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THE CONDUCTANCE OF SOME HIGH VALENCE TYPE ELECTROLYTES

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In the interpretation of ultrasonic velocity and absorption measurements in equilibrium chemical systems it is desirable to know other thermodynamic parameters of the systems as accurately as possible. Our work on ultrasonic measurements in solutions of electrolytes demands that we know the association constants of these electrolytes in the solvent systems of interest as well as any other parameters obtainable.

Therefore, Mr. Hallada kindly consented to measure these association constants by precision conductance techniques and apply the extended Fuoss-Onsager theory to the results. This resulted in the following technical report.

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INTRODUCTION

In electrolyte solutions, the interactions usually incorporated into theoretical models and experimental interpretations are of three categories: long range ion-ion, short range ion-ion, and short range ion-solvent.

The first type has been extensively studied and is described by the Debye-Hückel theory (1) set forth in 1923. For unassociated 1:1 electrolytes in dilute solutions, this theory and experimental data are in excellent agreement. Differences however, between measured activity coefficients and those calculated from the Debye-Hückel theory for some strong electrolytes led N. Bjerrum in 1926 to propose a model for short range ion-ion interaction (2). Since his proposal, many other attempts have been made to describe ion-ion association (3,4,5); however, none of these theories has been entirely satisfactory. To help clarify ion-ion association and, at the same time, extend the validity of long range ion-ion interaction beyond the Debye-Hückel theory, short range ion-solvent interaction must be considered.

An interesting approach to the study of ion-solvent interaction was made in 1953 and 1954 by J. Bjerrum and C. K. Jorgensen (6,7) when they applied the J. Bjerrum method of treating step-wise complexation (8) to the aquo-ion formation of several first row transition metal ions in solution. Their objective was to determine the successive formation constants, $\underline{k}_1$ through $\underline{k}_{\underline{N}}$, involved in the presumed selective solvation of the cation by water over an organic solvent (methanol). The method employs ultraviolet and visible spectral shifts obtained when the solvent composition is changed at constant ion concentration.

The major objections to their work are: (1) they assumed a value for $\underline{N}$ (the maximum number of waters coordinated by the cation), although this is unnecessary if the treatment is valid and a sufficiently extensive range of solvent mixtures is used, (2) they disregarded any anion-solvent interaction and any ion-ion association; the latter, even while the bulk dielectric constant of the solvent (and thus the coulombic force) was continuously being varied (9).

Following J. Bjerrum and C. K. Jorgensen, this investigator, employing spectral shifts, attempted to determine rather than assume $\underline{N}$. Again, first row transition metal ions were used, but now in a salt with a very large anion: p-toluenesulfonate (to be abbreviated PTS^-) as opposed to the previously used Cl^-

and NO_3^- anions. The thought was that a larger anion, with its consequent smaller charge density, would possibly relegate ion-ion association and anion-solvent interaction to such minor roles that they could be ignored. If treatment of the spectral data from such salts in mixed solvents proved a valid method of determining N, then the same treatment could be used on data from other physical measurements (such as nuclear magnetic resonance and vapor pressure) so that N could be found by several independent methods.

However, this work did not give the sought-after indication of an abrupt completion of a step-wise aquation process, even when the experiments were carried out over the entire range of solvent mixtures from pure water to pure methanol, at constant ion concentration. That no N was reached can be explained in two ways: either the cation exhibited no selectivity towards water over the organic solvent or, ion-ion association was still taking place in the changing dielectric media to such an extent that it could not be ignored.

From electrostatic considerations, the fact that water has a larger dipole than methanol would lead to the belief that the cation should show a greater selectivity towards water over methanol. It is apparent then, that one must return to the problem of ion-ion association before any conclusions are to be drawn about the interaction of ion and solvent from the mixed solvent method.

Association constants have been determined in an attempt to clarify the problem of ion association. However, except for those electrolytes known to be completely unassociated (such as KCl) and those highly associated (such as the covalently bonded carboxylic acids), the meaning of these association constants has been vague. This ambiguity has arisen from the fact that for a given electrolyte, widely divergent values for its association constant have been obtained. Not only from varying physical measurements are there found different values for an association constant of a particular electrolyte, but even from one technique can such a result occur.

In 1938, Owen and Gurry (10) demonstrated that from conductance measurements on $CuSO_4$ and $ZnSO_4$, several association constants for each salt could be found simply by varying the technique of curve fitting. As late as 1957, Prue and his associates (11,12) showed that spectrophotometric data on $CuSO_4$ could be so manipulated that the dissociation constant for this electrolyte could be given any value from 8.0×10^{-3} to 3.5×10^{-3} from the same set of experimental results.

Differences for the association constant of a given electrolyte obtained from varying experimental techniques may be attributed to the inherent differences in the techniques themselves. However, when such differences occur even by the use of a single technique, the problem is much more acute.

Taking a unique attitude, Guggenheim (13) in 1957, went so far as to question whether an electrolyte like $CuSO_4$ was even associated at all. Others have instead tried to fit experimental data on associated electrolytes to the numerous theories by the method of simply adding empirical terms to the theoretical equations to accommodate the behavior of each electrolyte, thus making every electrolyte a separate case, practically unrelated to any other electrolyte (14).

It is this investigator's feeling that the far-reaching dilemma existent in the study of ion association must be due to a lack of a suitable baseline. That is, one must know unambiguously, either theoretically or experimentally, how a given associated electrolyte would behave if it were not associated. Only then can an association constant have some meaning.

Without the use of any unreasonable parameters, the Onsager-Fuoss conductance theory (15,16,17) agrees with conductance data for the entire range of 1:1 electrolytes, from the completely unassociated, through the weakly associated, to the highly associated. This theory, which is an extension of the Onsager limiting law (18), describes the behavior of unassociated and of pair-wise associated electrolytes by the following equations for equivalent conductance:

Unassociated:

$$\Lambda = \Lambda^{o} - S\,c^{1/2} + E\,c\log c + J\,c$$

Associated:

$$\Lambda = \alpha(\Lambda^{o} - S\,(c\alpha)^{1/2} + E\,c\alpha\log c\alpha + J\,c\alpha)$$

where Λ = equivalent conductance, ohm^{-1} cm^{2} equivalent^{-1}

Λ^{o} = equivalent conductance at infinite dilution, ohm^{-1}cm^{2} equivalent^{-1}

S = the Onsager limiting law slope; a function of Λ^{o}, temperature, dielectric constant and viscosity of the solvent, the valence type of the solute, and universal constants

c = molarity; $c\alpha$ = molarity of the ions

E = a constant defined by the same variables as S; it is a term resulting from the mathematical extension of the Onsager limiting law

J = a constant defined by the same variables as S and E, and also the closest distance of approach of the ions, $\mathring{a}$; it results from both mathematical extensions of the Onsager limiting law and the inclusion of the size parameter

$(1-\alpha)$ = the fraction of ions pair-wise associated.

(For a more complete definition of terms, see Appendix I)

Although the mathematical treatment employed in reaching the final equations from the assumed model is very complex, the agreement of the theory with data on 1:1 electrolytes is excellent. This fact leads to the belief that the theory might also apply to higher valence type electrolytes, even if in more dilute solutions (so that the mathematical approximations are not exceeded).

STATEMENT OF THE PROBLEM

Because of the success of the Onsager-Fuoss theory on 1:1 electrolytes, conductance measurements were proposed to study the association of higher valence type electrolytes. The determined association constants for these species would then have some consistency since the Onsager-Fuoss model would describe how associated ions would behave if they were unassociated.

Most electrolyte solution theories are more valid for symmetrical electrolytes because of the form of the distribution function used in their derivations. Therefore, this type of electrolyte was chosen for the association studies.

Although there has not been found any symmetrical unassociated electrolyte of higher charge type than 1:1, the ideal complement to the determination of association constants for these electrolytes would be the discovery of a completely unassociated higher charged electrolyte. Such a fortunate discovery would lead the way for the use of different physical measurements (on the unassociated electrolyte) to test the validity of other theories beyond the simple case of the 1:1.

It was felt that the best possibility for obtaining an electrolyte which might be unassociated in water would be to select a salt containing the large anion of a strong acid. Because m-benzenedisulfonic acid (to be abbreviated H_2BDS) is a well-known strong acid, and because the charge on the m-benzenedisulfonate ion ($BDS^=$) is spread over a large framework, CuBDS was prepared.

If the comparison of the conductance data of a salt such as CuBDS (in water) to its limiting law indicated that it might be unassociated, an attempt to fit its data to the extended theory equation could be made. Furthermore, the study of the conductance of this electrolyte could be carried to mixed solvents where higher association would be forced. It would then be possible to determine whether the Onsager-Fuoss theory could handle the transition smoothly. In conjunction with this, the conductance of another salt, like $CuSO_4$, could be studied to see if it and CuBDS showed consistent behavior in the mixed solvents. Also, if the $BDS^=$ salt was found to be unassociated, it would be interesting to see if an unassociated 3:3 sulfonate salt could be found.

EXPERIMENTAL

Preparation of Acids and Salts

m-Benzenedisulfonic Acid and m-Benzenedisulfonate Salts

Two methods of purification were used on the crude commercial H_2BDS (Matheson, Coleman and Bell, Norwood, Ohio, Item T-1164) which contains a large H_2SO_4 impurity.

In the first method, $Ca(OH)_2$ was neutralized with the acid (H_2BDS) to form the soluble salt CaBDS and thus remove the large $SO_4^=$ impurity. Since the CaBDS was very difficultly recrystallized, it was converted to K_2BDS by use of K_2CO_3. The K_2BDS was recrystallized twice from water. Part of this purified K_2BDS was reconverted to H_2BDS by passing it through a column containing cation exchange resin in the acid form. The cation exchange resin used throughout the experimental work was Dowex 50. Next, a portion of this acid was used to prepare CuBDS and Na_2BDS by reaction with $CuCO_3$ and NaOH respectively. The final salts (K_2BDS, CuBDS and Na_2BDS) were recrystallized twice from conductivity water and dried over $CaCl_2$ at room temperature.

The second method adopted was much less tedious. The crude H_2BDS was reacted with $Ba(OH)_2$ to remove the $SO_4^=$ impurity. The resulting BaBDS was recrystallized and then converted to the acid using a cation exchange resin.

1,3,6-Naphthalenetrisulfonic Acid and 1,3,6-Naphthalenetrisulfonate Salts

Sodium 1,3,6-naphthalenetrisulfonate (Na_3NTS) is available commercially (Aldrich Chemical Co., Milwaukee 10, Wisconsin) and, like the crude H_2BDS, contains $SO_4^=$ as its major impurity. In this case, the Na^+ salt was converted to the acid by ion exchange. The acid was then reacted with La_2O_3. The resulting LaNTS, with $La_2(SO_4)_3$ impurity, was recrystallized twice from hot water. The much lower solubility of $La_2(SO_4)_3$ (over LaNTS) and its retrograde temperature dependence allowed a good separation. This LaNTS was used, in part, to prepare the acid, Na^+ and K^+ salts by ion exchange. These salts were recrystallized from conductivity water and dried over $CaCl_2$ at room temperature.

Analyses of Acids and Salts

None of the purified $BDS^=$ and $NTS^{\equiv}$ salts and acids showed any traces of $SO_4^=$ when tested with $Ba(NO_3)_2$.

A check of the isomer purity of the m-benzenedisulfonate anion was made by converting a sample of the anhydrous K^+ salt to the sulfonyl chloride by use of PCl_5. The product obtained was recrystallized from petroleum ether. Since the para isomer has a sulfonyl chloride which is much less soluble than either the ortho or meta isomer, its presence could be noted during recrystallization. The product obtained was free of this para isomer. The melting point of the sulfonyl chloride was found to be 62°C; the literature value of the meta product is 63°C and that of the ortho is 132°C (19).

Analyses for total cation content in the salts were performed by quantitative conversion to the acids (H_2BDS and H_3NTS) by ion exchange technique and subsequent titrations of the acids with standard NaOH, using a Beckman GS pH meter. Both H_2BDS and H_3NTS are strong acids giving single endpoints. A check of the accuracy of the method, using analytical grade KCl, showed no systematic errors. The precision of the total cation measurements was ± 0.1 %.

To ensure that the total cation was Cu^{++} in CuBDS, K^{+} in K_2BDS, Mn^{++} in MnBDS, and La^{+++} in LaNTS, separate determinations of these ions were performed. Copper was determined by electrodeposition, while the K^{+} content of the K_2BDS salt was found by using the sodium tetraphenyl boron technique. The pyrophosphate method was employed in the Mn^{++} determination. Lanthanum was analyzed by precipitation as the oxalate and ignition to the oxide.

For all the salts but CuBDS, water of hydration was determined by the Karl Fischer method, using a Pt-W electrode pair and a potentiometer for endpoint detection (20). Because the Cu^{++} ion reacts with the Karl Fischer reagent, its water of hydration was determined by heating the hydrated salt to 140°C. The weight loss agreed with the reported (21) change from a six hydrate to a one hydrate.

Both acids were extremely difficult to obtain in a good weighing form by recrystallization; they were therefore, not analyzed from solid samples. In the actual conductance work, concentrated solutions were used to make up stock solutions which were then analyzed for acid strength.

The Na^+ and K^+ salts of $NTS^{\equiv}$ are hygroscopic and difficulty was again encountered in attempting any weighing of the solid forms. Therefore, as with the acid, the stock solutions used were analyzed: first by ion exchange to the acid, followed by titration with standard NaOH.

The copper, potassium, manganese and lanthanum analyses agreed with their respective total cation determinations within two parts per thousand. The precision of the Karl Fischer analyses was less than 2% in all cases. Total content was based on the fact that each salt or acid contained the proper anion ($BDS^=$ or $NTS^{\equiv}$). The error in total content ranged from as low as 0.2% to a maximum of 0.5% for each substance, the magnitude of the error being dependent on the precision of the Karl Fischer analysis for the particular substance.

Both the $MnSO_4$ and the $CuSO_4$ were Baker and Adamson reagent grade, recrystallized twice from conductivity water and dried at 110°C to their monohydrates.

The weighing forms of the salts (on which analyses were possible) were, upon drying over $CaCl_2$ at room temperature: $Na_2BDS \cdot 4H_2O$, $K_2BDS \cdot H_2O$, $CuBDS \cdot 6H_2O$, $MnBDS \cdot 3\text{-}1/2H_2O$, $LaNTS \cdot 5\text{-}1/2H_2O$.

Preparation of Solvents

Water

The conductivity water was prepared by redistilling distilled water from permanganate (block-tin condenser). This gave water with a specific conductance from 1.0 x 10^{-6} to 1.5 x 10^{-6} $ohm^{-1}cm^{-1}$. The water was then passed through a Barnstead Bantam demineralizing column which gave water with a final specific conductance of about 0.7 x 10^{-6} $ohm^{-1}cm^{-1}$ at 25°C.

