ABSTRACT

ACID-BASE EQUILIBRIA IN NONAQUEOUS SOLVENTS
PART I: 1,1,3,3-TETRAMETHYLGUANIDINE
PART II: ADIPONITRILE

by Joseph Anthony Caruso

Electrical conductances of tetrazole, nine 5-substituted tetrazoles, picric acid, tetrabutylammonium iodide and triisoamyl-n-butylammonium tetraphenylborate were measured in 1,1,3,3-tetramethylguanidine (TMG) at 25°. Overall dissociation constants of these compounds were determined from the conductance data and were found to be in the range of 10^{-3} to 10^{-5}. The values of the limiting equivalent conductances ranged from about 30 to 45. The inductive effect of the substituent groups in 5-substituted tetrazoles is illustrated by a reasonable linearity of the Taft plot. The dielectric constant of TMG was found to be 11.00 ± 0.02 at 25°.

In addition, potentiometric studies using a hydrogen indicator electrode and a mercury-mercury (II) chloride reference electrode, were made on four 5-substituted tetrazoles, perchloric acid, m-chlorobenzoic acid, and phenol. The overall dissociation constants ranged from 10^{-7} for phenol to approximately 10^{-3} for perchloric acid. The values

obtained by the potentiometric method were in good agreement with those obtained from the electrical conductance measurements.

The use of TMG as a medium for the titrations of weak acids has been also investigated. It has been found that the hydrogen electrode behaves reversibly in this solvent and can serve as an indicator electrode in the titration reactions. The titrant was a 0.1 M solution of tetrabutylammonium hydroxide in a 90-10% mixture of TMG and methanol. Hydrogen electrode, dipping into a TMG solution saturated with benzoic acid, served as the reference electrode. Potentiometric titrations of a number of weak acids gave results accurate to at least ± 0.5%. It was found that in most cases curcumin could be used as an end-point indicator with an accuracy comparable to that of the potentiometric titration.

Electrical conductances of five sodium and potassium salts and twelve quaternary ammonium salts in adiponitrile have been measured at 25°. The data were analyzed by the Fuoss-Onsager conductance equation using Kay's Fortran computer program for both nonassociated and associated electrolytes. The dissociating nature of adiponitrile is reflected by fourteen of the salts showing no association and the other three having association constants of 28 or less. Limiting ionic equivalent conductances have been evaluated by the method of Coplan and Fuoss using triisoamyl-n-butylammonium

tetraphenylborate as a reference electrolyte. The dielectric constant of adiponitrile was found to be 32.45 at 25°.

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A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1967

ACKNOWLEDGMENTS

The author wishes to extend his thanks to Professor Alexander I. Popov for his guidance, encouragement, and enthusiasm throughout this study.

He also wishes to express his appreciation to Professor Paul G. Sears of the University of Kentucky for his comments and guidance.

Thanks are extended to Professor R. M. Herbst and Mr. Thomas Wehman of this Laboratory for providing the 5-substituted tetrazoles.

Thanks also go to the National Institutes of Health of the Department of Health, Education, and Welfare for partial support of this investigation.

Special thanks go to Dr. Robert L. Kay of the Mellon Institute for the use of his Fortran computer program in part of this study.

Many thanks and appreciation go to the author's wife, Judy, for her patience, understanding, and encouragement throughout the years of graduate study.

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INTRODUCTION

The usefulness of nonaqueous solvents in the study of acid-base equilibria (particularly in the Brönsted-Lowry sense) is clearly illustrated by the large number of analytical techniques which utilize either pure nonaqueous solvents or their mixtures for a wide variety of titrations of substances which, for one reason or another, cannot be analyzed in aqueous solutions.

With few exceptions, the development of the theory of acid-base equilibria in nonaqueous solvents, however, has not kept pace with the practical applications. Acidic solvents such as acetic acid and sulfuric acid have been studied very intensively and the nature of acid-base equilibria in these solvents have been elucidated particularly by the classical investigations of Kolthoff and Bruckenstein in acetic acid solutions (1) and of Gillespie and his coworkers (2) in sulfuric acid. On the other hand, acid-base equilibria in basic solvents seem to have been studied less completely, although of course, there are significant publications on such solvents as pyridine (3-6), ethylenediamine (7-12), and ammonia (13-15).

While 1,1,3,3-tetramethylguanidine (hereafter abbreviated as TMG) has been known for over seventy years (16) its application as a nonaqueous solvent has not been explored to any

significant extent. There are only two short reports in the literature which describe its use as a medium for the titration of weak acids (17). Valuable data on the solvent properties of TMG can also be found in an unpublished Ph.D. thesis of M. L. Anderson of this Laboratory (18).

It seemed quite obvious that further study of the solvent properties of TMG would be a useful contribution to the field of nonaqueous solvents. Three objectives were defined:

1. The study of the dissociation and ionization equilibria of some typical electrolytes in TMG.
2. Identification of some useful electrode systems in the solvent.
3. Study of acid-base equilibria.

Parallel with the general study of nonaqueous solvents, a comprehensive study of the chemistry of tetrazoles is being carried out in this laboratory. It is well known that 5-substituted tetrazoles behave as weak acids, but their relative acidity constants have not been determined with sufficient accuracy; and therefore, the influence of the substituent groups on the acidity constants is not known. In part this is due to the insolubility of most of the 5-R-tetrazoles in water, in part to the inherent weakness of the acid properties. Since TMG, as a strongly basic solvent, should enhance considerably the acidic character of these tetrazoles, it was decided to include these compounds in the study of acid-base equilibria in TMG.

HISTORICAL

I. 1,1,3,3-Tetramethylguanidine

A. Physical Constants

At room temperature TMG is a colorless liquid whose physical properties are given in Table I. The solvent has a rather wide liquid range. Its density is intermediate between water and ethylenediamine. The dielectric constant of 11.00 is within the useful range for an ionizing solvent and is quite comparable to those of ethylenediamine and pyridine, 12.9 and 12.3 respectively (12a). The specific conductance and viscosity are such that useful conductance measurements can be made. The high heat of vaporization, the Trouton constant, and the formation of "glass" at low temperatures indicate that the liquid must be highly associated, very likely through hydrogen bonding. It should also be noted that the C=N infrared absorption band in TMG is shifted to lower energy than that generally found in guanidines (19) which also indicates the possibility of hydrogen bonding.

Most of the properties thus far mentioned are quite comparable to those for ethylenediamine. The differences of aqueous basicities for the two are quite marked, however, and are reflected by comparing the pK_b values of 0.4 for TMG (20) as opposed to 4.15 for ethylenediamine (21),

Table I. Physical constants for 1,1,3,3-tetramethylguanidine.

Property	Physical constant	Reference
Freezing point ("glass" formation)	∿-70 to -80°C.	18
Boiling point	159.5°C.	18
Density (25°)	0.9136 g. ml^{-1}.	18
Dielectric constant (25°)	11.00	this study
Specific conductance(25°)	3.54 x 10^{-8} $ohm^{-1}cm^{-1}$.	this study
Viscosity (25°)	1.40 cp.	18
Refractive index	1.4658	18
Heat of vaporization	11.2 kcal. $mole^{-1}$	18
Trouton constant	25.9 cal. $mole^{-1}deg^{-1}$.	18
Aqueous pK_b	0.4	20

indicating TMG is a considerably stronger base than ethylenediamine and therefore would probably be an even better leveling solvent toward protogenic species.

B. Solubilities

Anderson found that, in general, solubilities of inorganic salts in TMG parallel the order found in liquid ammonia. The influence of the lower dielectric constant of TMG is reflected in somewhat lower solubilities for most salts. Salts with large anions in conjunction with small cations show enhanced solubility as evidenced by the following orders

cations: $NH_4^+ \lesssim Li^+ > Na^+ > K^+ > Ca^{2+} > Sr^{2+} > Ba^{2+}$

anions: $CNS^- > ClO_4^- > NO_3^- > I^- > Br^- > C_2H_3O_2^- > Cl^- > SO_4^{2-}$

Organic compounds are reasonably soluble in TMG and complete miscibility was found with most common organic solvents.

C. Chemical Properties

Tetramethylguanidine undergoes slow hydrolysis at room temperature in the presence of atmospheric moisture forming 1,1-dimethylurea and dimethylamine. Anderson indicates that water may be removed from TMG by the addition of carbon dioxide to form the insoluble bicarbonate salt according to the following reaction

$$(H_3C)_2N\text{-}\overset{\overset{NH}{\|}}{C}\text{-}N(CH_3)_2 + CO_2 + H_2O \longrightarrow (H_3C)_2N\text{-}\overset{\overset{H_2N^+H\ CO_3^-}{\|}}{C}\text{-}N(CH_3)_2$$

He found that reactions of TMG with acids are vigorous and exothermic producing the species with a protonated imine nitrogen and localized charge on the central carbon atom, $[(CH_3)_2N]_2C^+NH_2$. Chloride, bromide, acetate, and bicarbonate salts of the above cation were isolated. Attempts to prepare alkali metal guanidides of the type, $M^+NC[N(CH_3)_2]_2^-$, were unsuccessful.

D. Metal Complexes

In his study of metal complexes of TMG Anderson reports that a maximum of four molecules of tetramethylguanidine can coordinate with a transition metal ion such as cobalt (II), His study was not concerned with the coordination site, but Drago claims that complexation takes place through the imine nitrogen (22).

E. Acid-Base Titrations

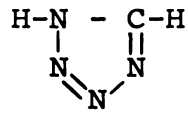
Anderson performed both conductometric and indicator titrations in TMG using tetra-n-butylammonium hydroxide in methanol solution as the titrant. He found several acid-base indicators which exhibit color changes in TMG solutions with changes in the acid-base concentration.

Titration of o-nitrophenol in TMG resulted in more than one conductometric end point supposedly because of hydroxyl ion addition to the aromatic ring. He claims excellent resolution of all three protons of citric acid. It would seem, however, that this observation would lead to the

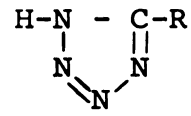
conclusion that TMG is a differentiating rather than leveling solvent toward acids.

II. Tetrazole and The 5-Substituted Tetrazoles

While it has been known for some time that tetrazole (I) and the 5-substituted tetrazoles (II) have definite acidic properties, the influence of structure factors upon the proton-donor ability of these compounds have not been thoroughly investigated.



(I)



(II)

Dissociation constants of some water-soluble tetrazoles have been determined conductometrically by Oliveri-Mandala (23) who found that unsubstituted tetrazole had approximately the same acid strength (K_a = 1.54 x 10^{-5}) as acetic acid. More recently, the acidic dissociation constants of a number of alkyl- and aryl-substituted tetrazoles have been determined potentiometrically by Herbst and co-workers (24). In the case of tetrazole, the K_a value of 1.62 x 10^{-5} agrees well with the value of Oliveri-Mandala. In a number of cases, however, the tetrazole derivatives were insoluble in water and water-alcohol mixtures of varying composition were used as solution media. Since the change in the composition of the solvent should also change the liquid junction potential (aqueous SCE was used as the reference electrode), it is

possible that the relative acid strengths of the tetrazoles may have been altered by this procedure.

THEORETICAL

1. Conductance Methods

Since tetramethylguanidine has a relatively low dielectric constant of 11.00 (see p. 26) it is to be expected that ionic equilibria in this solvent would be substantially influenced by ion-pairing. It has been shown by Kolthoff and Bruckenstein (1) that in such cases the overall dissociation of a weak acid HX will proceed in two steps as shown below

$$HX \underset{}{\overset{K_i}{\rightleftharpoons}} H^+X^- \overset{K_d}{\rightleftharpoons} H^+ + X^- \qquad 1.$$

where HX represents the molecular form of the acid, H^+X^- the ion pair resulting from the ionization process, H^+ the solvated proton, and X^- the conjugate base of the acid HX. The constants K_i and K_d represent the thermodynamic ionization and dissociation constants respectively,

$$K_i = \frac{a_{H^+X^-}}{a_{HX}} \qquad 2.$$

and

$$K_d = \frac{a_{H^+}a_{X^-}}{a_{H^+X^-}} \qquad 3.$$

These two relationships may be combined to give the overall dissociation constant, K_{HX}

$$K_{HX} = \frac{a_{H^+} a_{X^-}}{a_{HX} + a_{H^+X^-}} = \frac{K_i K_d}{1 + K_i} \qquad 4.$$

From the mass balance relationship we have

$$(C_{HX})_t = [H^+] + [H^+X^-] + [HX] \qquad 5.$$

where $(C_{HX})_t$ is the total analytical concentration of the acid HX and the terms in brackets represent the equilibrium concentrations of the respective species. If we assume that the activity coefficients of uncharged species equal unity, Expression 4 becomes

$$K_{HX} = \frac{a_{H^+} a_{X^-}}{[HX] + [H^+X^-]} \qquad 6.$$

and therefore from relationships 5 and 6 we have

$$K_{HX} = \frac{a_{H^+} a_{X^-}}{(C_{HX})_t - [H^+]} \qquad 7.$$

or, assuming that $a_{H^+} = a_{X^-}$

$$K_{HX} = \frac{a^2_{H^+}}{(C_{HX})_t - [H^+]} \qquad 8.$$

Equation 8 may be rewritten as the mass action law

$$K_{HX} = \frac{\gamma^2 C f^2}{1 - \gamma} \qquad 9.$$

where γ represents the degree of dissociation, f the mean activity coefficient, and C, the total analytical concentration of the acid HX.

A. Application of the Ostwald Dilution Law to Conductance Studies

It has been shown by Arrhennius that the degree of dissociation of a binary electrolyte can be obtained from the ratio of equivalent conductance at a given concentration to the equivalent conductance at infinite dilution

$$\gamma = \frac{\Lambda}{\Lambda_o} \qquad 10.$$

Substituting this relationship into Equation 9 and assuming that f = 1, we obtain

$$K_{HX} = \frac{\Lambda^2 C}{\Lambda_o(\Lambda_o - \Lambda)} \qquad 11.$$

or, by rearrangement

$$K_{HX}\,\Lambda_o^2 = \Lambda^2 C + K_{HX}\Lambda\Lambda_o \qquad 12.$$

Dividing Equation 12 by $K_{HX}\Lambda_o^2\Lambda$, we get

$$\frac{1}{\Lambda} = \frac{C\Lambda}{K_{HX}\Lambda_o^2} + \frac{1}{\Lambda_o} \qquad 13.$$

A plot of $1/\Lambda$ vs. $C\Lambda$ yields an intercept of $1/\Lambda_o$ and a slope of $1/K_{HX}\Lambda_o^2$. The values of Λ_o and K_{HX} may then be calculated. This equation gives approximate values of K_{HX} for dilute solutions of weak electrolytes, however, in most cases it is unsatisfactory because it does not take into account interionic effects.

B. The Shedlovsky Iteration Technique

Following the lead taken by Fuoss and Kraus in 1933 and 1935 (25), Shedlovsky in 1938 proposed the following

conductance equation for weak electrolytes (26)

$$\Lambda = \gamma \Lambda_o - S \frac{\Lambda}{\Lambda_o} (\gamma C)^{\frac{1}{2}} \qquad 14.$$

where the Onsager slope, S, is given by

$$S = \alpha\Lambda_o + \beta \qquad 15.$$

This parameter takes into account the relaxation and the electrophoretic effects, α and β respectively (27) which are given by

$$\alpha = \frac{8.203 \times 10^5}{(DT)^{\frac{3}{2}}} \qquad 16.$$

and

$$\beta = \frac{82.43}{\eta(DT)^{\frac{1}{2}}} \qquad 17.$$

where D is the dielectric constant, η the viscosity, and T the absolute temperature. He defined a function, S_z, where

$$z = \frac{S(C\Lambda)^{\frac{1}{2}}}{\Lambda_o^{\frac{3}{2}}} \qquad 18.$$

and

$$S_z = 1 + z + \tfrac{1}{2} z^2 + \ldots \qquad 19.$$

Then a solution of Equation 14 was written as

$$\gamma = \frac{S_z \Lambda}{\Lambda_o} \qquad 20.$$

Substitution in the mass action law, Equation 9, and rearrangement yielded

$$\frac{1}{\Lambda S_z} = \frac{1}{\Lambda_o} + \frac{C\Lambda S_z f^2}{K_{HX}\Lambda_o^2} \qquad 21.$$

As seen from Equation 21 a plot of $1/\Lambda S_z$ vs. $C\Lambda S_z f^2$ yields a straight line with an intercept of $1/\Lambda_o$ and a slope of $1/K_{HX}\Lambda_o^2$. The procedure in applying this technique is to assume a value for Λ_o, solve for z and S_z, and plot the appropriate functions. From the intercept a new value of Λ_o is obtained which is used to recalculate z and S_z. The process is repeated until consecutive Λ_o values agree to within an acceptable tolerance. It was shown by Fuoss and Shedlovsky (28) that the above procedure for the evaluation of Λ_o and the dissociation constant is more reliable than the older method of Fuoss and Kraus (25).

