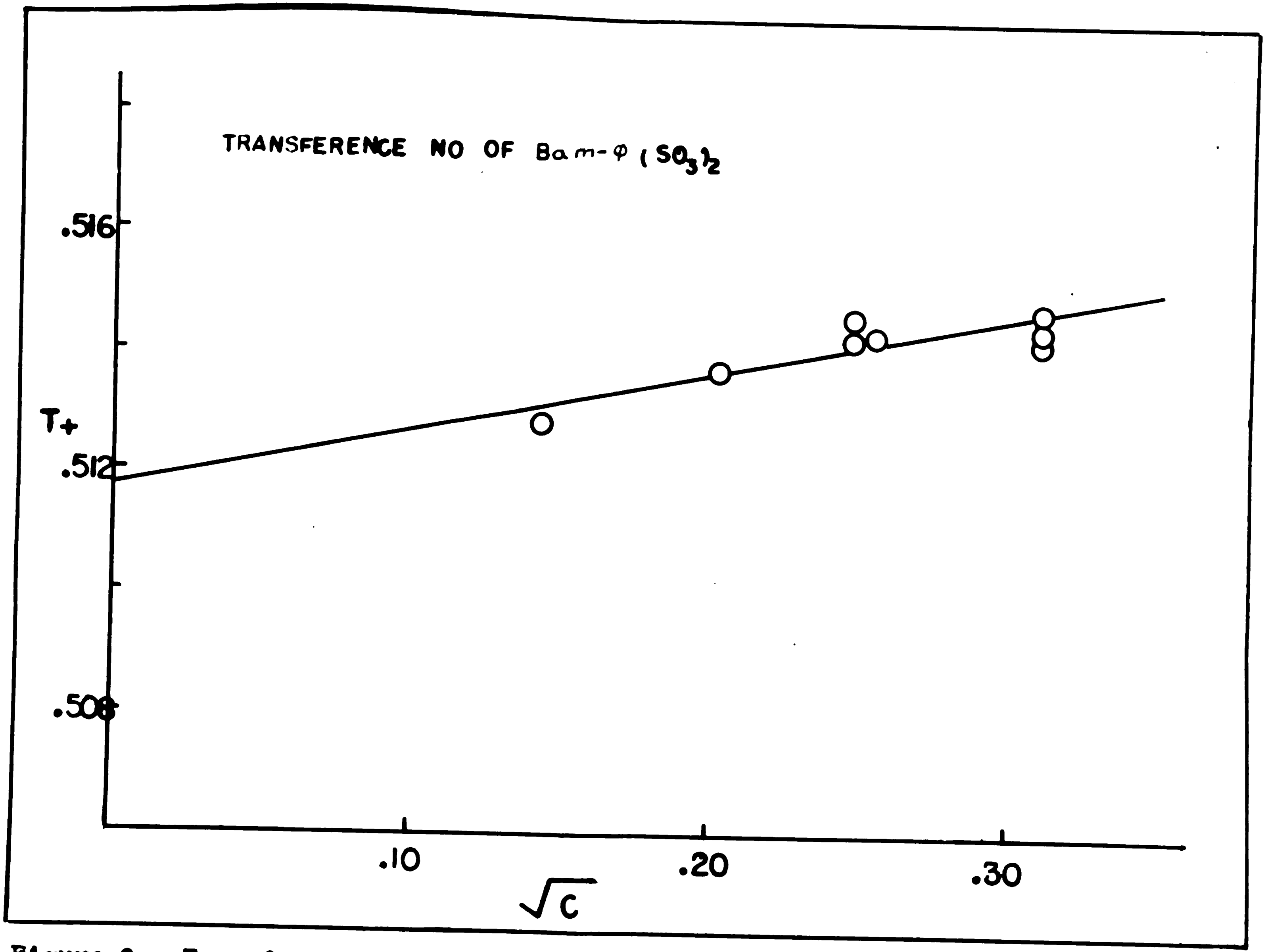

Figure 3. Transference number of Barium-metabenzenedisfonate.

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