Methanol

The starting methanol was Baker analyzed reagent whose main impurities are about 0.1% H_2O and lesser amounts of aldehydes and ketones. The test for aldehydes and ketones outlined by Hartley and Raikes (22) using $Hg(CN)_2$ in strong base, which is reportedly sensitive to 0.002% ketones and 0.004% aldehydes, was employed on the solvent. The test proved negative for the Baker reagent. The H_2O was eliminated by refluxing over Mg for an hour and fractionating, the center cut of about 60-70% being taken. At first, the methanol thus obtained was stored over molecular sieves. However, the conductance of the methanol was considerably higher than could be tolerated for a conductance solvent. When the methanol was not stored over molecular sieves, the measured conductance was suitable for a conductance solvent. Therefore, the purified methanol was not stored over molecular sieves. The physical properties of the purified solvent as compared with literature values were:

	Experimental	Literature (23)
Boiling Point	64.5 - 64.7°C at 743mm	64.7°C at 760mm
Density	0.7876 g/ml	0.7872 g/ml

Conductance Measurements

General Equipment

The bridge arrangement for the resistance measurements consisted of a General Radio 1301A variable frequency oscillator, a Leeds and Northrup Jones Bridge, a Fisher TR-1 battery-powered preamplifier and a DuMont 304H oscilloscope for null detection. A large (approximately 18 gallon) fish tank filled with transformer oil served as the constant temperature bath. The thermoregulator used was a differential range type made by the Precision Scientific Company. This thermoregulator was connected through a thyratron relay to a heating lamp outside the bath. Cooling was accomplished by several turns of copper wire through which tap water was run. By these means, the bath gave a constant temperature of 25.000 ± 0.005°C.

The bridge and bath were placed on a large copper sheet to obtain adequate grounding. The oscillator, bridge and preamplifier were set up as specified by Dike (24).

Cells

Two flask type cells were used for the conductance measurements, that is, erlenmeyer flasks with the electrodes contained in a side arm. The electrodes were made of smooth platinum and were so spaced to give cell constants of about 0.10 and 0.25 cm^{-1}. These two cells were calibrated with KCl solutions using the Fuoss equation for KCl (25):

$$\Lambda = 149.93 - 94.65\ c^{1/2} + 58.74\ c \log c + 198.4\ c$$

where c is the molar concentration of KCl. The cell constants were determined as functions of the measured specific conductance (26) and were:

$$\text{Cell 1:} \quad k = (0.26390 - 0.45\ L_m)\ cm^{-1}$$

$$\text{Cell 2:} \quad k = (0.08808 - 0.04\ L_m)\ cm^{-1}$$

where L_m is the measured specific conductance.

Preparation of Solutions

The solutions whose resistances were measured were made up in the conductance cell by a weight dilution method. Conductivity water was weighed into the cell and allowed to come to equilibrium (indicated by a constant resistance reading). Four to seven successive weighed amounts of stock solution were added, each time allowing the solution to equilibrate. The resistance was measured at 1000, 2000, 4000 and 10,000 cycles/sec, and a plot of resistance versus $\omega^{-1/2}$ (ω = frequency in cycles/sec) extrapolated to infinite frequency (27) gave the resistance at infinite frequency, R_∞.

The weight dilution method has the advantage that resistance measurements at several concentrations can be made in a relatively short period of time. Also, the correction for solvent conductance is for that specific batch of solvent on that day and not just the average correction for several batches. This is especially significant in the very dilute solutions where the solvent contributes a considerable part of the measured resistance.

Each stock solution was run in both cells at least once; at least two different stock solutions were used for each electrolyte-solvent system.

When possible, the stock solutions were made up by weight: when the solute had a definite weighing form or, in the case of the mixed solvent work, when the solute could be dried to not higher than a one hydrate. The latter corresponds to only about 0.001% change in the percentage of water in the solvent used, so that no correction would then be necessary for the percentage of water in the mixed solvent. Those materials (H_2BDS, H_3NTS, Na_3NTS and K_3NTS in water, and MnBDS in mixed solvent) whose stock solutions could not be made up by weight, were analyzed for concentration by titration with standard NaOH; the salt solutions were first converted to the acid by the ion exchange technique.

The density of each stock solution and each mixed solvent was measured in a pycnometer, giving results to $\pm 5 \times 10^{-5}$ g/ml at 25°C.

RESULTS

Treatment of Raw Data

The measured resistances and solution concentrations are treated to obtain sets of equivalent conductance, concentration ($\underline{\Lambda}$, $\underline{c}$) data.

In using the weight dilution technique, it is assumed that the volume of the solution is simply the sum of the volume of the solvent used and the volume of the stock solution added:

$$V_{\text{solution}} = V_{\text{solvent}} + V_{\text{stock solution}} \tag{1}$$

The concentration (in moles/l) of the stock solution is obtained: in the case of the salts with known weighing form, by use of molality and density; for the other, by titration of the acid form with standard NaOH. The weights of solvent and stock solution introduced into the conductance cell, along with their densities, readily give the volumes of these solutions. Thus, the concentration of the solution whose resistance is measured is calculated:

$$c_{\text{solution(moles/l)}} = \frac{c_{\text{stock(moles/l)}} \times V_{\text{stock(ml)}}}{V_{\text{solution(ml)}}} \, . \tag{2}$$

As successive weighed amounts of stock solution are added to the cell, the resistance of each of a series of solutions can be measured. It is evident then, that the weight dilution method greatly facilitates obtaining an entire set of resistances and concentrations.

As mentioned previously (see page 16), the resistances measured are extrapolated to give the resistance at infinite frequency, R_∞. Since the specific conductance L, is given by:

$$L = \frac{k_{cell}}{R_\infty} \tag{3}$$

where k_{cell} is the cell constant, a simple calculation converts the resistances of the solvent and the solution to their specific conductances. Then, the specific conductance of the solute is:

$$L_{solute} = L_{solution} - L_{solvent}. \tag{4}$$

The equivalent conductance of the solute is calculated from L_{solute} and the normality of the solution (N):

$$\Lambda_{solute} = \frac{1000\ L_{solute}}{N}. \tag{5}$$

When there are no other effects which could change the values of L or c, a set of Λ, c data is thus found. However, solutes containing one or more substances which hydrolyze, force a reconsideration of L_{solute} and $c_{solution}$. The Λ, c data needed must apply to the solute existing as such, that is, exclusive of any hydrolysis products.

Comparison of the conductances of H_2BDS and H_3NTS with the Onsager-Fuoss extended law indicates these acids are completely dissociated in water. Therefore, for the

$BDS^{=}$ and $NTS^{\equiv}$ ions, hydrolysis need not be considered. But hydrolysis must be considered for the Cu^{++}, Mn^{++}, La^{+++} and $SO_4^{=}$ ions, and the CO_2 absorbed from the air.

The Cu^{++}, Mn^{++} and La^{+++} hydrolysis constants were obtained by measuring the pH of solutions of their salts (CuBDS, MnBDS, LaNTS). The solutions on which pH measurements were made, corresponded to the solutions used in resistance measurements, that is, a series of solutions of a given salt were made up by the weight dilution method and the pH of each solution was read with a Beckman GS pH meter.

The $[H^+]$ of the solvent is assumed to be due entirely to the CO_2-H_2O equilibrium. Since the amount of stock solution used in all cases is small (dilute solutions), no $[H^+]$ contribution from a CO_2-H_2O equilibrium is designated to the stock solution. It is also assumed that the CO_2 content of the solvent does not change during the addition of the solute. This last assumption was checked by following the conductance of the solvent for a day while periodically opening the cell cap. The change in conductance was negligible.

The hydrolysis constants thus found ($Cu^{++} = 1.5 \times 10^{-8}$, $Mn^{++} = 2.5 \times 10^{-11}$, $La^{+++} = 1.2 \times 10^{-9}$) were in good agreement with the literature (28,29,30). The hydrolysis constant used for $SO_4^{=}$ was 8.3×10^{-11} (31) and the dissociation constant used for H_2CO_3 was 4.3×10^{-7} (32).

An outline of a typical calculation using CuBDS will indicate the method for correcting $\underline{c_{solution}}$ and $\underline{L_{solute}}$.

The concentration of the solution, given in equation (2) must be corrected for the moles of solute hydrolyzed, that is, the amount of $CuOH^+$ present must be subtracted. The interdependent equilibria involved in the dissociation of H_2CO_3 and the hydrolysis of Cu^{++}, along with the conditions:

$$[HCO_3^-] + [H_2CO_3] = \text{total hydrolyzed } CO_2 \qquad (6)$$

and $$[HCO_3^-] + [CuOH^+] = [H^+]_{solution} \qquad (7)$$

must be simultaneously satisfied in the determination of the amount of $CuOH^+$ present. The technique of obtaining this correction was to pick values for $[H^+]_{solution}$ to be used in the dissociation expression for H_2CO_3 and the hydrolysis expression for Cu^{++} until the final conditions, given by equations (6) and (7) were satisfied. This is a very tedious, but valid process of calculation which not only gives $[CuOH^+]$ needed for correction to $\underline{c_{solution}}$, but also $[H^+]$ and $[HCO_3^-]$ needed for the corrections to $\underline{L_{solute}}$.

The specific conductances of the ions H^+ and HCO_3^- and whatever residual species are present, make up the measured $\underline{L_{solvent}}$:

$$L_{solvent} = L_{H^+} + L_{HCO_3^-} + L_{residual} \qquad (8)$$

where $\underline{L_{residual}}$ is the specific conductance of any impurities other than CO_2 in the solvent, plus the specific conductance of the solvent itself.

But when solute is added to the solvent, the specific conductances of the $CuOH^+$ present and an amount of $BDS^=$ equal to the amount of Cu^{++} ions removed by hydrolysis, as well as the specific conductances of $L_{residual}$ and of the changed concentrations of HCO_3^- and H^+ (as found in the $c_{solution}$ correction), now totally constitute the specific conductances to be accounted for in calculating L_{solute}. Equation (4) now must be changed to read:

$$L_{solute} = L_{solution} - L_s \tag{9}$$

where

$$L_s = L_{H^+} + L_{HCO_3^-} + L_{residual} + L_{CuOH^+} + L_{BDS^=}. \tag{10}$$

The evaluation of L_s involves the calculations of L for each ion and $L_{residual}$. For each of the ions:

$$L_{ion} = \frac{\lambda\ N_{ion}}{1000}$$

or, since the corrections are so small:

$$L_{ion} \approx \frac{\lambda^o\ N_{ion}}{1000} \tag{11}$$

where λ is the equivalent ionic conductance and λ^o is the limiting equivalent ionic conductance.

To obtain $L_{residual}$, the resistance of the solvent is measured and $L_{solvent}$ calculated. The $[H^+]$ in the solvent is determined by pH measurements before each run. Since the $[H^+]$ is assumed to be due solely to the CO_2-H_2O equilibrium, $[H^+] = [HCO_3^-]$, and $L_{H_2CO_3}$ can be found:

$$L_{H_2CO_3} = L_{H^+} + L_{HCO_3^-}$$

$$L_{H_2CO_3} = \frac{\lambda^o_{H^+}[H^+] + \lambda^o_{HCO_3^-}[HCO_3^-]}{1000}$$

$$L_{H_2CO_3} = \frac{(\lambda^o_{H^+} + \lambda^o_{HCO_3^-})\ [H^+]}{1000}$$

$$L_{H_2CO_3} = \frac{\Lambda^o_{H_2CO_3}\ [H^+]}{1000} \qquad (12)$$

Rearranging equation (8):

$$L_{residual} = L_{solvent} - L_{H_2CO_3} \qquad (13)$$

and the value for $\underline{L_{residual}}$ is obtained.

Thus, having the corrected $\underline{L_{solute}}$ and the corrected $\underline{c_{solution}}$, the equivalent conductance of the solute may now be calculated. One finally obtains a set of $\underline{\Lambda}$, $\underline{c}$ data for the CuBDS present as such, exclusive of hydrolysis products.

The corrections for hydrolysis, although tedious, were indeed necessary: for CuBDS, the correction to $\underline{\Lambda}$ ranged from 0.8% at 10^{-4} $\underline{M}$ to 0.2% at 5×10^{-3} $\underline{M}$, and for LaNTS, from 0.1% at 5×10^{-5} $\underline{M}$ to 0.06% at 2×10^{-3} $\underline{M}$. Although the corrections for LaNTS are near the limit of the over-all precision of the $\underline{\Lambda}$ results for this substance (0.1%), the corrections were made. However, the $SO_4^=$ and Mn^{++} hydrolysis corrections to $\underline{\Lambda}$ are <0.03% at the lowest concentrations. This is well below the over-all reproducibility of the measurements on these substances, and therefore no hydrolysis corrections were warranted for these ions. For H_2BDS and H_3NTS, no solvent corrections were made since the major conducting species in the solvent are from the dissociation of H_2CO_3; this dissociation is suppressed by the addition of strong acid.

It may be noted here that in all solutions, whether hydrolysis corrections were applied or not, data for which $\underline{L_s} > 3\% \ \underline{L_{solution}}$ were dropped for all calculations. This is a rather arbitrary cut-off point, but those solutions in which $\underline{L_s} > 3\% \ \underline{L_{solution}}$ were also the least concentrated solutions, the precision of whose $\underline{\Lambda}$ data is quite poor.

Tables showing the sets of $\underline{\Lambda}$, $\underline{c}$ data for H_2BDS and the $BDS^=$ salts (Table I), H_3NTS and the $NTS^{\equiv}$ salts (Table II), $MnSO_4$ and $CuSO_4$ (Table III) in water are now presented, followed by the mixed solvent $\underline{\Lambda}$, $\underline{c}$ data for MnBDS (Table IV) and $MnSO_4$ (Table V).

TABLE I

Equivalent Conductance, Concentration Data

m-Benzenedisulfonic Acid and m-Benzenedisulfonate Salts in Water

H_2BDS

10^4c (moles/liter)	Λ
0.746	408.5
2.438	405.6
5.372	402.1
12.007	397.7
18.576	394.8
25.890	392.1
37.558	388.6

Na_2BDS		K_2BDS	
10^4c (moles/liter)	Λ	10^4c (moles/liter)	Λ
1.3672	106.90	0.7512	131.33
3.6213	105.25	1.5726	130.25
5.4140	104.27	2.4585	129.53
7.2115	103.27	4.3921	128.12
10.304	102.52	8.2340	126.32
14.455	101.36	12.881	124.68
18.072	100.39	20.344	122.69
23.788	99.36	31.483	120.54
32.127	98.03	46.236	118.39
46.720	96.10	59.180	116.68

TABLE I
(continued)

CuBDS		MnBDS	
$10^4 c$ (moles/liter)	Λ	$10^4 c$ (moles/liter)	Λ
0.9035	109.57	1.6202	107.02
1.4132	108.73	3.0881	104.39
1.8535	107.74	4.5834	102.71
4.6921	103.40	7.2762	100.12
5.6935	102.05	8.7987	99.03
7.2820	100.61	15.667	95.04
13.158	97.15	17.335	94.35
17.489	95.63	30.710	89.82
21.650	92.99	50.255[a]	85.66
26.781	91.80		
31.177	90.31		
43.553[a]	87.75		
54.560[a]	85.89		
66.830[a]	84.09		

[a] For completeness of data, these points are included. However, the validity of applying theoretical calculations to them is questionable since, at these concentrations, $\kappa \mathring{a} > 0.2$ (see Appendix I).