Both the Ostwald and the Shedlovsky methods are best applied using the method of least squares and hence evaluation of Λ_o and K_{HX} is easily handled on modern digital computers. A Fortran program listing which evaluates conductance data by both techniques is given in Appendix I.

II. Potentiometric Methods

Potentiometric studies of acids in TMG were carried out by means of a galvanic cell

$$\text{Ref. Electrode} \;\Big\|\; HX(C_{HX})_t \text{ (TMG)} \;\Big|\; H_2(1 \text{ atm.}), \text{ Pt}$$

The reference electrode consisted of a mercury-mercury (II) couple, which was composed of a mercury layer in contact with a saturated solution of mercury (II) chloride in TMG.

The e.m.f. generated by this cell is given by the equation

$$E_{HX} = E_H^{o'} + 0.0592 \log a_{H^+} \qquad 22.$$

where

$$E_H^{o'} = E^o_{H^+, \frac{1}{2}H_2} + E_{l.j.} + E_{ref.} \qquad 23.$$

It is possible to interpret the experimental results by assuming the ionization and dissociation equilibria as given on page 9. By assuming $a_{H^+} = [H^+]$ Equation 8 becomes

$$K_{HX} = \frac{a^2_{H^+}}{(C_{HX})_t - a_{H^+}} \qquad 24.$$

from which,

$$a_{H^+} = (K_{HX}[(C_{HX})_t - a_{H^+}])^{\frac{1}{2}} \qquad 25.$$

Substituting Equation 25 into Equation 22 yields

$$E_{HX} = E_H^{o'} + 0.0296 \log K_{HX} + 0.0296 \log [(C_{HX})_t - a_{H^+}] \qquad 26.$$

It is seen that a plot of E_{HX} vs. $\log [(C_{HX})_t - a_{H^+}]$ gives a straight line with slope of 0.0296 and intercept of $E_H^{o'} + 0.0296 \log K_{HX}$. If K_{HX} of an acid is known from independent measurements, the value of $E_H^{o'}$ may be calculated (assuming that the liquid junction potential remains constant). Essentially the same technique is then used in an iterative process to calculate K_{HX} values for other substances. As the first approximation we can write

$[(C_{HX})_t - a_{H^+}] = (C_{HX})_t$. The e.m.f. values are then plotted *vs.* $\log (C_{HX})_t$ and a value of K_{HX} obtained. From this value of K_{HX} a first value of a_{H^+} is calculated and E_{HX} plotted *vs.* $\log [(C_{HX})_t - a_{H^+}]$ from which a new value of K_{HX} is obtained. The process is repeated until the consecutive K_{HX} values are within an acceptable tolerance. This method usually requires four or five iterative steps and is easily handled by a digital computer. A Fortran program listing for this procedure is given in Appendix I.

In a similar potentiometric study using ethylenediamine as solvent, Bruckenstein and Mukherjee (12a), have postulated the following conjugate ion equilibrium

$$X^- + HX \rightleftharpoons HX_2^- \qquad 27.$$

where

$$K_{HX_2^-} = \frac{a_{HX_2^-}}{a_{X^-} a_{HX}} \qquad 28.$$

For cases where the conjugate ion equilibrium is present a plot of E_{HX} *vs.* $\log(C_{HX})_t$ yields two linear portions, one of slope 0.0296 representing Equilibria 1, and one of slope 0.0592 representing Equilibrium 27. At the point of intersection of the two linear segments we have the relationship

$$K_{HX_2^-} = \frac{1}{(C_{HX})'_t} \qquad 29.$$

where $(C_{HX})'_t$ gives the concentration of the acid at the point of intersection.

EXPERIMENTAL

I. Reagents

The solvent, 1,1,3,3-tetramethylguanidine was obtained from American Cyanamid and it was purified by vacuum distillation from granulated barium oxide through a 70 cm. column packed with glass helices. The distillation was carried out at 36-38° under ∽0.1 mm. pressure. The system containing about 2 liters of TMG was first refluxed for several hours, then a first fraction of 100 ml. collected and discarded. Subsequent fractions of 500-700 ml. each were then collected for each experiment until approximately 100 ml. remained in the distilling flask. After use the solvent was redistilled. Solvent prepared in such manner exhibited specific conductances within the range of 4-10 x 10^{-8}ohms^{-1}cm^{-1}. Gas chromatograms taken on an F & M Model 700 gas chromatograph equipped with a hydrogen flame detector, showed only one peak, while solvent purified at atmospheric pressure exhibited three peaks with the area ratios of about 2:2:96.

Conductance water for potassium chloride solutions was prepared by passing distilled water through a mixed bed resin obtained from Crystalab Research Laboratories. The specific conductance of such water ranged from 5-7 x 10^{-7} ohms^{-1}cm^{-1}.

Potassium chloride, Matheson Coleman and Bell "Reagent, A.C.S., Crystals" was fused in a platinum crucible, ground in an agate mortar, oven dried and stored.

The preparation and purification of triisoamyl-n-butylammonium tetraphenylborate was carried out by a previously described technique (29). The melting point of the final product was 264-265° instead of 274-275° reported in the literature. The melting point, however, remained constant on several recrystallizations. It seems likely, therefore, that the literature value may be in error.

Picric acid, Matheson, Coleman and Bell "Reagent Crystals," was recrystallized twice from ethanol and dried to constant weight *in vacuo*.

Some of the 5-substituted tetrazoles were available as a result of previous work in this Laboratory (24), others were prepared according to the procedure of Finnegan *et al.* (30). The compounds were purified as follows:

5-Ethyl(m.p. = 86.5 - 89.5°), and 5-n-propyl(m.p. = 60 - 62°)tetrazoles were purified by triple sublimation. Since they were in such short supply, further purification was not attempted and consequently their purity may not be as high as would be desirable.

5-p-Nitrophenyl(m.p. = 226 - 227°d.), 5-p-chlorophenyl (m.p. = 260 - 261°d.), 5-p-methoxyphenyl(m.p. 239 - 240°), 5-phenyl(m.p. = 221 - 222°), 5-methyl(m.p. = 148°), 5-benzyl(m.p. = 124 - 125°), and 5-p-chlorobenzyl(m.p. =

162 - 163°) tetrazoles were all recrystallized twice. The respective tetrazole was added to 1,2-dichlorethane and the mixture brought to boiling. Just enough methanol was then added to dissolve the tetrazole. The solution was allowed to cool and the needle-like crystals filtered. The crystals were then dried in a vacuum desiccator for 24 hrs. The melting points, as given above, compare favorably with the literature values (24).

Tetrazole was obtained from City Chemical Company and was purified by recrystallization from a 1:5 methanol-benzene mixture. The needle-like crystals were dried to constant weight in vacuo. The melting point of 155° coincided with the literature value (31).

Baker Analyzed Reagent mercury and perchloric acid, G. F. Smith sodium perchlorate, and Fisher Certified Reagent mercury (II) chloride were used without further purification.

Matheson Co., Inc. prepurified hydrogen was passed through a flow meter to assure constant delivery to the hydrogen electrode half cell. It was then passed through a column of Ascarite and a column of Drierite before use.

Tetra-n-butylammonium hydroxide (TBAH) was obtained from Eastman Chemical Company as a 25% solution in methanol. Since preliminary results indicated that pure methanolic solutions could not be used as titrants, a solution of TBAH

in TMG-MeOH mixture was prepared by adding ~13 ml. of the stock TBAH solution to 87 ml. of TMG. The solution was somewhat unstable and showed a definite change in titer after standing for 24 hours. It was necessary, therefore, to standardize it at the onset of each series of titrations. Dahmen and van der Heijde (32) indicate that TBAH is unstable in pyridine as a consequence of the "Hofmann degradation." This may also be the case for the TBAH-TMG solutions.

Curcumin (turmeric), 1,7-bis(4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione was obtained from Eastman (m.p. 179-181°) and was not further purified. Indicator solution for the titrations was prepared at a concentration of approximately 0.2 mg./ml. in TMG.

Benzoic acid and the substituted benzoic acids were recrystallized from water-ethanol mixtures and dried to constant weight *in vacuo*.

Phenol and *p*-chlorophenol, obtained from Eastman Chemical Co., were purified by vacuum distillation in a micro distillation apparatus; *o*-cresol was purified by sublimation.

II. Apparatus

All melting points were taken on a Fisher-Johns melting point block for which the usual stem corrections were made.

The conductance bridge used in this investigation was constructed in this Laboratory and has been described in a previous publication (33). The bridge was operated at a frequency of 2000 cycles/sec.

The cells were similar to those described by Daggett, Bair, and Kraus (34).

The electrodes were platinized according to the technique of Jones and Bollinger (35). Potassium chloride solutions were made up by weight, and molar concentrations calculated, and the equivalent conductances calculated from the Lind, Zwolenik, and Fuoss equation (36). The constants of the four cells used in this investigation were calculated in the usual manner and are as follows: 0.2409 ± 0.0001; 0.2320 ± 0.0001; 0.1216 ± 0.0002; and 0.4421 ± 0.0004 cm^{-1}.

The temperature of 25.00 ± 0.03 was provided by a Sargent S-84805 thermostatic bath assembly filled with light mineral oil.

The e.m.f. readings were taken on a Beckman Expanded Scale pH Meter. The 0 to 200 mv. full scale was extended by recalibrating the 0 against the output of a Biddle-Gray Portable Potentiometer Model 605014. Readings were good to ± 0.2 mv.

Potentiometric titrations were carried out in the concentration cell shown in Figure 1. Hydrogen electrode immersed in a saturated solution of benzoic acid in TMG served as the reference electrode. All titrations were performed using 10 ml. burets equipped with teflon stop-cocks.

The cell used in the e.m.f. measurements is illustrated in Figure 2. The reference electrode consisted of a

Figure 1. Diagram of the cell used in potentiometric titrations.

a: platinum electrode
b: hydrogen bubbler
c: outlet bubbler
d: teflon stopcock
e: fine porosity frit
f: electrolyte chamber
g: buret
h: $\frac{10}{30}$

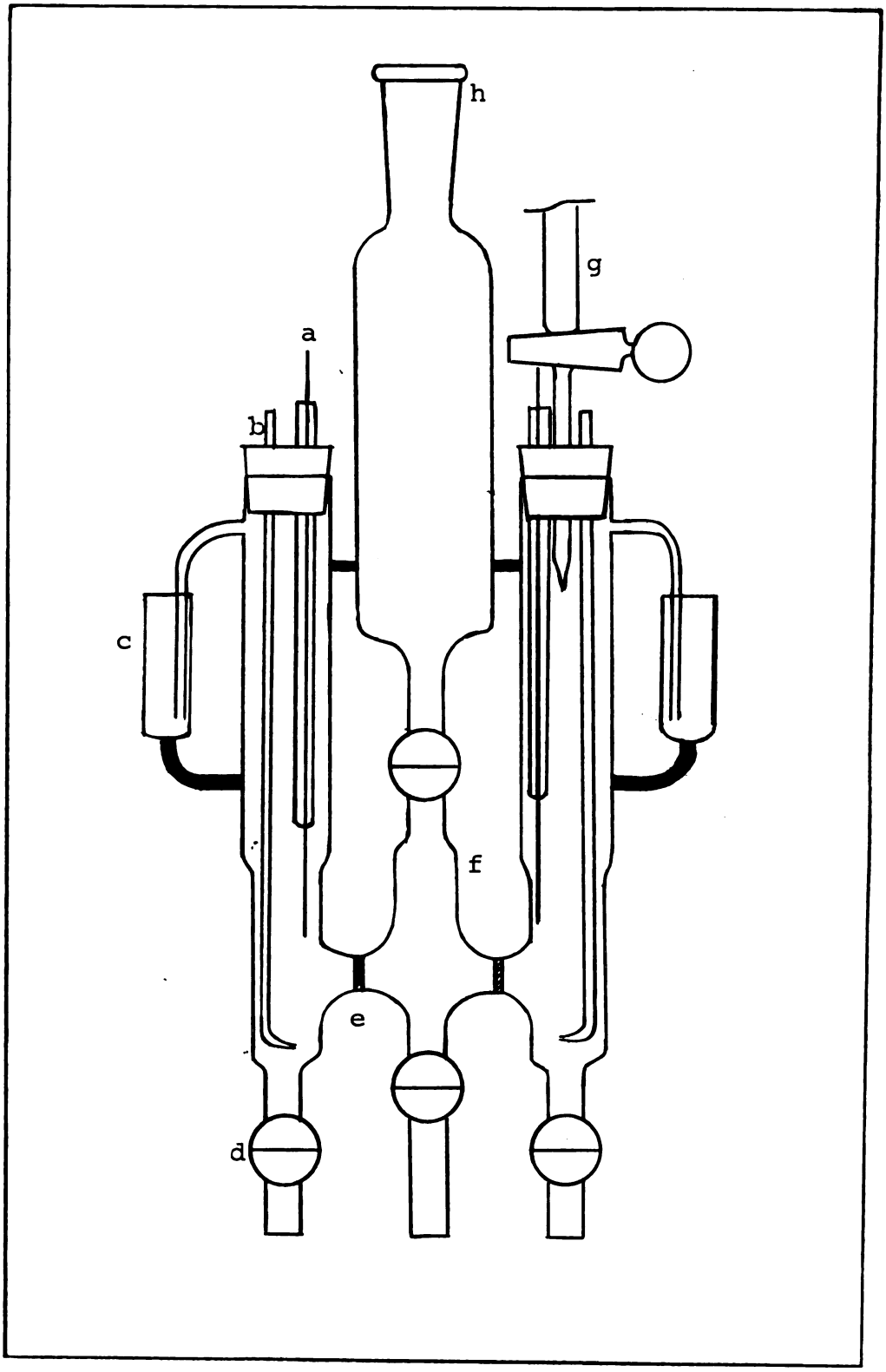


Figure 1

Figure 2. Diagram of the cell used in e.m.f. studies.

a: ⧲ 10/30
b: platinum electrode with mercury contact
c: hydrogen outlet capillary
d: gas dispersion tube; course frit
e: hydrogen electrode half cell
f: fine porosity frit
g: teflon stopcock
h: ⧲ 14/20
i: reference electrode half cell
j: filler hole
k: teflon stopper
l: platinum contact
m: ⧲ 19/20
n: electrolyte chamber

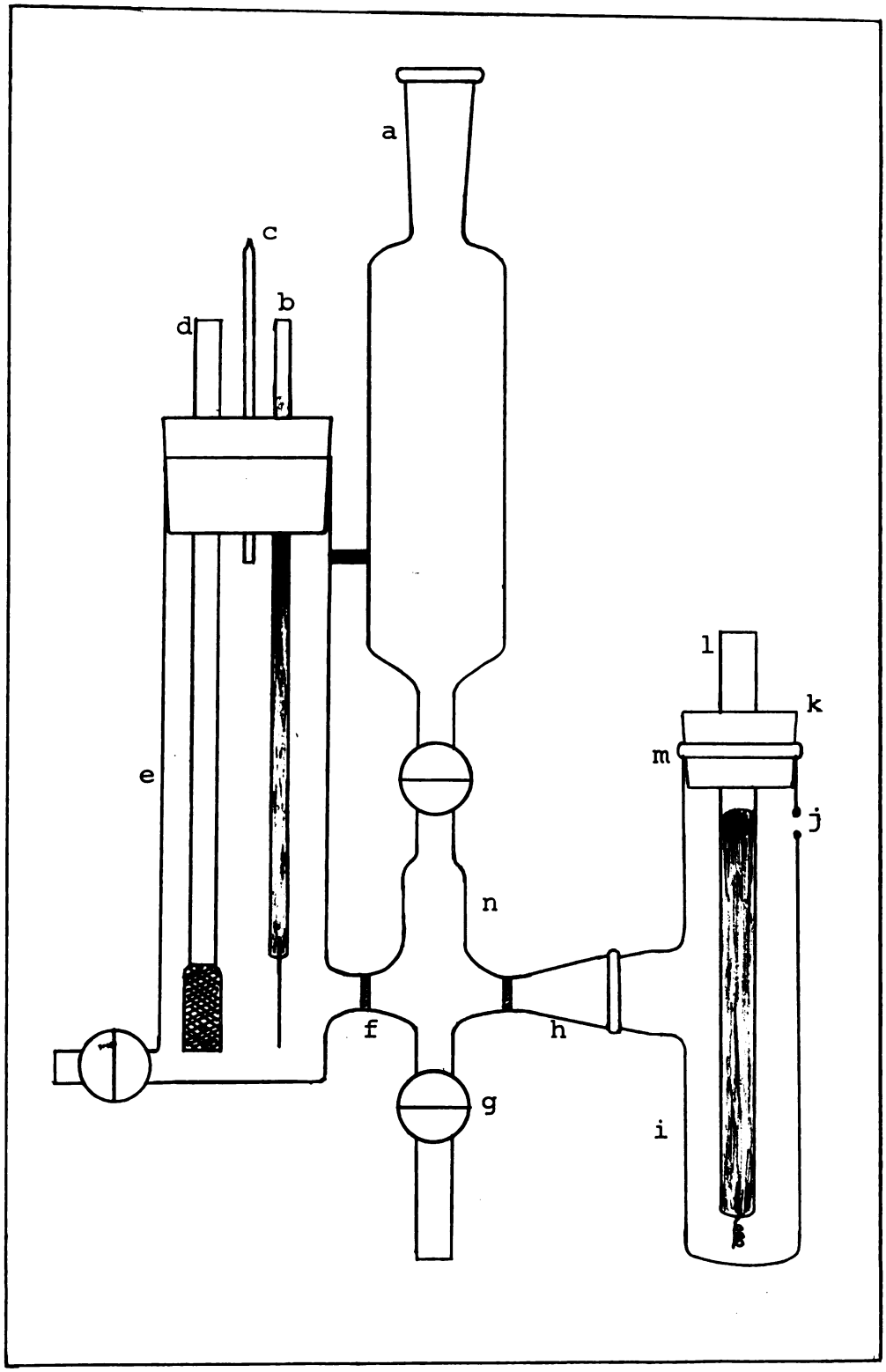


Figure 2

mercury-mercury (II) couple which was composed of a mercury layer in contact with a saturated solution of mercury (II) chloride in TMG.

