

1973

The Conductance of Some Polyvalent Electrolytes

Jack Lee Worthington

Eastern Illinois University

This research is a product of the graduate program in [Chemistry](#) at Eastern Illinois University. [Find out more](#) about the program.

Recommended Citation

Worthington, Jack Lee, "The Conductance of Some Polyvalent Electrolytes" (1973). *Masters Theses*. 3766.
<https://thekeep.eiu.edu/theses/3766>

This is brought to you for free and open access by the Student Theses & Publications at The Keep. It has been accepted for inclusion in Masters Theses by an authorized administrator of The Keep. For more information, please contact tabruns@eiu.edu.

PAPER CERTIFICATE

TO: Graduate Degree Candidates who have written formal theses.

SUBJECT: Permission to reproduce theses.

The University Library is receiving a number of requests from other institutions asking permission to reproduce dissertations for inclusion in their library holdings. Although no copyright laws are involved, we feel that professional courtesy demands that permission be obtained from the author before we allow theses to be copied.

Please sign one of the following statements.

Booth Library of Eastern Illinois University has my permission to lend my thesis to a reputable college or university for the purpose of copying it for inclusion in that institution's library or research holdings.

May 21, 1973
Date

I respectfully request Booth Library of Eastern Illinois University not allow my thesis be reproduced because _____

Date

Author

THE CONDUCTANCE OF SOME

POLYVALENT ELECTROLYTES

(TITLE)

BY

Jack Lee Worthington

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

MASTER OF SCIENCE, DEPARTMENT OF CHEMISTRY

IN THE GRADUATE SCHOOL, EASTERN ILLINOIS UNIVERSITY
CHARLESTON, ILLINOIS

1973

YEAR

I HEREBY RECOMMEND THIS THESIS BE ACCEPTED AS FULFILLING
THIS PART OF THE GRADUATE DEGREE CITED ABOVE

May 19, 1973
DATE

May 19, 1973
DATE

ACKNOWLEDGEMENTS

The author respectfully thanks Dr. David W. Ebdon for suggesting this problem and for his guidance, cooperation, and comradeship in the course of the investigation.

In addition, special thanks are extended to Dr. Jerry Ellis for glass blowing new equipment and for the repair of old and broken glassware.

Also, the author would like to express appreciation to Larry Shadwick for writing computer programs to handle the Murphy-Cohen equation and the Fuoss-Onsager extended equation.

Finally, the author would like to acknowledge the Council on Faculty Research of Eastern Illinois University for financial grants which supported this investigation.

TABLE OF CONTENTS

	Page
ACKNOWLEDGEMENTS	ii
TABLE OF CONTENTS	iii
LIST OF FIGURES	v
LIST OF TABLES	vi
ABSTRACT	vii
GLOSSARY OF SYMBOLS	ix
INTRODUCTION	1
STATEMENT OF PROBLEM	13
EXPERIMENTAL	15
Preparation of Sulfonic Acids and Their Salts	15
Sodium 1,3,5-Benzenetrisulfonate	15
Potassium 1,3,5-Benzenetrisulfonate	15
Lanthanum 1,3,5-Benzenetrisulfonate	18
1,3,5-Triphenylbenzene-4',4'',4'''-trisulfonic Acid (H ₃ TTS)	18
Sodium, Potassium, and Lanthanum Salts of 1,3,5- Triphenylbenzene-4',4'',4'''-trisulfonic Acid	22
Characterization of H ₃ TTS	23
1,3,5-Tri(p-hydroxyphenyl)benzene Derivative	23
1,3,5-Tri(p-methoxyphenyl)benzene	24
1,3,5-Tri(p-methoxyphenyl)benzene	25
Purification of Water	31

	Page
Conductance Measurements	32
Equipment	32
Cells	32
Preparation of Solutions	39
RESULTS	40
Treatment of Raw Data	40
Concentration	43
Resistance	43
Equivalent Conductance	44
Application of Data to Theory	45
Experimental Phoreograms	45
Theoretical Fit Using the Murphy-Cohen Equation . .	45
Theoretical Fit Using the Fuoss-Onsager Equation . .	48
Experimental Solute Parameters	48
Theoretical Solute Parameters	49
SUMMARY	57
LIST OF REFERENCES	59
VITA	61

LIST OF FIGURES

Figure	Page
1. Theoretical Behavior for KCl at 25°	5
2. Phoreograms of Sodium m-Benzenedisulfonate, Potassium m-Benzenedisulfonate and Sodium Sulfate .	10
3. Phoreograms of Copper m-Benzenedisulfonate and Copper Sulfate	11
4. Reactions	16
5. Apparatus for Synthesis of 1,3,5-Triphenylbenzene- 4',4'',4'''-trisulfonic Acid	21
6. Infrared Spectrum of 1,3,5-tri(p-hydroxyphenyl)- benzene, a Derivative	26
7. Infrared Spectrum of 1,3,5-tri(p-hydroxyphenyl)- benzene	28
8. Cell Calibration	36
9. Typical Data Sheet	41
10. Typical Data Sheet	42
11. Phoreogram of Sodium 1,3,5-Benzenetrisulfonate . .	50
12. Phoreogram of Potassium 1,3,5-Benzenetrisulfonate .	51
13. Phoreogram of Lanthanum 1,3,5-Benzenetrisulfonate .	52
14. Phoreogram of Sodium 1,3,5-Triphenylbenzene-4',4'', 4'''-trisulfonate	53
15. Phoreogram of Potassium 1,3,5-Triphenylbenzene- 4',4'',4'''-trisulfonate	54
16. Phoreogram of Lanthanum 1,3,5-Triphenylbenzene- 4',4'',4'''-trisulfonate	55

LIST OF TABLES

Table	Page
I. Calculated Limiting Equivalent Conductance and Distance of Closest Approach	7
II. Elemental and Cation-Exchange Analyses	31
III. Cell Constant Variation with Concentration	38
IV. [Λ^{exp} , C] Data Sets for Salts of 1,3,5-Benzene-trisulfonic Acid in Water	46
V. [Λ^{exp} , C] Data Sets for Salts of 1,3,5-Triphenylbenzene-4',4'',4'''-trisulfonic Acid in Water	47
VI. Experimentally Determined Solute Parameters	56
VII. Theoretically Determined Solute Parameters	56

ABSTRACT

Title of Thesis: The Conductance of Some Polyvalent Electrolytes

Jack Lee Worthington, Master of Science, 1973

Thesis directed by: David W. Ebdon, Assistant Professor of Chemistry

A new compound, 1,3,5-triphenylbenzene-4',4'',4'''-trisulfonic acid, was synthesized by treating triphenylbenzene in 1,2-dichloroethane with chlorosulfonic acid. The reaction appears to be quantitative. Conductance measurements were then made on the sodium, potassium, and lanthanum salts of this new acid and of 1,3,5-benzene-trisulfonic acid.

The choice of these acids was based on two factors:

1) the desire to prepare a 3-3 symmetrical unassociated electrolyte which would allow the determination of a more reliable equivalent ionic conductance value for La^{3+} and 2) an interest in using the Murphy-Cohen equation to determine solute parameters such as association constants if association is present.

Conductance measurements were done in water at 25°C using the weight dilution technique and phoreograms of each salt were drawn. From the phoreograms of the sodium, potassium, and lanthanum salts of 1,3,5-triphenylbenzene-4',4'',4'''-trisulfonic acid values of Λ_0 found are 99.35 ($\text{ohm}^{-1}\text{-cm}^2\text{-equiv}^{-1}$), 122.65 ($\text{ohm}^{-1}\text{-cm}^2\text{-equiv}^{-1}$), and 119.25 ($\text{ohm}^{-1}\text{-cm}^2\text{-equiv}^{-1}$), respectively. The value of the limiting equivalent ionic conductance, λ_0^- , of 1,3,5-triphenylbenzene-

4',4'',4'''-trisulfonate ion found is $49.25 \pm .01$ ($\text{ohm}^{-1}\text{-cm}^2\text{-equiv}^{-1}$). A value of λ_0^+ for La^{3+} as determined from λ_0^- is 70.0 ($\text{ohm}^{-1}\text{-cm}^2\text{-equiv}^{-1}$).

Similarly, Λ_0 's for the sodium and potassium salts of 1,3,5-benzenetrisulfonic acid were found to be 80.69 ($\text{ohm}^{-1}\text{-cm}^2\text{-equiv}$) and 80.88 ($\text{ohm}^{-1}\text{-cm}^2\text{-equiv}^{-1}$) respectively. The value of λ_0^- for 1,3,5-benzenetrisulfonate ion was found to be $80.78 \pm .1$ ($\text{ohm}^{-1}\text{-cm}^2\text{-equiv}^{-1}$).

The Murphy-Cohen equation qualitatively shows these salts to be unassociated; however, there is a real possibility of very slight association.

GLOSSARY OF SYMBOLS

a	mean distance of approach of ions ($\overset{\circ}{a}$ same in $\overset{\circ}{\text{Angstr\AA}ms}$)
C	concentration in conductance cell in moles per liter
\bar{C}	concentration of stock solution in moles per gram solution
D	dielectric constant of water (78.303)
e	electronic charge (4.803×10^{-10} esu)
E	conductance equation coefficient, a function of D, η , and T
G	mass (grams)
J	conductance equation coefficient, a function of a, D, η , T and ionic charge
K Ω	1000 ohms
K _A	association constant
k _{cell}	cell constant
k	Boltzmann's constant
M	molar concentration
N	concentration in equivalents per liter
n _i	concentration in ions/cc
R _{msolv}	measured resistance of solvent (ohms)
R _{msoln}	measured resistance of solution (ohms)
R _{msolv} [∞]	resistance of solvent extrapolated to infinite frequency (ohms)
R _{msoln} [∞]	resistance of solution extrapolated to infinite frequency (ohms)
R _{solv} [∞]	resistance of solvent corrected for 30 K Ω in parallel (ohms)
R _{solute} [∞]	resistance of solute (ohms)

S	conductance equation parameter, a function of α and β
T	absolute temperature, °K
V	volume, milliliters
z_i	ionic charge
z_1	cation charge
z_2	anion charge
α	limiting law, time of relaxation coefficient, a function of ionic charge, D and T
ρ	density of water at 25° (.997075 grams/ml)
η	viscosity of water at 25°, in poise (.008903)
ω	frequency of alternating electrical field, in hertz
κ^*	reciprocal of average radius of ionic atmosphere, $[\kappa^{*2} = (4\pi e^2/DkT) \sum_{i=1}^{\infty} \eta_i z_i^2]$
κ	specific conductance in $\text{ohm}^{-1}\text{-cm}^{-1}$
σ	standard deviation
Λ	equivalent conductance, $\text{ohm}^{-1}\text{-cm}^2\text{-equiv}^{-1}$
Λ_o	limiting equivalent conductance (equivalent conductance at infinite dilution)
Λ^{exp}	experimentally determined equivalent conductance
Λ^{MC}	theoretically determined equivalent conductance using the Murphy-Cohen equation
Λ^{FO}	theoretically determined equivalent conductance using the Fuoss-Onsager extended equation
λ_o^+	equivalent ionic conductance of cation at infinite dilution
λ_o^-	equivalent ionic conductance of anion at infinite dilution
γ	dissociation constant, fraction of ions unassociated
β	limiting law, electrophoretic coefficient, a function of ionic charge, D, T, and η

INTRODUCTION

The interpretation of electrolytic conductance measurements is predicated on the mathematical relations developed by Debye and Hückel in their theory of interionic attraction for dilute solutions of electrolytes. From the Debye-Hückel theory Onsager¹ and Fuoss and Onsager² derived equations to describe the equivalent conductance of symmetrical associated and unassociated electrolytes for solutions of concentrations less than $10^{-2}M$. A comparison of various conductance theories by other researchers³ has demonstrated that the Fuoss-Onsager extended equation best fits the experimental data.

The Fuoss-Onsager extended equation has been tested with data for 1-1 and 2-2 unassociated electrolytes as will be discussed; however, to our knowledge no conductivity measurements have been made on a 3-3 unassociated electrolyte. We thought it would be interesting to measure two 3-3 electrolytes of different charge density and then use the Fuoss-Onsager extended equation to determine whether they are associated or unassociated and at the same time establish the validity of this equation for a symmetrical electrolyte of such a high charge type. In addition, recent modifications of the Fuoss-Onsager theory by Murphy and Cohen⁴ allow the theory to handle unsymmetrical electrolytes i.e. 1-2, 2-1, and 3-1, etc. Therefore, it would also be of interest to compare the data fitting ability of the Murphy-Cohen equation to that of the Fuoss-Onsager extended equation for symmetrical electrolytes as well as to examine the ability of the Murphy-Cohen

equation to reproduce conductivity data for unsymmetrical electrolytes.

Historical Background

Debye and Hückel in the early 1920's were aware that the theory of electrolytic solutions must depend on knowing the forces that affect ions in solution, namely coulombic, thermal, and local flow of the solvent (hydrodynamic). By putting Coulomb's Law in the form of Poisson's equation and assuming a value of $1/\kappa^*$ for the radius of the "ionic atmosphere" they derived exact relations from which the behavior of dilute electrolyte solutions could be quantitatively predicted.⁵

When considering the forces that influence ionic motion Debye and Hückel recognized two important effects: 1) The time of relaxation effect and 2) the electrophoretic effect.

The Time of Relaxation Effect: When an external force is applied (to an electrolytic solution) the ions begin to move; if the response were instantaneous, the spherical symmetry of the unperturbed solution at rest would be retained because the ions of the atmosphere would then be able to readjust their locations promptly in order to follow the motion of the central ion. But by assuming a friction coefficient different from zero, we are requiring the ions to take a non-zero time to move a given distance. Hence, the distribution in the ion atmosphere will always lag behind that corresponding to the instantaneous position

of the reference ion; the distribution becomes asymmetric in a direction determined by the direction of the external force which produces the motion.

It then becomes clear that the asymmetry which the external field produces in the distribution will lead to a diminution of conductance, because the net change in the equilibrium distribution must be exactly equal and opposite to the charge on the reference ion. If the distribution becomes unsymmetrical, it must be because not quite enough opposite charge is ahead of the moving reference ion and because not quite all of the ions of opposite charge behind it have reverted to a random distribution (with respect to the moving ion). The result is that a moving ion always carries with itself an electric field which is directly opposed to the external field. On account of its origin in the finite time required for a perturbed distribution to revert to a uniform one, this electrostatic braking effect is called the relaxation field.⁶

The Electrophoretic Effect: When an external electric field is applied to an electrolytic solution, force is exerted on the ions and these forces are transmitted to the solvent, which in turn causes other ions to move. Since anions and cations move in opposite directions and are electrostatically coupled the local flow pattern becomes complicated when an external force initiates ionic motion. At the surface of the ion the medium is moving with the same velocity as the ion. Since the ion occupies volume, it will push solvent away

directly in front and drag it along behind. At the plane through the center, perpendicular to the field direction, there will be no radial displacement of the liquid, but in any other direction the liquid will be displaced both radially with respect to the ion and parallel to the field. Hence, any other ion located by co-ordinates (r, θ) with respect to the reference ion will be in a medium which is moving due to motion of the reference ion.⁶

Onsager was the first to successfully analyze the conductance problem. Into the two effects just mentioned he incorporated the phenomenon of Brownian motion in his mathematical treatment, with ions considered as point charges. Onsager's result is known as the limiting law for electrolytic conductance:

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

In the mid 1950's Fuoss and Onsager derived a more complete conductance equation for unassociated symmetrical electrolytes:⁷

$$\Lambda = \Lambda_0 - SC^{1/2} + EC\log C + JC$$

The inclusion of the parameter, a , in the coefficient, J , is an improvement in the conductance equation, because it represents an attempt to account for the finite size of ions in solution rather than considering them as point charges.

Using the extended equation Fuoss and Onsager calculated theoretical Λ values⁷ for KCl (a 1-1 electrolyte) at 25°C and demonstrated that it reproduces the experimental data up to $C \sim .01M$.