TABLE II

Equivalent Conductance, Concentration Data

1,3,6-Naphthalenetrisulfonic Acid and 1,3,6-Naphthalenetrisulfonate Salts in Water

H_3NTS		LaNTS	
10^4c (moles/liter)	Λ	10^4c (moles/liter)	Λ
0.928	413.6	0.5202	118.39
4.263	405.8	1.0450	109.70
5.283	403.6	1.8211	101.23
9.151	398.9	3.5221	90.65
10.528	397.1	5.0143	84.90
17.069	392.0	6.7760	80.30
24.722[a]	386.8	10.453	73.61
28.064[a]	385.4	14.037[a]	69.65
		21.088[a]	64.40
		32.455[a]	59.65

[a] For completeness of data, these points are included. However, the validity of applying theoretical calculations to them is questionable since, at these concentrations, $\kappa^{0}a>0.2$ (see Appendix I).

TABLE II
(continued)

Na_3NTS		K_3NTS	
10^4c (moles/liter)	Λ	10^4c (moles/liter)	Λ
1.0199	116.63	1.0574	139.96
1.7592	115.38	5.2771	134.39
4.4823	112.13	9.4206	131.27
5.8743	110.97	15.021	128.19
9.4072	108.54	24.905[a]	124.36
11.449	107.45	34.682[a]	121.63
18.365	104.51	40.437[a]	120.36
23.983[a]	102.69		
27.905[a]	101.53		
31.847[a]	100.62		

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[a] For completeness of data, these points are included. However, the validity of applying theoretical calculations to them is questionable since, at these concentrations, $\kappa\mathring{a}>0.2$ (see Appendix I).

TABLE III

Equivalent Conductance, Concentration Data

Copper Sulfate and Manganese Sulfate in Water

$CuSO_4$		$MnSO_4$	
10^4c (moles/liter)	Λ	10^4c (moles/liter)	Λ
4.0000[a]	117.52	2.0134	122.84
9.0000[a]	108.55	2.6134	121.39
16.000[a]	100.74	3.2881	119.89
25.000[a]	94.07	3.9939	118.01
36.000[a,b]	88.35	5.0626	115.98
1.7554	123.73	7.6176	111.81
2.5373	119.43	8.9728	109.94
4.8951	115.59	13.945	104.54
12.618	103.84	19.570	100.00
22.449	95.65	23.732	97.14
28.273	92.70	28.230	94.56
		31.411	93.02

[a] Values from Owen and Gurry (10).

[b] For completeness of data, these points are included. However, the validity of applying theoretical calculations to them is questionable since, at these concentrations, $\kappa \mathring{a} > 0.2$ (see Appendix I).

TABLE IV

Equivalent Conductance, Concentration Data

Manganese m-Benzenedisulfonate in Methanol-Water

100% Methanol (weight %)		80% Methanol (weight %)	
10^4c (moles/liter)	Λ	10^4c (moles/liter)	Λ
2.4312	27.89	1.8569	56.49
7.3039	19.95	2.4658	53.89
9.1328	18.36	3.1599	51.55
13.162	16.09	4.9331	47.21
17.249[a]	14.62	7.8202	42.63
23.867[a]	13.08	15.397	36.33
		19.477[a]	34.30
		22.646[a]	33.03

60% Methanol (weight %)		40% Methanol (weight %)	
10^4c (moles/liter)	Λ	10^4c (moles/liter)	Λ
1.4611	55.78	1.6284	55.73
5.4190	48.27	5.9389	51.04
7.4454	46.95	13.119	47.07
12.403	42.74	17.769	45.39
18.031	40.15	22.640	44.00
23.729[a]	38.27	27.530[a]	42.88
28.084[a]	37.13	32.809[a]	41.87
		39.418[a]	40.80

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[a] For completeness of data, these points are included. However, the validity of applying theoretical calculations to them is questionable since, at these concentrations, $\kappa \mathring{a} > 0.2$ (see Appendix I).

TABLE IV
(continued)

30% Methanol
(weight %)

$10^4 c$ (moles/liter)	Λ
2.0449	58.48
5.0302	55.71
9.1027	53.14
14.352	50.89
18.989	49.40
24.685[a]	47.95

20% Methanol (weight %)		10% Methanol (weight %)	
$10^4 c$ (moles/liter)	Λ	$10^4 c$ (moles/liter)	Λ
1.2249	67.96	1.7387	82.85
2.9912	65.58	4.5360	79.45
6.7493	62.52	10.182	75.51
10.498	60.53	16.903	72.55
14.879	58.75	21.694	70.94
20.221	57.04	25.843[a]	69.81
24.799[a]	55.91	29.480[a]	68.89

[a] For completeness of data, these points are included. However, the validity of applying theoretical calculations to them is questionable since, at these concentrations, $\kappa\mathring{a}>0.2$ (see Appendix I).

TABLE V

Equivalent Conductance, Concentration Data

Manganese Sulfate in Methanol-Water

40% Methanol (weight %)		30% Methanol (weight %)	
10^4c (moles/liter)	Λ	10^4c (moles/liter)	Λ
2.2748	52.11	0.9595	66.96
4.5601	45.72	2.6435	60.47
6.6662	42.00	6.1582	53.04
8.7040	39.38	9.9216	48.32
10.716	37.32	12.869	45.69
		16.531	43.15

20% Methanol (weight %)		10% Methanol (weight %)	
10^4c (moles/liter)	Λ	10^4c (moles/liter)	Λ
2.0589	75.45	1.3726	97.22
5.8421	67.25	5.0088	88.44
11.814	60.13	10.598	80.81
17.857	55.58	17.950	74.56
23.318	52.60	24.324	70.73
28.154[a]	50.48	29.461[a]	68.24

[a] For completeness of data, these points are included. However, the validity of applying theoretical calculations to them is questionable since, at these concentrations, $\kappa \mathring{a}>0.2$ (see Appendix I).

Application of Data to Theory

Conductance in Water

The phoreogram (Λ vs $c^{1/2}$ plot) of H_2BDS is compared to that of H_2SO_4 in Figure 1; Na_2BDS, K_2BDS and Na_2SO_4 are similarly compared in Figure 2. The Λ, c data for Na_2SO_4 are those quoted by MacInnes (33) from the unpublished work of Shedlovsky and Longsworth. The old criterion for an unassociated electrolyte (34) is that its equivalent conductance data approach the limiting law tangent from above. H_2BDS, Na_2BDS and K_2BDS all exhibit this behavior, indicating essentially no association. Because of this fact, the H_2BDS, Na_2BDS and K_2BDS data were fitted to the extended equation for unassociated electrolytes. Since

$$\Lambda = \Lambda^{o} - S\,c^{1/2} + E\,c\,\log c + J\,c \qquad (14)$$

for an unassociated electrolyte, and

$$\Lambda' \equiv \Lambda + S\,c - E\,c\,\log c, \qquad (15)$$

then

$$\Lambda' = \Lambda^{o} + J\,c\ . \qquad (16)$$

Using the proper values for S and E (see Appendix III), Λ' is easily calculated. If the data fit the extended theory for unassociated electrolytes, a plot of Λ' vs c (called the Fuoss plot) should give a straight line where Λ^{o} is the intercept and J the slope. In actual practise, since S and E are dependent on Λ^{o}, a Λ^{o} from the phoreogram is chosen

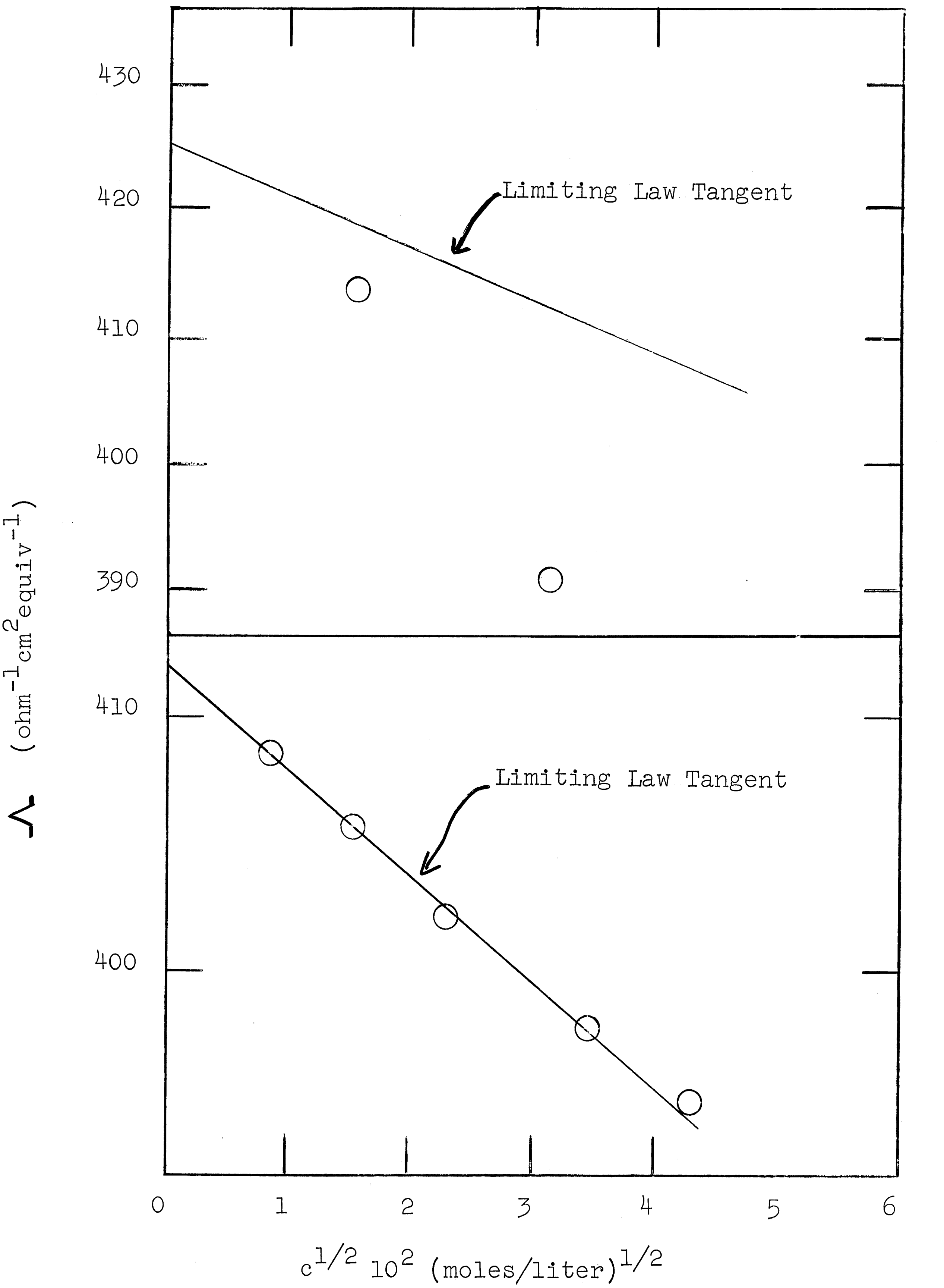

Fig. 1--Phoreograms of m-Benzenedisulfonic Acid (bottom) and Sulfuric Acid (top).

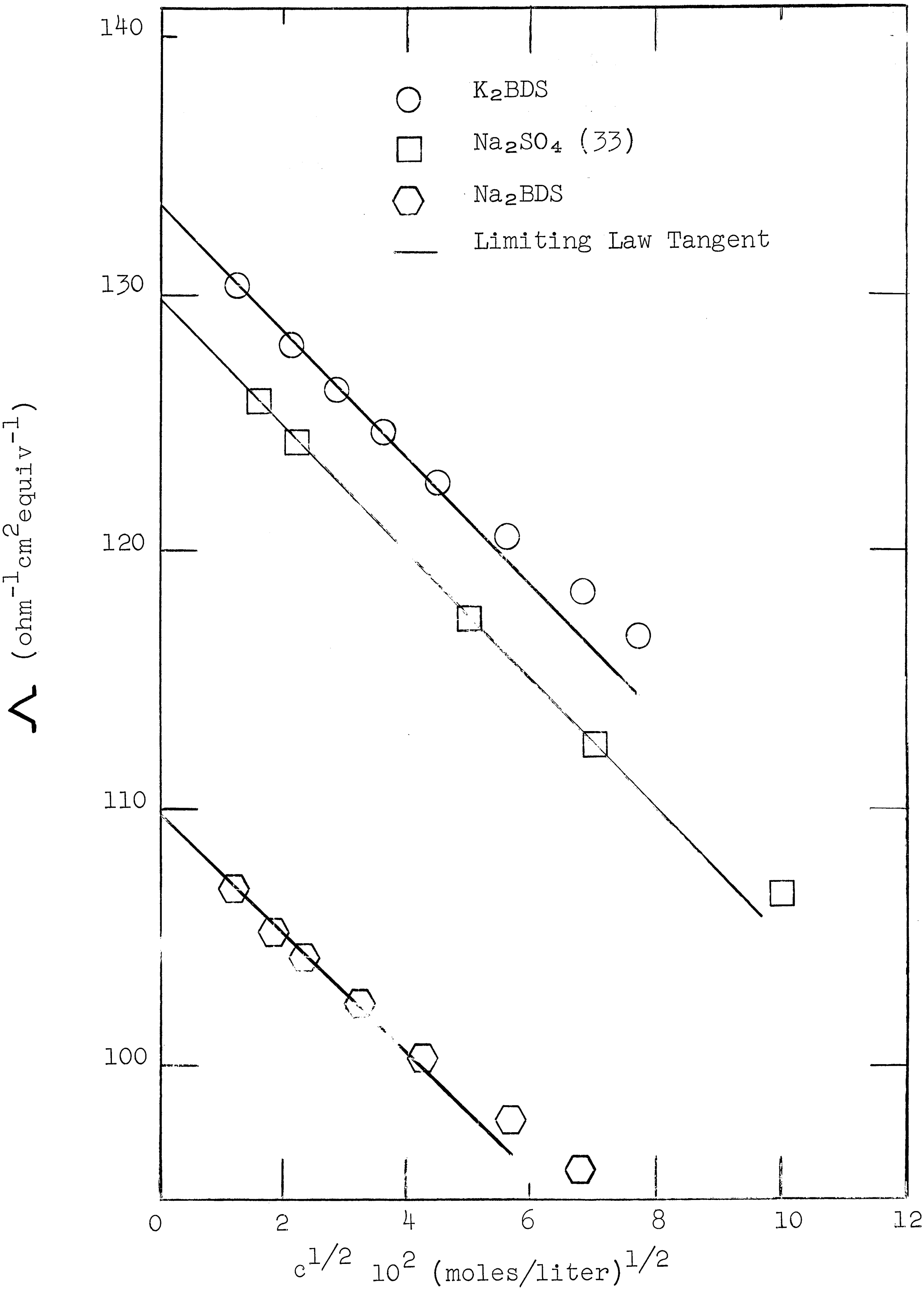

Fig. 2.--Phoreograms of Sodium m-Benzenedisulfonate, Potassium m-Benzenedisulfonate and Sodium Sulfate.

and the Fuoss plot is made. If the Λ^{o} obtained from this plot is different from that first chosen, this new Λ^{o} can be used to recalculate S and E and obtain new values. This process is repeated until Λ^{o} becomes consistent.