III. Procedures

A. Conductance Measurements

Freshly distilled solvent was weighed into a cell which had been previously steamed, rinsed with acetone and dried by a stream of dry nitrogen. The cells were then immersed into the thermostatic bath and allowed sufficient time to attain temperature equilibrium. Since the resistance readings for the pure solvent as well as for the solutions were generally above 30,000 ohms, the cell was shunted with a resistance of 30,000 ohms. The parallel resistance readings were then taken and converted to series cell resistances. The specific conductance of the solvent was then calculated. Stock solutions were prepared by weighing solvent into a flask containing previously weighed solute. The stock solution was then added to the cell by means of a weight buret and the contents of the cell thoroughly mixed. After temperature equilibration the contents of the cell were remixed in the bath and the resistance readings taken. An additional amount of the stock solution was then added to the cell and a new measurement was taken. In this manner it was possible to measure the conductance of a series of solutions of varying concentration.

When solutions were prepared by the usual volumetric techniques rather than by weight, considerably more scatter was observed in the Shedlovsky plots.

The dielectric constant of 11.00 ± 0.02 for TMG was measured by a previously described technique (37).

B. Potentiometric Measurements

Solutions of various acids in TMG were prepared by the usual volumetric technique, but the manipulations were carried out in a dry box under a dry nitrogen atmosphere.

It was found that mercury-mercury (II) electrode had a steady and reproducible potential when used in conjunction with a hydrogen electrode. A saturated solution of mercury (II) chloride was prepared by suspending 2.00 g. of dry salt in 100 ml. of solvent and stirring the mixture for two hours. The solutions appeared to be stable for at least 24 hours. After the solution had been aged for several days, however, a black deposit was formed on the bottom of the flask. In order to avoid a possible source of error fresh saturated solutions of mercury (II) chloride were prepared just prior to use.

Attempts to prepare a calomel reference electrode in TMG were unsuccessful since addition of calomel to TMG instantly produced a black precipitate.

The reference electrode half cell (shown in Figure 2) was filled to $\backsim$1 cm. from the bottom with mercury and a platinum contact inserted into the mercury. Saturated

mercury (II) chloride solution was then added to the reference electrode compartment.

Sixteen gage platinum wires of 1 to 1.5 inches in length were sealed into soft glass tubes and subsequently coated with platinum black by electrolysis in the previously described solution (p. 20) for 5 min. at 10 ma. The electrodes were then charged with hydrogen by cathodizing in a dilute sulfuric acid solution. As the measurements were taken electrodes were interchanged to compare their response. Fresh electrodes were used when readings became erratic or when readings did not agree to within ± 0.5 mv. between fresh and previously used electrodes. Immediately before use, the platinum electrodes were washed with distilled water, rinsed in acetone, and air dried.

A gas dispersion tube was inserted into the hydrogen electrode half cell (Figure 2) and the half cell purged with hydrogen for 5 minutes. The reference electrode compartment was then filled with saturated mercury (II) solution. Finally, the hydrogen electrode compartment was filled with the solution to be studied. The bridging compartment was also filled with the same solution to minimize errors due to diffusion. A current of hydrogen was allowed to stream through the solution for at least 20 minutes. The readings were taken when changes in potential were about 2 mv. or less over a 20 to 30 minute recording interval. This behavior may be due to the hydrogen electrode coming slowly into equilibrium with

the solution. Even in aqueous solutions this electrode occasionally shows erratic behavior (38). It was found that when the system was thermostated in a constant temperature bath the accuracy of the measurements did not improve. Reproducible measurements could be obtained in a water thermostat only after 40 to 45 minutes. The reported e.m.f. values are the mean values of the best four readings and have average deviations of ± 0.5 to ± 1.0 mv. The hydrogen partial pressure correction to the observed e.m.f. was ignored since it would be less than experimental error.

C. Titration Procedures

Solutions were prepared by weighing an amount of acid to be titrated and diluting it with 25 to 50 ml. of TMG. This solution was then transferred to the cell for subsequent titration. The titrant was always standardized against benzoic acid.

The hydrogen bubbling rate did not appear to have a significant influence on the potential readings and, therefore, the tank output regulated so as to maintain a slow passage of hydrogen through the solution throughout the titration. After the solutions were saturated with hydrogen (usually 15 to 30 min.) the titration was begun. The potential values were taken after the highest scale reading was reached (usually about one minute). Near the equivalence point the potentials were more unsteady and it took somewhat longer to reach the peak reading. After the equivalence point, the

readings were generally unsteady until a relatively large excess of titrant had been added. Again, the peak scale readings were taken. When curcumin indicator was used for the detection of the end-point, the titrations were carried out under nitrogen atmosphere because of the high affinity of the solvent for moisture and carbon dioxide. To insure that the color change corresponded to the potentiometric equivalence point, preliminary titrations were done potentiometrically with the indicator added to the cell. Initially, the solutions to be titrated had a red-violet color (3 or 4 drops of indicator solution per 50 ml. of solvent). The color changed to an intense blue upon addition of a small amount of base and turned very sharply to yellow or gold at the equivalence point. Blank corrections were not made in as much as the experimental conditions, volume of solutions, and volume of indicator were kept the same during the standardization of the titrant solution and the titrations of the acids. Fresh indicator solution was prepared prior to each series of titrations since on standing for long periods of time the indicator solution tended to decompose.

RESULTS AND DISCUSSION

I. Conductance Results

Conductance data were obtained for tetrazole, nine 5-substituted tetrazoles, tetrabutylammonium iodide, triisoamyl-n-butylammonium tetraphenylborate and picric acid solutions in TMG. These data are shown in Table II. It should be noted that the concentration range of these solutions is, perhaps, somewhat narrower than that usually found in similar studies. In general, the upper limit of concentration was determined by the Fuoss equation, $C_{max.} = 3.2 \times 10^{-7} D^3$ (39), since at higher concentrations the simple laws of dilute solutions of electrolytes may no longer be obeyed. The lower limit was taken such that the specific conductance of the solvent would be less than 5% of the specific conductance of the most dilute solution. Under these conditions, the solvent correction was made by subtracting the specific conductance of the solvent from that of the respective solution.

The experimental data were evaluated according to the Fuoss-Shedlovsky method as previously described using a Fortran computer program run on the Control Data Corporation Model 3600 computer. The results including the respective standard deviations, are given in Table III, and the

Table II. Equivalent conductances in TMG at 25°
(Superscripts designate series of determinations)

10^4C	Λ	10^4C	Λ	10^4C	Λ
5-p-NO_2PhTz		5-p-MeOPhTz		5-p-ClPhTz	
0.4551	26.93[a]	0.6704	19.01[a]	0.6051	24.40[a]
1.297	23.32	1.618	14.66	1.517	20.11
1.731	21.66	2.427	12.78	2.809	17.03
2.401	20.04	3.399	11.33	3.547	15.90
3.166	18.87	4.152	10.54	0.8480	22.97[b]
4.112	17.68	4.666	10.09	1.773	19.36
0.3510	27.75[b]	1.210	16.08[b]	3.051	16.64
1.165	23.89	2.369	12.89	3.841	15.51
1.737	22.07	3.357	11.39		
2.585	20.17	4.367	10.35		
3.223	19.10	5.202	9.705		
4.303	17.72	5.876	9.279		
5-PhTz		Tetrazole		5-MeTz	
1.525	17.39[a]	1.703	16.75[a]	2.878	10.41[a]
2.435	15.02	3.359	13.15	5.014	8.364
3.560	13.29	5.038	11.26	8.835	6.708
4.858	11.97	6.575	10.20	1.546	12.84[b]
5.542	11.45	7.922	9.530	3.864	9.314
1.381	17.84[b]	9.451	8.913	4.961	8.419
2.126	15.67	2.089	15.71[b]	6.253	7.705
3.322	13.57	3.733	12.74	7.667	7.122
4.487	12.28	5.885	10.72	9.140	6.637
5.372	11.53	7.633	9.707		
		9.382	8.986		
		11.21	8.388		

continued

Table II -- Continued

10^4C	Λ	10^4C	Λ	10^4C	Λ
5-EtTz		5-PrTz		5-BzTz	
1.799	11.43[a]	1.889	10.80[a]	1.251	13.71[a]
2.330	10.38	3.437	8.647	2.823	10.23
3.349	9.053	4.954	7.485	4.319	8.695
4.678	7.990	6.923	6.572	5.467	7.925
5.417	7.515	8.687	5.996	6.569	7.370
7.220	6.710	10.03	5.617	7.609	6.948
1.883	11.17[b]	1.944	10.73[b]	1.070	14.40[b]
2.414	10.19	3.505	8.597	2.320	10.97
3.739	8.633	5.715	7.098	3.380	9.524
5.108	7.648	7.400	6.417	4.274	8.705
5.704	7.328	9.075	5.912	5.337	7.986
7.253	6.669	10.60	5.563	6.186	7.538
5-*p*-ClBzTz		Picric Acid		(*i*-Am)$_3$BuNBPh$_4$	
1.525	14.55[a]	0.7588	33.30[a]	0.3702	24.60[a]
3.008	11.69	1.720	30.64	0.6467	24.15
5.031	9.748	3.334	27.84	1.246	23.38
6.331	8.985	4.342	26.66	2.916	21.67
7.540	8.419	5.475	25.57	4.044	20.86
8.578	8.023	6.487	24.98	1.979	22.52
1.172	15.79[b]	0.4806	34.04[b]	0.3295	24.78[b]
2.178	13.05	1.188	31.96	0.5731	24.35
3.169	11.48	2.504	29.10	1.078	23.58
3.978	10.61	3.508	27.63	1.695	22.75
4.842	9.892	5.190	25.85	2.484	21.98
5.671	9.343	5.912	25.25	3.542	21.14

continued

Table II -- Continued

10^4C	Λ	10^4C	Λ	10^4C	Λ
Bu_4NI					
0.4366	22.97[a]				
1.226	16.50				
1.779	14.41				
2.641	12.49				
3.220	11.58				
3.673	11.04				
0.4259	23.38[b]				
1.042	17.61				
1.739	14.68				
2.373	13.11				
2.910	12.14				
3.617	11.19				

Tz = tetrazole; Bz = benzyl; Ph = phenyl; Bu = n-butyl; i-Am = isoamyl; Me = methyl; Et = ethyl; Pr = n-propyl; MeO = methoxy.

Table III. Conductance results in TMG at 25°

Substance	Λ_o	$\sigma\Lambda_o$	$K_{HX} \times 10^5$	$\sigma K_{HX} \times 10^5$
Tetrazole	45.5	1.2	2.94	0.16
5-MeTz	36.3	1.5	2.52	0.21
5-EtTz	34.9	1.0	2.31	0.14
5-PrTz[a]	34.6	0.5	2.18	0.08
5-BzTz	36.0	0.5	2.45	0.07
5-p-ClBzTz[a]	32.6	---	4.56	--
5-PhTz	35.5	0.3	5.77	0.10
5-p-MeOPhTz	35.1	0.4	3.89	0.10
5-p-ClPhTz	34.1	0.3	10.5	0.25
5-p-NO_2PhTz	33.0	0.5	18.9	0.72
Picric acid	38.2	0.2	55.8	1.2
(i-Am)$_3$BuNBPh$_4$	26.4	0.1	179.0	8.9
Bu_4NI	42.7	0.9	2.48	0.11

[a]Evaluated by taking the mean of both data sets; all others were evaluated by combining both data sets.

Shedlovsky plots for the systems investigated are given in Figures 3-6. The plots, as taken from the computer print out, clearly reflect the linearity and reproducibility of the data. Bellobono and Favini, studied conductances of several electrolytes in ethylenediamine solutions (40) and reported that satisfactory values of Λo and K_{HX} were obtained by the simple application of the Ostwald dilution law (Equation 13), as well as by the Fuoss and Kraus technique. Upon evaluation of their potassium iodide data with our computer program a rather surprising result was obtained, namely that over the concentration range they chose, the $1/\Lambda$ vs. $c\Lambda$ plot was quite linear while the Shedlovsky plot was linear only for the most dilute solutions. Thus it appears as if better results were obtained by ignoring interionic effects and activity corrections!

The Ostwald method was applied to the data in this investigation but the plots were curved and the extrapolated values were much more uncertain than those obtained by the Fuoss-Shedlovsky treatment.

As expected for a solvent with a dielectric constant of 11.00, all of the compounds studied are rather weak electrolytes. The leveling effect of the basic solvent on acids is also evident from the relatively narrow range of the acid dissociation constants. For example, while the dissociation constants of picric acid and of tetrazole differ by a factor of 140,000 in aqueous solutions (41,23) (2.2 and 1.54×10^{-5}, respectively), the factor is reduced to only 19.5 in TMG

Figure 3. Shedlovsky plots for A, 5-BzTz, B, 5-p-ClBzTz, and C, tetrazole in TMG.