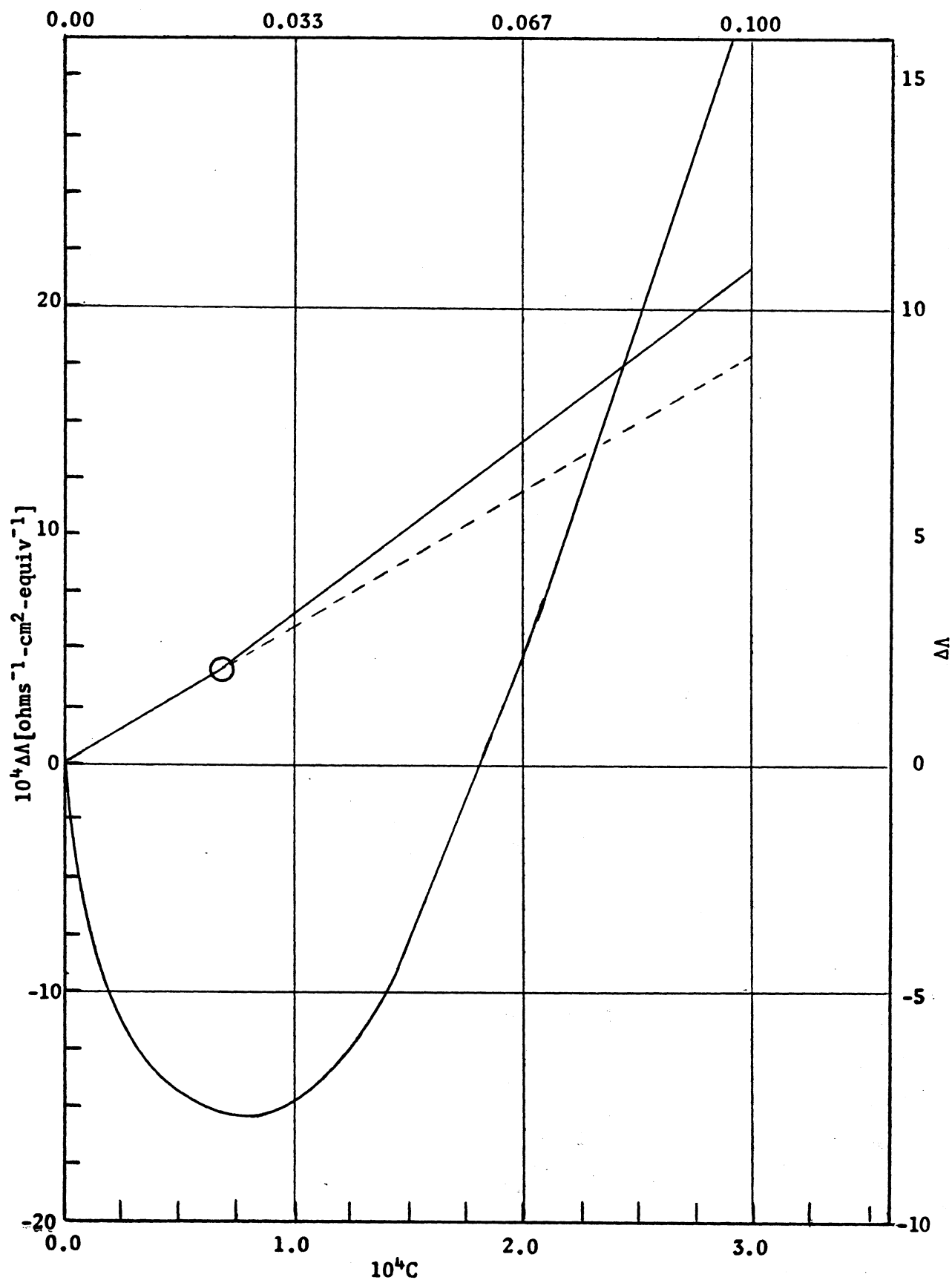


Figure 1. Theoretical behavior for KCl at 25°; scales for lower curve ($0 < C < 3 \times 10^{-4}$) left and below; scales for upper curve ($0 < C < .10$) right and above; points, Shedlovsky data.*

*From R. M. Fuoss and L. Onsager, J. Phys. Chem., 61, 668(1957).

They let $\Delta\Lambda$ denote the distance from the Onsager tangent to the conductance curve:

$$\Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta)C^{1/2} + EC\log C + JC$$

$$\Delta\Lambda = \Lambda + (\alpha\Lambda_0 + \beta)C^{1/2} - \Lambda_0 = EC\log C + JC$$

Figure 1 shows $\Delta\Lambda$ vs. 10^4C for theoretical and experimental data and on an expanded scale low concentration behavior of unassociated salts, specifically, the conductance curve crosses the limiting tangent from above at low concentrations and then approaches the tangent from below as zero concentration is approached.

In 1960 Kay⁸ used data on some 1-1 electrolytes from several researchers to investigate the ability of the extended equation to reproduce the concentration dependence of the equivalent conductance. Table 1 shows results for 3 salts(selected from a group of 22). The standard deviations, $\sigma(\Lambda_0)$ and $\sigma(\underline{a})$, were calculated to demonstrate the internal consistency of the extended equation and how well the calculated values of Λ and \underline{a} agree with the experimental(\underline{a} was compared to crystallographic radii and to values obtained by other empirical methods).

Two years later Hallada⁹ and Atkinson, Yokoi, and Hallada¹⁰ published reports on the conductance of some 2-2 and 3-3 electrolytes. They were concerned that different experimental methods gave wide variations in association constants, for example K_A for CuSO_4 was variously reported as 230, 170 and 125.

Table I. Calculated Limiting Equivalent Conductance and Distance of Closest Approach.*

H₂O, 25°

<u>Salt</u>	<u>Λ_o</u>	<u>$\sigma(\Lambda_o)$</u>	<u>$10^8 a$</u>	<u>$10^8 \sigma(a)$</u>
KCl	149.94	.01	3.10	.02
KCl	.94	.01	3.11	.01
KCl	.91	.02	3.16	.03
KCl	.98	.01	3.12	.06
KCl	.98	.02	2.99	.02
KCl	.99	.02	2.90	.15
KBr	151.767	.004	3.26	.01
KBr	.76	.03	3.36	.06
KBr	.77	.03	3.28	.06
KI	150.53	.01	3.86	.05
KI	.50	.03	3.53	.07
KI	.57	.03	3.67	.06

Calculations Based on the Equation

$$\Lambda = \Lambda_o - SC^{1/2} + EC\log C + JC$$

*Taken from R. L. Kay, J. Amer. Chem. Soc.,
82, 2099[1960]

A possible explanation for the difference in K_A values as proposed by Atkinson, Yokoi and Hallada was the lack of a well-defined base-line for the calculation of K_A ; that is, there was no mathematically proved theory that could define a property such as the conductance of a partially dissociated high charge type salt as if it were completely dissociated. However, since the extended Fuoss-Onsager equation had already worked well for defining the theoretical conductivity of 1-1 electrolytes, they speculated that it could also be used for symmetrical electrolytes of higher charge type. If the idea could be verified experimentally then the use of the extended equation as a base-line would be established.

The first question they had to answer was what kind of 2-2 or 3-3 salt might be unassociated. They surmised that an anion composed of single charges separated by a large inert framework would lessen the charge density such that the electrolyte would then be expected to show smaller short-range ion-ion interactions with the concomitant reduction or elimination of association. It would however retain long-range ion-ion and ion-solvent interactions which contribute to the conductance.

Atkinson, Yokoi and Hallada selected m-benzenedisulfonate (to be abbreviated BDS^{2-}) for their 2-2 salts and 1,3,6-naphthalene-trisulfonate (NTS^{3-}) for their 3-3 salts. They studied 3 BDS^{2-} salts in water at 25°C. Na_2BDS , K_2BDS , and $CuBDS$. A phoreogram (graph of Λ^{exp} vs. $C^{1/2}$) of each salt was plotted along with the respective

limiting law tangent to determine if the salt was unassociated (Figs. 2 and 3) and CuSO_4 , a known associated salt, was plotted for comparison. In addition the cross-over parameters (Ref. 9, p. 41) for CuBDS were calculated from the extended equation, interpolated from the phoreogram and compared. The results indicated that the extended equation could reproduce the experimental data. Since the Fuoss-Onsager extended equation had not been solved for unsymmetrical electrolytes the theoretical data for the potassium and sodium salts could not be calculated.

For the NTS^{3-} salts the same procedure was followed. The sodium and potassium salts were prepared and a 3-3 salt, LaNTS. The Λ_o^{exp} for LaNTS obtained from the phoreogram did not agree with that calculated, Λ_o^{FO} , using the extended equation. This result could be explained either by postulating association or by assuming that the Fuoss-Onsager equation broke down for such a high charge electrolyte in the concentration range studied.

The derivation of a new conductance equation by Murphy and Cohen⁴ provided a new theoretical curve for the investigation of such highly charged electrolytes as well as the first extended equation for treating data of unsymmetrical electrolytes. We therefore decided to attempt the synthesis of a 3-3 electrolyte which would show markedly less association compared to LaNTS and perhaps to demonstrate that this salt was indeed unassociated using the Murphy-Cohen conductance equation. Utilizing Atkinson's idea of widely separated single charges

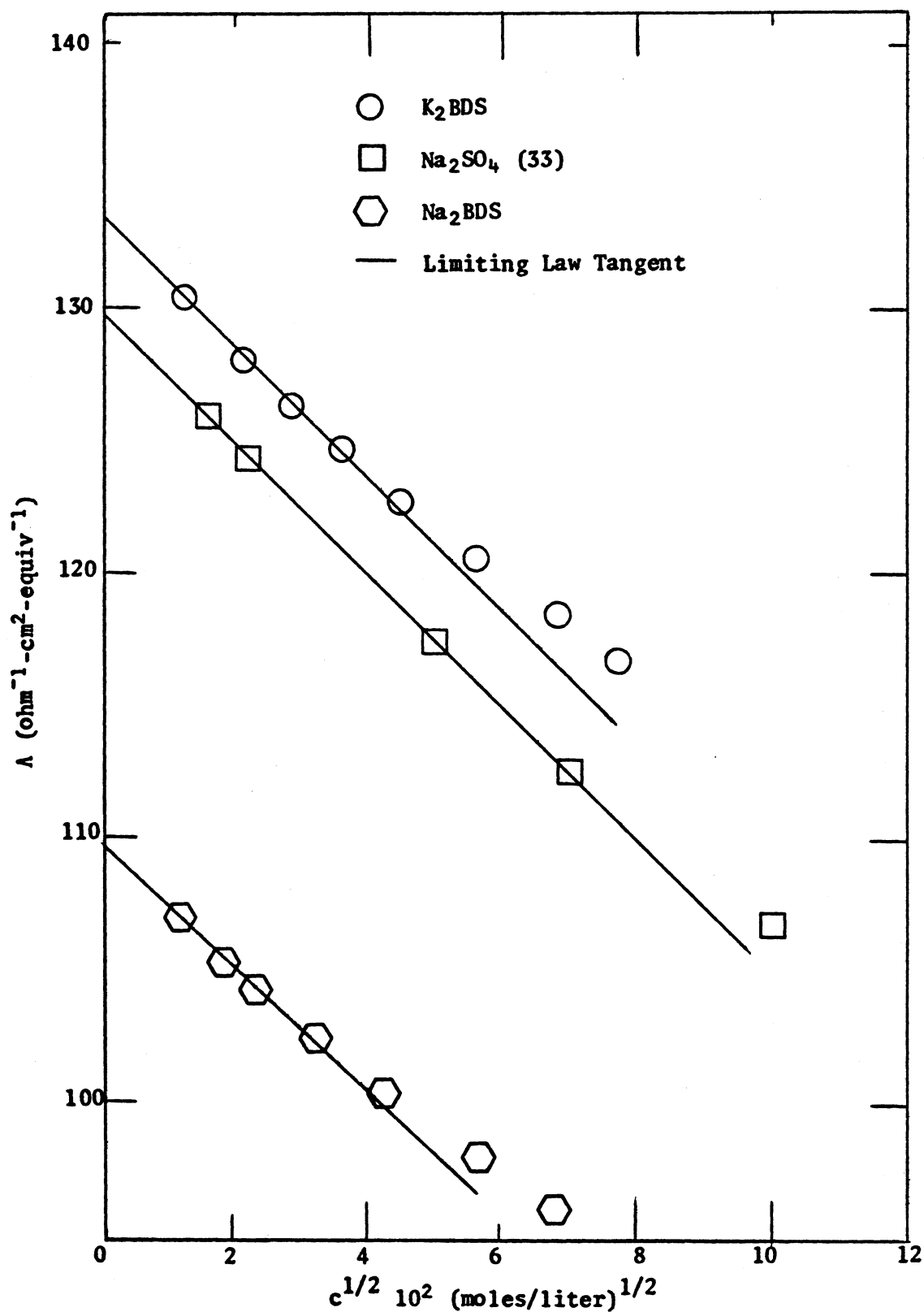


Figure 2. Phoreograms of Sodium m-Benzenedisulfonate, Potassium m-Benzenedisulfonate and Sodium Sulfate.*

*From G. Atkinson, M. Yokoi and C. J. Hallada, J. Amer. Chem. Soc., 83, 1570(1961).

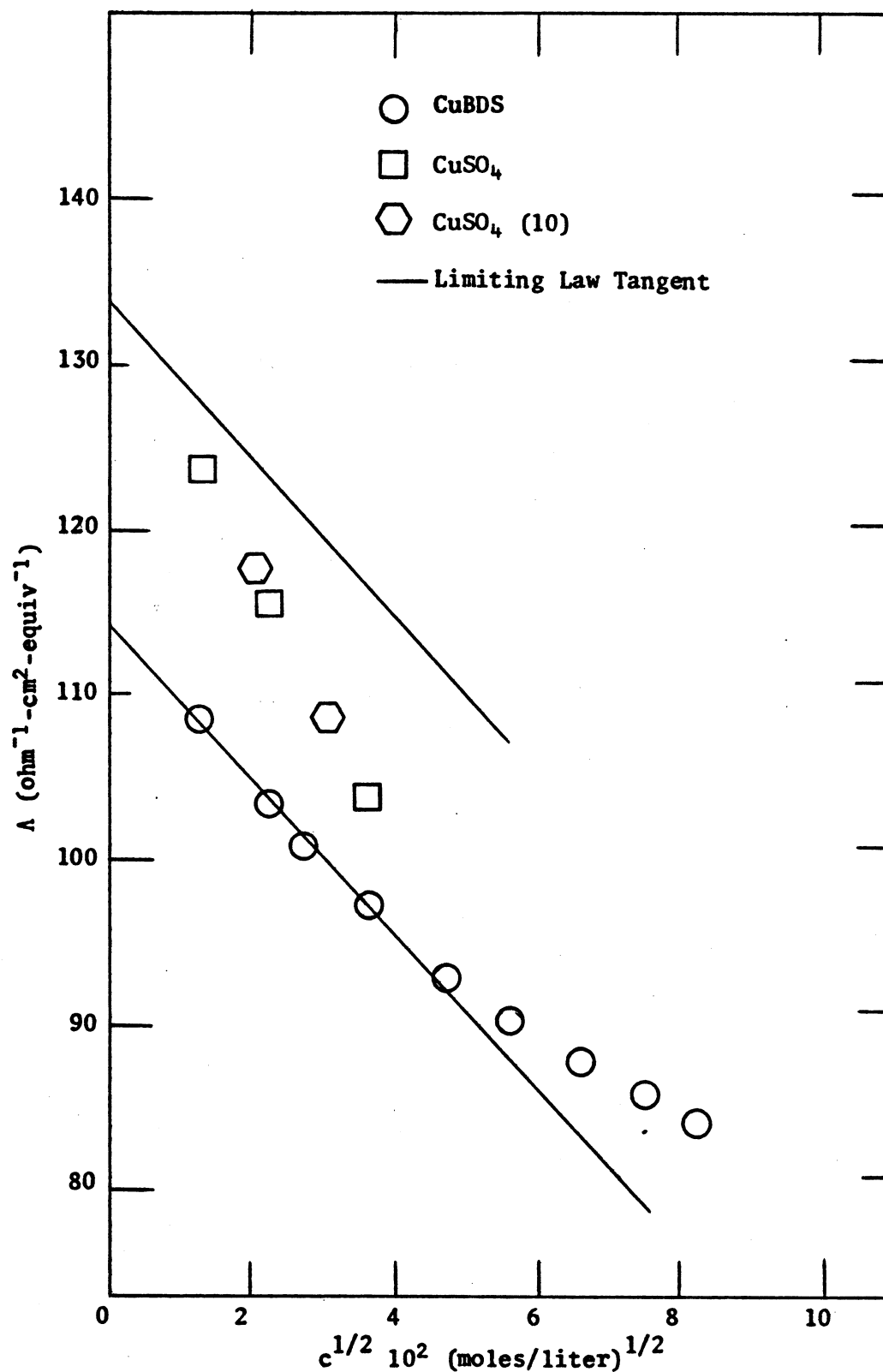


Figure 3. Phoreograms of Copper m-Benzenedisulfonate and Copper Sulfate.*

*From G. Atkinson, M. Yokoi and C. J. Hallada, J. Amer. Chem. Soc., 83, 1570 (1961).

in an inert framework, we set out to prepare Lanthanum 1,3,5-triphenylbenzene-4',4'',4'''-trisulfonate with the hope that it would prove to be the first unassociated 3-3 electrolyte reported.