Figure 3 shows the final Fuoss plots for Na_2BDS and K_2BDS. Deviations from linearity only occur at the highest concentrations. The slight downward curvature occurring at these concentrations could be due to any or all of several reasons: (1) a small amount of association, (2) non-inclusion of an extra viscosity correction due to large ions, (3) a general breakdown of the theory at these concentrations for unsymmetrical electrolytes (35).

Despite the curvature at high concentrations however, this plot affords a very fine method of extrapolation for Λ^{o}. Since the reason for making the conductance measurements on Na_2BDS and K_2BDS is primarily to obtain a value for Λ^{o}, the Fuoss plot is of great importance.

The phoreograms of CuBDS and $CuSO_4$ are shown in Figure 4 and their Fuoss plots in Figure 5. The $CuSO_4$ data were checked against the data of Owen and Gurry (10) for this salt, since they include hydrolysis corrections in their work. The excellent agreement can be seen in Figure 4. The figure also shows that the CuBDS data definitely approach the salt's limiting tangent from above in marked contrast to the behavior of $CuSO_4$. However, although the CuBDS curve approaches its limiting tangent from above, it then crosses the tangent and approaches Λ^{o} from below the tangent.

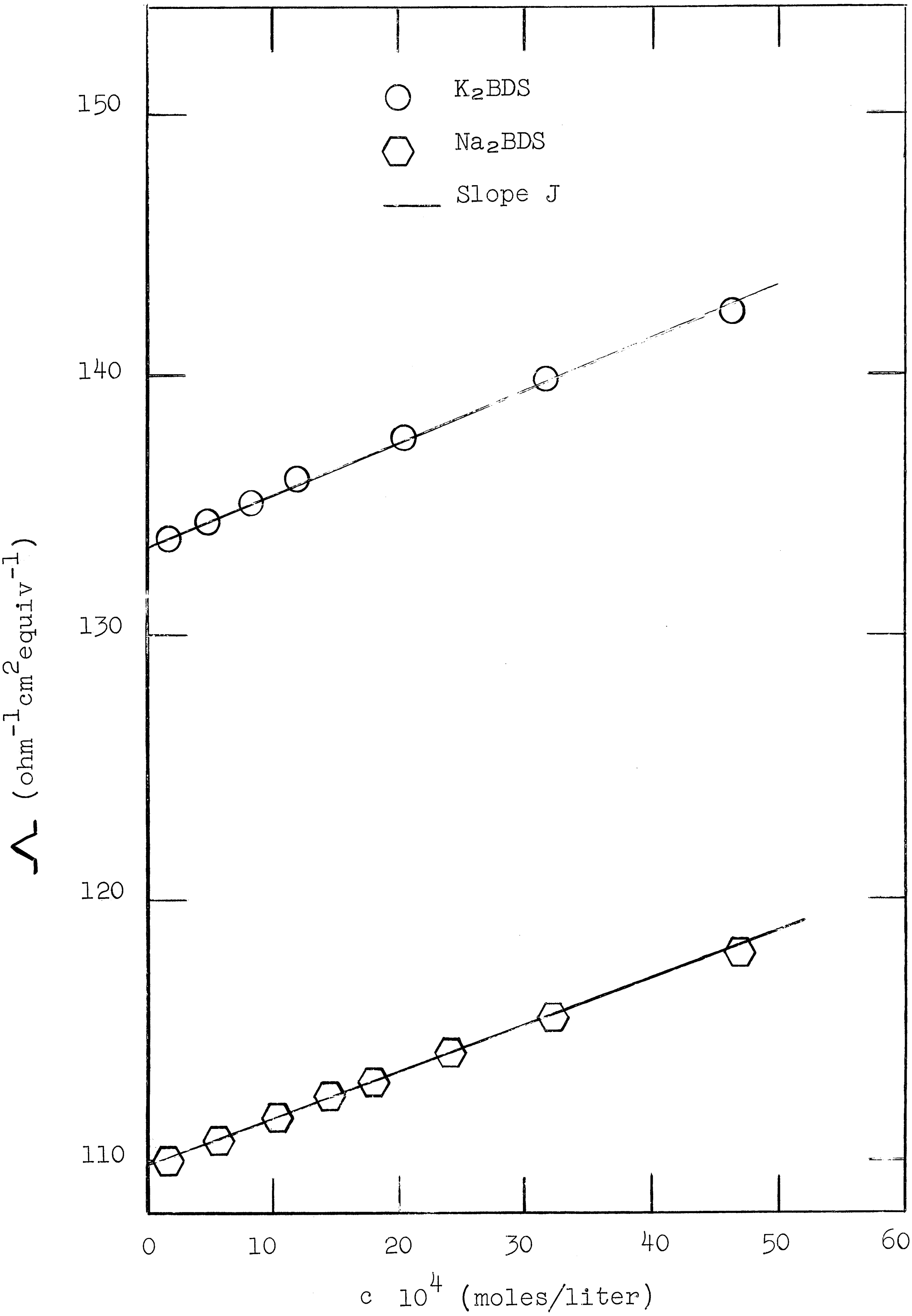

Fig. 3--Fuoss Plots of Sodium m-Benzenedisulfonate and Potassium m-Benzenedisulfonate.

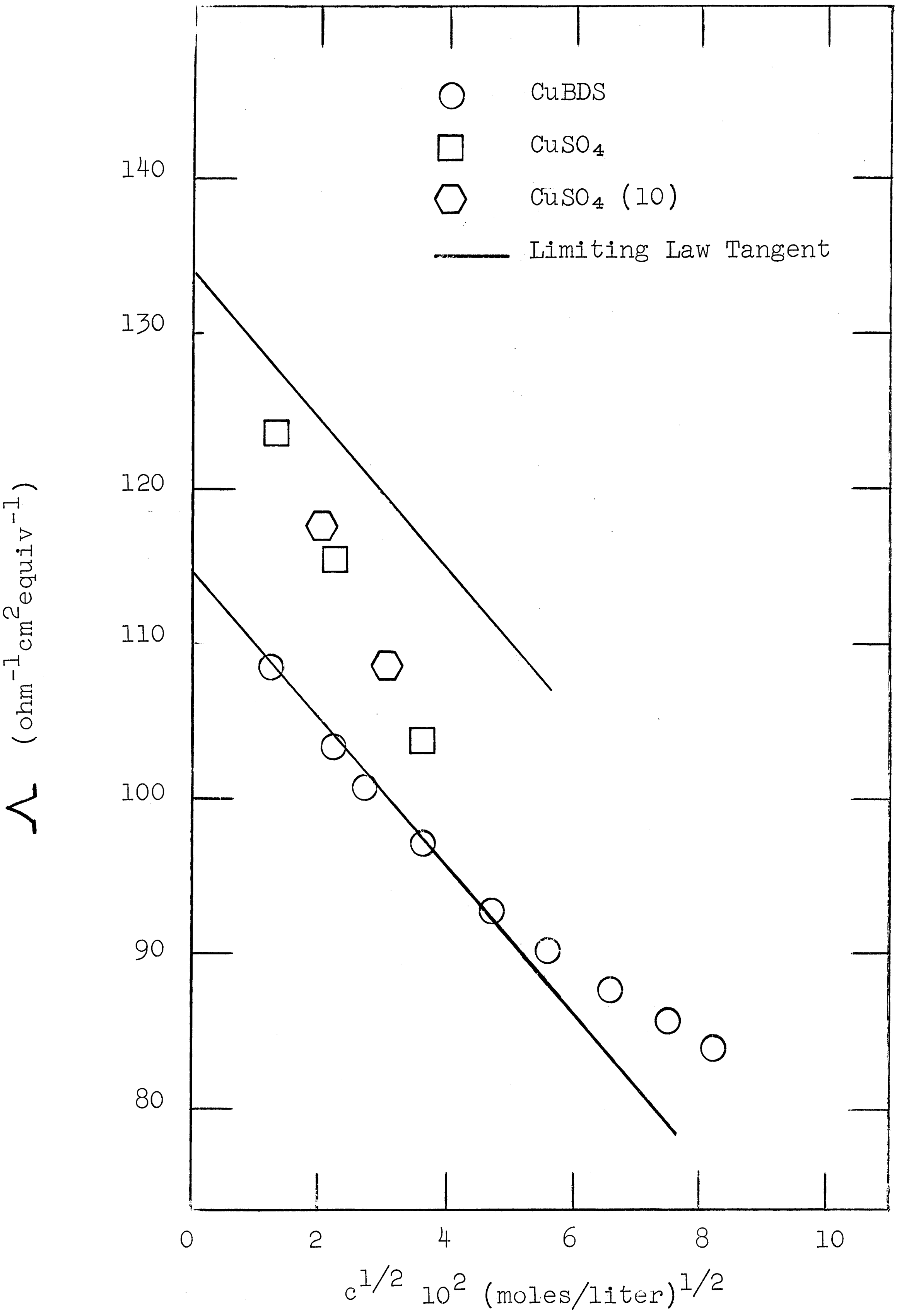

Fig. 4--Phoreograms of Copper m-Benzenedisulfonate and Copper Sulfate.

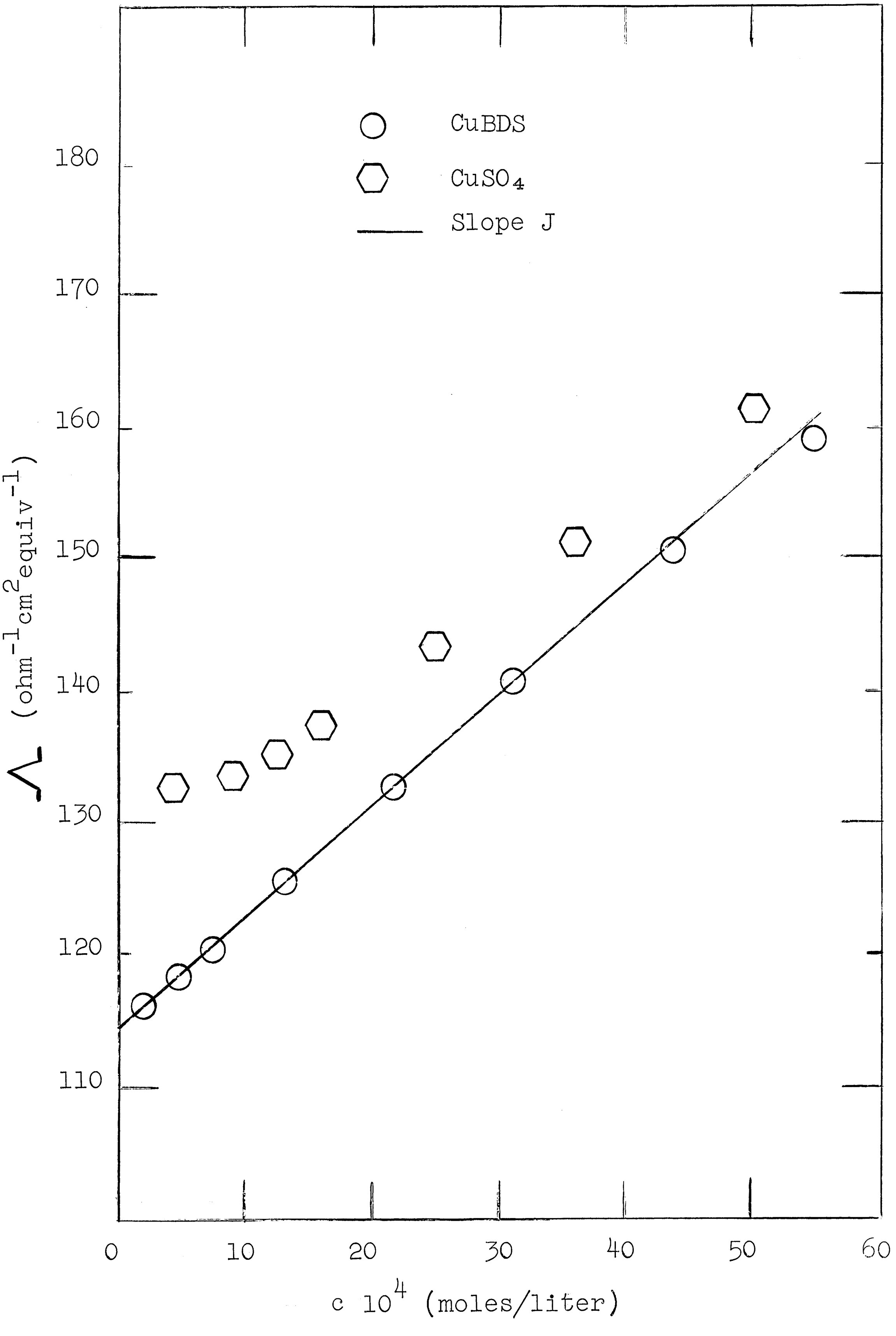

Fig. 5--Fuoss Plots of Copper m-Benzenedisulfonate and Copper Sulfate.

This raises some question concerning association or specific effects, or both. Nonetheless, the Fuoss plot (Figure 5) of CuBDS is a straight line, indicating it may be an unassociated electrolyte. Again, as with the Na^+ and K^+ salts, deviation from linearity occurs only at the highest concentrations.

Further examination shows that the seemingly odd behavior exhibited in the phoreogram (Figure 4) is simply a result of the $\underline{E}$ and $\underline{J}$ terms of the extended equation. Over the valid range of concentrations (see Appendix I), the term $\underline{E\ c\ \log c}$ is always negative, and the $\underline{J\ c}$ term positive. As opposed to the case of the 1:1 electrolyte, the higher charge types have $\underline{E}$ and $\underline{J}$ terms which are extremely large and therefore, these terms in the extended equation become the determining factors in the shape of the curve even at very low concentrations. For these high valence type salts, $\underline{E\ c\ \log c}$ is more important at low concentrations and $\underline{J\ c}$ at higher concentrations. The extended theory thus predicts that the phoreogram of an unassociated 2:2 salt should cross the limiting law tangent just as the phoreogram of CuBDS does.

It is interesting to consider this behavior in more detail. The limiting law and the extended law have two points in common: $\underline{c = 0}$ and $\underline{c = c_x}$ (c_x is the crossover point). At the crossover point,

$$\Lambda^{o} - S\, c_x^{1/2} = \Lambda^{o} - S\, c_x^{1/2} + E\, c_x \log c_x + J\, c_x \qquad (17)$$

(limiting law) (extended law)

and thus <u>log c_x = - J/E</u>. The value of $\underline{c_x}$ is therefore characteristic of a given electrolyte. Between c = 0 and c = c_x,

$$\Delta\Lambda \equiv \Lambda_{\text{extended law}} - \Lambda_{\text{limiting law}} \qquad (18)$$

$$\Delta\Lambda = E\, c \log c + J\, c \qquad (19)$$

and $\underline{\Delta\Lambda}$ must have a maximum value, $\underline{\Delta\Lambda_{max}}$. This maximum value should occur at a concentration such that:

$$\log c_{max} = -(0.4343 + \frac{J}{E}) \qquad (20)$$

and at $\underline{c_{max}}$,

$$\Delta\Lambda_{max} = E\, c_{max} \log c_{max} + J\, c_{max}. \qquad (21)$$

Table VI gives the values of $\underline{c_x}$, $\underline{c_{max}}$ and $\underline{\Delta\Lambda_{max}}$ for KCl and CuBDS calculated from the above equations as compared to these values when taken from a large phoreogram. The KCl values are those of Fuoss and Onsager (15) who first noticed this consequence of the theory.