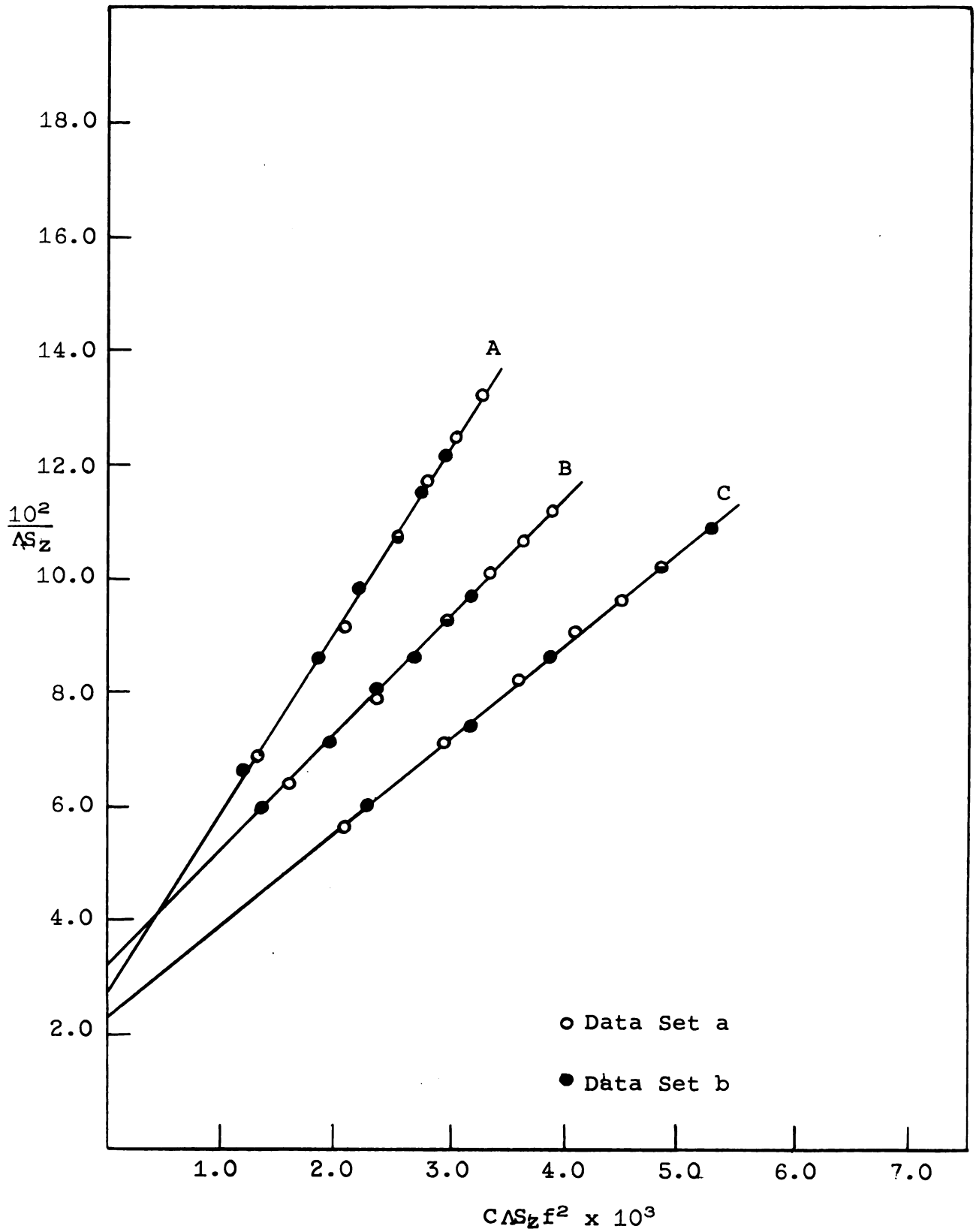

18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
$\frac{10^2}{\Delta S_z}$
A
B
C
o Data Set a
• Data Set b
1.0
2.0
3.0
4.0
5.0
6.0
7.0
$C\Delta S_z f^2 \times 10^3$

Figure 3

Figure 4. Shedlovsky plots for A, 5-MeTz, B, 5-p-MeOPhTz, and C, picric acid in TMG.

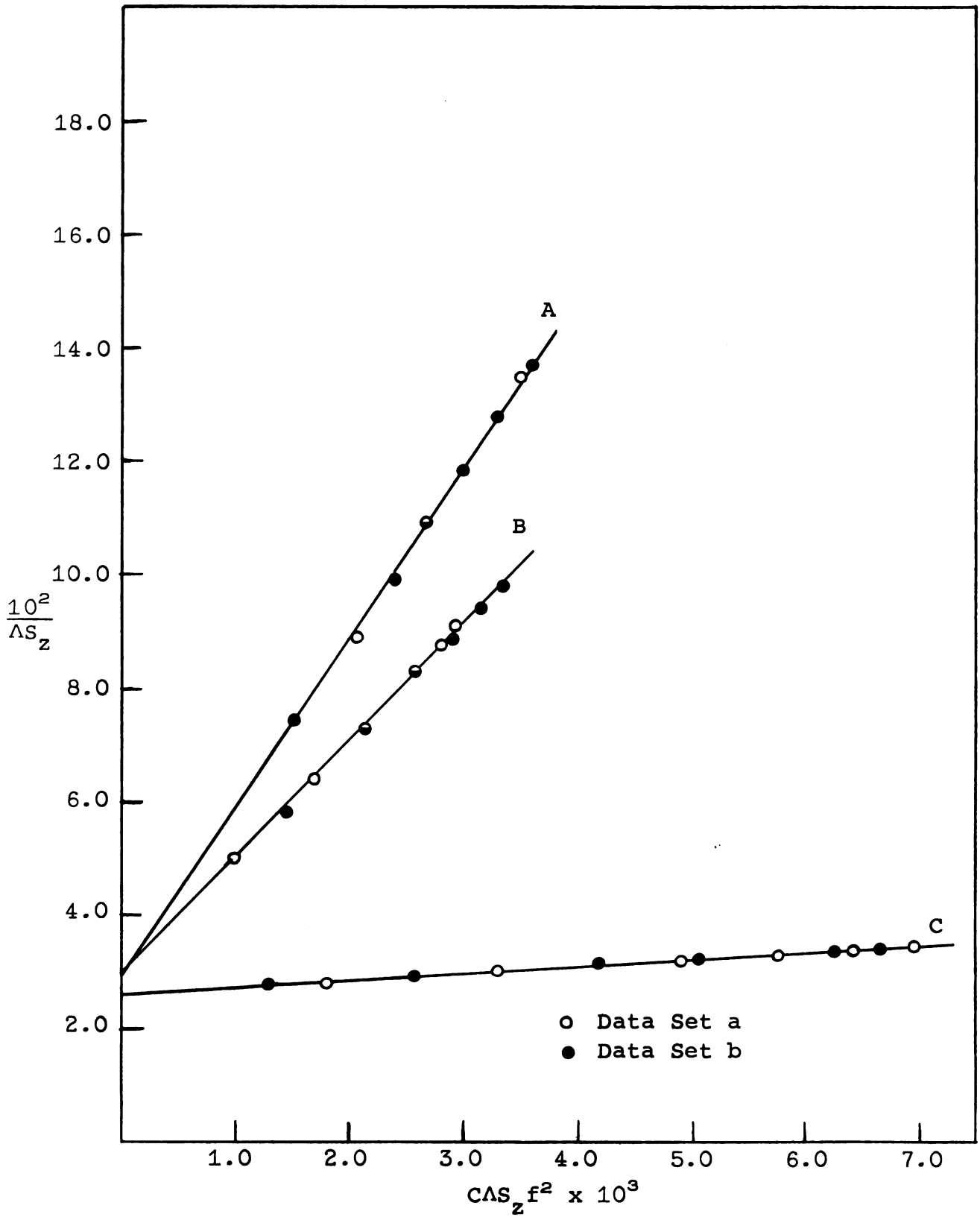

18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
$\frac{10^2}{\Lambda S_z}$
A
B
C
o Data Set a
● Data Set b
1.0
2.0
3.0
4.0
5.0
6.0
7.0
$C\Lambda S_z f^2 \times 10^3$

Figure 4

Figure 5. Shedlovsky plots for A, 5-PrTz, B, Bu_4NI, and C, $(\underline{i}\text{-Am})_3BuNBPh_4$ in TMG.

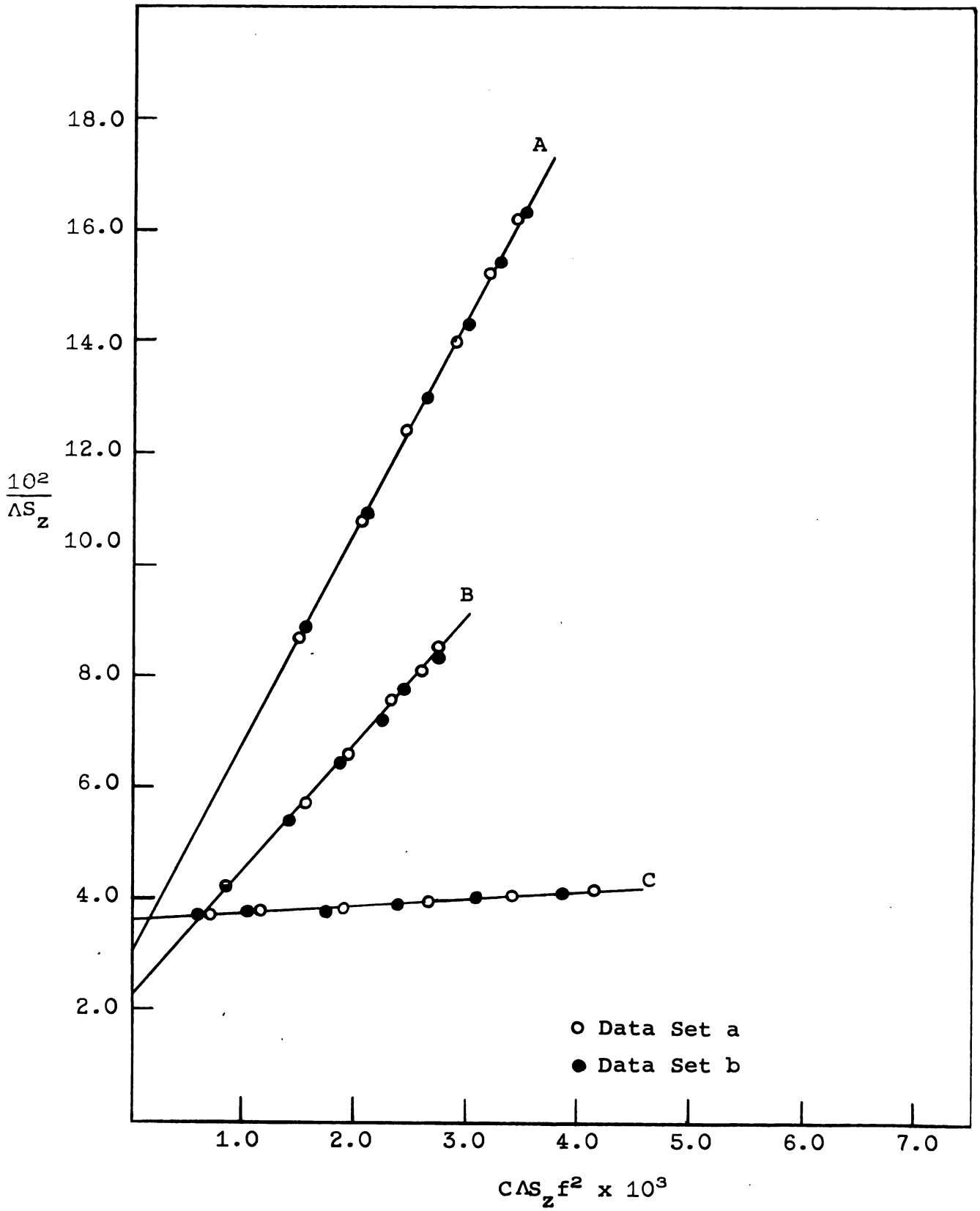

18.0
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
$\frac{10^2}{\Lambda S_z}$
A
B
C
o Data Set a
● Data Set b
1.0
2.0
3.0
4.0
5.0
6.0
7.0
$C\Lambda S_z f^2 \times 10^3$

Figure 5

Figure 6. Shedlovsky plots for A, 5-EtTz, B, 5-PhTz, C, 5-p-ClPhTz, and D, 5-p-NO_2PhTz in TMG.

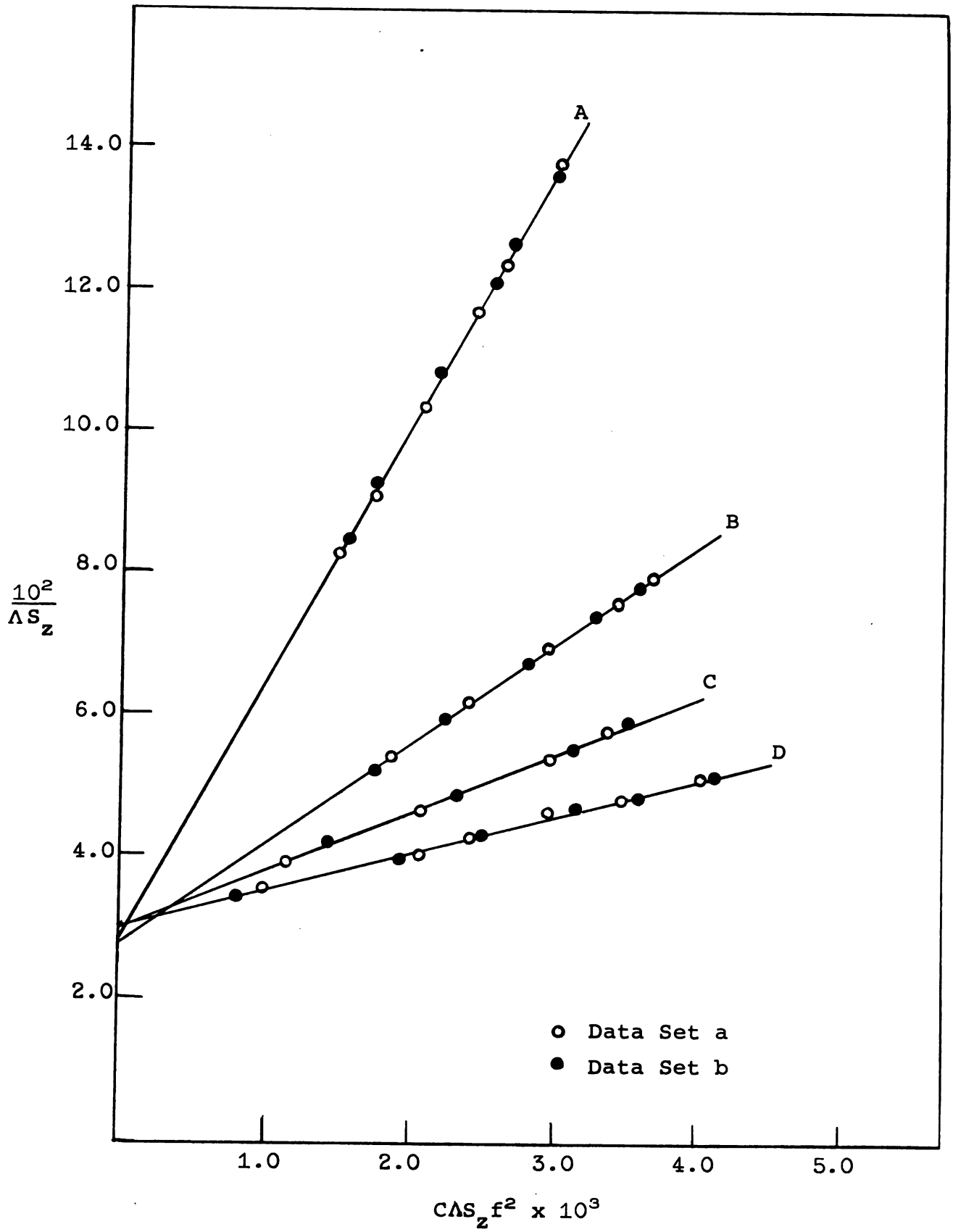

A
B
C
D
14.0
12.0
10.0
8.0
6.0
4.0
2.0
$\frac{10^2}{\Lambda S_z}$
Data Set a
Data Set b
1.0
2.0
3.0
4.0
5.0
$C\Lambda S_z f^2 \times 10^3$

Figure 6

Figure 6. Shedlovsky plots for A, 5-EtTz, B, 5-PhTz, C, 5-p-ClPhTz, and D, 5-p-NO_2PhTz in TMG.