STATEMENT OF PROBLEM

This research has three objectives: 1) to prepare a new aromatic trisulfonic acid, 1,3,5-triphenylbenzene-4',4'',4'''-trisulfonic acid (H_3TTS); 2) to determine the equivalent conductances of the sodium, potassium and lanthanum salts of both this acid and 1,3,5-benzenetrisulfonic acid (H_3BTS); and 3) to determine the extent of association of the symmetrical lanthanum salts using the Murphy-Cohen and Fuoss-Onsager equations in both the associated and unassociated forms.

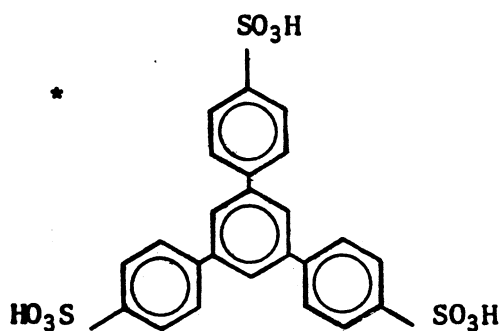
The H_3TTS was selected for synthesis with the following objectives in mind:

- 1) The acid is tribasic thus allowing for the preparation of symmetrical salts with the lanthanides.
- 2) The anion is the conjugate base of a strong acid and should not exhibit hydrolysis.
- 3) The charges on the anion are separated by a large inert hydrocarbon framework which should tend to decrease ion pairing since the charge density is lowered.

From the work of Hallada and Atkinson it seems reasonable that if triphenylbenzene ($T\phi B$) can be sulfonated in the three para positions of the terminal phenyl groups, the salts of the resulting acid should show markedly decreased ion association compared to that expected for a typical 3-3 electrolyte. The new acid structure should appear as drawn below.*

Conductivity experiments will then be done on six salts: Na_3TTS , K_3TTS , LaTTS , Na_3BTS , K_3BTS and LaBTS and data pairs, $(\Lambda^{\text{exp}}, C^{1/2})$, calculated and graphed for each salt. With proper care 6-8 data pairs are expected per salt.

Using a computer program the conductance-concentration data will be fitted to the Fuoss-Onsager and Murphy-Cohen equations in the associated and unassociated forms and solute parameters will be calculated. The program is designed to evaluate the fit internally in terms of standard deviations and least squares. A table will be drawn to show the values of the solute parameters: Λ_0 , λ_0^+ , λ_0^- , K_A (if associated), and λ_0^+ of La^{3+} calculated.



EXPERIMENTAL

Preparation of Salts

Sodium 1,3,5-Benzenetrisulfonate:¹¹ The sodium salt of 1,3,5-benzenetrisulfonic acid was prepared in the following manner. Fifty grams of m-benzenedisulfonic acid (Eastman, Item #T4147) was heated with 50 ml of 15% oleum (Fig. 4a) and 2 grams of mercury in a round bottom flask fitted with condenser and placed in a sand bath for twelve hours at 275-300°C. The reaction mixture was then carefully poured on cracked ice and the resultant solution was neutralized with CaCO_3 . The excess CaCO_3 and the CaSO_4 precipitate were removed by suction filtration and the filtrate was then treated with Na_2CO_3 (Fig. 4b) until the solution tested slightly basic. The CaCO_3 precipitate was removed by suction filtration and the filtrate after clarification with Norit was evaporated to the point where crystals began to form. The resultant sodium 1,3,5-benzenetrisulfonate (Na_3BTS) was recrystallized three times from conductivity water before use.

Potassium 1,3,5-Benzenetrisulfonate: The potassium salt was prepared from the purified sodium salt by converting the latter to the acid H_3BTS using Dowex 50W-X8 ion exchange resin (Fig. 4c) and neutralizing with either K_2CO_3 or KOH to obtain a solution of K_3BTS (Fig. 4d). Evaporation and recrystallization from conductance water followed by drying in the oven at 110° produced crystals which

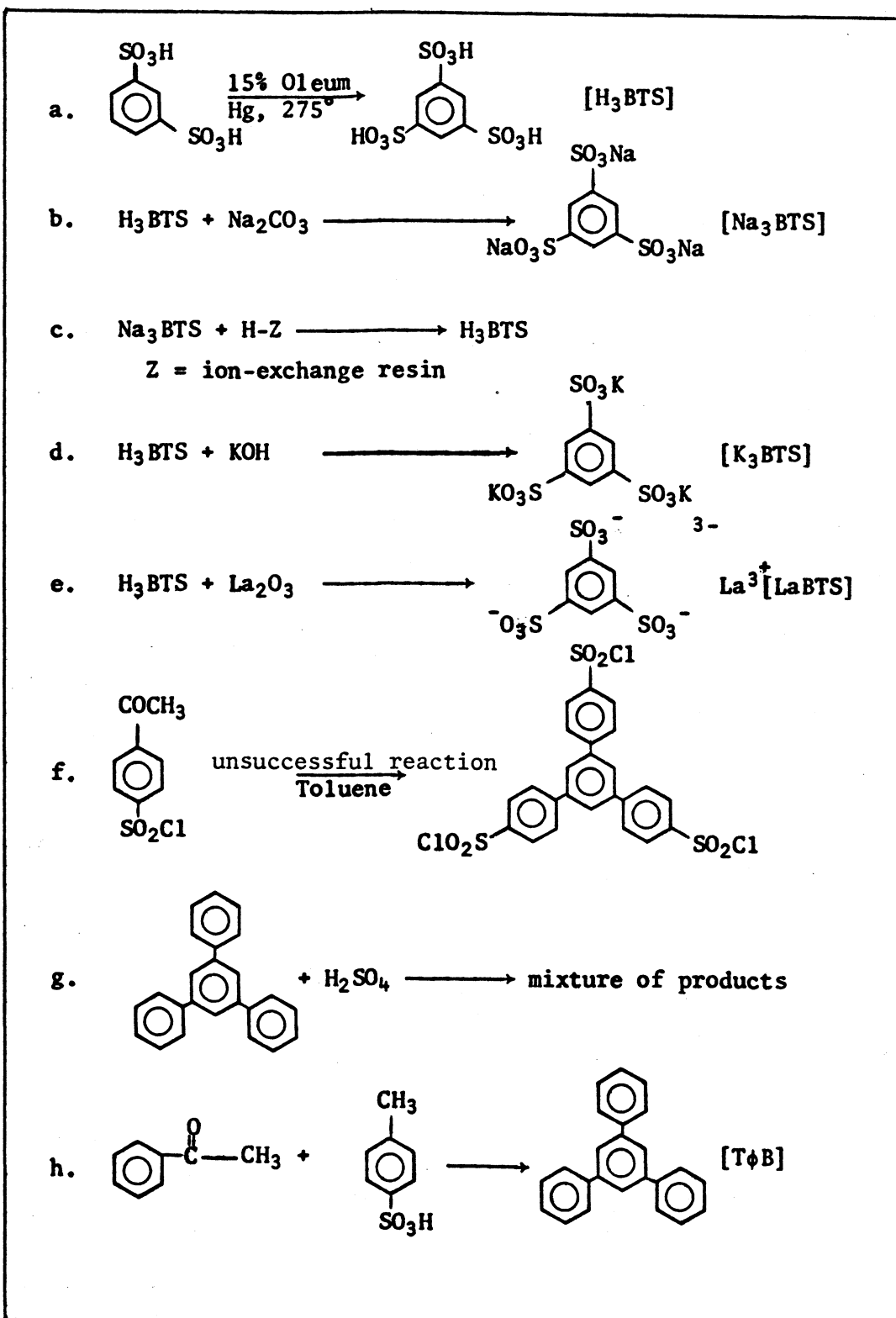


Figure 4. Reactions

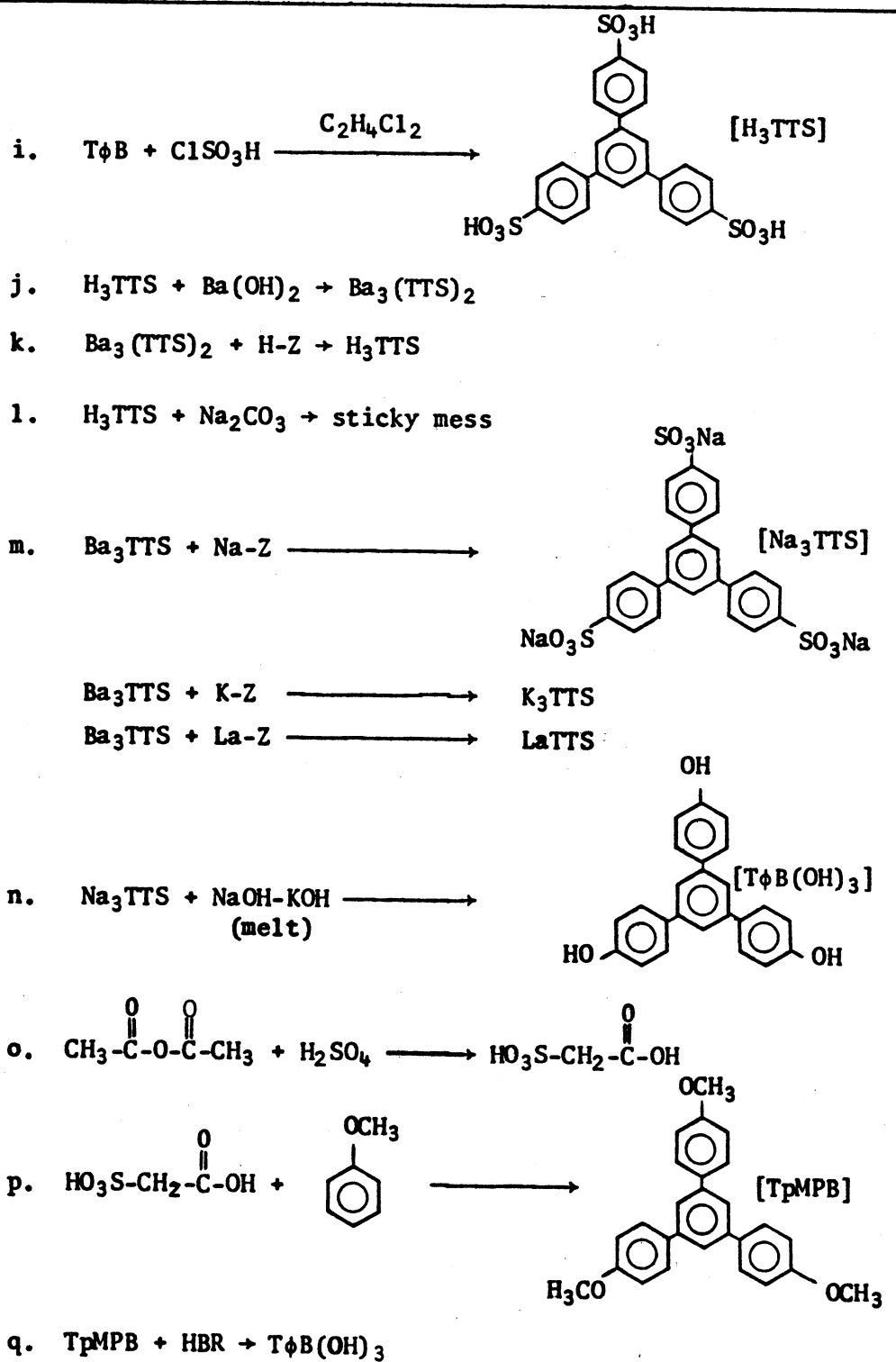


Figure 4. Reactions (Continued).

upon analysis proved to be the anhydrous K_3BTS .

Lanthanum 1,3,5-Benzenetrisulfonate: The lanthanum salt was also prepared from H_3BTS obtained by ion exchange of the sodium salt. The acid was then neutralized with a slurry of La_2O_3 (Fig. 4e). When the pH tested approximately 6 by hydriion paper the solution was filtered in a sintered glass funnel and the filtrate reduced in volume using the Roto-Vac. The salt was not recrystallized but was diluted to the desired concentration with conductance water and used immediately for the conductance run.

1,3,5-Triphenylbenzene-4',4'',4'''-trisulfonic Acid (H_3TTS):

Several attempts to synthesize H_3TTS met with difficulty. Cyclization of p-acetylbenzenesulfonyl chloride in toluene was attempted without success (Fig. 4f). Direct sulfonations of triphenylbenzene with various concentrations of sulfuric acid at different temperatures were performed, but this procedure gave a mixture of products (Fig. 4g) and posed an interesting, if not insoluble, separation problem. An easier method of preparation had to be found.

From the literature¹² it was found that: 1) chlorosulfonic acid had been shown to be an effective sulfonating agent for benzene and other aromatic compounds in chlorinated hydrocarbon solvents and 2) 1,2-dichloroethane was employed as a solvent when biphenyl was sulfonated with $ClSO_3H$ to obtain the monosulfonated product. We then decided to try sulfonating triphenylbenzene

with ClSO_3H in 1,2-dichloroethane and in chloroform.

Triphenylbenzene is produced commercially and 500 grams were obtained from Aldrich Chemical Co., Inc., Milwaukee, Wisconsin. However, this supply was quickly exhausted and we decided to prepare our own. To a 3000 ml round bottom flask were added 100 grams of p-toluenesulfonic acid, 1500 ml sulfur-free toluene and several boilerezers. The flask was then fitted with a Barrett trap and a double surface condenser and the solution was refluxed at 110°C until about 7 ml of water had been collected. The mixture was then cooled to room temperature, 600 g of acetophenone was added, and the mixture refluxed at 110° until 72-81 ml of water had been collected (Fig. 4h). On cooling white crystals of triphenylbenzene formed on the bottom of the flask. Successive recrystallizations from benzene were done until a clear supernatant could be seen. The crystals of triphenylbenzene were dried in the air and ground to a coarse powder and dried in the Roto-Vac to remove any trace of benzene. Yield is ~50%.

Based on the account of the sulfonation of biphenyl using ClSO_3H given in the literature we calculated the corresponding quantities of triphenylbenzene, ClSO_3H , and $\text{C}_2\text{H}_4\text{Cl}_2$ necessary to synthesize H_3TTS . The crude H_3TTS was prepared as follows: To a stirred solution (Fig. 4i) of triphenylbenzene (50g; .16 mole) in 600 ml of 1,2-dichloroethane or chloroform we slowly added (dropwise) a solution of chlorosulfonic acid (70g; .80 mole) in

100 ml of 1,2-dichloroethane. The excess ClSO_3H is necessary to correct for the partial hydrolysis of ClSO_3H to H_2SO_4 and HCl . The addition is done in a 1000 ml, 3-necked, round bottom flask with one neck connected to a water aspirator for control of HCl fumes. The reaction was cooled by an ice bath to reduce formation of unwanted side products, particularly sulfones. Precipitation of H_3TTS begins almost immediately. A blood red color appears as the ClSO_3H -1,2-dichloroethane solution strikes the solution of triphenylbenzene in 1,2-dichloroethane and eventually the mass of product takes on a lavender color. If CHCl_3 is used as a solvent the product is cream-colored. Completion of the reaction is assumed when the blood red color can no longer be observed on addition of the ClSO_3H -1,2-dichloroethane solution. The reaction mixture was stirred for 1 hour after completion. The precipitate was filtered in a sintered glass funnel, washed with solvent, and dried in the Roto-Vac to remove the remaining solvent. A yield was difficult to determine because the acid is exceedingly hygroscopic, however the reaction seems to be quantitative. Figure 5 shows the apparatus used in synthesizing the acid.