As seen, the $\underline{\Delta\Lambda_{max}}$ for the 1:1 electrolyte is so small as to be essentially not measurable, and $\underline{c_x}$ and $\underline{c_{max}}$ are almost at the lower limit of the experimental concentration range. However, this behavior is quite sensitive to charge type and, due to the large size of the <u>E</u> and <u>J</u> terms

TABLE VI

The Crossover Parameters

Salt	$10^4 c_x$		$10^4 c_{max}$		$\Delta\Lambda_{max}$	
	Calc.	Plot	Calc.	Plot	Calc.	Plot
KCl	1.8	-	0.7	-	0.002	-
CuBDS	26.1	25.5	9.6	10.1	1.3	1.5

for a 2:2 electrolyte, a detectable $\Delta\Lambda_{max}$ is observed.

The agreement between the observed and calculated values of these quantities in the case of CuBDS is additional evidence that this may indeed be an unassociated 2:2 electrolyte. The Fuoss plot of $CuSO_4$ (Figure 5) in contrast to that of CuBDS, shows the behavior of an associated electrolyte when an attempt is made to fit its conductance data to the equations for an unassociated electrolyte. When treated as an associated electrolyte, the K_a obtained for $CuSO_4$ (see the following section for the method employed in calculating K_a) is 1.91×10^2. This is smaller than the value of 2.32×10^2 obtained by Owen and Gurry (10), who used the Shedlovsky method for determining K_a (36). This method forces the theoretical curve to approach the limiting law tangent from above by multiplying the $S c^{1/2}$ term of the limiting law equation by the factor Λ/Λ^o. The extended theory curve for an unassociated 2:2 electrolyte however, drops below the limiting law tangent and approaches Λ^o from below the tangent. Therefore, the difference between the data for an associated electrolyte and the extended theory curve is less than the difference between that data and the Shedlovsky curve. It is not surprising then, that the value of $\underline{K_a}$ for $CuSO_4$ obtained by using the extended theory is lower than the $\underline{K_a}$ obtained by Owen and Gurry.

Table VII gives a summary of parameters for H_2BDS, the $BDS^=$ salts and $CuSO_4$.

TABLE VII

Experimental Parameters

m-Benzenedisulfonic Acid, m-Benzenedisulfonate Salts and Copper Sulfate

Salt	Λ^o	λ^o_-	λ^o_+	$J \times 10^3$	$\overset{o}{a}$ ($\overset{o}{A}$)
H_2BDS	412.3	-	-	6.65	5.0
Na_2BDS	109.99	59.88	50.11[a]	1.775	4.5
K_2BDS	133.52	60.00	73.52[a]	1.975	4.1
CuBDS	114.55	59.94	54.6	8.35	5.0
$CuSO_4$	134.1	79.8[b]	54.3	10.51	5.7
$CuSO_4$	133.6[c]	79.8[c]	53.8[c]	-	-

[a] Values from Harned and Owen (37)

[b] Values from MacInnes (38)

[c] Values from Owen and Gurry (10)

The $\underline{\lambda^o_-}$ of the $BDS^=$ ion is estimated from the $\underline{\Lambda^o}$ values of the Na^+ and K^+ salts using Kohlrausch's Law (39) and the $\underline{\lambda^o}$'s of the well characterized Na^+ and K^+ ions.

The value for λ°_{-} of $BDS^{=}$ thus found is used to estimate the λ°_{+} of Cu^{++}. The λ°_{+} of Cu^{++} obtained from the Λ° of $CuSO_4$ and the λ°_{-} of the $SO_4^{=}$ ion is 0.3 conductance units lower than that from the Λ° of CuBDS, compared to a difference of 0.8 units from the Λ° that Owen and Gurry obtained in treating $CuSO_4$ by the Shedlovsky method.

It is interesting that the order of values of $\overset{\circ}{a}$ for H_2BDS, Na_2BDS and K_2BDS agree qualitatively with the order of values of $\overset{\circ}{a}$ obtained for HCl, NaCl and KCl when their activity coefficient data are fitted to the extended forms of the Debye-Huckel theory. No comparison is available for the $\overset{\circ}{a}$ for the Cu^{++} salt, but it is at least reasonable as compared to the values of $\overset{\circ}{a}$ for the H^{+}, Na^{+} and K^{+} values. The reason for the higher $\overset{\circ}{a}$ value for $CuSO_4$ over CuBDS is not immediately apparent.

The successful fitting of the conductance data of CuBDS to the extended equation, with the result that it appears to be a completely unassociated salt, made most intriguing the possibility of discovering a strong 3:3 electrolyte.

The same pattern as was used in treating the $BDS^{=}$ salts was used on the $NTS^{\equiv}$ salts. The acid conductance was used to qualitatively show whether hydrolysis of the anion would be important; it proved not to be. The conductance data for H_3NTS are very close to the limiting law tangent and so the acid was treated with the extended equation for unassociated electrolytes. The Fuoss plots of Na_3NTS and

K_3NTS (Figure 6) show the same type of behavior as the corresponding $BDS^=$ salts, the plots being curved at higher concentrations.

Figure 7 shows the phoreogram of LaNTS. Although the limit of validity of the extended theory is, at best, about 1 x 10^{-3} M, it is seen that over a large range of concentrations, the conductance of LaNTS shows a behavior qualitatively similar to CuBDS. However, the Fuoss plot of LaNTS (Figure 8) looks more like that of $CuSO_4$ than CuBDS (Figure 5). Besides this, the slope is so large that it is even difficult to guess what Λ^o might be. The data of LaNTS were therefore fitted to the equation for associated electrolytes and the association constant obtained is 1.73 x 10^3.

Table VIII gives a summary of parameters for H_3NTS and the $NTS^{\equiv}$ salts.

TABLE VIII

Experimental Parameters

1,3,6-Naphthalenetrisulfonic Acid and 1,3,6-Naphthalenetrisulfonate Salts

Salt	Λ^o	λ^o_-	λ^o_+	Jx10^{-3}	$\mathring{a}$(Å)
H_3NTS	421.8	-	-	33.8	6.2
Na_3NTS	121.55	71.44	50.11[a]	9.85	6.2
K_3NTS	145.05	71.53	73.52[a]	11.95	6.4
LaNTS	137.5	71.5	69.1[b]	157.9	10.0

[a] Values from Harned and Owen (37)

[b] Values from Spedding and Atkinson (40)

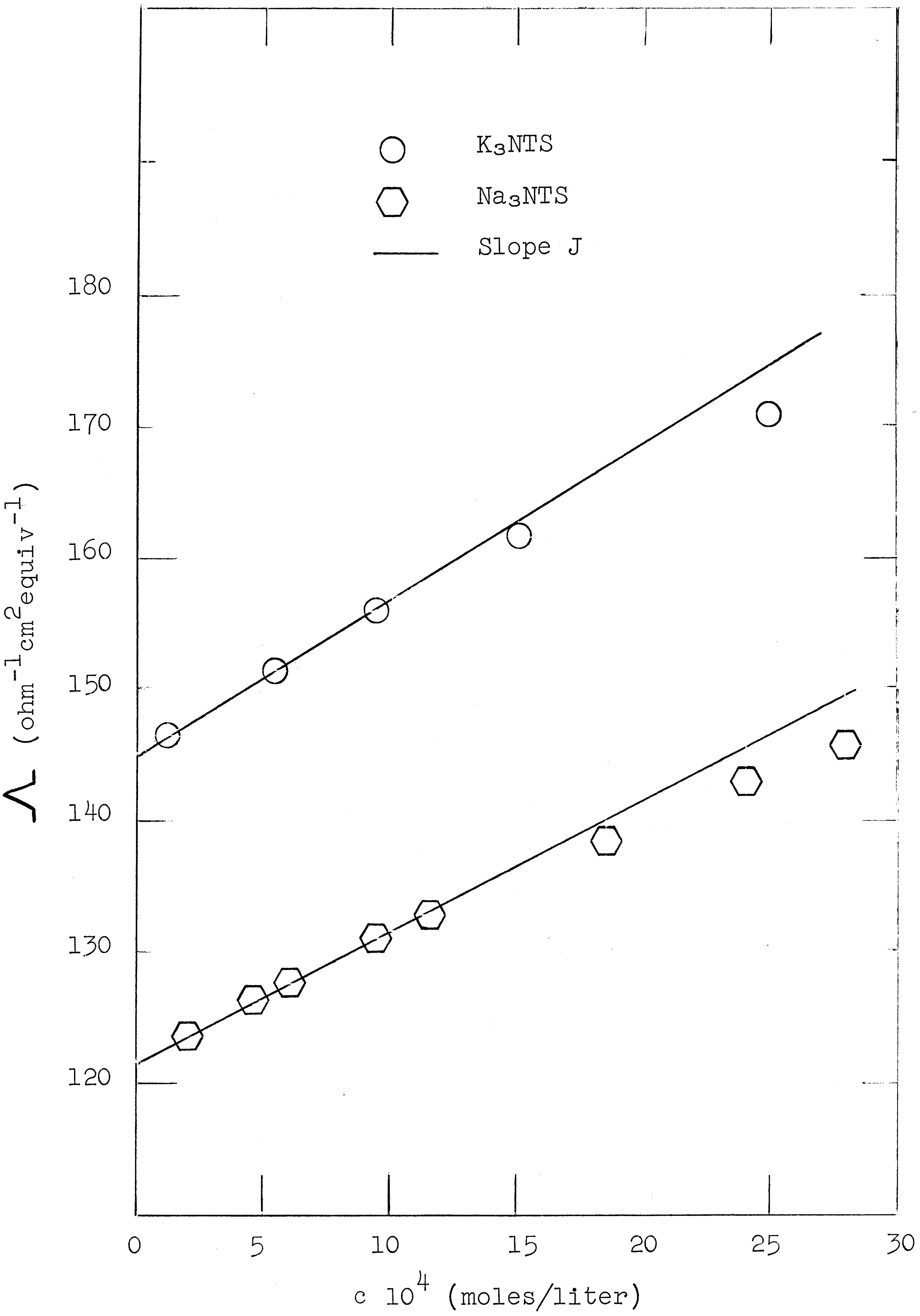

Fig. 6--Fuoss Plots of Sodium 1,3,6-Naphthalenetrisulfonate and Potassium 1,3,6-Naphthalenetrisulfonate.

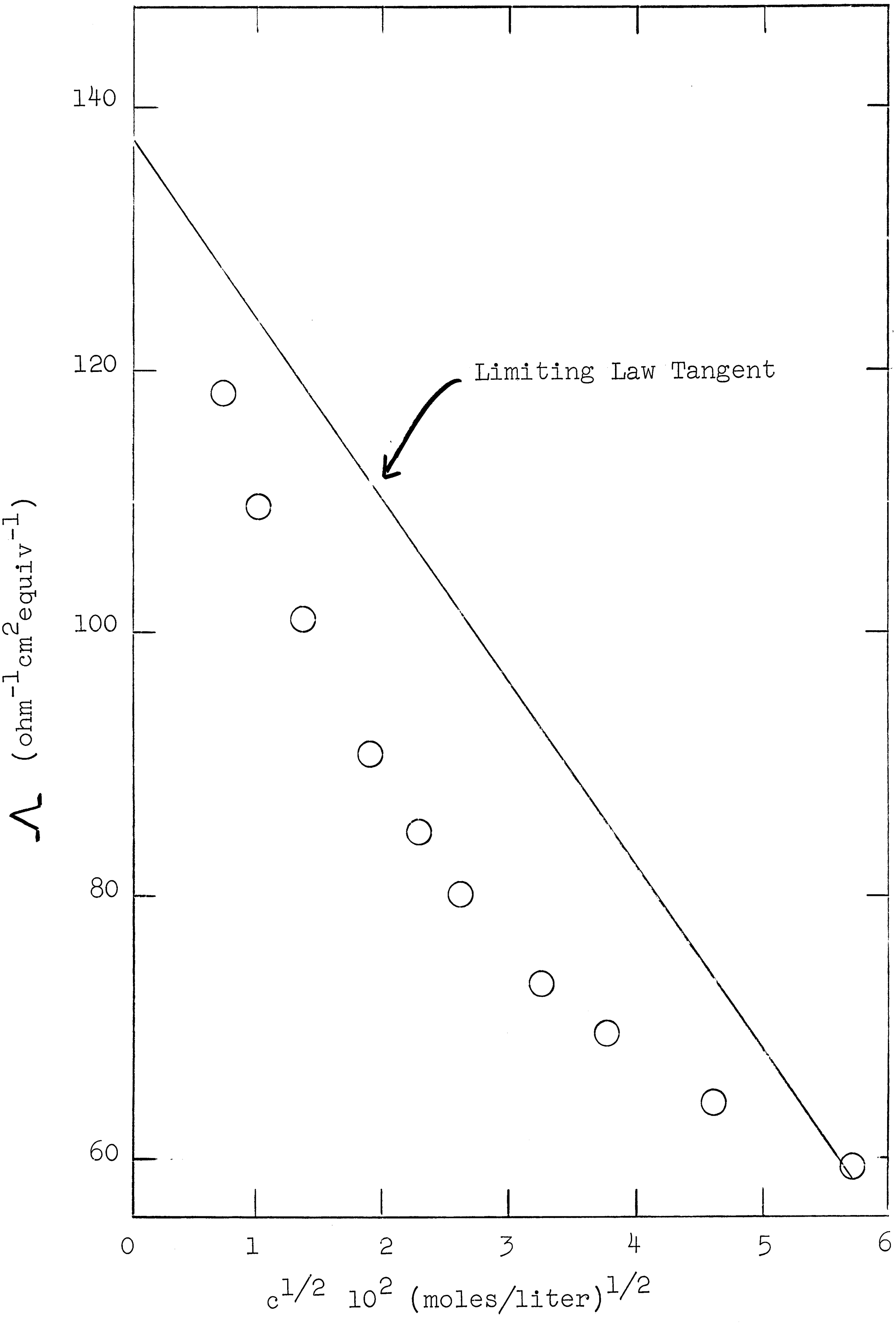

Fig. 7--Phoreogram of Lanthanum 1,3,6-Naphthalene-trisulfonate.