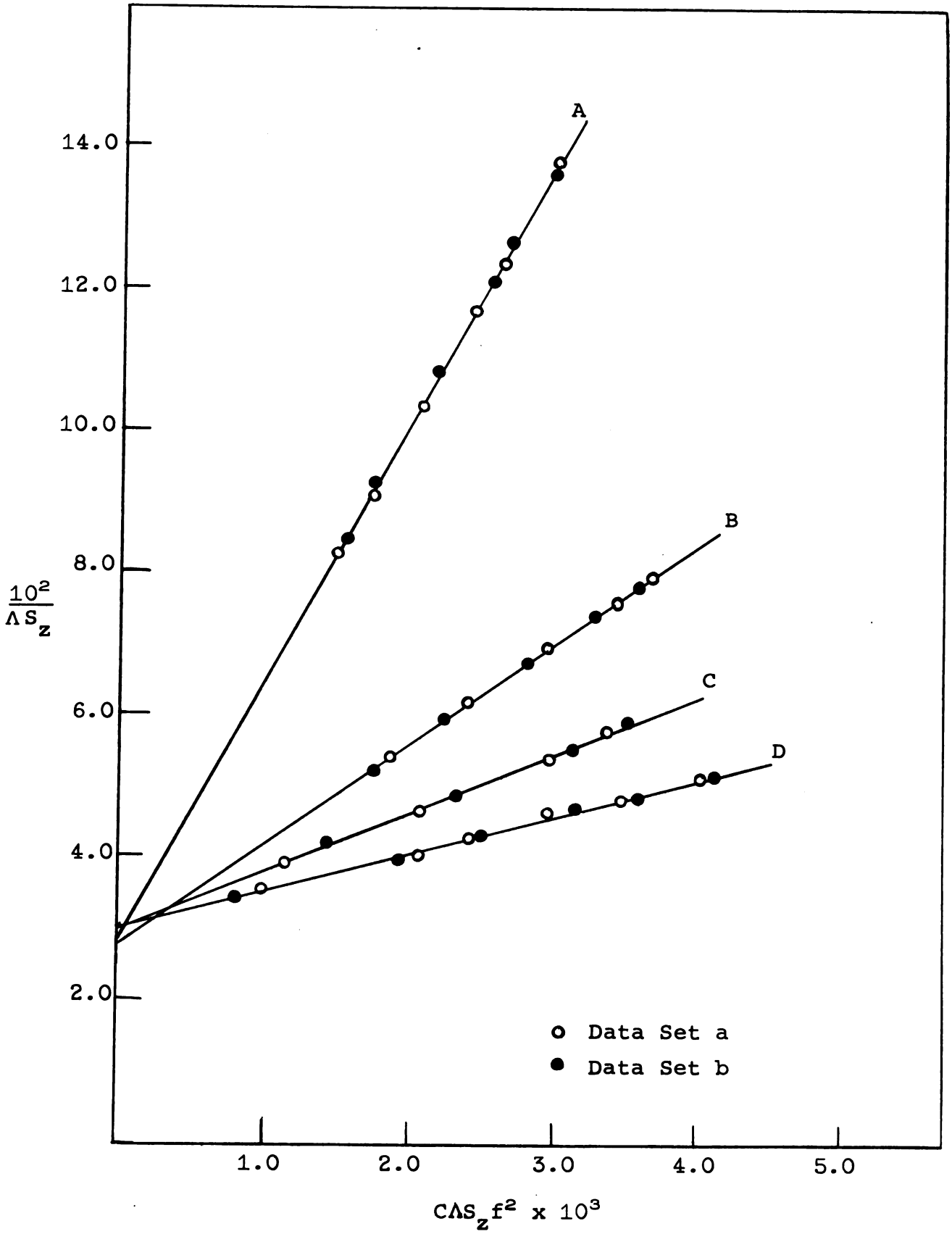

A
B
C
D
14.0
12.0
10.0
8.0
6.0
4.0
2.0
$\frac{10^2}{\Lambda S_z}$
Data Set a
Data Set b
1.0
2.0
3.0
4.0
5.0
$C\Lambda S_z f^2 \times 10^3$

Figure 6

solutions. In the case of tetrazole the overall acidity constant in TMG is greater than in water because of the basic nature of the solvent and therefore $K_i^{TMG} >> K_i^{H_2O}$ and this factor more than compensates for the ion-pair formation in TMG. On the other hand, picric acid is a strong acid in water and, therefore, $K_i^{TMG} \gtrsim K_i^{H_2O}$ but the overall constant is smaller in TMG than in water because of the low dielectric constant of the former solvent ($K_d^{TMG} << K_d^{H_2O}$). The overall acidity constant, however, still reflects the inductive effect of the substituent group on the acidity of the tetrazoles. Thus, for example, the acid strength varies in the order: HTz > 5-MeTz > 5-EtTz > 5-PrTz. With the phenyl derivatives the order is 5-p-NO_2PhTz > 5-p-ClPhTz > 5-PhTz > 5-p-MeOPhTz, and with benzyl derivatives, 5-p-ClBzTz > 5-BzTz.

The discrepancy between the ion-pair dissociation constants of triisoamyl-n-butylammonium tetraphenylborate and tetrabutylammonium iodide is puzzling, especially in view of the fact that both electrolytes exhibit normal behavior in adiponitrile solutions.[1] It should be pointed out, however, that tetralkylammonium halides show appreciable association even in solvents of high dielectric constant such as acetonitrile (42) where the ion-pair dissociation constant for tetramethylammonium iodide, for example, is 3.62×10^{-2}.

The limiting conductance follows the usual trend of varying inversely with the size of the ions. In this respect

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[1]See Part II of this work.

it is interesting to compare our results with those of Bellobono and Favini (40) since ethylenediamine has approximately the same dielectric constant as TMG and both solvents are basic in nature. Their results indicate, for example, that the conductances of alkali metal halides in ethylenediamine solutions, in general, increase with the size of the ions. Thus they obtain the following orders

$$\Lambda_o^{LiI} < \Lambda_o^{NaI} \lessapprox \Lambda_o^{CsI}$$

and

$$\Lambda_o^{LiBr} < \Lambda_o^{NaBr} < \Lambda_o^{KBr} > \Lambda_o^{CsBr}$$

Also the limiting conductances of the bromides are, in general, lower than those of the iodides. The limiting conductances of organic acids and their alkali metal salts showed little correlation with ionic size.

An attempt was made to correlate the inductive effect of the substituent groups with the Taft σ^* constant for the series of 5-aliphatic substituted tetrazoles. With tetrazole as a reference, σ^* values (43) were plotted vs. log K_{HX}. As seen from Figure 7, the result is a fairly reasonable linear plot which may be described by the equation

$$\log K_{HX} = \rho^* \sigma^* + \log K^o_{HX} = 0.173\ \sigma^* - 4.53 \qquad 30.$$

These data, also shown in Table IV, support the conclusion that the Taft σ^* values provide a useful correlation for the estimation of acid strengths of weak acids, although as given

Figure 7. Relationship between log K_{HX} and σ^* for some 5-aliphatic substituted tetrazoles.

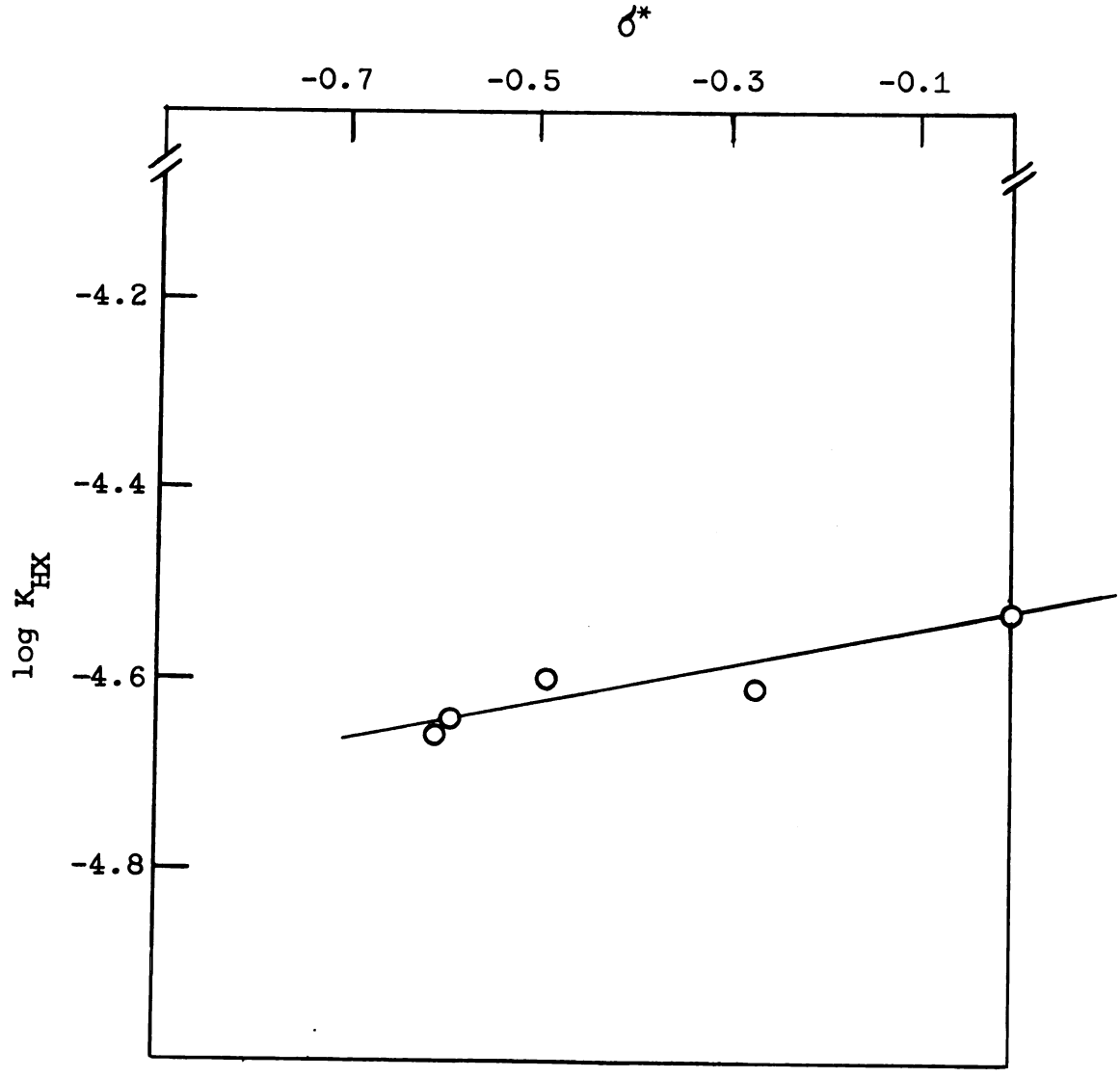


Figure 7

Table IV. σ^* Constants for various tetrazoles[a,b]

Substance	Log K_{HX}	σ^*
5-MeTz	-4.60	-0.490
5-EtTz	-4.64	-0.590
5-PrTz	-4.66	-0.605
5-BzTz	-4.61	-0.275
Tetrazole	-4.53 (log K^o_{HX})	0.000

[a]The above σ^* values are relative to tetrazole (containing the hydrogen substituent) with the reference value of 0.000. Taft gives the methyl substituent as the reference. To convert these values to those given by Taft (43), 0.490 is added to each value.

[b]Taft gives median deviations for the σ^* values of ± 0.02 to ± 0.04.

by Taft, the σ^* values refer to the hydrolysis of esters in acidic or basic solutions. It has also been previously shown that log K_f is a linear function of the Taft σ^* constant, where K_f is the formation constant of various halogen complexes (44).

II. Potentiometric Results

Overall dissociation constants of 5-MeTz, 5-BzTz, 5-PhTz, 5-p-ClBzTz, perchloric and m-chlorobenzoic acids, and phenol were determined potentiometrically by the procedure outlined on pp. 26-28. Unfortunately, in a number of cases limited solubilities of acids in TMG precluded their study. For example, attempts have been made to study the dissociation of acetic acid, hydrochloric acid, and hydrobromic acid in TMG but the experiments could not be carried out due to the low solubility of these acids in TMG.

The experimental data are given in Table V. The value for $E_H^{\circ\prime}$ was calculated from the K_{HX} value for 5-BzTz obtained from the electrical conductance measurements. The e.m.f. data were fitted by the method of least squares to yield a straight line with a slope of 0.0288 (± 0.0012) and an intercept of -0.8021 (± 0.0015), where the numbers in parenthesis represent the respective standard deviations. Recalling that intercept = $E_H^{\circ\prime}$ + 0.0296 log K_{HX}, the value of $E_H^{\circ\prime}$ was calculated to be -0.6657 v. This value for $E_H^{\circ\prime}$ was then used in conjunction with the data in Table V to calculate the overall acidity constants for the other systems. The results are given

Table V. Experimental data from potentiometric measurements in TMG.

10^3C	E_{HX}(v.)	10^3C	E_{HX}(v.)
Phenol[a]		$HClO_4$	
422.5	-0.8490	142.9	-0.7829
283.3	-0.8622	36.69	-0.8083
194.3	-0.8779	24.09	-0.8035
189.7	-0.8763	19.3	-0.8156
106.8	-0.9066	5.04	-0.8357
105.3	-0.8965	3.56	-0.8411
36.11	-0.9315	2.51	-0.8404
31.16	-0.9278	1.17	-0.8575
10.6	-0.9467		
3.00	-0.9590		
5-p-ClBzTz		m-Chlorobenzoic Acid	
12.7	-0.8485	23.61	-0.8547
7.81	-0.8575	16.07	-0.8615
4.72	-0.8619	9.47	-0.8710
2.82	-0.8679	5.84	-0.8815
2.19	-0.8719	3.40	-0.8808
1.88	-0.8794	1.43	-0.8936
0.916	-0.8854		

continued

Table V -- Continued

10^3C	E_{HX} (v.)	10^3C	E_{HX}(v.)
5-MeTz		5-PhTz	
38.52	-0.8420	32.46	-0.8326
31.17	-0.8442	17.26	-0.8397
22.6	-0.8470	14.2	-0.8393
20.7	-0.8503	9.88	-0.8486
14.9	-0.8550	9.81	-0.8452
11.9	-0.8560	8.11	-0.8484
11.6	-0.8568	5.91	-0.8515
8.73	-0.8592	5.79	-0.8555
7.38	-0.8631	5.61	-0.8565
3.81	-0.8694	5.32	-0.8579
3.16	-0.8730	4.06	-0.8581
2.90	-0.8750	3.53	-0.8635
		2.24	-0.8642
		1.94	-0.8681
5-BzTz		5-BzTz (cont.)	
32.0	-0.8440	4.95	-0.8675
17.7	-0.8522	4.43	-0.8708
17.5	-0.8488	4.42	-0.8694
13.8	-0.8558	3.48	-0.8695
10.3	-0.8566	3.33	-0.8755
10.2	-0.8603	2.16	-0.8784
9.58	-0.8585	1.79	-0.8835
5.77	-0.8645		
5.62	-0.8658		

[a]The last four data combinations listed were those used to evaluate pK_{HX} for phenol.

in Table VI. It is seen that there is good agreement between the potentiometric and conductometric methods. The behavior of all substances listed, except phenol, is characteristic of weakly acidic substances in the concentration range of $\backsim$0.002 to 0.03 M. The same behavior was found for the conductance measurements which were done at $\leq$ 0.001 M. The potentiometric method has lead to pK_{HX} values for systems which could not be readily studied conductometrically, i.e., phenol and m-chlorobenzoic acid. In the case of tetrazoles the inductive nature of the substituent groups is reflected in their pK_{HX} values. Perchloric acid, the strongest acid studied (pK_{HX} of 3.11) does not differ greatly in acid strength from the rest of the substances with the exception of phenol. Even in the latter case the leveling effect of the solvent is clearly noted considering that aqueous phenol has a pK_a of 10 while aqueous perchloric acid is completely dissociated. The pK_{HX} value of perchloric acid also compares favorably with the value of 3.28 for picric acid as measured above. This is not surprising, however, since both are strong acids in aqueous solution and it would be expected that they exhibit similar acidic character in a strongly basic solvent such as TMG. The linearity of the E_{HX} vs. log $[(C_{HX})_t - a_{H^+}]$ plots is shown in Figures 8 and 9. Measurements at low concentrations ($<$ 0.001 M) for hydrogen bromide solutions in TMG indicated that a pK_{HX} value of $\backsim$4 might be expected. Mukherjee found that hydrogen bromide had a pK_{HX} of 3.28 in ethylenediamine (45).

Table VI. Results of potentiometric study in TMG [a]

Substance	Intercept (v.)	Slope	$pK_{HX}^{(e.m.f.)}$	$pK_{HX}^{(cond.)}$
5-BzTz (reference)	-0.8021(0.0015)	0.0288(0.0012)	--	4.61
5-MeTz	-0.8019(0.0015)	0.0280(0.0007)	4.60	4.60
5-p-ClBzTz	-0.7921(0.0085)	0.0298(0.0033)	4.28	4.34
5-PhTz	-0.7881(0.0036)	0.0288(0.0016)	4.13	4.24
m-Chlorobenzoic acid	-0.8076(0.0076)	0.0303(0.0034)	4.80	--
Phenol	-0.8887(0.0073)	0.0282(0.0038)	7.54	--
$HClO_4$	-0.7580(0.0044)	0.0305(0.0019)	3.11	--

[a] Numbers in parentheses represent the respective standard deviations.