The H_3TTS was neutralized with a saturated solution of $\text{Ba}(\text{OH})_2$ to form moderately soluble $\text{Ba}_3(\text{TTS})_2$ (Fig. 4j). The sulfate impurity was precipitated as insoluble BaSO_4 . The slurry of $\text{Ba}_3(\text{TTS})_2$ and BaSO_4 was then filtered in a large Buchner funnel through Celite filter-aid. The filtrate was then reduced in volume in the

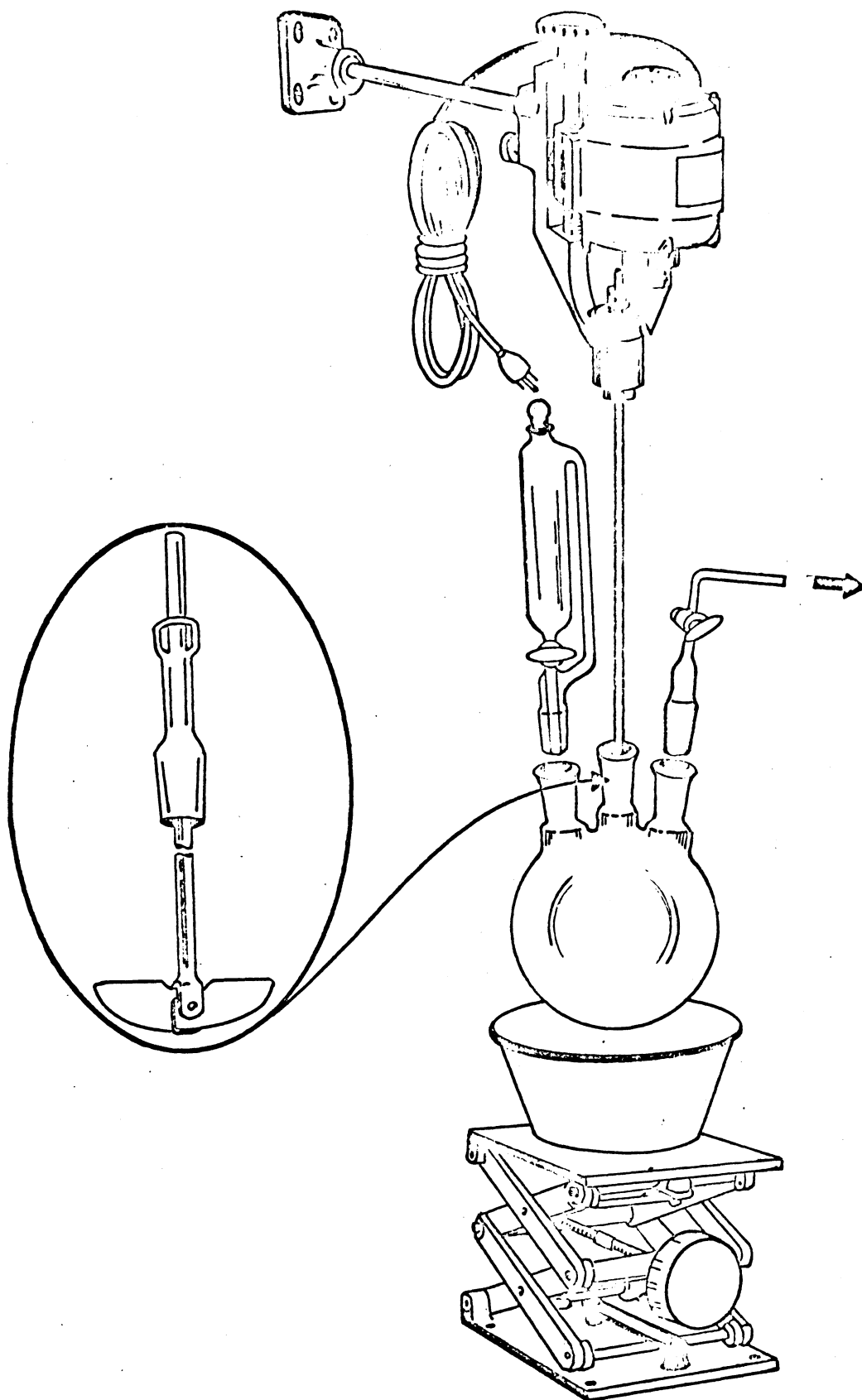


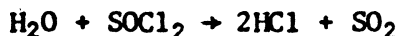
Figure 5. Apparatus for Synthesis of 1,3,5-Triphenylbenzene-4',4'',4'''-trisulfonic Acid.

Roto-Vac until $\text{Ba}_3(\text{TTS})_2$ just began to precipitate, warmed on a steam cone to re-dissolve the salt, and set aside for crystallization. The solid white $\text{Ba}_3(\text{TTS})_2$ was recrystallized from deionized water until the salt solution gave negative Cl^- tests with .2N AgNO_3 and then recrystallized 3 times from conductance grade water.

A later search of the literature showed the value of using ClSO_3H as the sulfonating reagent.

Benzene and other aromatic compounds can be sulfonated with concentrated H_2SO_4 , but as the concentration of the water increased, during the reaction, the rate of sulfonation steadily decreases, the rate being inversely proportional to the square of the water concentration. Reaction ceases when the acid concentration reaches a level characteristic of each compound, in the case of benzene about 78% H_2SO_4 .¹³

The second approach for completing sulfonation involves a chemical method for removing the water as formed (58) by the following reaction:¹³



Similar information was reported by Gilbert.¹⁴

Sodium, Potassium and Lanthanum Salts of 1,3,5-Triphenyl-benzene-4',4'',4'''-trisulfonic Acid: Initially, 3-5 grams of the barium salt were ion-exchanged to the acid (Fig. 4k) form and the acid neutralized by adding dropwise a saturated aqueous solution of Na_2CO_3 or NaOH (Fig. 4l). The pH was monitored with hydron paper and the neutralization considered complete at a pH of 6. After filtering in a Buchner funnel, the filtrate volume was reduced by Roto-Vac. However, a soupy, sticky mess formed instead

of white crystals. It was concluded that the sodium salt was too hygroscopic to crystallize. Similar results were obtained with the potassium salt. For the lanthanum salt the acid was neutralized with an aqueous slurry of lanthanum oxide and again a sticky soup formed.

In view of the results above, it was decided to prepare stock salt solutions by ion-exchange. Weighed samples of $\text{Ba}_3(\text{TTS})_2$ were dissolved in a minimum amount of conductance water and introduced into a column of Dowex 50W-X8 ion-exchange resin (Fig. 4m). To form the appropriate salt the resin was regenerated with 2M NaCl, KCl, or LaCl_3 .

Weighed aliquots of each stock solution were ion-exchanged to the acid and analyzed by potentiometric titration with standardized NaOH. For pH measurements we used a Corning Model 12 pH Meter and for titrant delivery a Metrohm Piston Burette.

Characterization of H_3TTS : Once a good supply (100 g) of the purified Ba salt had been collected several approaches were employed to establish its identity: 1) melting point comparison, 2) infrared spectra comparison, and 3) elemental analysis.

1,3,5-Tri(p-hydroxyphenyl)benzene Derivative: A standard derivative of a sulfonic acid is the phenol, which is prepared by alkali fusion of a salt of the acid (Fig. 4n). Ten grams of the Ba salt had previously been converted to the Na salt by ion-exchange. The salt was ground to a powder with mortar and

pestle and 1 gram was added to a melt of 5 grams of NaOH and 5 grams of KOH in a crucible. Heating was done by bunsen burner. After a brown solution was obtained the crucible was set aside to cool to room temperature. When cool several milliliters of water were added to cover the precipitate and it was allowed to stand several days. The solution was then carefully acidified with concentrated HCl and filtered in a sintered glass funnel. The solid material was then recrystallized from ethanol triturated with H₂O. The slightly brown crystals gave a melting point of 228-229°C indicating the derivative, 1,3,5-tri(p-hydroxyphenyl)-benzene.¹⁵

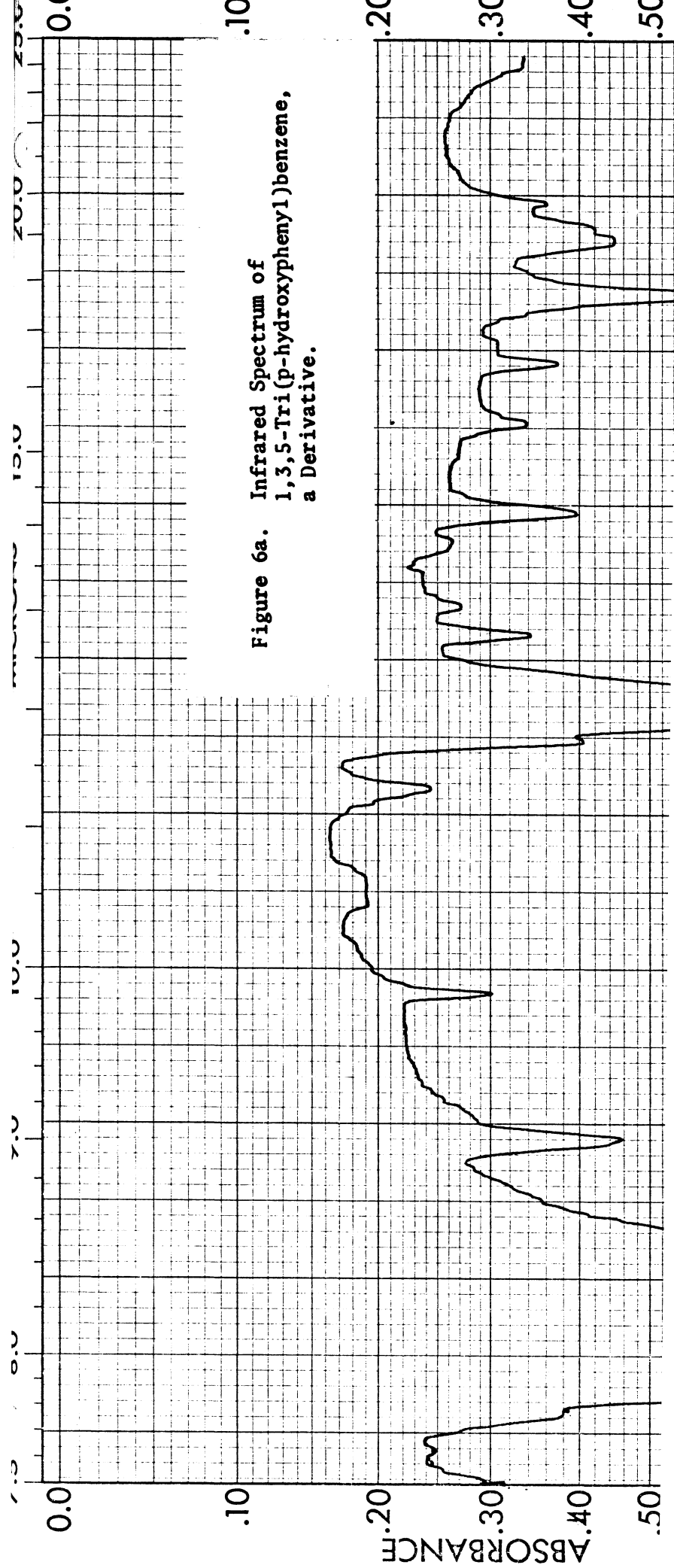
As a further check it was decided to prepare 1,3,5-tri-(p-hydroxyphenyl)benzene by a known method and compare its melting point and infrared spectrum with those of the derivative. The substance is prepared from 1,3,5-tri(p-methoxyphenyl)benzene, which was prepared according to a method outlined in the literature.

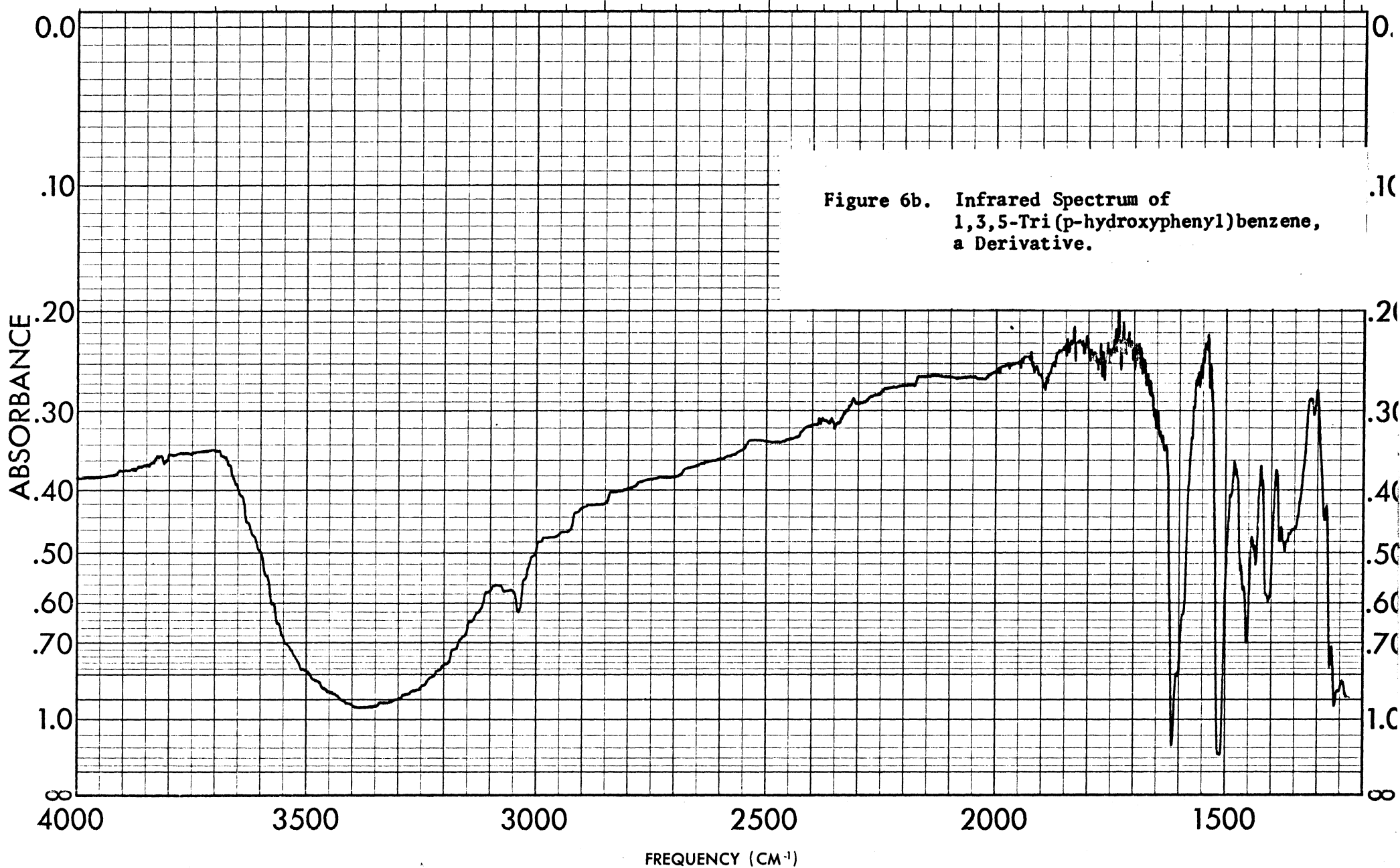
1,3,5-Tri(p-methoxyphenyl)benzene:¹⁵ To 100 ml of dry acetic anhydride in a 200 ml, two-neck, round bottom flask was added slowly 30 ml of conc. H₂SO₄. Two layers formed. Care must be taken to keep the temperature below 50°C (Fig. 4o). The flask was fitted with a thermometer and an air condenser and stirring was done by magnetic stirrer. The flask was partially immersed in an ice bath to provide cooling. Once the H₂SO₄ had been added and the two layers had disappeared, the solution was warmed to 75-80°C

by heating mantle and refluxed for several hours, care being taken to prevent the temperature from rising above 80°C. After refluxing, the solution was cooled to room temperature and 30 ml of anisole was added (Fig. 4p) while keeping the flask in the ice bath. Two layers formed. The temperature was not allowed to rise above 45°C. When the two layers disappeared, the solution was allowed to stir gently at 45-50°C for 24 hours. The solution was set aside to cool to room temperature and when a solid mass formed, 150-180 ml of pure ethanol was added and the solution allowed to stand for 1 day. The alcohol first dissolved the crystal mass which then recrystallized on cooling in an ice bath. The solid mass was then filtered in a Buchner funnel and the crystals dissolved in a minimum amount of boiling ethanol. The resulting solution was triturated with water and set aside for crystallization. Colorless, needle shaped crystals gave a melting point of 143-144.5°C (uncorr.) compared with 142° for the literature value. Yield: 33%. Subsequent attempts to prepare the compound met with difficulty and only once in nine times did we produce the desired product.