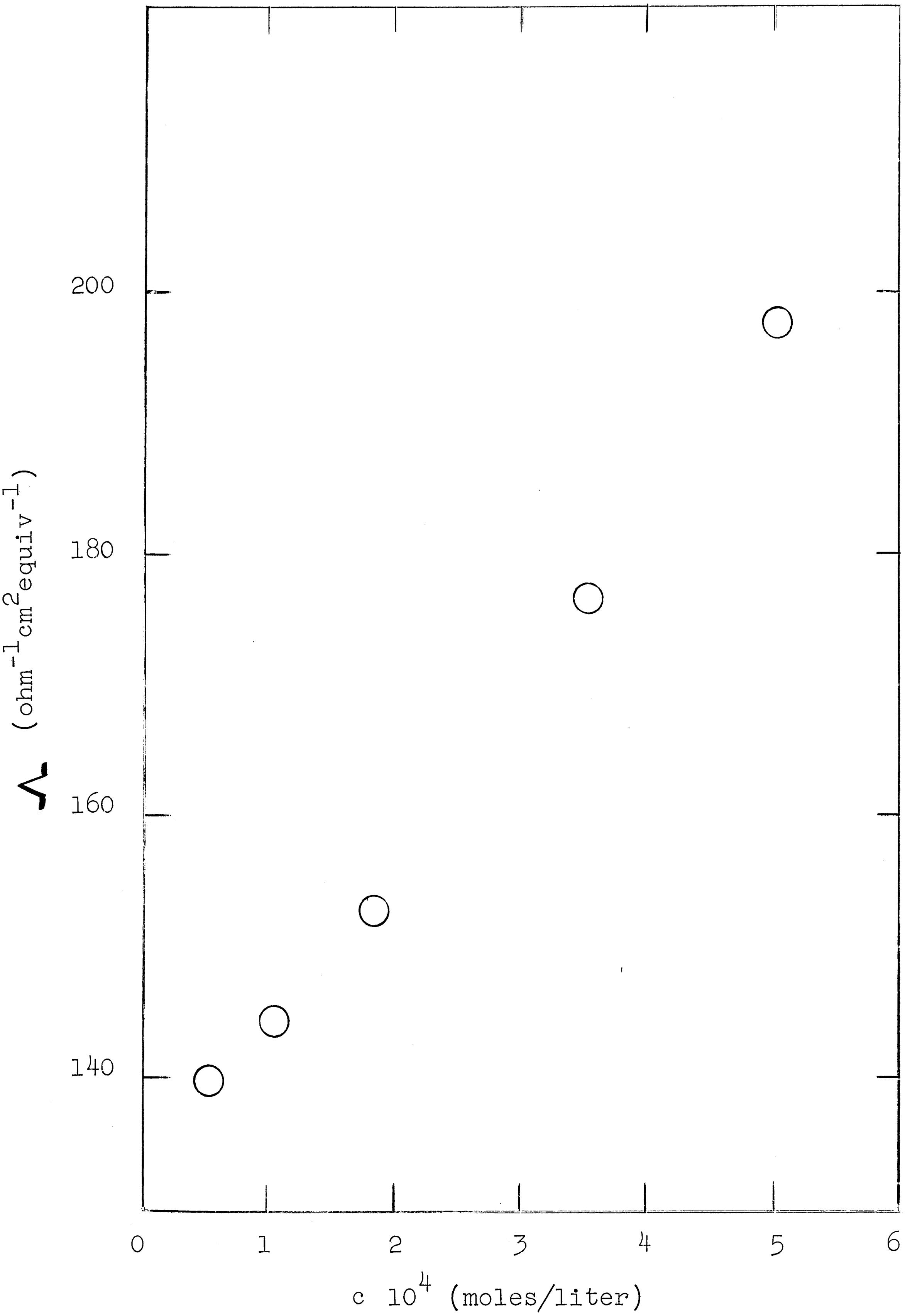

Fig. 8.--Fuoss Plot of Lanthanum 1,3,6-Naphthalenetrisulfonate.

As for the $BDS^=$ salts, the Na^+ and K^+ salts were used to find λ^o_- of the $NTS^{\equiv}$ ion. The Λ^o of LaNTS is not in good agreement with that expected from the limiting ionic conductances of the cation and anion. However, it was noted from the phoreogram of LaNTS that when the lower concentration points were included (that is, those points which were actually dropped from the calculations because $L_s > 3\%\ L_{solution}$), the curve then seemed to be approaching a higher Λ^o (about 140) value; this value would be in better agreement. Nonetheless, the disagreement between the Λ^o obtained from the addition of λ^o_+ and λ^o_-, and the Λ^o obtained by treating the LaNTS data with the extended equation for associated electrolytes, may well be an indication that the extended theory cannot be applied to 3:3 electrolytes.

The $\overset{o}{a}$ values of H^+, Na^+, and K^+ for all practical purposes, are constant. But the $\overset{o}{a}$ obtained for LaNTS is considerably higher. This may again be an indication that the theory has been pushed beyond the limit of its validity.

Conductance in Mixed Solvents

Although the conductance data for CuBDS in water were successfully fitted to the equation for an unassociated electrolyte, caution still had to be exercised before suggesting that the conductance theory showed this electrolyte to be completely unassociated, or conversely that the electrolyte proved the validity of the theory.

For 1:1 electrolytes, the size of the J term varies between about 50 and 100; for 2:2 electrolytes, it becomes about 5000 to 10,000. Therefore, for 1:1 electrolytes which are associated to any appreciable extent, a Fuoss plot would easily indicate that the electrolyte could not be fitted to the equation for unassociated electrolytes. Similarly, for the 2:2 which is strongly associated, the Fuoss plot would not be linear. However, for a 2:2 electrolyte which might be only slightly associated, the size of the $\underline{J}$ term would obscure the small degree of association and the Fuoss plot would still be linear, except at the higher concentrations (35).

The data for CuBDS fit this last example almost exactly: the $\underline{J}$ term is large and suspicion is aroused since, at the highest concentrations used, curvature appears on the Fuoss plot. For a case such as this, conductance measurements in mixed solvents may serve as the experimental technique needed to check whether this kind of electrolyte is or is not associated to some degree in water. At the same time, such measurements would indicate whether the theory handles the transition to associated electrolytes smoothly.

By changing the solvent mixtures, varying degrees of association are forced and association constants may be obtained by applying the $\underline{\Lambda}$, $\underline{c}$ data to the equation for associated electrolytes. If a smooth extrapolation of these constants back to pure water can be performed, then some significant information is obtained. Depending on the reliability of the extrapolation, an electrolyte, if it is indeed unassociated in water, would yield an extrapolated $\underline{K_a}$ of zero or very close to zero.

Because of the tedious hydrolysis corrections required in arriving at the sets of $\underline{\Lambda}$, $\underline{c}$ data when CuBDS was used, it was decided that the mixed solvent conductance work would be performed on MnBDS; the Mn^{++} ion requires no hydrolysis correction.

In water, MnBDS shows the same type of behavior as CuBDS. The phoreogram of MnBDS as compared to that of $MnSO_4$ is shown in Figure 9. As with CuBDS, the data for MnBDS approaches the limiting law tangent from above, then crosses the tangent and approaches $\underline{\Lambda^o}$ from below the tangent. The Fuoss plot for MnBDS (Figure 10) shows a straight line except at the highest concentrations used. Thus, the same conclusions can be drawn for MnBDS as for CuBDS: the conductance data in water can be successfully fitted to the equation for an unassociated electrolyte, but the slight curvature at the high concentrations indicates the need for mixed solvent techniques in an attempt to determine whether any small degree of association is taking place.

To test both the consistency of the treatment of 2:2 electrolytes and the method of extrapolation, the conductance of an electrolyte known to be associated in water was also measured in the mixed solvents. For this work, $MnSO_4$ was chosen; again, no hydrolysis corrections are needed for this salt. If the extrapolation technique is valid (and the theory applies to mixed solvents), the extrapolated $\underline{K_a}$

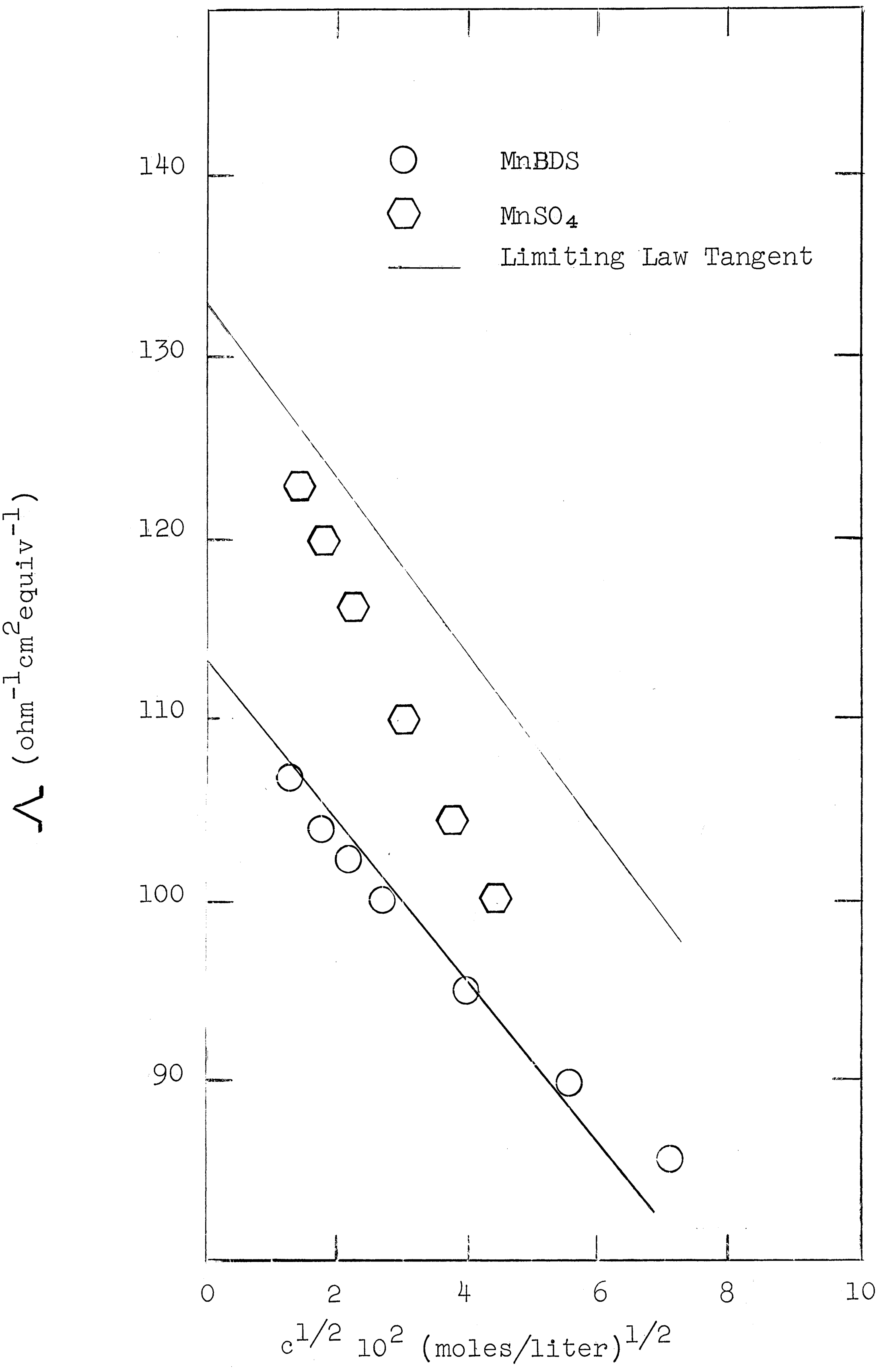

Fig. 9--Phoreograms of Manganese m-Benzenedisulfonate and Manganese Sulfate.

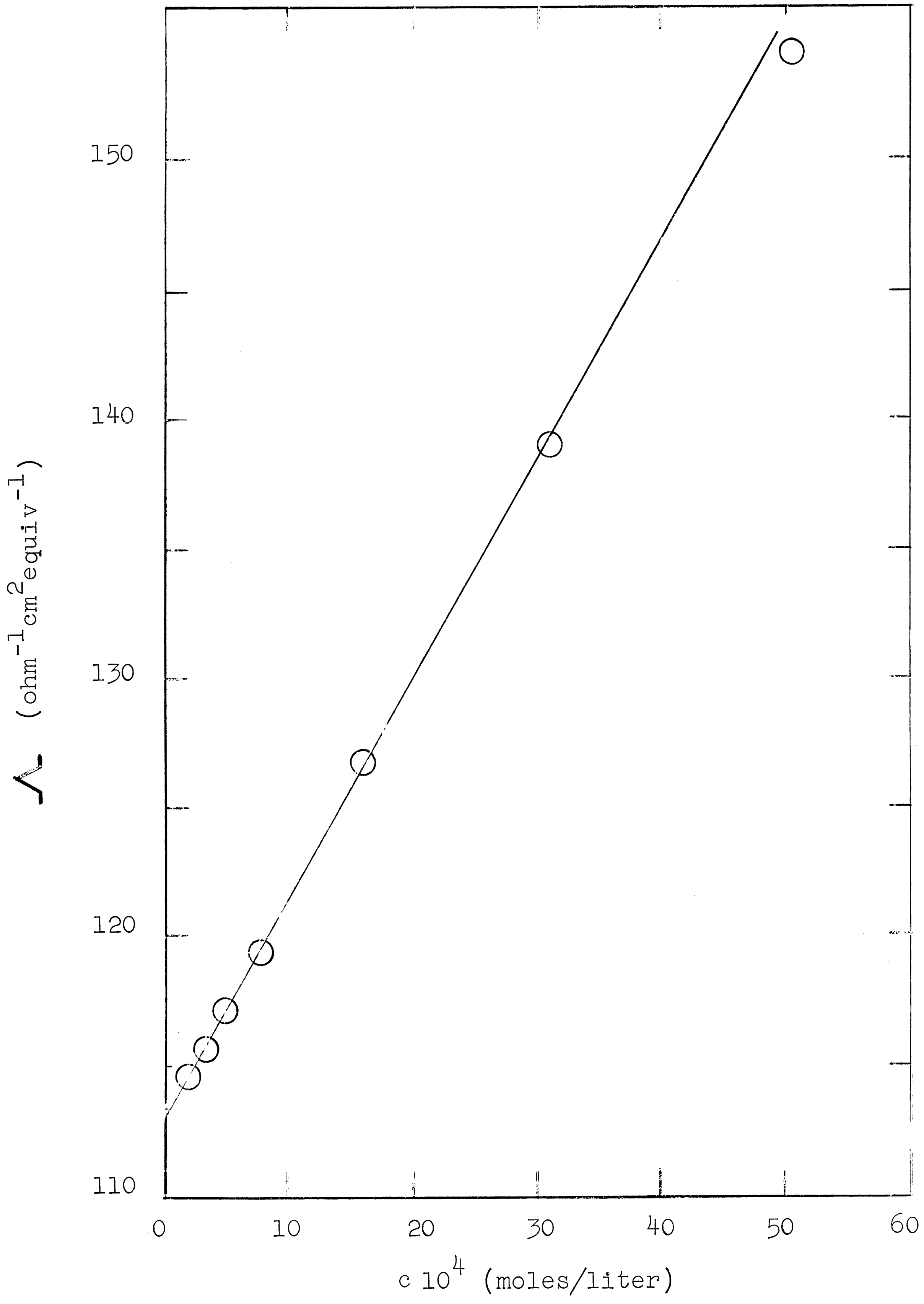

Fig. 10--Fuoss Plot of Manganese m-Benzenedisulfonate.

for $MnSO_4$ should be compatible with the K_a obtained when $MnSO_4$ conductance data (in water) were fitted to the equation for associated electrolytes.