Figure 8. E_{HX} *vs.* $\log[(C_{HX})_t - a_{H^+}]$ for TMG solutions of A, 5-PhTz, B, 5-BzTz, and C, *m*-chlorobenzoic acid.

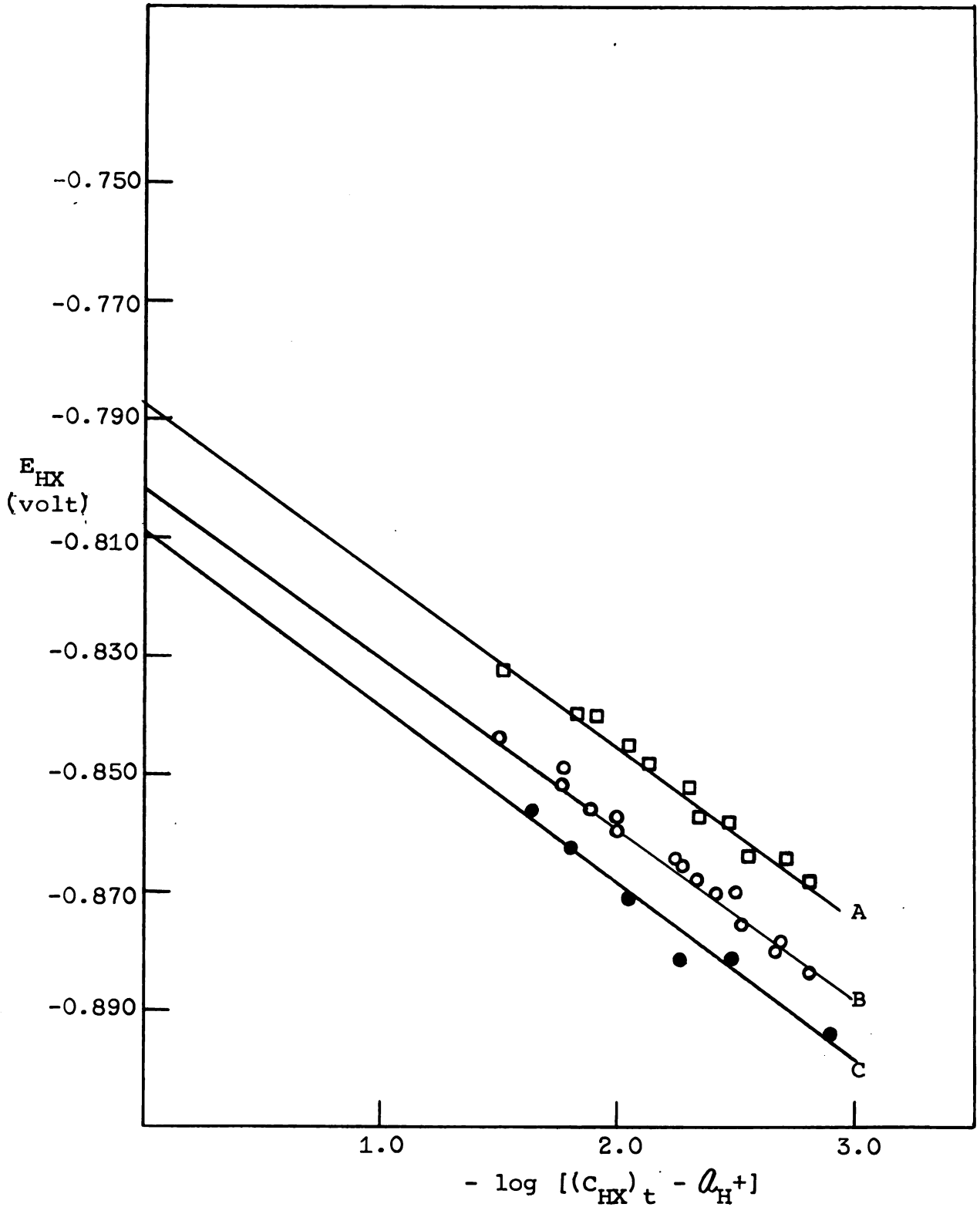

-0.750
-0.770
-0.790
-0.810
-0.830
-0.850
-0.870
-0.890
E_HX (volt)
A
B
C
1.0
2.0
3.0
- log [(C_HX)_t - a_H+]

Figure 8

Figure 9. E_{HX} *vs.* $\log[(C_{HX})_t - a_{H^+}]$ for TMG solutions of A, $HClO_4$, B, 5-*p*-ClBzTz, and C, 5-MeTz.

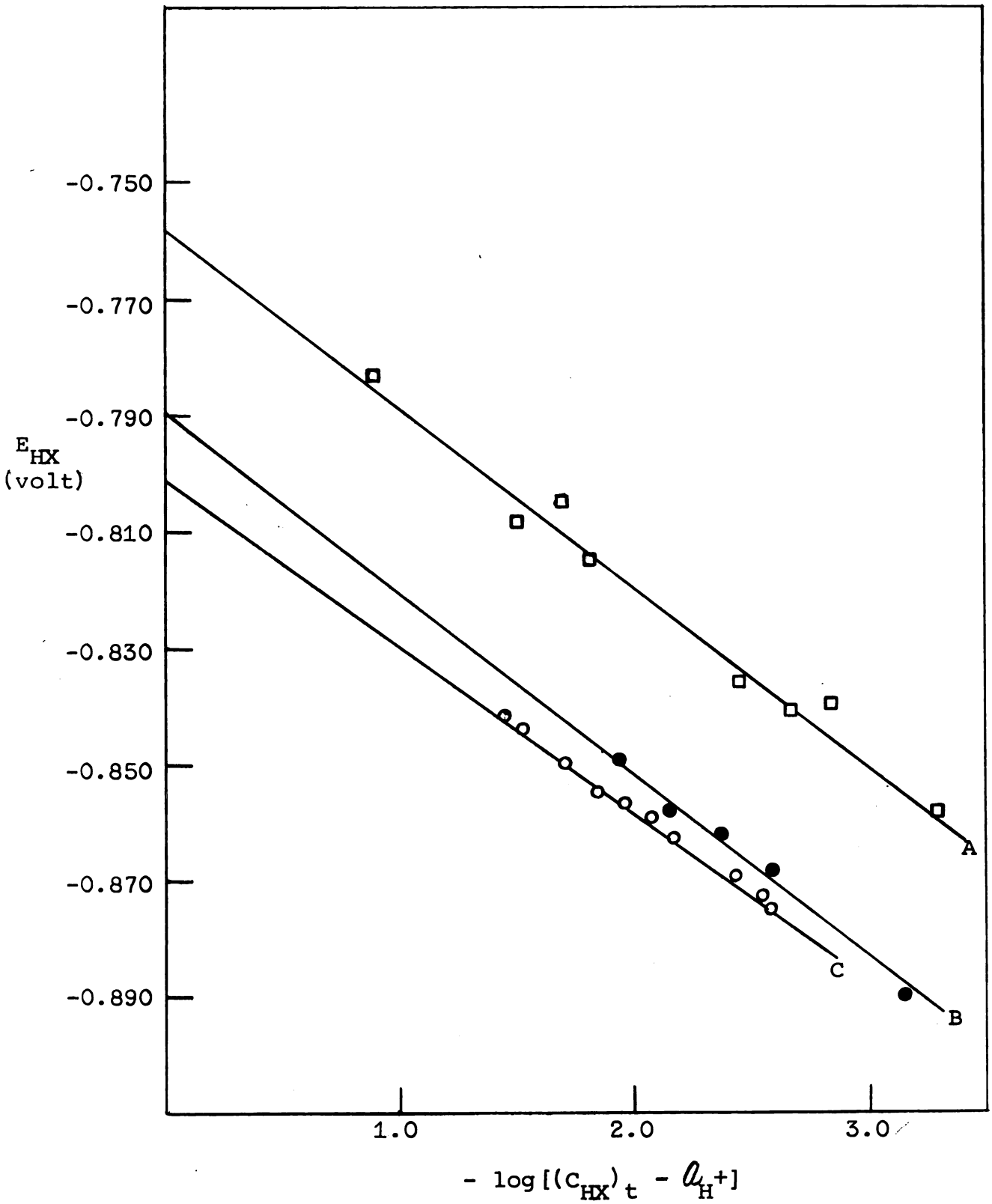

-0.750
-0.770
-0.790
-0.810
-0.830
-0.850
-0.870
-0.890
E_HX (volt)
1.0
2.0
3.0
- log[(C_HX)_t - a_H+]
A
B
C

Figure 9

The importance of the iterative process in evaluating the data may be illustrated by comparing the following data for perchloric acid. The original plot of E_{HX} vs. log $(C_{HX})_t$ yielded a slope of 0.0349, an intercept of -0.7537v., and a pK_{HX} value of 2.98, whereas in the final iterative step, for which E_{HX} was plotted vs. log $[(C_{HX})_t - a_{H^+}]$ a slope of 0.0305, an intercept of -0.7579 v., and a pK_{HX} value of 3.11 were obtained.

The pK_{HX} value of phenol of 7.54 indicates that it behaves as a stronger acid in TMG than in ethylenediamine for which the corresponding value is 8.23 (45). This behavior would be expected in as much as TMG is a considerably stronger base than ethylenediamine (aqueous pK_a = 0.4 as opposed to an aqueous pK_a of 4.15 (21), respectively.

The data illustrated in Figure 10 indicate that the conjugate ion, HX_2^-, may be one of the species present in the more concentrated phenol-TMG solutions. It would appear that the discussion given by Bruckenstein (12a) regarding phenolic ions of the HX_2^- type would also be pertinent in this work, since he points out that ions of this type have been previously reported on the basis of photometric, potentiometric, and conductometric information. The value for $pK_{HX_2^-}$ was found from the data shown in Figure 10 to be 1.52 ($K_{HX_2^-}$ = 34.2).

Figure 10. E_{HX} *vs.* log $(C_{HX})_t$ for phenol solutions in TMG.

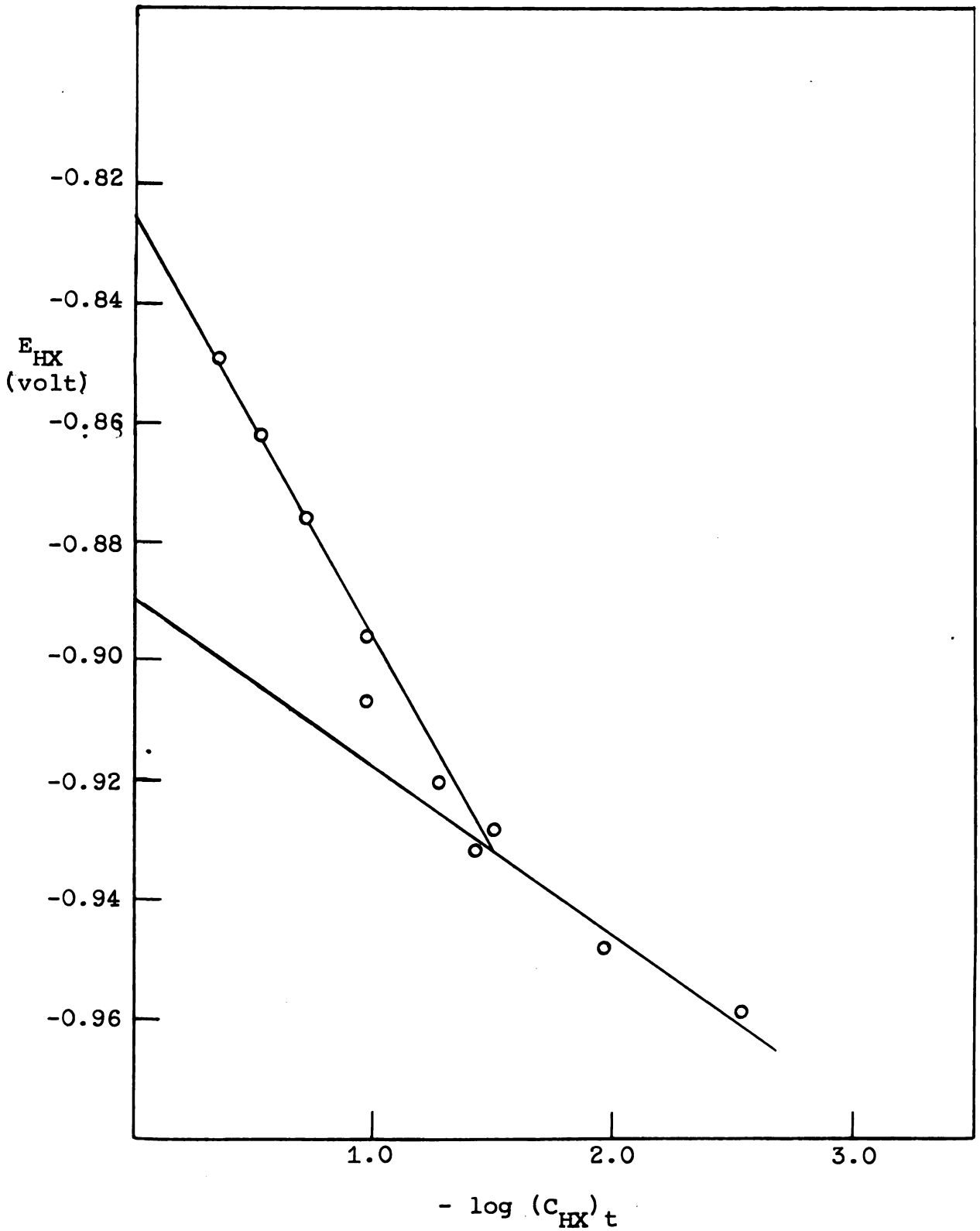


Figure 10

III. Titration Results

In the initial phases of this investigation an attempt was made to use methanolic solutions of tetrabutylammonium hydroxide as the titrant. The titration curves, however, were erratic and it was evident that methanol was undergoing a slow reaction with TMG. In order to minimize these effects, titrations were performed with TBAH in a 90-10% mixture of TMG with methanol.

The experimental data are listed in Tables VII and VIII, while the respective titration curves are shown in Figures 11-13. As expected, with weak acids, a sharp decrease in potential is observed in the initial stages of titration. Thus for phenol ($pK_a^{H_2O} \lessapprox 10$) a sharp rise at the beginning of the titration is seen, while for m-chlorobenzoic acid ($pK_a^{H_2O} \lessapprox 4$) no noticeable inflection is observed at the start of the titration. A titration curve similar to that of phenol was observed for o-cresol. Likewise, in the case of the substituted benzoic acids, the titration curves are similar to that of m-chlorobenzoic acid. While it is difficult to compare directly acid strength in TMG to acid strength in water, it appears that the substituted benzoic acids titrate in TMG as strong acids do in water, while phenol and the substituted phenols yield titration curves similar to those of weak acids in aqueous solutions.