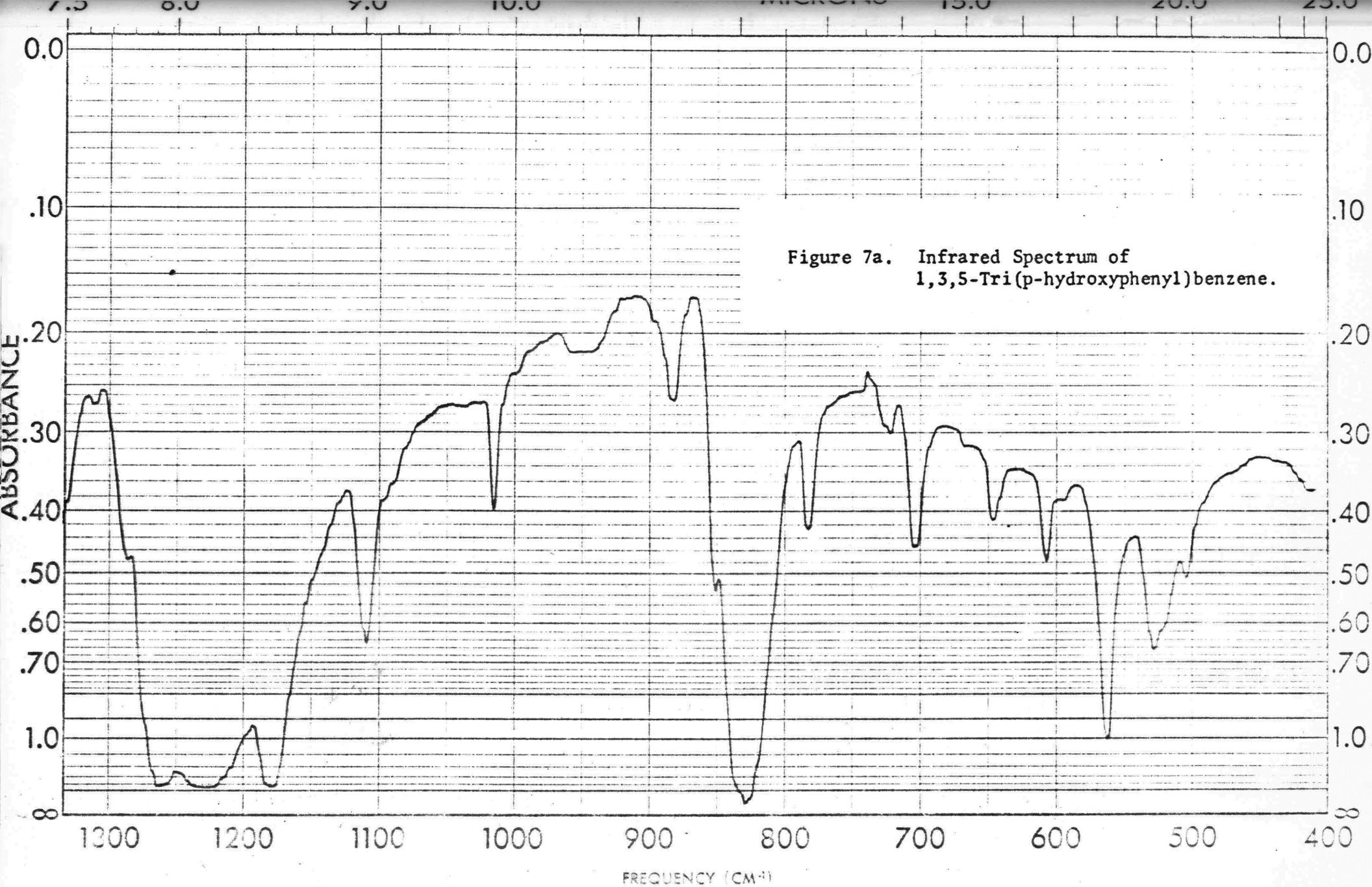
1,3,5-Tri(p-hydroxyphenyl)benzene: This compound was prepared as follows: 3 grams of the recrystallized 1,3,5-tri-(p-methoxyphenyl)benzene were treated with 46 ml of conc. HBr (Fig. 4q) in a 100 ml, 3-necked, round bottom flask fitted with a condenser and thermometer. Stirring was done by magnetic stirrer and heating by heating mantle. The solution was refluxed at 125°C

Figure 6a. Infrared Spectrum of
1,3,5-Tri(p-hydroxyphenyl)benzene,
a Derivative.

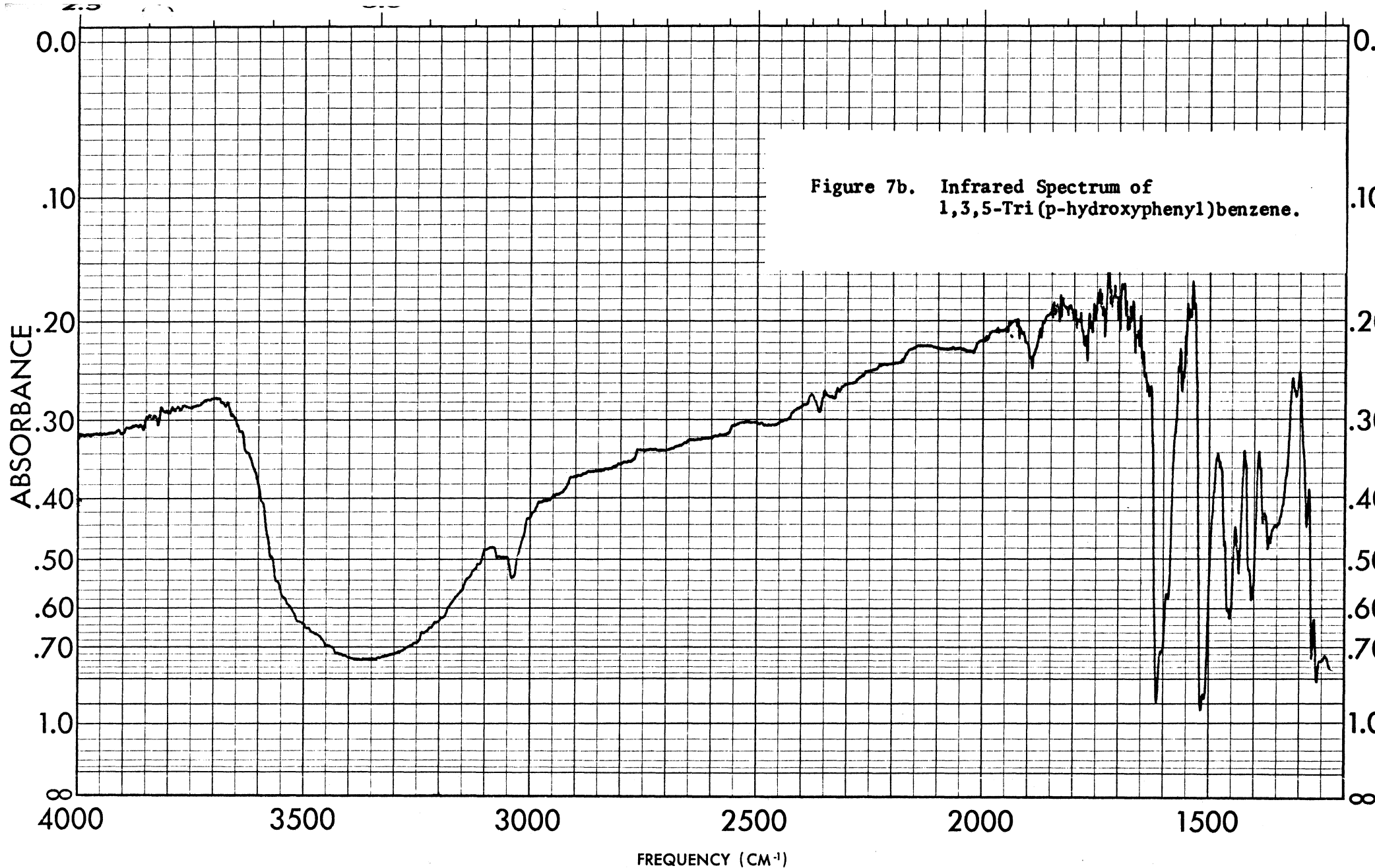




SAMPLE <u>Unk 'Phenol'</u>	CURVE NO. _____	SCAN SPEED _____	OPERATOR <u>SW</u>
<chem>Oc1ccc(cc1)-c2ccc(O)cc2</chem>	CONC. _____	SLIT _____	DATE <u>3/14/71</u>
ORIGIN _____	CELL PATH _____	REMARKS _____	
SOLVENT <u>KBr pellet</u>	REFERENCE _____		



SAMPLE <u>Known Phenol</u>	CURVE NO. _____	SCAN SPEED _____	OPERATOR <u>Joe</u>
ORIGIN _____	CONC. _____	SLIT _____	DATE <u>5/15/51</u>
SOLVENT <u>KBr pellet</u>	CELL PATH _____	REMARKS _____	
REFERENCE _____			



SAMPLE <u>Known Phenol</u>	CURVE NO. _____	SCAN SPEED _____	OPERATOR <u>SW</u>
ORIGIN _____	CONC. _____	SLIT _____	DATE <u>3/12/71</u>
SOLVENT <u>KBr. Pellet</u>	CELL PATH _____	REMARKS _____	
	REFERENCE _____		

for about 2 days and set aside to cool. A brown precipitate formed, was filtered in a sintered glass funnel, washed with water, and recrystallized from pure ethanol 3 times. The product melted at 229°C, the same value as reported in the literature.

Samples of the 1,3,5-tri(p-hydroxyphenyl)benzene from the derivative prepared by alkali fusion and from the above synthesis were used in the formation of KBr pellets and the infrared spectrum of each sample was taken using a Perkin-Elmer Model 337 Grating Infrared Spectrophotometer. Figures 6a and 7a are the IR spectra of the derivative and the known, respectively, for the 400-1300 cm^{-1} region. Figures 6b and 7b are the corresponding spectra for the 1400-4000 cm^{-1} region. Careful examination showed the spectra for the derivative and the known to be almost perfect overlays, peak for peak, for a given region and identification of peaks was deemed unnecessary, the overlay character being assumed conclusive.

It was then decided to analyze the barium salt, $\text{Ba}_3(\text{TTS})_2$, by cation-exchange. Two grams of $\text{Ba}_3(\text{TTS})_2$ were dissolved in a minimum amount of water and ion-exchanged to the acid, H_3TTS , using Dowex 50W-X8 regenerated with 2N HCl. An equivalent weight of 259.5 grams was found to be 9 grams higher than the theoretical value, 250 grams, which suggested the possibility of there being 3 waters of hydration per mole of barium salt.

As a final check a dried sample of the barium salt was sent to Galbraith Laboratories, Inc., Knoxville, Tennessee for elemental

analysis. The results are shown in Table II with the theoretically calculated analysis based on three waters of hydration. In addition, the analysis based on our cation-exchange is also shown.

Table II. Elemental and Cation-Exchange Analyses.

	<u>C</u>	<u>H</u>	<u>O</u>	Per Cent		<u>Equiv. Wt. Ba₃(TTS)₂</u>
				<u>S</u>	<u>Ba</u>	
Theoretical Analysis	37.11	2.33	21.63	12.38	26.52	258.8
Elemental Analysis	37.04	2.70	--	12.19	--	--
Cation-Exchange	--	--	--	--	--	259.5

Purification of Water

Conductance grade water was initially obtained by passing the house deionized water through two Illinois Water Treatment Model I Research Cartridge Deionizers. This "polishing" technique produced water with a specific conductance of $1 \times 10^{-6} \text{ ohm}^{-1}\text{-cm}^{-1}$ and was used for recrystallization of all salts and for a complete set of conductance runs.

Later it was discovered that this conductance water was contaminated with iron hydroxide and the "polishing" technique for purifying the house DI water was discontinued. Conductance water was then collected from an all glass Corning AG-1b water distillation apparatus using the house deionized water as feed stock to limit scaling.

Conductance Measurements

Equipment: Resistance measurements were made with a Beckman Model RC-18A Conductivity Bridge. The bridge was modified after the first set of conductance runs so that the tenths decade was replaced by a variable, 1-ohm, 50 watt, Model J, Series A, Ohmite resistor which extended the accuracy of our resistance readings to $\pm .02$ ohm. A 10 gallon, glass lined, styrofoam insulated aquarium, 3 feet long by 1 foot wide by 2 feet deep filled with transformer oil, served as a constant temperature bath. Heating was regulated by a Sargent Thermonitor Model ST thermostat (sensitivity, $\pm .002^{\circ}\text{C}$). Cooling was accomplished by using a Forma Scientific Model 2095 Refrigerated and Heated Bath and Circulator to pump chilled water (20°C) through a coil of copper tubing on the floor of the bath. The transformer oil was stirred by a Lightnin Model F Mixer. In the bottom of the bath two magnetic stirrers were located to provide stirring for the conductance cells. Solvent and solution weighings were done with a Sartorius Model 2254 top loading balance and salt and weighed solution additions were weighed on a Mettler Model H20 semi-micro balance.

Cells: Two Beckman Model CEL-3L-025, 500 ml Erlenmeyer type flasks with electrode compartments and side arms (Kraus-type cells) were used for the conductance measurements. The electrodes were etched platinum disks with back flared rims.

To determine the cell constants, as outlined in the literature,^{16,17,18} successive weighed amounts of a KCl stock solution were added to each cell, which initially contained a weighed amount of water. Equilibration of each point was indicated by a constant resistance reading and the solution measured at 1 and 3 KHz. The KCl stock solution was prepared by dissolving a weighed sample, 1 to 1.2 grams, of the primary standard KCl (Anachemia Ltd., Montreal) in enough solvent to give a solution weight of 475-500 grams. The concentrations were then calculated correcting all weights to vacuo and the equivalent conductance calculated using the Fuoss⁶ equation:

$$\Lambda = 149.93 - 94.56C^{1/2} + 58.74C\log C + 198.4C$$

where C is the molar concentration of KCl.

C is calculated as follows:

$$C[\text{moles/liter}] = \frac{\sum G_i \times \bar{C} \times \rho \times 1000}{[\sum G_i + G_{\text{solv}}] \times 1.001043}$$

where $\sum G_i$ is the sum of the masses of the weighed additions of stock KCl solution in grams; G_{solv} is the mass in grams of water in the cell initially; ρ , the density of water at 25°C, is assumed to be the density of the solution, an assumption applied to all solutions in subsequent calculations; and \bar{C} is the concentration of the stock KCl solution,

$$\bar{C}[\text{moles/gram solution}] = \frac{\text{wt. KCl} \times 1.0004714}{74.55 \times \text{wt. soln.} \times 1.001043}$$

where wt. KCl is the mass in grams of KCl, wt. soln. is the mass in grams of KCl stock solution, and 1.0004714 and 1.001043 are correction factors for the buoyancy of air for KCl and water, respectively.

The equivalent conductance by definition is:

$$\Lambda = \frac{1000\kappa}{N}$$

and $\Lambda_{\text{solute}} = \frac{1000\kappa_{\text{solute}}}{N}$

Furthermore, by definition:

$$\kappa = \frac{k_{\text{cell}}}{R}$$

and $\kappa_{\text{solute}} = \frac{k_{\text{cell}}}{R_{\text{solute}}^{\infty}}$

$$\therefore k_{\text{cell}} = \frac{\Lambda_{\text{solute}} N R_{\text{solute}}^{\infty}}{1000}$$

Graphs of k_{cell} vs. $10^5 \kappa_{\text{soln}}$ were then drawn and we expected to see a linear relation, however this did not happen (Fig. 8). Numerous attempts were unsuccessful and in addition even the calibration graphs were not entirely reproducible for the different runs.

In an effort to solve the problem of non-constant "cell constants" we first looked at the graph of k_{cell} versus $10^5 \kappa_{\text{soln}}$. In the higher concentration regions k_{cell} is apparently constant and therefore we assumed that the real problem is associated with the low concentration region. In view of this assumption and the

behavior of the graph we concluded that the cell constant in the low concentration regions was lower than it should be (This may seem apparent from the graph, however it is also possible that the high concentration points should really be lower due, perhaps, to polarization; but, this seems unlikely.).

Assuming the cell constant is low, it is necessary to consider what affects the cell constant. By definition:

$$k_{\text{soln}} = \frac{k_{\text{cell}}}{R_{\text{msoln}}^{\infty}}$$

and immediately it is obvious that if C and/or $R_{\text{msoln}}^{\infty}$ (derived from R measured) are low then k_{cell} will be low. Almost as quickly, variations in C were ruled out since the KCl is weighed to $\pm .0002$ grams accuracy and the salt solution is weighed to $\pm .005$ grams in 500.000 grams, unless the primary standard was contaminated, which seemed improbable. Thus we concluded that the cell constant was low because the solution resistance was low in the low concentration regions.