The solvents employed were methanol-water mixtures. Methanol was chosen because dielectric and viscosity data on the complete range of weight percentage mixtures are available (see Appendix II).

Sets of Λ, c data from the mixed solvent resistance measurements were obtained (Tables IV and V). Figure 11 compares the phoreograms of MnBDS in pure water, two methanol-water mixtures and in pure methanol. That more and more association has been forced by changing the solvent from 100% water to 100% methanol is evident from the figure.

From the Λ, c data, values for Λ^o, $\overset{o}{a}$ and K_a for MnBDS and $MnSO_4$ in the various solvent mixtures may now be calculated by the method of Fuoss (35). The equation for the equivalent conductance of associated electrolytes is:

$$\Lambda = \alpha\,(\Lambda^o - S\,(c\alpha)^{1/2} + E\,c\alpha \log c\alpha + J\,c\alpha) \qquad (22)$$

where all the terms are defined as on page 6 and in Appendix I. By introducing the mass action equation for association:

$$K_a = \frac{1 - \alpha}{c\alpha^2 f_\pm^{\,2}} \qquad (23)$$

where $f_\pm$ is the activity coefficient, equation (22) can be written:

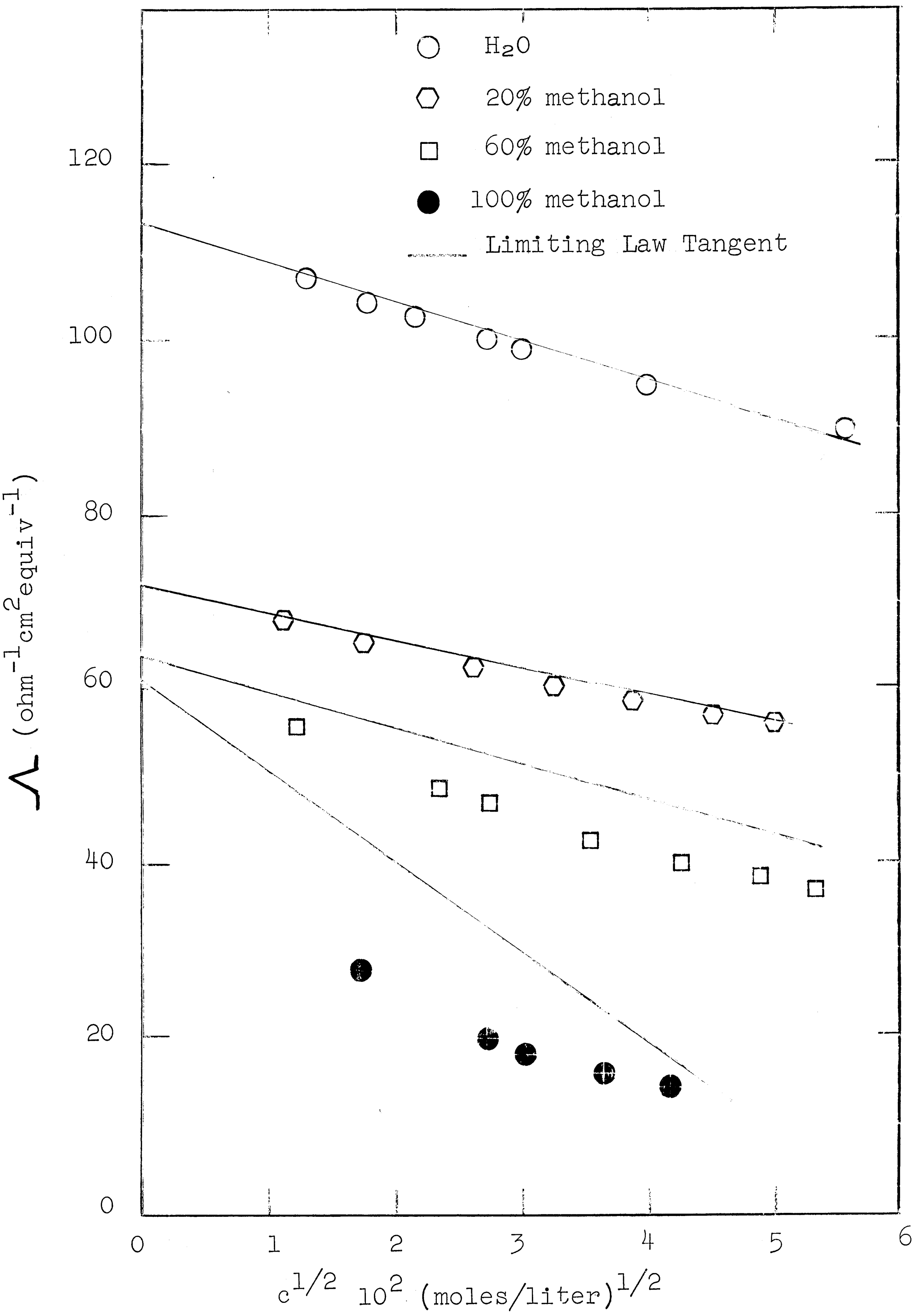

Fig. 11--Phoreograms of Manganese m-Benzenedisulfonate in Methanol-Water Systems.

$$\Lambda = \Lambda^{\circ} - S\,(c\alpha)^{1/2} + E\,c\alpha \log c\alpha + J\,c\alpha - K_a \Lambda f_{\pm}^{2}\,c\alpha. \qquad (24)$$

The procedure for finding the three unknowns $\underline{\alpha}$, $\underline{\Lambda^{\circ}}$ and $\underline{\overset{\circ}{a}}$ will now be outlined.

If the proper $\underline{\Lambda^{\circ}}$ and $\underline{\overset{\circ}{a}}$ were known, the value of $\underline{\alpha}$ could be found for each $\underline{\Lambda}$, $\underline{c}$ point. First, an opening $\underline{\alpha_o}$ is chosen from

$$\alpha_o = \left(\frac{\Lambda}{\Lambda^{\circ}}\right)^{1/2} \qquad (25)$$

Next,

$$\alpha_1 = \frac{\Lambda}{\Lambda^{\circ} - S\,c^{1/2}\,\alpha_o} \qquad (26)$$

is found. Using the value obtained for $\underline{\alpha_1}$ from equation (26), $\underline{\alpha_2}$, $\underline{\alpha_3}$, ..., $\underline{\alpha_n}$ are calculated:

$$\alpha_2 = \frac{\Lambda}{\Lambda^{\circ} - S\,(c\alpha_1)^{1/2} + E\,c\alpha_1 \log c\alpha_1 + J\,c\alpha_1} \qquad (27)$$

$$\alpha_3 = \frac{\Lambda}{\Lambda^{\circ} - S\,(c\alpha_2)^{1/2} + E\,c\alpha_2 \log c\alpha_2 + J\,c\alpha_2} \qquad (28)$$

$$\vdots$$

$$\alpha_n = \frac{\Lambda}{\Lambda^{\circ} - S\,(c\alpha_{n-1})^{1/2} + E\,c\alpha_{n-1} \log c\alpha_{n-1} + J\,c\alpha_{n-1}} \qquad (29)$$

until

$$\alpha_n \approx \alpha_{n-1} = \alpha \;; \qquad (30)$$

this $\underline{\alpha}$ is the fraction of ions unassociated in the solution.

With the value of α now determined, the following definitions are made:

$$\Lambda' \equiv \Lambda + S\,(c\alpha)^{1/2} - E\,c\alpha \log c\alpha\ , \qquad (31)$$

$$\Delta\Lambda \equiv \Lambda' - \Lambda^{o}\ , \qquad (32)$$

$$y \equiv \frac{\Delta\Lambda}{c\alpha}\ , \qquad (33)$$

and

$$x \equiv f_{\pm}^{\,2} \qquad (34)$$

where $f_{\pm}$ is calculated from the Debye-Hückel theory using the proper $\overset{\circ}{a}$ value.

Equation (24) therefore becomes:

$$y = J - K_{a}x\ . \qquad (35)$$

This procedure for determining α, assuming that $\overset{\circ}{a}$ and Λ^{o} are known, is the same as is used in the actual case when $\overset{\circ}{a}$ and Λ^{o} are not known. Note that the three unknowns are included in equation (35): J (that is, $\overset{\circ}{a}$) and K_{a} explicitly and Λ^{o} implicitly.

Picking a reasonable series of $\overset{\circ}{a}$ values, a correct Λ^{o} must be found, and only when this correct Λ^{o} is used in calculating α and y, is a plot of y vs x a straight line. If the trial value of Λ^{o} is smaller than the unknown (that is, correct) Λ^{o}, the numerator of y approaches a positive constant as c decreases (x increases), and since the denominator of y is approaching zero in this case, the y vs x plot will be sharply concave upward as c decreases. If the trial value of Λ° is too large, the numerator of y becomes zero before the concentration does, and the y vs x plot will be concave downward as the concentration decreases. Therefore, a series of Λ° values must be used before the correct one is found. With the proper Λ° in the y vs x plot, the intercept J is obtained; this J must be made compatible with the $\mathring{a}$ value used in finding α and $f_\pm$. Now these best Λ° and J values can be used to find the best α and all the parameters are thus found.

This procedure for finding Λ°, $\mathring{a}$ and K_a is obviously an extremely lengthy process to follow manually for each system studied. A computer program was written to handle the problem of varying $\mathring{a}$, Λ° and α until the plot of y vs x was found to be linear.

Table IX presents the final K_a, Λ° and $\mathring{a}$ values thus obtained.

Having the values of K_a, the extrapolation of K_a to water for MnBDS may be attempted. As suggested by Fuoss (35), $\log K_a$ vs $1/D$ (D is the dielectric constant of the solvent) was plotted for both MnBDS and MnSO$_4$ (Figure 12) in the series of mixed solvents employed. Both the MnSO$_4$ and MnBDS data show curvature at lower dielectric constant, but are close to linear as they approach the dielectric constant of water. The MnSO$_4$ data in the mixed solvents extrapolate very close to the K_a in water determined previously. A linear extrapolation of the high D points of

TABLE IX

Experimental Parameters

Manganese m-Benzenedisulfonate and Manganese Sulfate in Methanol-Water

Salt	% Methanol (weight %)	$K_a \times 10^{-2}$	Λ^o	$\mathring{a}$ (Å)
$MnSO_4$	0	1.33	133.2	5.0
	10	2.37	104.9	5.2
	20	4.39	85.8	5.8
	30	8.81	74.7	8.0
	40	17.1	68.9	8.2
MnBDS	0	-	113.3	5.4
	10	0.08	88.3	5.4
	20	0.16	72.1	5.8
	30	0.21	63.9	5.5
	40	0.56	60.8	5.7
	60	5.13	64.1	8.2
	80	14.9	74.2	7.3
	100	81.7	61.6	8.0

MnBDS leads to the value of K_a of 4.5, corresponding to an α of about 0.995 at a concentration of 3×10^{-3} M. This value is entirely consistent with the previously obtained conclusion from the conductance data in water that MnBDS may be a completely unassociated electrolyte.

From Table IX, it is apparent that the values obtained for $\mathring{a}$ vary considerably and that there is a large general

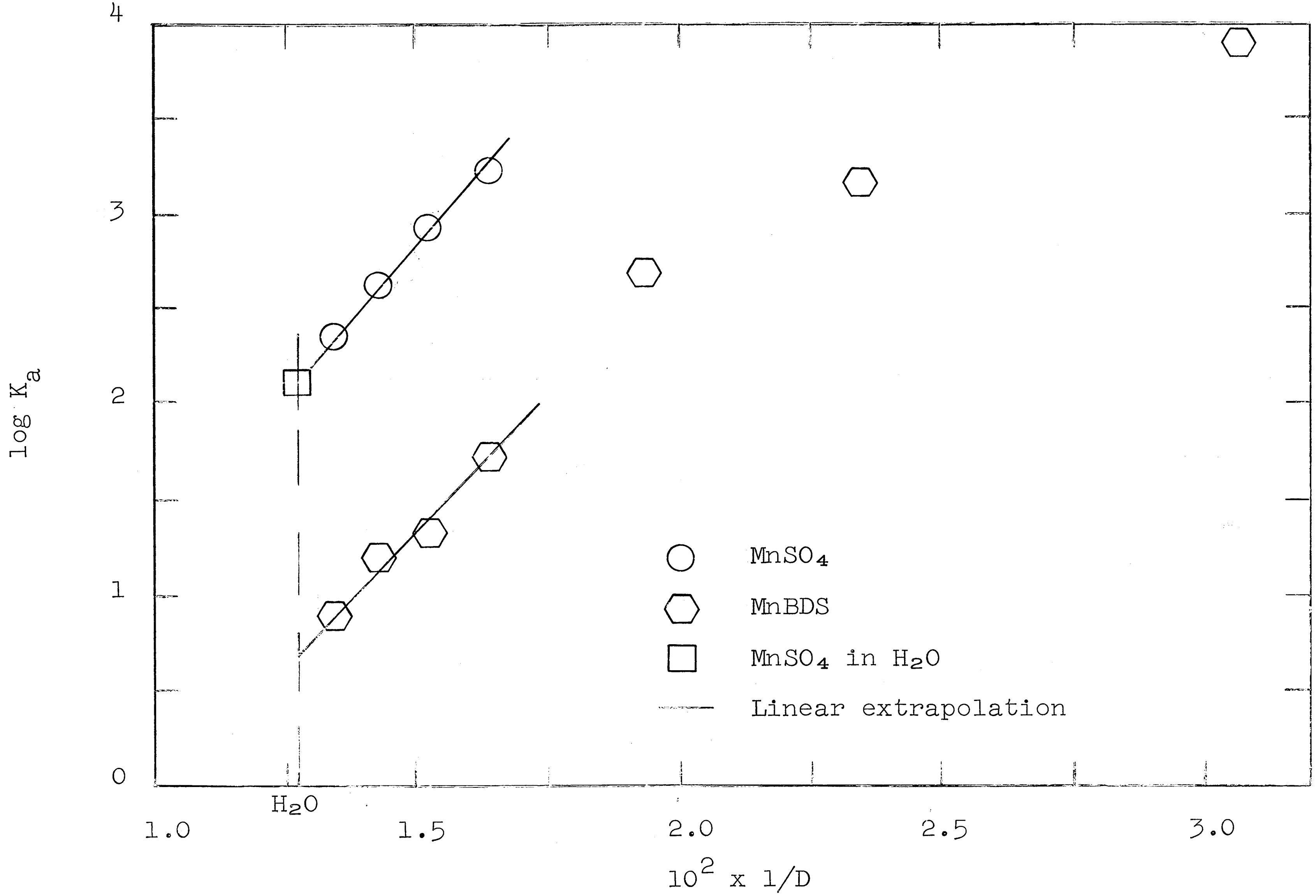

Fig. 12--The Association Constants of Manganese m-Benzenedisulfonate and Manganese Sulfate as a Function of Dielectric Constant.

jump in the value of $\overset{\circ}{a}$ from 40% methanol to 60% methanol. Fuoss has stated (35) however, that the $\overset{\circ}{a}$ for a particular electrolyte should be nearly constant even in different solvent mixtures, and that any variance in $\overset{\circ}{a}$ only indicates the necessity for an extra viscosity correction due to large ions. The Fuoss method for applying this correction makes use of the Einstein volume (41) for large ions. The value of this correction for these salts, according to the Fuoss method, would then be about $1.4\,\Lambda^{\circ}$; this amounts to a change of about 150 in the J term. However, in order to keep $\overset{\circ}{a}$ constant in the MnBDS mixed solvent work, the needed correction is closer to $20\,\Lambda^{\circ}$, or a change of about 2000 in the J term. It seems ill-advised to add such a large single correction without considering other factors which might be causing the variance in $\overset{\circ}{a}$. Higher terms in the equation which had been dropped in the case of 1:1 electrolytes, for instance the $c^{3/2}$ term, could possibly have some significance in the case of the 2:2 electrolytes. Also, recalling the large value for $\overset{\circ}{a}$ obtained for LaNTS, where K_a is quite large, the reason for the variance in $\overset{\circ}{a}$ may be the fact that the equation does not completely describe the behavior of strongly associated electrolytes.