Because of the relatively low dielectric constant of TMG, it would be expected that most of the electrolytes are

Table VII. Titration data for monoprotic acids in TMG.[a]

ml.	mv.	ml.	mv.	ml.	mv.
Phenol		o-cresol		p-chlorophenol	
0.0	+2.0	0.0	+18.0	0.0	0.0
0.84	113	0.26	14.0	1.00	20.0
3.00	154	0.50	108	3.00	45.0
5.00	173	1.00	150	5.50	73.0
7.00	186	3.01	201	7.50	105
9.00	218	5.00	237	10.00	128
10.00	250	6.00	274	14.25	196
10.10	259	6.10	284	14.85	245
10.25	277	6.20	306	14.90	265
10.50	301	6.30	331	15.00	290
11.00	327	6.40	359	15.10	310
13.00	330	6.50	370	15.25	321
		6.75	389	15.50	328
		8.00	409		
		9.00	415		
5-MeTz					
0.0	+26.0				
3.00	+22.0				
7.00	+3.0				
9.00	31.0				
9.67	93.0				
9.70	95.0				
9.72	102				
9.77	171				
9.85	310				
10.00	351				
10.20	366				
10.40	376				
11.30	392				
12.80	403				

Continued

Table VII -- Continued

ml.	mv.	ml.	mv.	ml.	mv.
o-Chlorobenzoic acid		m-Chlorobenzoic acid		p-chlorobenzoic acid	
0.0	+31.0	0.0	+20.0	0.0	29.0
0.50	+20.0	1.00	2.0	1.00	44.0
1.00	+6.0	2.00	19.0	2.00	68.0
2.50	54.0	3.00	53.0	2.50	100.
2.75	82.0	3.15	67.0	2.62	127
2.86	203	3.34	128	2.65	139
2.89	271	3.36	147	2.70	206
2.91	312	3.39	254	2.73	295
2.95	359	3.42	319	2.75	335
3.05	396	3.46	363	2.80	385
3.25	429	3.51	379	2.90	398
4.00	455	3.58	392	3.00	406
5.00	459	4.00	412	3.25	425
		4.50	421	3.80	430
		5.00	425	4.50	435

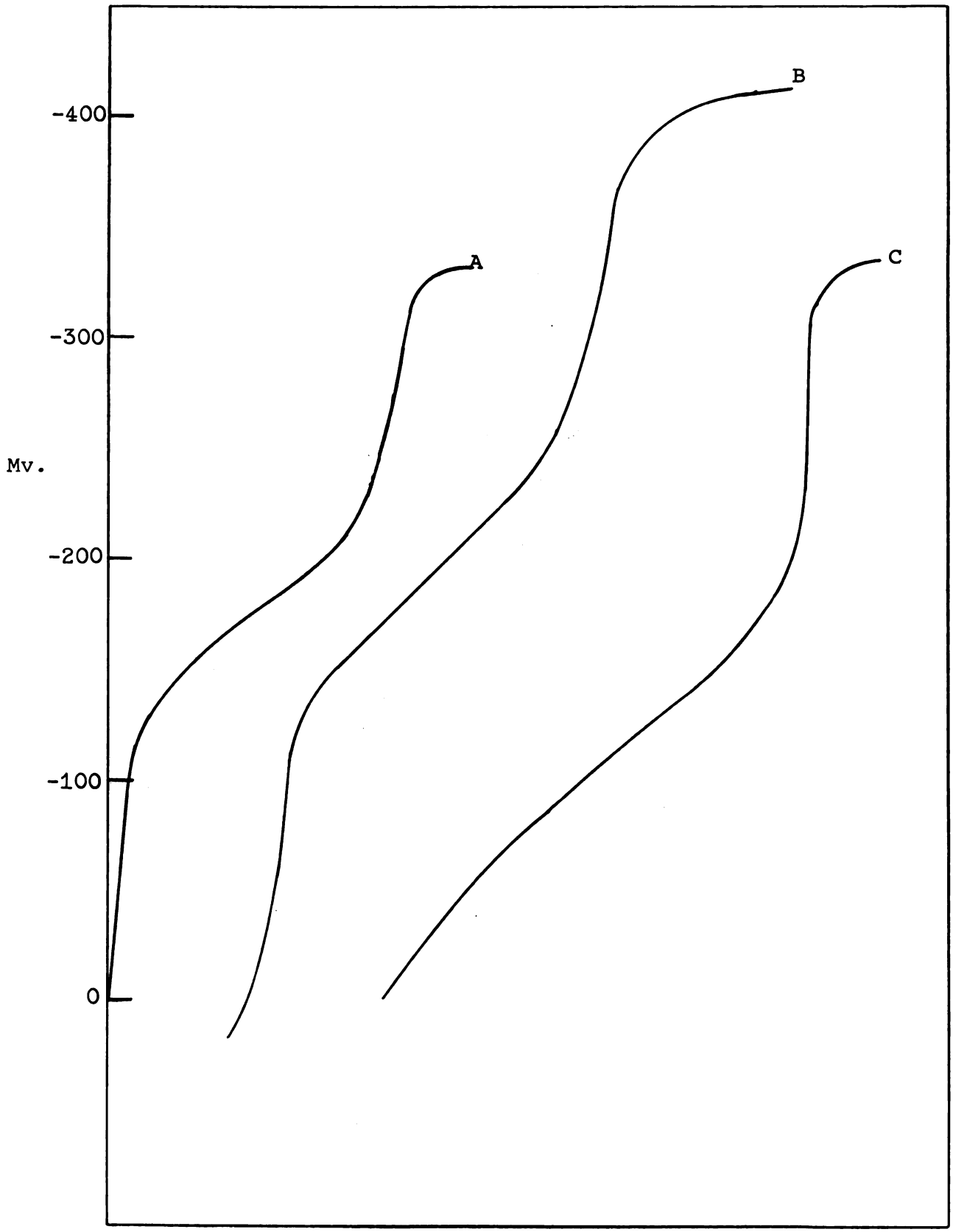
[a]No sign before data in the mv. column indicates a negative reading (-).

Table VIII. Titration data for binary mixtures of acids in TMG.[a]

Phenol-benzoic acid		Phenol-*m*-chlorobenzoic acid		*o*-Cresol-m-chlorobenzoic acid	
ml.	mv.	ml.	mv.	ml.	mv.
0.0	+2.0	0.0	+9.0	0.0	+12.0
0.50	+1.0	0.80	15.0	0.50	4.0
1.00	14.0	1.75	69.0	1.50	50.0
1.50	31.0	1.85	82.0	1.85	87.0
2.50	84.0	1.95	96.0	1.95	112
2.66	100	2.05	112	2.05	135
2.75	113	2.25	138	2.15	158
3.00	140	3.00	177	2.25	180
3.75	179	4.50	221	2.50	189
4.25	195	6.00	272	3.00	212
6.00	254	6.20	289	4.50	252
6.25	271	6.30	301	5.20	294
6.45	296	6.40	332	5.30	320
6.55	322	6.50	376	5.40	360
6.60	343	6.60	396	5.50	395
6.70	379	6.80	419	5.60	415
6.80	401	7.25	435	5.80	428
7.50	435	8.00	444	6.00	435
9.50	448	9.00	447	7.00	446
				8.00	448

[a]No sign before data in the mv. column indicates a negative reading (-).

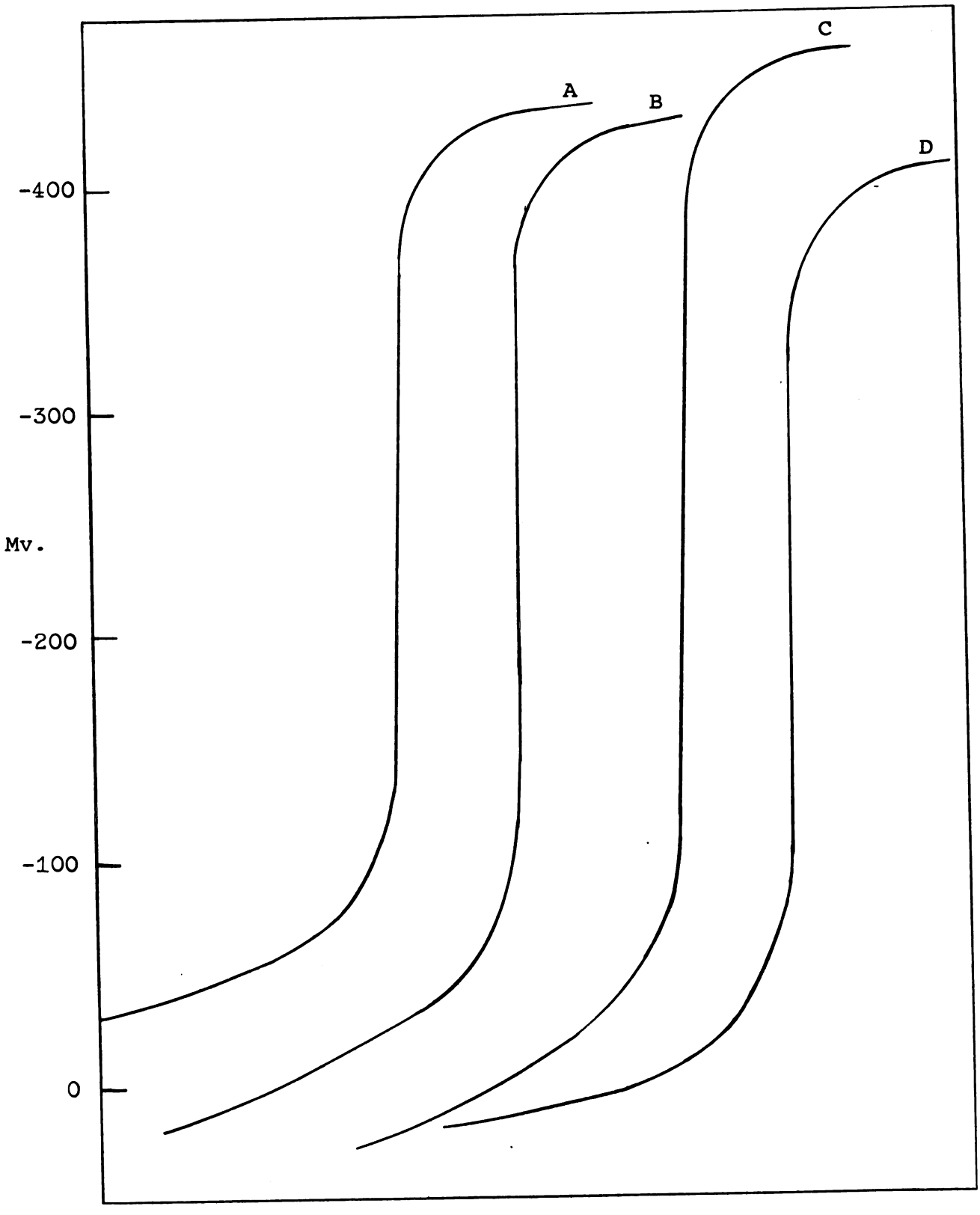
Figure 11. **Titration curves for A, phenol, B, o-cresol, and C, p-chlorophenol.**



Volume of titrant

Figure 11

Figure 12. Titration curves for A, p-chlorobenzoic acid, B, m-chlorobenzoic acid, C, o-chlorobenzoic acid, and D, 5-MeTz.



Volume of titrant

Figure 12

present in this solvent as ion-pairs. Conductance measurements (pp. 30-49) have shown that the overall dissociation constant, K_{HX}, for picric acid is 5.6×10^{-4} while the ion-pair dissociation constant for a strong electrolyte, tri-isoamyl-n-butylammonium tetraphenylborate was 1.8×10^{-3}. It is seen, therefore, that picric acid in TMG is essentially completely ionized, but, because of the low dielectric constant of the solvent, it is incompletely dissociated. On the basis of the potentiometric study, which supported the conclusions reached in the conductance study, similar behavior is expected for the substituted benzoic acids. Thus, as would be expected, the titration curves are indicative of the ionization rather than of the dissociation process.

The results of the titrations are shown in Table IX. It is seen that the results are quite acceptable and that the error is always less than 1%. Addition of 0.1% of water did not change significantly the results, but larger amounts produced increasing errors. The results were quite unreliable when 1% or more of water was added.

All titration curves were reproducible with starting potentials for identical solutions reproducible to within 10 mv.

It was found that curcumin indicator exhibited a color change in the -170 to -250 mv. region. Acidic solutions were an intense blue color which turned very sharply to yellow at the equivalence point. In the titrations of o-cresol and

Table IX. Results of potentiometric and indicator titrations of weak acids in TMG.

Substance	Meq. taken	Meq. found	Recovery, %
Phenol[a]	0.659	0.656	99.5
o-Cresol[a]	0.513	0.513	100
p-Chlorophenol	0.475	0.475	100
5-MeTz	1.215	1.212	99.75
	0.7630	0.7650	100.3
o-Nitrobenzoic acid[b]	0.660	0.660	100
	0.414	0.412	99.4
m-Chlorobenzoic acid	0.6662	0.6667	100.1
p-Chlorobenzoic acid	0.6591	0.6585	99.91
	0.9069	0.9055	99.85
o-Chlorobenzoic acid	0.6853	0.6856	100.0
	0.7798	0.7771	99.65

[a]Potentiometric titrations only.

[b]Indicator titration only.

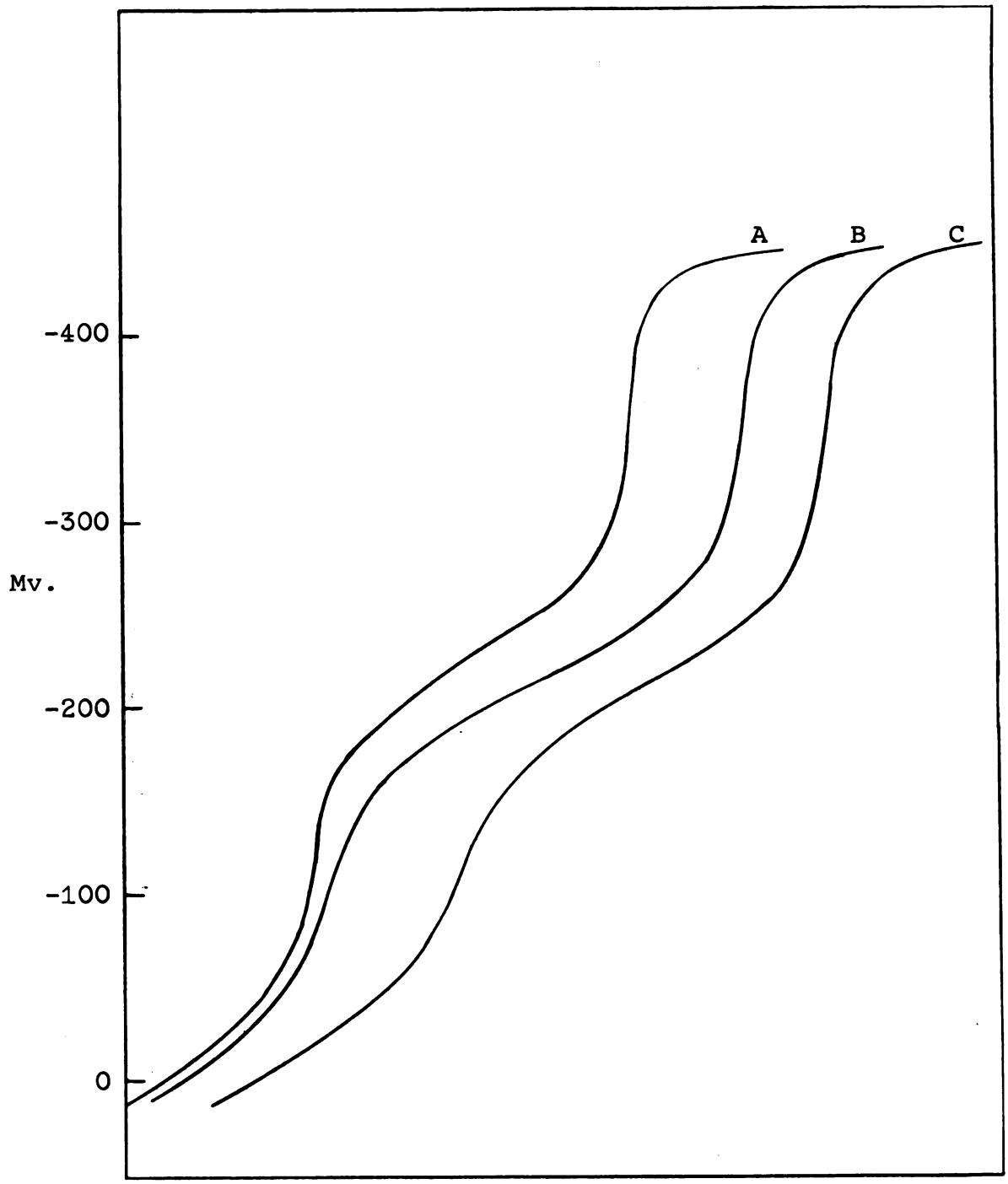
phenol, however, the equivalence points occurred below -250 mv. and consequently curcumin was unsuitable as an indicator for these species. In all other cases the equivalence points occurred at higher potentials and, therefore, the indicator method gave the same end-point as the potentiometric titration.

The indicator solution had sufficient stability to be useful over a twenty-four hour period. After this period it was discarded and fresh solution was prepared. An attempt was made to determine the indicator constants by the spectrophotometric technique introduced by Lagowski and coworkers (46). It was found, however, that the dilute indicator solutions in TMG were too unstable to yield a reproducible absorbance spectrum.