The problem then became one of trying to think of all factors which might lower the resistance in the low concentration range but whose affects would be masked in the higher concentration range and testing these hypotheses. Immediate factors which we thought might lower the resistance are: 1) dirty cells, 2) electrode shape, 3) degree of platinization of electrodes, and 4) electrode surface, shiny as opposed to etched.

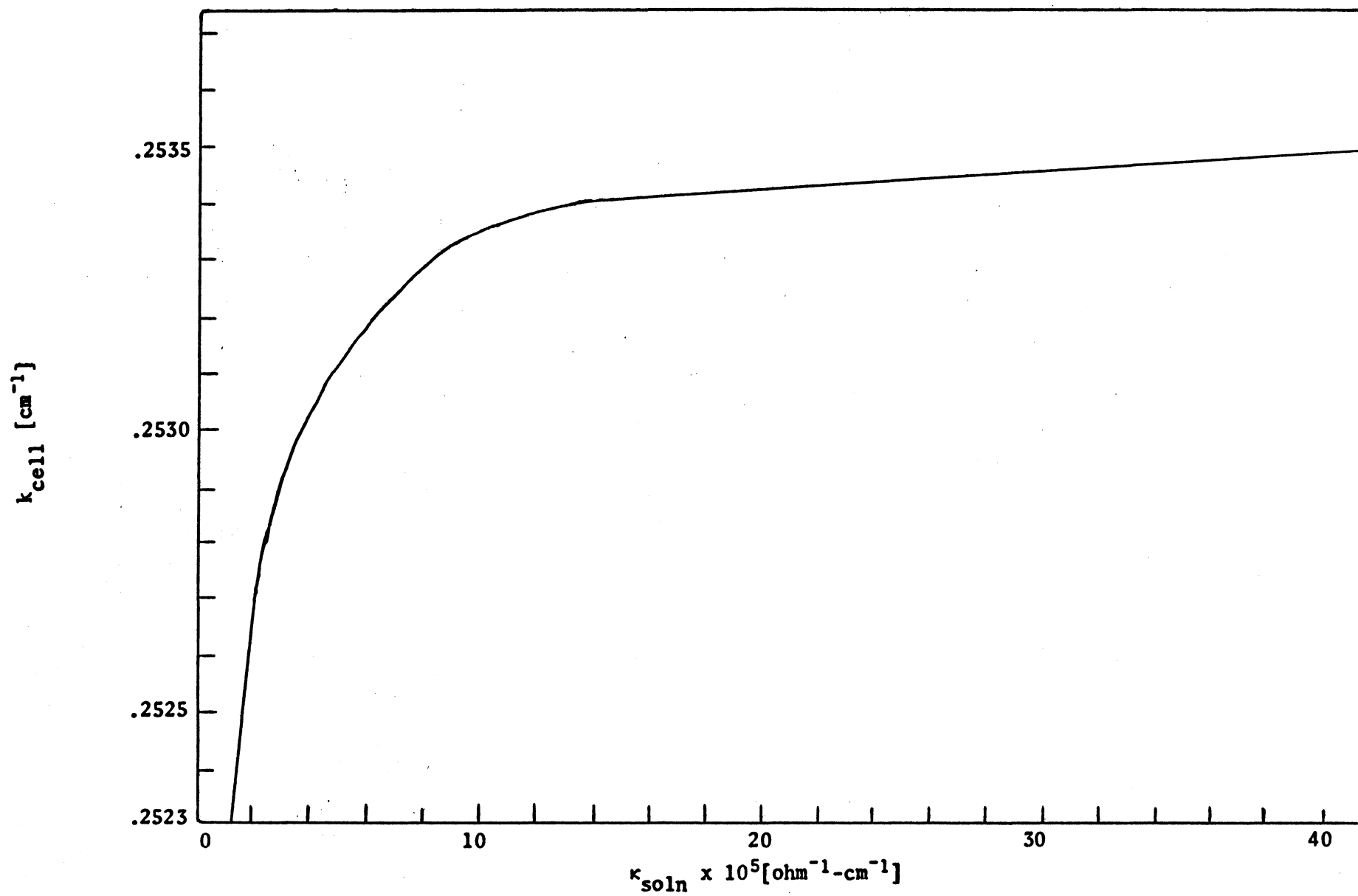


Figure 8. Cell Calibration.

In the first case cleaning was done with detergent and then with alcoholic-KOH. In one instance another researcher achieved outstanding results with this technique but attempts to repeat met with the "normal", non-constant behavior. In the second, third and fourth cases we used a different set of conductance cell with flat, shiny electrodes and varying degrees of platinization. The only difference seemed to be a marked decrease in the internal capacitance of the cell with increasing degrees of platinization.

In the course of this work we discovered that co-axial leads cause high external capacitance. We therefore changed to single separate leads as a matter of convenience.

Other ideas tested include: using N_2 - atmosphere to eliminate CO_2 - H_2O equilibrium and ionization contribution to the conductivity; varying water levels in the cell at the start of the run; using a Jones bridge to measure resistance at 1, 2, 3, 5, and 10 KHz; and doing conductance runs in a water bath. None of these ideas changed the general behavior of the "cell constant", although markedly high solvent resistances were obtained under an N_2 atmosphere and serious capacitance problems developed with the water bath.

The last area to be investigated involved the constant temperature bath. Three things were tried: 1) grounding all metal parts of the bath to a copper sheet, 2) wrapping the cells in aluminum foil, and 3) setting up a Faraday shield. The reason for

trying these approaches stems from an experiment in which we attached the bridge leads to the electrodes of different cells in the oil bath. Normally, one would expect to see an infinite resistance. However, a measurable resistance was obtained and suggested the possibility of "cross-talk" between the cells.

The first two approaches did not yield especially different results from past work, however the Faraday shield built of copper sheet seemed to give different results indicating perhaps that at least we were on the right track in solving this problem.

However, a cell constant was necessary and hence, was determined using the appropriate calibration graph of the cell used for the conductance measurements. To determine the "cell constant" for a given concentration point an interative technique was used in which a value close to the expected cell constant was selected and divided by R_{msoln}^{∞} to get κ_{soln} , then a new k_{cell} was interpolated from the calibration graph and the cycle repeated until κ_{soln} converged. Data sets were then compiled such that for each concentration there was an appropriate cell constant. A typical set of data is shown in Table III.

Table III. Cell Constant Variation with Concentration.

k_{cell}	$C \times 10^4$
.25195	2.4506
.25273	4.6313
.25294	8.2967
.25315	14.0865
.25334	25.0015
.25340	40.8432

Preparation of Solutions: The salt solutions whose resistances were measured were made up in the conductance cell by a weight dilution method. The conductance cells were weighed, filled with approximately 300 ml of conductance water and weighed again to determine weight of water in the cell. Once the water had equilibrated (as indicated by constant resistance) the resistance was recorded and successive additions of stock salt solution were made using a 30 ml Lab-Crest weight burette (Fischer & Porter Co.) each time allowing the solution to equilibrate. Solvent and solution resistances were measured at 1 and 3 KHz and then extrapolated algebraically to infinite resistance versus $1/\omega$.

By using the weight dilution method all resistance measurements for a single run were completed in about 12 hours with the last concentration points (#5, 6, 7, 8) coming to equilibrium quite rapidly (15-30 minutes). Since a run is completed in a short time the corrections for solvent conductance are specific for that run, not an average for several different days. Specificity of the solvent corrections is important for dilute solutions where the solvent contributes a large portion of the measured resistance.

Much time was expended in trying to solve the cell constant problem, thus, the reported results are for single conductance runs for each of the six salts. This procedure seemed justified since we had already done crude measurements of all six salts and knew approximately what kind of behavior to expect from each.

RESULTS

Treatment of Raw Data

For each conductance run of the six salts the data include: weight of water initially in the conductance cell and its resistance at 1 and 3 KHz, weight of stock salt solution added and the resistance of each cell solution at 1 and 3 KHz, and from the potentiometric titration of the cation-exchanged stock salt solution the weight of stock solution titrated and the (pH, ml standard NaOH) pairs. Data sets of $[\Lambda^{\text{exp}}, C]$ were then calculated. Figures 9 and 10 show typical data sheet format.

The concentrations of the stock salt solutions were determined graphically by plotting pH versus ml and $\Delta\text{pH}/\Delta\text{ml}$ versus $\bar{\text{ml}}$ (average milliliters). From the graphs the mls of standard NaOH at the equivalence point were interpolated and the concentration of the stock solution calculated in terms of moles of solute per gram of solution with all weights corrected to vacuo.

$$\bar{C}[\text{moles/gram soln}] = \frac{V_{\text{NaOH}} \times N_{\text{NaOH}}}{3 \times 1000 \times G_1 \times 1.001043}$$

where V_{NaOH} is the volume of standardized NaOH in milliliters at the equivalence point, 3 stands for 3 equivalents/mole, 1000 is a conversion factor, 1000 ml/liter, G_1 is the grams of stock salt solution titrated for Na_3BTS , K_3TTS , or LaTTS , etc., and N_{NaOH} is the normality of the standardized base, and is calculated as follows:

Date:

Salt Measured:

Cell #

E1

E2

Weight Cell, Stirrer, and Water(g)

Weight Cell and Stirrer(g)

Weight Water(g)

If Cell Constant Run:

Weight weighing bottle, cap, and KCl(g)

Weight weighing bottle and cap(g)

Weight KCl(g)

Weight 500 ml Volumetric flask magnetic stirrer, and KCl solution(g)

Weight 500 ml Volumetric flask and magnetic stirrer(g)

Weight KCl stock solution(g)

If Salt Run: Concentrations determined by potentiometric titration (Fig. 10)

Solvent Resistance (30K in parallel):

Time Cell E1

Cell E2

1KHz: ____ Ω 3KHz: ____ Ω 1KHz: ____ Ω 3KHz: ____ Ω

Addition #1

Initial wt. burette & soln.(g)

Final wt. burette & soln.(g)

Weight soln. added(g)

Figure 9. Typical Data Sheet.

$$N_{\text{NaOH}}[\text{equiv/liter}] = \frac{G_{\text{KHP}} \times 1.0005914 \times 1000}{V_{\text{NaOH}} \times 1.001043 \times 204.23}$$

where G_{KHP} is the mass of potassium hydrogen phthalate in grams, 1.0005914 is the correction to vacuo for KHP, 1000 is a conversion factor, 1000 ml/liter, V_{NaOH} is the volume in milliliters of sodium hydroxide stock solution at the equivalence point, and 204.23 is the equivalent weight of KHP.

Values of Λ^{exp} and C are calculated as follows:

Concentration: The concentration of the salt solution in the conductance cell is given by,

$$C[\text{moles/liter}] = \frac{\sum G_i \times \bar{C} \times \rho \times 1000 \times 1.001043}{[\sum G_i + G_{\text{solv}}]}$$

where $\sum G_i$ is the sum of the mass of stock salt solution in grams added to the cell and G_{solv} is the mass of water in the cell initially.

Resistance: The resistances at infinite frequency for both water, solutions, and solutes were found by algebraically extrapolating the measured resistances at 1 and 3 KHz versus $1/\omega$. For the solvent resistance it was necessary to use $30\text{K}\Omega$ in parallel with the water resistance because the resistance was too large for the bridge to measure directly. The water resistance is determined as follows: we first extrapolate the measured resistances to infinite frequency,

$$\frac{R_{\text{msolv}}^{3\text{KHz}} - R_{\text{msolv}}^{1\text{KHz}}}{1/3\text{KHz} - 1/1\text{KHz}} = \frac{R_{\text{msolv}} - R_{\text{msolv}}^{1\text{KHz}}}{1/\infty - 1/1\text{KHz}}$$

$$R_{\text{msolv}}^{\infty} = R_{\text{msolv}}^{1\text{KHz}} + 1.5[R_{\text{msolv}}^{3\text{KHz}} - R_{\text{msolv}}^{1\text{KHz}}]$$

then, correct for the 30K Ω in parallel,

$$\frac{1}{R_{\text{msolv}}^{\infty}} = \frac{1}{R_{\text{solv}}^{\infty}} + \frac{1}{30\text{K}}$$

$$R_{\text{solv}}^{\infty} = \frac{30\text{K} \times R_{\text{msolv}}^{\infty}}{30\text{K} - R_{\text{msolv}}^{\infty}}$$

The solution resistances are calculated in a similar way;

first the measured resistances are extrapolated to infinite frequency,

$$\frac{R_{\text{msoln}}^{1\text{KHz}} - R_{\text{msoln}}^{3\text{KHz}}}{1/1\text{KHz} - 1/3\text{KHz}} = \frac{R_{\text{msoln}}^{1\text{KHz}} - R_{\text{msoln}}^{\infty}}{1/1\text{KHz} - 1/\infty}$$

$$R_{\text{msoln}}^{\infty} = R_{\text{msoln}}^{1\text{KHz}} - 1.5[R_{\text{msoln}}^{1\text{KHz}} - R_{\text{msoln}}^{3\text{KHz}}]$$

then, correcting for the solvent resistance, the solute resistance is calculated as follows:

$$\frac{1}{R_{\text{msoln}}^{\infty}} = \frac{1}{R_{\text{solute}}^{\infty}} + \frac{1}{R_{\text{solv}}^{\infty}}$$

$$R_{\text{solute}}^{\infty} = \frac{R_{\text{solv}}^{\infty} \times R_{\text{msolute}}^{\infty}}{R_{\text{solv}}^{\infty} - R_{\text{msolute}}^{\infty}}$$

Equivalent Conductance: The experimental equivalent

conductance is given by,

$$\Lambda^{\text{exp}} = \frac{1000\kappa_{\text{solute}}}{N}$$

$$\text{but } \kappa_{\text{solute}} = \frac{k_{\text{cell}}}{R_{\text{solute}}^{\infty}}$$

$$\Lambda^{\text{exp}} = \frac{1000 k_{\text{cell}}}{NR_{\text{solute}}^{\infty}}$$

The data sets, $[\Lambda^{\text{exp}}, C]$, are shown in Tables IV and V for the six salts measured. It was assumed that factors such as, changes in CO_2 content of the solvent, hydrolysis, or $[\text{H}^+]$ in the solvent due to $\text{CO}_2\text{-H}_2\text{O}$ equilibrium do not affect our measurements significantly.

Application of Data to Theory

Experimental Phoreograms: Combining Λ^{exp} , calculated from the equation, $\Lambda = \frac{1000\kappa}{N}$, with the square root of the concentration, $C^{1/2}$, data pairs $[\Lambda^{\text{exp}}, C^{1/2}]$ were formed and phoreograms for all six salts were plotted (Figures 11 through 16). From these graphs values of Λ_0 , were estimated (Table VI). Normally, the limiting law tangent for each salt would now be plotted to determine whether the salt is associated or unassociated, however our interest is in the ability of the Murphy-Cohen equation and the Fuoss-Onsager extended equation to fit the data and, therefore, we proceeded directly to this problem.

Theoretical Fit Using the Murphy-Cohen Equation: A computer program was written¹⁹ to fit the conductance-concentration data to the Murphy-Cohen equation for associated electrolytes and a similar program¹⁹ was written to do the same for the Murphy-Cohen equation for unassociated electrolytes.

Table IV. [Λ^{exp} , C] Data Sets for Salts of
1,3,5-Benzenetrisulfonic Acid in Water

$C \times 10^4$	Λ^{exp} Na_3BTS	$C \times 10^4$	Λ^{exp} K_3BTS
3.7148	125.81	.7690	151.17
5.4049	124.64	1.6830	150.51
8.4357	122.89	3.3963	148.63
13.5820	120.75	4.4894	147.97
19.7002	118.78	6.3791	146.65
30.0131	116.29	9.6607	144.79
		15.1966	142.42
		23.1511	139.86

$10^4 C$	Λ^{exp} LaBTS
1.6189	158.68
2.6928	154.79
3.9528	151.34
6.6583	146.21
10.1271	141.76
14.0623	138.26
18.8046	135.15
35.8056	128.26
44.5556	125.91

Table V. [Λ^{exp} , C] Data Sets for Salts of
1,3,5-Triphenylbenzene-4',4'',4'''-
trisulfonic Acid in Water

10^4C	Na_3TTS Λ^{exp}	10^4C	K_3TTS Λ^{exp}
1.5494	97.1646	3.3175	119.15
3.4409	96.46	4.2229	118.71
6.1357	95.23	5.2283	118.27
9.6397	94.09	6.4522	117.77
14.3011	93.02	9.9792	116.44
20.8133	91.78	16.6441	114.58
31.1641	90.31	25.3371	112.82
41.0566	89.15	36.9485	111.13

10^4C	LaTTS Λ^{exp}
1.1795	108.12
2.2165	103.65
3.9330	98.06
6.5788	92.31
11.3597	85.37
17.8546	78.76
28.7004	70.61

$$\text{Associated: } \Lambda^{MC} = \gamma(\Lambda_0 - S^{MC}(C\gamma)^{1/2} + E^{MC}C\gamma\log(C\gamma) + J^{MC}C\gamma)$$

$$\text{Unassociated: } \Lambda^{MC} = \Lambda_0 - S^{MC}C^{1/2} + E^{MC}C\log C + J^{MC}C$$

The solute parameters: Λ_0 , J^{MC} , α and K_A (if associated) were evaluated internally.