In any event, when variation in $\overset{\circ}{a}$ is witnessed, a correction of such large proportions cannot be attributed to one factor such as viscosity until the actual viscosity measurements have been made. The difficulty in this is that the measurement of viscosity in dilute solutions is of itself, a major research project. Until these measurements are made however, the reason why $\mathring{a}$ is not constant will be only speculatively evaluated.

The Λ° values obtained for MnBDS in the various solvent mixtures deserve some comment also. Up to 40% methanol, the values for Λ° decrease in such a manner as to make their Walden product, $\Lambda^\circ\eta$ (42), almost constant (η is the viscosity of the solvent). In 60, 80 and 100% methanol, the values of Λ° for MnBDS vary such that the Walden product falls sharply and $\Lambda^\circ\eta$ in pure methanol is only about one-third $\Lambda^\circ\eta$ in pure water. This behavior is qualitatively similar to the behavior noted by others (43) for different salts in methanol-water solvent mixtures.

SUMMARY

Within the concentration range of applicability, the conductance theory of Onsager and Fuoss for unassociated electrolytes has proved quite valid for the examined 1:2, 2:2 and 1:3 sulfonates in water. In addition, for these salts, generally consistent values for the closest distance of approach of the ions, $\mathring{a}$, have been obtained, and the conductance data for the 2:2 sulfonates cross the limiting law tangent as predicted by the theory. The application of the Onsager-Fuoss extended theory to the associated 2:2 sulfates has also given reasonable results for Λ^o and $\mathring{a}$. However, the associated 3:3 sulfonate studied did not give Λ^o and $\mathring{a}$ parameters in good agreement with the 1:3 salts.

When MnBDS was forced to associate by employing mixed solvents, the association constants were obtained by use of the extended theory for associated electrolytes. The extrapolation of these constants back to the dielectric constant of water indicated that MnBDS was only slightly associated in water ($\alpha = 0.995$ at 3×10^{-3} M). In conjunction with the work on MnBDS, the higher association of $MnSO_4$ in mixed solvents was studied; the results obtained from this salt exemplified the consistency of the extrapolation for both 2:2 electrolytes. The large variation in $\mathring{a}$

values found from the mixed solvent work raises the question of the roles of the viscosity correction for large ions and the inclusion of higher terms in the theoretical equation for 2:2 electrolytes.

As indicated by their low field conductance, both CuBDS and MnBDS must now be designated as much stronger electrolytes than their corresponding sulfates. In connection with this, investigation of the high field conductances of CuBDS and $CuSO_4$ has been begun (44). These measurements have been used to give some indication of the extent of ion association in solution (45), and the initial findings indicate that, substantiating the low field work, CuBDS is less associated than $CuSO_4$ in water solutions. This preliminary result was obtained by comparing the experimental data of CuBDS and $CuSO_4$ with the Onsager-Wilson theory for the high field conductance of completely unassociated electrolytes (45).

However, even with the conclusions drawn from the low field conductance studies in water and mixed solvents, this work has not shed any light on the actual question of what is involved on the microscopic scale in ion association. The Fuoss (5) and Denison-Ramsay (3) theories would predict that a plot of <u>log K_a</u> vs <u>1/D</u> be linear:

$$K_a \propto e^b \quad ; \quad b = \frac{z_1 z_2}{\mathring{a} D k T}$$

But the plots of $\underline{\log K_a}$ vs $\underline{1/D}$ are not linear throughout; only approaching linearity in the high dielectric range. Also, the values for $\underline{\mathring{a}}$, calculated for MnBDS, using the Bjerrum theory separate into two groups: from 10% to 40% methanol, the $\underline{\mathring{a}}$ is about 15 Å; from 60% to 100% methanol, the $\underline{\mathring{a}}$ is about 7.5 Å. Not only is there a great variation in the values of $\underline{\mathring{a}}$ thus found (as there was in the $\underline{\mathring{a}}$ values from the Fuoss theory), but the order of their relative sizes is inverted from the order found using the conductance theory. The Bjerrum $\underline{\mathring{a}}$'s for $MnSO_4$ also vary considerably with percentage methanol, and like the $\underline{\mathring{a}}$'s of MnBDS, change in the inverse order from the corresponding conductance values. The explanation for the differences in behavior in methanol-water from that predicted by the theories may be a specific solvation effect or a reflection of the changes in the physical properties of the methanol-water solvent itself.

The results from this research investigation of the low field conductance of various salts in water and methanol-water, along with the questions raised, point to the need for a variety of physical measurements to help clarify the behavior observed. A conductance study of other salts and solvent systems, and viscosity measurements are the next steps in pursuit of the problem. In this laboratory, preliminary conductance experiments have been begun with dioxane-water solvent mixtures and with o- and p-benzene-disulfonate salts. To help clarify the general problem of ion association in these systems, ultrasonic absorption, high field conductance, and near ultraviolet and visible spectra should be examined.

APPENDIX I

Definition of Terms in the Limiting Law and Extended Law Equations for Unassociated Electrolytes

In attempting to describe the behavior of an ionic solution when a field is applied, the problem is the determination of the ionic velocities. If there were no ionic atmosphere, the velocity of a reference ion, *j*, would be directly proportional to the external force applied. Since an ionic atmosphere exists around the ion in solution, two effects must be considered:

1. The electrophoretic effect: When an external field is applied, the ionic atmosphere, carrying solvent medium with it, moves in a direction opposite to the reference ion. Therefore, *j* is not moving in a medium at rest, and its net velocity is decreased.
2. The relaxation effect: Before the external field is applied, the atmosphere surrounding *j* is spherically symmetrical. Once the field is applied, *j* begins to move but the ionic atmosphere, attempting to re-form around *j*, does so in a time *t*, not equal to zero, therefore giving rise to an asymmetric atmosphere around *j*. This asymmetry

produces a field on j opposing the external field and therefore causes the velocity of j to be decreased.

Taking these two effects into account, the limiting law for the equivalent conductance of unassociated electrolytes (assuming the ions to be point charges) in solution was derived by Onsager:(18):

$$\Lambda = \Lambda^{\circ} - S\ c^{1/2} \quad . \tag{1}$$

By considering these same two effects, but using a model in which the ions are represented by charged spheres rather than by point charges, and carrying the mathematical treatment further, Onsager and Fuoss developed the extended law equation for unassociated electrolytes:(15,16,17):

$$\Lambda = \Lambda^{\circ} - S\ c^{1/2} + E\ c \log c + J\ c\ . \tag{2}$$

The constants S, E and J are given by the following equations:

$$S = \alpha^{*} \Lambda^{\circ} + \beta^{*} \tag{3}$$

$$\alpha^{*} = \frac{e^{2} \kappa}{6\ D\ k\ T\ (1 + q)\ c^{1/2}} \tag{3a}$$

$$\beta^{*} = \frac{\mathcal{F}\ e\ \kappa}{3\pi \eta\ C\ c^{1/2}\ (10^{-8})} \tag{3b}$$

$$E = E_{1} \Lambda^{\circ} - E_{2} \tag{4}$$

$$0.4343\ E_{1} = \frac{\kappa^{2}\ \mathring{a}^{2}\ b^{2}}{24\ c} \tag{4a}$$

$$0.4343\ E_2 = \frac{\kappa\ \mathring{a}\ b\ \beta^*}{16\ c^{1/2}} \tag{4b}$$

$$J = \sigma_1\ \Lambda^o + \sigma_2 \tag{5}$$

$$\sigma_1 = \left(\frac{\kappa^2\ \mathring{a}^2\ b^2}{12\ c}\right) \left[h(b) + 0.9074 + \ln\left(\frac{\kappa\ \mathring{a}}{c^{1/2}}\right)\right] \tag{5a}$$

$$h(b) = \frac{2b^2 + 2b - 1}{b^3} \tag{5b}$$

$$\sigma_2 = \alpha^*\ \beta^* + \frac{11\beta^*\ \kappa\ \mathring{a}}{12\ c^{1/2}} - \frac{\kappa\ \mathring{a}\ b\ \beta^*}{8\ c^{1/2}} \left[1.0170 + \ln\left(\frac{\kappa\ \mathring{a}}{c^{1/2}}\right)\right] \tag{5c}$$

where e = electronic charge = 4.8022×10^{-10} esu

κ = reciprocal of the radius of the ionic atmosphere; defined by Debye and Huckel:

$$\kappa \equiv \left[\frac{4\pi\ N\ e^2}{1000\ D\ k\ T} \sum_i c_i\ z_i^{\ 2}\right]^{1/2}$$

N = Avogadro's number = 6.0238×10^{23} molecules/mole

z = ionic charge

D = dielectric constant

k = Boltzmann constant =
1.3803×10^{-16} erg/degree molecule

T = temperature, ° A

c = concentration, moles/liter

$$q = \left[\frac{|z_1\ z_2|\ (\lambda_1^o + \lambda_2^o)}{(\ |z_1| + |z_2|)\ (|z_2|\ \lambda_1^o + |z_1|\ \lambda_2^o)}\right]^{1/2}$$

$\mathcal{F}$ = Faraday constant = 96,493 absolute coulombs/equivalent

η = viscosity

C = velocity of light = 2.9979 cm/sec

$\mathring{a}$ = closest distance of approach of the ions, cm

b = Bjerrum parameter $\equiv \frac{|z_1 z_2| e^2}{\mathring{a} D k T}$

Because of mathematical approximations used in the derivation of the conductance equations, the theory should not be fitted to data whose $\kappa \mathring{a} > 0.2$ (46).

APPENDIX II

Viscosity and Dielectric Data for Methanol-Water Systems (47)

% Methanol (weight %)	$\eta \times 10^3$ (millipoise)	D
0	8.95	78.48
10	11.58	74.21
20	14.00	70.01
30	15.31	65.55
40	15.93	60.92
60	14.03	51.71
80	10.06	42.60
100	5.41	32.64

APPENDIX III

Calculated Values for the Conductance Equation Terms of the Systems Studied

Size Independent Terms for Water Systems

System	α^*	β^*	E_1	E_2
H_2BDS	0.6085	156.41	6.3312	133.53
Na_2BDS	0.7398	156.41	6.3312	133.53
K_2BDS	0.7038	156.41	6.3312	133.53
H_3NTS	1.0577	294.93	28.491	731.67
Na_3NTS	1.4373	294.93	28.491	731.67
K_3NTS	1.3264	294.93	28.491	731.67
2:2 electrolytes	1.8312	240.96	33.766	650.60
3:3 electrolytes	6.1803	541.74	384.62	4940.2

Size Independent Terms for 2:2 Electrolytes in Methanol-Water

% Methanol (weight %)	α^*	β^*	E_1	E_2
0	1.8312	240.96	33.766	650.60
10	1.9915	191.52	39.933	562.43
20	2.1735	163.10	47.566	522.69
30	2.3990	154.14	57.954	545.22
40	2.6775	153.65	72.182	606.57
60	3.4237	189.35	118.04	955.81
80	4.5790	290.99	211.14	1964.6
100	6.8271	618.11	469.35	6222.1

Size Dependent Terms for Water Systems

System	$\mathring{a}$ (Å)	σ_1	σ_2
H_2BDS	4	13.372	129.6
	5	15.729	174.7
	6	17.930	227.8
Na_2BDS	4	13.372	150.1
	5	15.729	195.2
	6	17.930	248.3
K_2BDS	4	13.372	144.5
	5	15.729	189.6
	6	17.930	242.7
2:2 electrolytes	5	73.418	-79.6
	6	81.500	-37.5
	7	88.848	20.6
	8	95.690	90.4

System	$\mathring{a}$ (Å)	σ_1	σ_2
H_3NTS	6	78.64	-28.8
	7	85.87	90.5
	8	92.66	223.8
	9	99.16	852.7
Na_3NTS	6	78.64	83.1
	7	85.87	202.5
	8	92.66	335.7
	9	99.16	964.6
K_3NTS	6	78.64	50.3
	7	85.87	169.8
	8	92.66	303.0
	9	99.16	931.9
3:3 electrolytes	6	964.88	-5696
	7	1028.8	-5867
	8	1086.0	-5950
	9	1138.2	-5965
	10	1186.5	-5927

Size Dependent Terms for 2:2 Electrolytes in Methanol-Water

% Methanol (weight %)	$\mathring{a}$ (Å)	σ_1	σ_2	% Methanol (weight %)	$\mathring{a}$ (Å)	σ_1	σ_2
0	5	73.418	-79.6	40	5	158.63	-292.5
	6	81.500	-37.5		6	174.37	-283.5
	7	88.848	20.6		7	188.49	-259.6
	8	95.691	90.4		8	201.45	-224.8
	9	102.15	168.9		9	213.55	-181.8
10	5	86.943	-114.0	60	5	262.65	-654.0
	6	92.286	-83.8		6	287.16	-664.8
	7	104.76	-39.8		7	308.94	-652.2
	8	112.62	14.1		8	328.80	-622.5
	9	120.02	75.8		9	347.18	-579.6
20	5	103.76	-152.9	80	5	478.63	-1764.1
	6	114.65	-131.6		6	520.39	-1837.1
	7	124.49	-97.5		7	557.30	-1863.1
	8	133.59	-54.0		8	590.43	-1852.0
	9	142.13	-3.4		9	620.96	-1814.8
30	5	126.82	-209.8	100	5	1097.3	-7187.8
	6	139.79	-194.6		6	1185.3	-7595.9
	7	151.44	-165.8		7	1262.1	-7880.9
	8	162.18	-127.4		8	1330.8	-7994.9
	9	172.25	-81.6		9	1393.3	-8053.9

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