Theoretical Fit Using the Fuoss-Onsager Extended Equation:

As above, two computer programs were written³ to fit the conductance-concentration data of the symmetrical electrolytes, LaBTS and LaTTS, to the Fuoss-Onsager Extended Equation:

$$\text{Associated: } \Lambda^{FO} = \gamma(\Lambda_0 - S^{FO}(C\gamma)^{1/2} + E^{FO}C\gamma\log(C\gamma) + J^{FO}C\gamma)$$

$$\text{Unassociated: } \Lambda^{FO} = \Lambda_0 - S^{FO}C^{1/2} + E^{FO}C\log C + J^{FO}C$$

The solute parameters: Λ_0 , J^{FO} , α , and K_A (if associated) were evaluated internally.

Experimental Solute Parameters: The limiting ionic equivalent conductances, λ_0 's, of the anions, BTS^{3-} and TTS^{3-} , and the cation, La^{3+} , were determined as follows. The value of λ_0^- of the TTS^{3-} ion was estimated from the Λ_0 values of the Na^+ and K^+ salts using Kohlrausch's Law and the λ_0^+ values of the well characterized Na^+ and K^+ ions. The value of λ_0^- for TTS^{3-} thus found was used to calculate the value of λ_0^+ for La^{3+} .

In the same manner the value of λ_0^- for the BTS^{3-} ion was estimated. Then using the value of λ_0^- for BTS^{3-} thus found, the value of λ_0^+ for La^{3+} was calculated. The values of λ_0^+ and λ_0^- thus determined for La^{3+} and the anions, BTS^{3-} and TTS^{3-} are listed in Table VI.

In addition the values of λ_0^+ for the well characterized Na^+ and K^+ ions and the reported λ_0^+ of La^{3+} as listed in Harned and Owen⁵ are listed.

Theoretical Solute Parameters: By the method outlined above the values of λ_0^- for the anions and λ_0^+ for La^{3+} were determined from the Λ_0 's calculated using the computer programs for the Murphy-Cohen and Fuoss-Onsager extended equations. The values of the λ_0 's thus calculated are listed in Table VII.

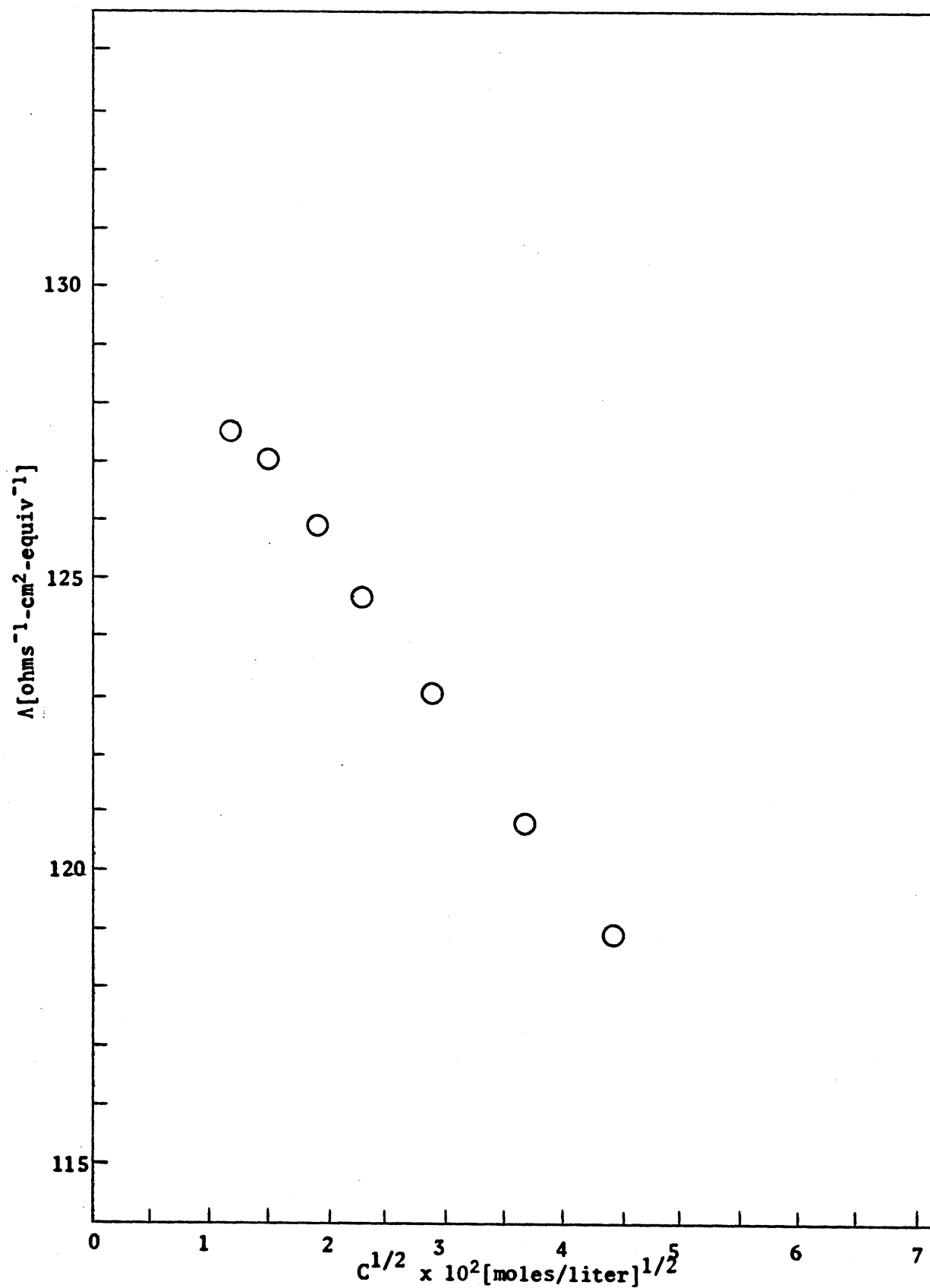


Figure 11. Phoreogram of Sodium 1,3,5-Benzenetrisulfonate.

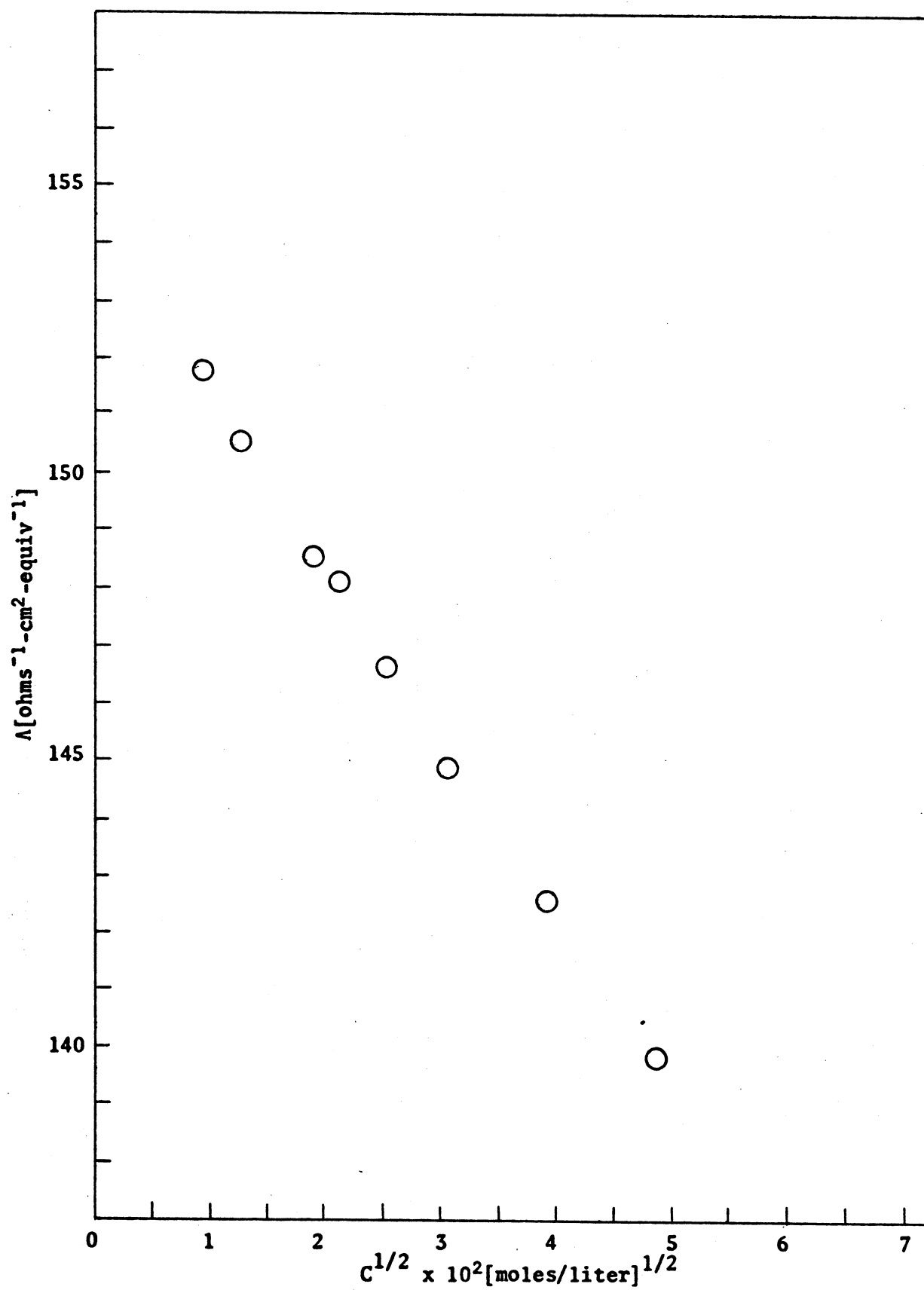


Figure 12. Phoreogram of Potassium 1,3,5-Benzenetrisulfonate.

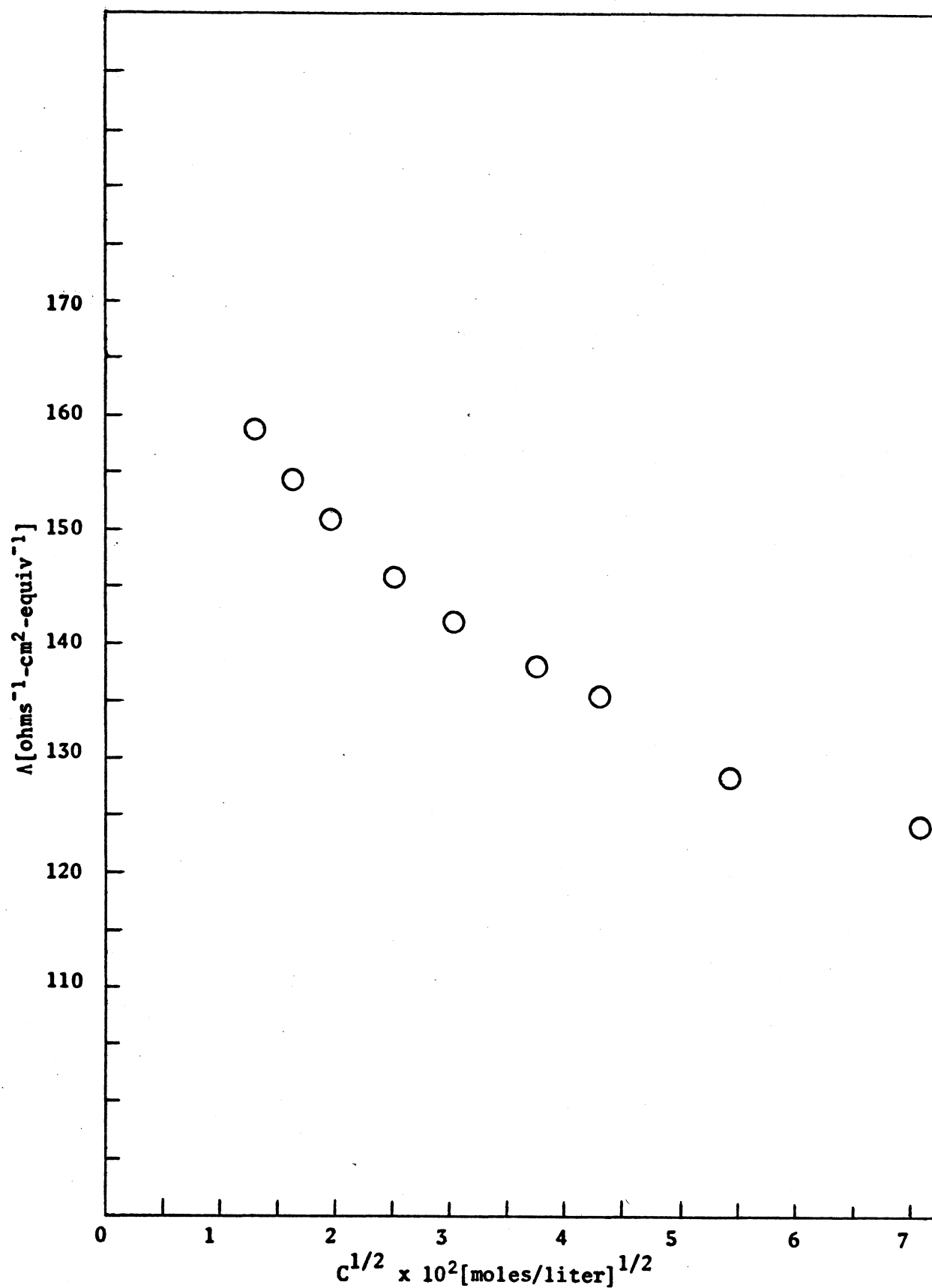


Figure 13. Phoreogram of Lanthanum 1,3,5-Benzenetrisulfonate.

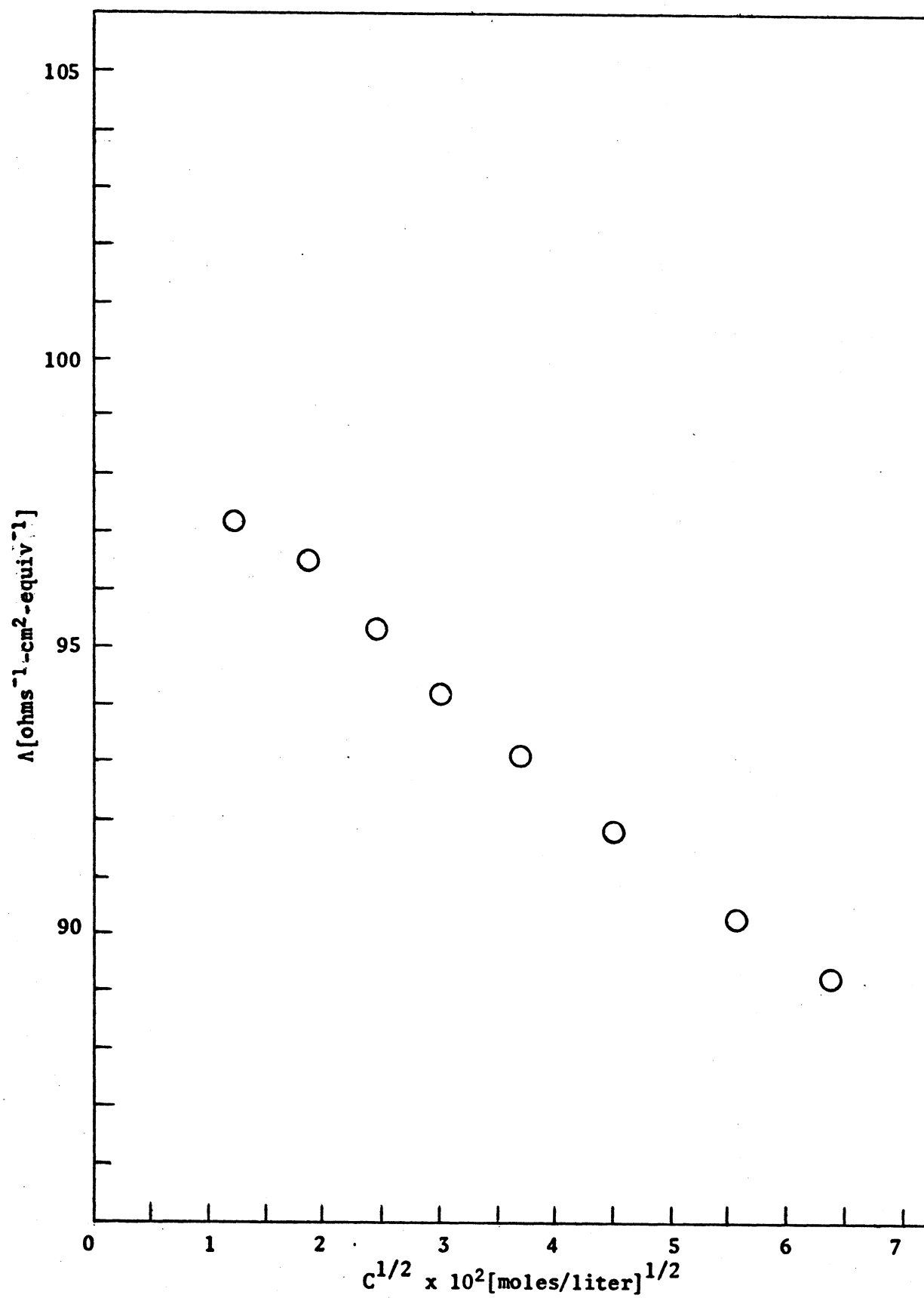


Figure 14. Phoreogram of Sodium 1,3,5-Triphenylbenzene-4',4'',4'''-trisulfonate.

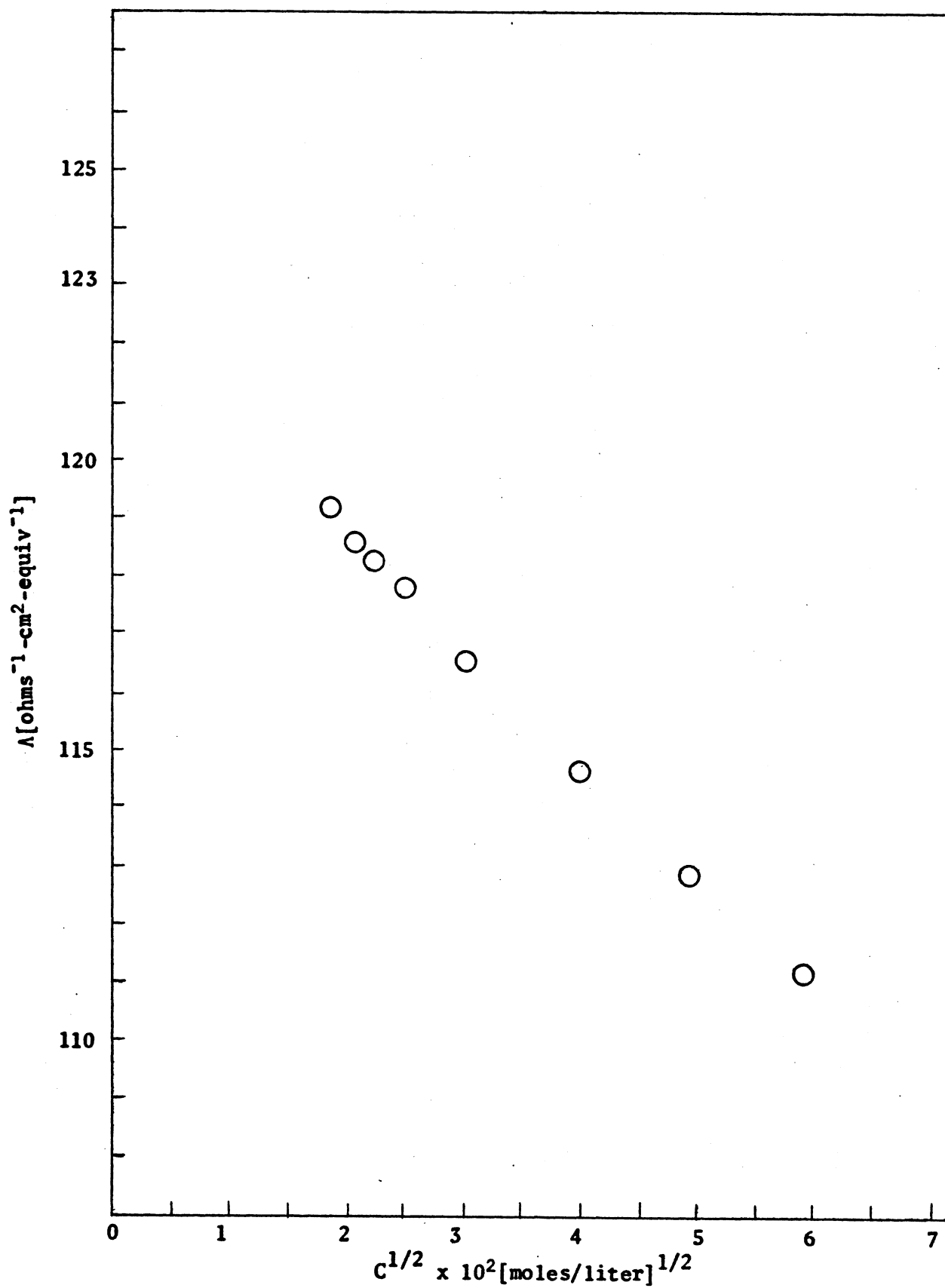


Figure 15. Phoreogram of Potassium 1,3,5-Triphenylbenzene-4',4'',4'''-trisulfonate.

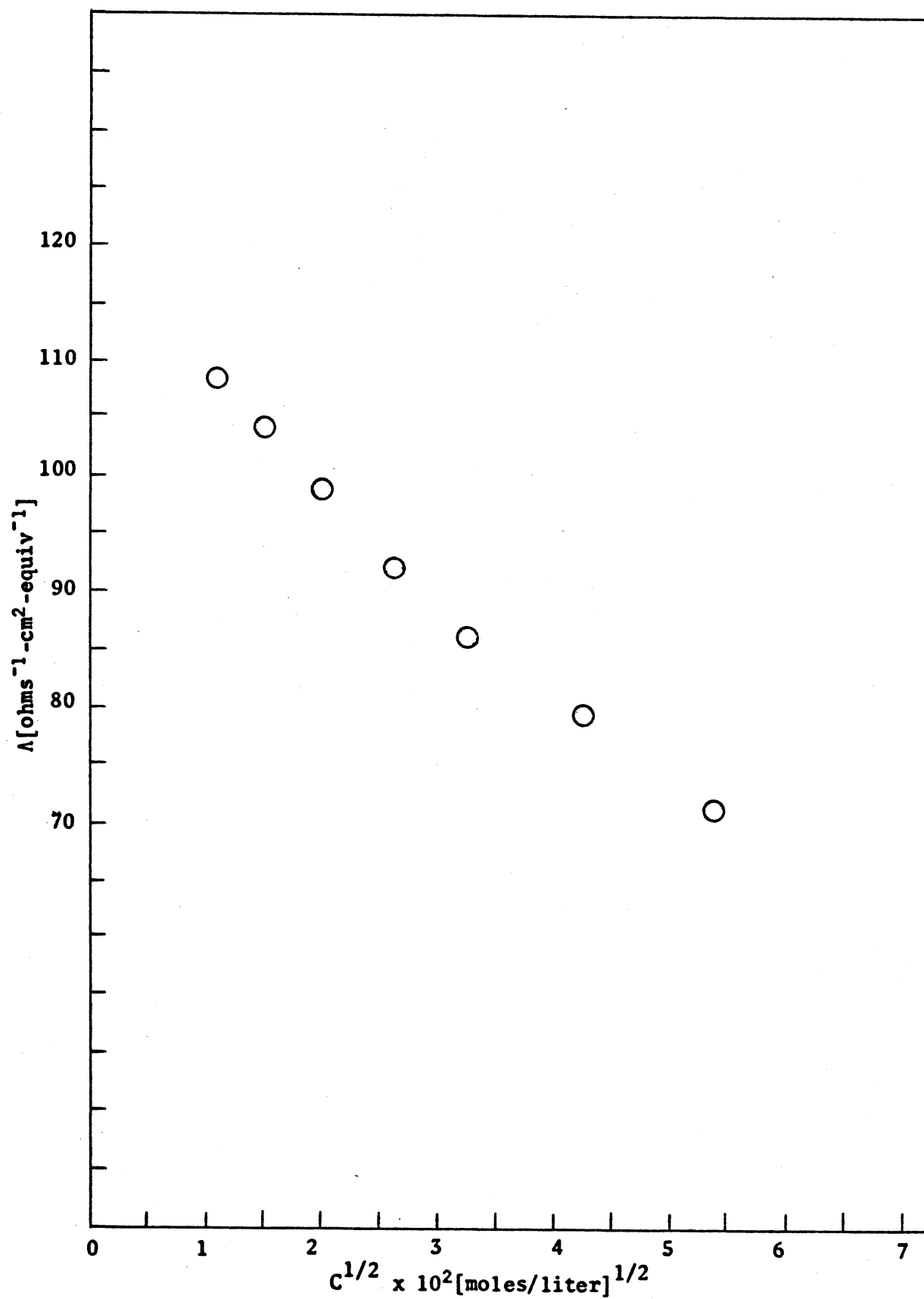


Figure 16. Phoreogram of Lanthanum 1,3,5-Triphenylbenzene-4',4'',4'''-trisulfonate.

Table VI. Experimentally Determined Solute Parameters.

Salt	Λ_o^{exp}	λ_o^-	λ_o^{+*}	$\lambda_o^+(\text{La}^{3+} \text{ calc.})$
Na ₃ BTS	130.80	80.69	50.11	
K ₃ BTS	154.40	80.88	73.52	
LaBTS	172.25	102.75	69.5	91.47
Na ₃ TTS	99.35	49.25	50.11	
K ₃ TTS	122.65	49.13	73.52	
LaTTS	119.25	49.19	69.52	70.06

*Values from Harned and Owen (5)

Table VII. Theoretically Determined Solute Parameters.

Salt	Λ_o^{MC}	λ_o^-	$\lambda_o^+(\text{La}^{3+} \text{ calc.})$	Λ^{FO}
Na ₃ BTS	132.79	82.68	--	--
K ₃ BTS	155.80	82.28	--	--
LaBTS	157.66	88.16	75.18	--
Na ₃ TTS	101.61	51.50	--	--
K ₃ TTS	125.09	51.57	--	--
LaTTS	121.33	51.83	69.80	--

SUMMARY

1. Synthesis: A new compound has been prepared 1,3,5-triphenylbenzene-4'-4''-4'''-trisulfonic acid and characterized using melting points, infrared spectra, cation-exchange analysis and elemental analysis. The barium salt is moderately soluble in water and the sodium potassium and lanthanum salt are soluble.

2. Experimental Data: Phoreograms were used to determine Λ_0 values for all six salts measured and values of the limiting equivalent ionic conductance of two anions were determined. A value of λ_0^+ for La^{3+} was also calculated.

3. Murphy-Cohen Theory: The Murphy-Cohen theory has been shown to correlate only moderately well with the experimental data, however, this could well be due to non-constant "cell constants" and the fact that the higher concentration points in the concentration ranges studied are too high for the theory.

4. Fuoss-Onsager Theory: No conclusive results were obtained from the computer program fit of the conductance-concentration data to the Fuoss-Onsager extended equation for the symmetrical lanthanum salts. This was due to poor quality LaBTS and problems with the computer program.

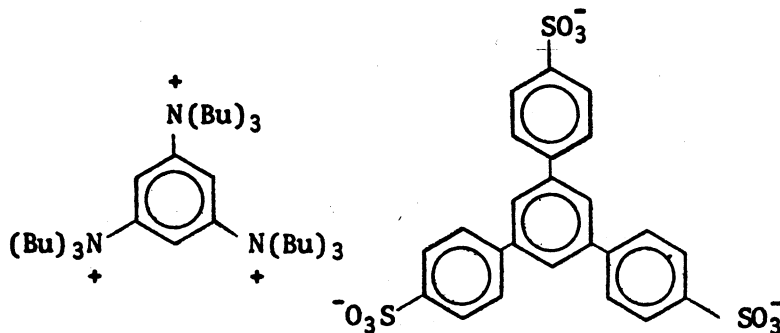
Proposal of Future Investigations

As a consequence of this investigation the following topics merit research:

1. The experiments should be repeated with Kraus-type conductance cells, which have "constant" cell constants. Measurements should be done at 1, 2, 3, 5 and 10 KHz and an all stainless steel constant temperature bath is recommended. This would clear up the ambiguity of the Murphy-Cohen and Fuoss-Onsager results.

2. More lanthanide series salts should be prepared and conductance measurements done. This would provide information on the properties of these salts without interference from ion-association.

3. A completely unassociated, 3-3 electrolyte might be produced by combining a tris quaternary ammonium cation, made from 1,3,5-triaminobenzene hydrochloride, with the TTS³⁻ anion as shown below.



Conductivity measurements could then be done on this compound and LaTTS and their K_A 's calculated for comparison.

LIST OF REFERENCES

1. L. Onsager, *Physik Z.*, 28, 277 [1927].
2. L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, 36, 2689 [1932].
3. D. W. Ebdon, Ph.D. Dissertation, University of Maryland, College Park, 1967.
4. T. J. Murphy and E. G. D. Cohen, *J. Chem. Phys.*, 53, 6 [1970].
5. H. S. Harned and B. B. Owen, The Physical Chemistry of Electrolytic Solutions, 3rd ed. Reinhold Publishing Corp., New York, 1968, pp. 232 and 697.
6. R. M. Fuoss and F. Accascina, Electrolytic Conductance, Interscience Publishers, Inc., New York, 1959.
7. R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, 61, 668 [1957].
8. R. L. Kay, *J. Amer. Chem. Soc.*, 82, 2099 [1960].
9. C. J. Hallada, Ph.D. Dissertation, The University of Michigan, Ann Arbor, 1961.
10. G. Atkinson, M. Yokoi, and C. Hallada, *J. Amer. Chem. Soc.*, 83, 1570 [1961].
11. C. M. Suter and G. A. Harrington, *J. Amer. Chem. Soc.*, 59, 2575 [1937].
12. C. M. Suter and A. W. Weston, Organic Reactions, Vol. III, J. Wiley and Sons, Inc., New York, 1937, pp. 141-197.
13. H. Cerfontain, Mechanistic Aspects in Aromatic Sulfonation and Desulfonation, Interscience Publishers, New York, 1968.
14. E. E. Gilbert, Sulfonation and Related Reactions, Interscience Publishers, New York, 1965.
15. W. Schneider and F. Seebach, *Chem. Ber.*, 54, 2298-2302 [1921].
16. R. A. Robinson and R. H. Stokes, Electrolyte Solutions, Butterworth & Co. Ltd., London.

17. S. Glasstone, Physical Chemistry, D. Van Nostrand Company, Inc., New York, 1940.
18. D. A. MacInnes, The Principles of Electrochemistry, Dover Publications, Inc., New York, 1961.
19. L. M. Shadwick, Masters Thesis, Eastern Illinois University, Charleston, 1973.

VITA

Name: Jack Lee Worthington.

Permanent Address: 604 W. Main, Urbana, Illinois 61801.

Degree and date to be conferred: M.S., 1973.

Date of birth: March 16, 1946.

Place of birth: Muscatine, Iowa.

Secondary education: Reedley Joint Union High School, Reedley,
California, 1960-1964.

Collegiate institution attended:	<u>Date</u>	<u>Degree</u>	<u>Date of Degree</u>
Eastern Illinois University	1964-1969	B.S.	August 1969
Eastern Illinois University	1970-1973	M.S.	May 1973

Major: Physical Chemistry.

Positions held: Chemist, Illinois State Water Survey, Champaign,
Illinois [1971-1973].
Teacher, Charleston Jr. High School, Charleston,
Illinois [1970-1971].
Teacher, Charleston High School, Charleston,
Illinois [Aug.-Dec. 1969].