Potentiometric titrations of organic acids with nitro groups, such as picric acid, were unsuccessful due to apparent reduction of the nitro group with hydrogen. The intense yellow color of picric acid obscured the indicator endpoint but other nitro-acids, such as o-nitrobenzoic acid, yielded clear and sharp end-points with curcumin.

An attempt was made to titrate binary mixtures of acids. Figure 13 illustrates the titrations of mixtures. Although the titration curves clearly illustrated stepwise neutralization, Table X shows that only the total acid present could be determined with any degree of accuracy. The leveling effect of TMG compresses the range of acid strengths and,

Figure 13. Titration curves for binary mixtures of A, o-cresol and benzoic acid, B, phenol and m-chlorobenzoic acid, and C, phenol and benzoic acid.



Volume of titrant

Figure 13

Table X. Results of potentiometric titrations of binary mixtures of acids in TMG.

Mixture	Meq. taken	Meq. found	Total taken	Total found	Total recovery, %
(1) Benzoic acid	0.200	0.213	0.489	0.491	100
Phenol	0.289	0.278			
(2) m-Chlorobenzoic acid	0.130	0.163	0.518	0.522	101
Phenol	0.388	0.359			
(3) m-Chlorobenzoic acid	0.123	0.158	0.391	0.400	102
o-Cresol	0.268	0.242			

for example, in the benzoic acid-phenol mixture, before all of the stronger acid, benzoic, is neutralized, the weaker acid, phenol, begins to react with the titrant.

CONCLUSIONS

The conductance and potentiometric studies have both shown conclusively that TMG is a suitable solvent for the study of acid-base equilibria even though it has a low dielectric constant of 11.00. The values of the overall dissociation constants, K_{HX}, were in the range of $\backsim 10^{-3}$ to 10^{-7} with the strongest acids being perchloric and picric acid while the weakest acid was phenol. These also reflect the leveling effect TMG has on acidic substances in as much as the K_{HX} values are very considerably compressed when compared to the same values for aqueous solutions.

The inductive effect of the tetrazole substituent groups is reflected in the K_{HX} values for tetrazole and the 5-substituted tetrazoles. This would be expected since K_{HX} is a function of the ionization constant K_i, as well as the dissociation constant, K_d.

The titration studies showed that the tetrazoles and substituted benzoic acids titrate in TMG as strong acids in water while phenol and the substituted phenols titrate in TMG as would weak acids in water. These results indicate that the former are essentially completely ionized to ion-pairs while the latter are only partially ionized. Analytical results, good to $\pm$ 0.5%, were obtained.

PART II

ADIPONITRILE

HISTORICAL INTRODUCTION

The use of mononitriles as nonaqueous solvents has been the subject of many investigations (47-56). Acetonitrile (47-53), benzonitrile (53-56), propionitrile (56), isobutyronitrile (52), and α-napthonitrile (53) have all been investigated, although, the greatest effort has been made with acetonitrile. As early as 1906 Walden studied the conductometric behavior of alkali metal and tetraalkylammonium salts in propionitrile, benzonitrile, and acetonitrile (56). Fuoss and Brown studied the behavior of tetrabutylammonium tetraphenylborate, a large symmetrical electrolyte with cation and anion of approximately the same size, in acetonitrile and isobutyronitrile as a means of determining limiting ionic conductances (52). French and Muggleton investigated the behavior of picric acid in acetonitrile, benzonitrile, and α-napthonitrile (50). They proposed the formation of the triple ion, $(Pi\text{-}H\text{-}Pi)^-$, to explain the conductance behavior over their chosen concentration range (Pi represents the picrate anion). Kay and co-workers found that tetraalkylammonium halides had similar ion size parameters, a, of about 3.6 ± 0.2 A° and that only the tetramethylammonium halides showed appreciable association in acetonitrile (47). The latter results are in accord with the earlier findings of Popov and Humphrey (42). Kay et al., evaluated their

acetonitrile data by the latest Fuoss-Onsager treatment (57), while Harkness and Daggett (48), who investigated many of the same salts in acetonitrile at about the same time, evaluated Λ_o by extrapolating the phoreograms and by Shedlovsky's iteration technique (26). The three treatments appear to yield comparable results for Λ_o while the results do not agree quite as well for the ion pair association constant, K_A. For example, Λ_o values for tetra-n-propylammonium iodide by the Fuoss-Onsager, Phoreogram, and Shedlovsky methods were respectively, 172.9, 173.2, and 173.1. The K_A values as determined by the Fuoss-Onsager and Shedlovsky treatments were respectively, 5 and 10.5. It should be pointed out, however, that in determining small association constants as such, the errors are quite large.

The use of nitriles as solvents in the study of acid-base equilibria has been limited with the exception of the studies of Coetzee et al. (58). No equilibrium studies have been undertaken using dinitriles as solvents. The work presented here involves initial use of a dinitrile as an electrolytic solvent. As a prelude to studying acid-base equilibria in this solvent an electrical conductance study of sodium, potassium, and tetraalkylammonium salt solutions was initiated.

Adiponitrile (abbreviated as ADN) presents an especially interesting case since it is a relatively polar solvent with

a high dielectric constant and an appreciable dipole moment. At the same time it has respectable donor properties toward Lewis acids such as transition metal ions and would probably act as a bidentate ligand.

Literature reports indicate that adiponitrile (1,4-dicyanobutane) has a density of 0.9579 g./1. (59), a viscosity of 0.0621 poise (sixfold greater than that of water) (59), and a dipole moment of 3.76 debyes (60). A dielectric constant of 32.45 was measured in this work (p. 26). It has a very broad liquid range (2^{o} to $\backsim 300^{o}$) and may be purified by fractional freezing or fractional distillation. Most quaternary ammonium salts dissolve in adiponitrile whereas alkali metal salts are generally much less soluble even though some such as sodium perchlorate and sodium iodide form solvates.

THEORETICAL

The Onsager conductance equation (61) is given as follows

$$\Lambda = \Lambda_o - (\alpha\Lambda_o + \beta)C^{\frac{1}{2}} \qquad 1.$$

where the terms have the same meanings as given in the previous section (p. 12). This equation is only a limiting law in as much as the higher terms have been neglected in the derivation. For dilute solutions of strong uni-univalent electrolytes, a plot of Λ vs. $C^{\frac{1}{2}}$ (phoreogram) generally yields a straight line with slope $S = \alpha\Lambda_o + \beta$. By rearranging Equation 1 and solving for Λ_o (62) one can obtain the expression

$$\Lambda_o = \frac{\Lambda + \beta C^{\frac{1}{2}}}{1 - \alpha C^{\frac{1}{2}}} \qquad 2.$$

Shedlovsky has found that Λ_o was not constant over any appreciable concentration range. Consequently he defined a new function, Λ_o', by the following equation

$$\Lambda_o' \equiv \frac{\Lambda + \beta C^{\frac{1}{2}}}{1 - \alpha C^{\frac{1}{2}}} \qquad 3.$$

If Λ_o' is plotted vs. C, a straight line given by Equation 4 is obtained

$$\Lambda_o' = \Lambda_o + BC \qquad 4.$$

The value of Λ_o' at infinite dilution is the true limiting conductance, Λ_o.

It should be recalled that Equation 1 assumes that the degree of dissociation, γ, equals unity and assigns the decrease of Λ with increasing concentration of the solutions to a decrease in ionic mobility arising from the interionic forces between the ions. The equation, however, only accounts for two interionic forces, the braking relaxation effect, α, and the electrophoretic effect, β. In the modern conductance theory (57) two additional interionic forces are considered. The asymmetry in the atmosphere of a moving ion also produces a virtual osmotic force which slightly increases conductance, and also a correction must generally be made for the increase in static viscosity of the solution due to the presence of the ions. Two conductance equations then, result from the Fuoss-Onsager derivation (57). The first, for unassociated electrolytes is

$$\Lambda = \Lambda_o - SC^{\frac{1}{2}} + EC \log C + JC - F\Lambda_o C \qquad 5.$$

where, E, J, and F are given by the following relationships

$$E = E_1\Lambda_o + E_2 \qquad 6.$$

$$J = \sigma_1\Lambda_o + \sigma_2 \qquad 7.$$

and

$$F = 6.308 \times 10^{21} R^3 \qquad 8.$$

The constants, E_1, E_2, σ_1, and σ_2 are functions of fundamental constants and are defined by Fuoss and Accascina (63). The parameter, R, is known as the "hydrodynamic radius" which Fuoss and Accascina describe as "the sphere around an ion, inside of which no other ion may penetrate." Equation 8 which defines F, the correction due to the increase of static viscosity of the solution with increasing concentration, is generally applied only when viscosity data for the individual solutions are unavailable. If viscosity data are available F may be calculated from these data (64).

In the case of associated electrolytes Fuoss and Onsager have shown that the conductance equation takes the form

$$\Lambda = \Lambda_0 - S(\gamma C)^{\frac{1}{2}} + E\gamma C \log \gamma C + J\gamma C - K_A\gamma C f^2 - F\Lambda_0 C \quad 9.$$

where K_A is the association constant and f the mean activity coefficient.

By ignoring the static viscosity correction, F, in dilute solutions, Equations 5 and 9 become

$$\Lambda = \Lambda_0 - SC^{\frac{1}{2}} + EC \log C + JC \quad 10.$$

and

$$\Lambda = \Lambda_0 - S(\gamma C)^{\frac{1}{2}} + E\gamma C \log \gamma C + J\gamma C - K_A\gamma C f^2 \quad 11.$$

The assumption that F is negligible would appear to be valid since in dilute solutions the static viscosity correction would be very small.

The application of Equations 10 and 11 to conductance data is aptly described by Fuoss and Accascina (65). Kay utilized the treatments in his least squares computer program, thereby making the modern conductance theories easily and readily applied.[1]

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[1]Dr. R. L. Kay of the Mellon Institute, Pittsburg, Pa., kindly provided the Fortran program which was used in the final treatment of our data.

EXPERIMENTAL

I. Reagents

Adiponitrile (hereafter referred to as ADN) was obtained from Eastman Chemical Co. and was subjected initially to successive fractional freezings until a constant freezing temperature of 2.15° was obtained. The solvent was then fractionally distilled from granulated barium oxide through a 24 in. Vigreaux column at 1 mm. pressure and 123°. The retained middle fractions had the following properties at 25°: specific conductance, 1-2 x 10^{-8}ohm^{-1}cm^{-1}; dielectric constant at 1 megacycle, 32.45; viscosity, 0.0599 poise; density, 0.9585 g./ml. The procedures for the measurement of the dielectric constant, viscosity, and density have been previously described in detail (37). Comparison data for the specific conductance and dielectric constant are unavailable. However, the values for the viscosity and density of ADN differ somewhat from the corresponding data of 0.0621 poise and 0.9579 g./ml. in the literature (59). The solvent was recovered for reuse by distillation.

The synthesis and purification of triisoamyl-n-butylammonium iodide and triisoamyl-n-butylammonium tetraphenylborate are described above (p. 17). Eastman Grade tetrabutylammonium iodide, tetrahexylammonium iodide and tetrahexylammonium bromide, as well as reagent grade potassium and

sodium salts, were used without further purification. The other seven quaternary ammonium salts were recrystallized from appropriate solvent systems. All salts were dried *in vacuo* at 50° to constant weight prior to their use in the preparation of stock solutions. The subsequent confirmation of additivity of ionic conductances indicated that the salts were generally pure.

II. Apparatus and Procedures

The apparatus and procedures have been described above (p. 20). The additions of stock solutions to the conductance cell were made under normal laboratory conditions since brief exposures of the non-hygroscopic solvent and solutions to the atmosphere caused no observable changes in resistances.

RESULTS AND DISCUSSION

The measured equivalent conductances of the solutions and the corresponding concentrations (in moles per liter) are summarized in Table XI. The data were all evaluated both as unassociated and associated electrolytes using Equations 10 and 11 respectively. The results report the individual species as associated or unassociated electrolytes based on the nature of the calculated degree of dissociations at various concentrations. If the degree of dissociation was greater than unity then the species was taken to be unassociated and the results reported in that manner. Because of the lack of information concerning the viscosities of solutions of salts in ADN, the normally small viscosity corrections associated with J were omitted. The viscosity correction in each case has no effect on Λ_o or on the association constant and, if applied, leads to only slightly higher values for J and $\underline{a}^o$. For each salt the upper concentration limit was below the concentration at which $\underline{K}\underline{a} = 0.2$, where $\underline{K}$ is the Debye-Huckel parameter and $\underline{a}$ is the ionic diameter.

The conductance parameters obtained from least squares analysis of the data in Table XI using a CDC-3600 Computer are summarized in Table XII. Included also in Table XII are data for $\sigma\Lambda$; the standard deviation associated with the individual Λ values. Calculations were made with unweighted values

Table XI. Conductances of salts in adiponitrile at 25° (Superscripts designate series of determinations)

10^4C	Λ	10^4C	Λ	10^4C	Λ
NaI		KI		KSCN	
2.461	12.07[a]	1.337	12.92[a]	2.538	15.36[a]
10.23	11.69	9.093	12.43	5.978	15.04
16.50	11.47	15.74	12.19	12.85	14.51
24.88	11.25	24.69	11.93	23.41	13.96
37.10	11.00	37.72	11.64	38.43	13.40
2.245	12.11[b]	4.441	12.68[b]	57.24	12.86
4.418	11.96	9.874	12.40	2.362	15.38[b]
8.944	11.74	17.15	12.14	5.675	15.03
14.95	11.53	27.72	11.85	12.05	14.56
23.38	11.31	41.78	11.57	22.95	14.01
35.56	11.05			36.96	13.48
				55.56	12.94
$NaClO_4$		$NaBPh_4$		Et_4NBr	
4.562	12.53[a]	4.535	8.68[a]	4.853	12.44[a]
11.04	12.21	9.013	8.52	10.38	12.17
18.29	11.94	14.68	8.38	18.00	11.90
28.05	11.67	22.95	8.21	28.17	11.61
42.03	11.34	34.52	8.04	42.52	11.32
6.606	12.43[b]	5.116	8.64[b]	3.893	12.51[b]
12.96	12.14	9.306	8.50	9.272	12.22
21.29	11.86	15.30	8.35	16.43	11.95
33.58	11.55	23.81	8.18	25.61	11.68
50.58	11.19	35.44	8.02	39.18	11.38

continued

Table XI -- Continued

10^4C	Λ	10^4C	Λ	10^4C	Λ
Me_3PhNBr		Me_3PhNI		Pr_4NBr	
2.778	12.38[a]	2.382	12.83[a]	1.921	11.33[a]
5.716	12.15	9.796	12.39	4.817	11.14
11.37	11.78	17.16	12.08	10.63	10.87
19.35	11.40	27.08	11.77	17.53	10.67
30.56	10.99	41.17	11.44	27.51	10.42
45.55	10.59	1.993	12.88[b]	41.37	10.18
2.401	12.43[b]	4.846	12.65	1.932	11.34[b]
5.202	12.19	9.693	12.37	5.301	11.11
11.65	11.76	17.19	12.08	10.26	10.90
19.29	11.40	26.40	11.78	17.67	10.67
30.79	10.98	40.54	11.46	26.94	10.44
46.66	10.56			41.24	10.19
Pr_4NI		Bu_4NBr		Bu_4NI	
2.181	11.67[a]	2.545	10.53[a]	2.688	10.87[a]
5.026	11.49	4.851	10.38	5.208	10.72
9.937	11.27	9.616	10.20	9.979	10.52
16.86	11.05	16.01	9.99	16.91	10.31
26.16	10.82	24.71	9.79	25.99	10.09
39.55	10.57	37.59	9.56	39.15	9.86
2.180	11.68[b]	2.560	10.53[b]	2.693	10.87[b]
4.980	11.50	4.869	10.39	5.083	10.73
9.756	11.28	9.745	10.19	10.03	10.52
16.43	11.07	16.53	9.98	16.69	10.32
25.62	10.83	25.54	9.77	25.32	10.13
38.80	10.58	38.50	9.55	38.67	9.88

continued

Table XI -- Continued

10^4C	Λ	10^4C	Λ	10^4C	Λ
Hex_4NBr		Hex_4NI		$(i\text{-Am})_3BuNI$	
3.434	9.60[a]	5.467	9.85[a]	2.492	10.49[a]
6.978	9.44	9.872	9.66	6.160	10.30
12.44	9.26	15.86	9.49	10.14	10.15
19.69	9.08	25.00	9.29	16.84	9.95
29.21	8.90	36.95	9.09	25.84	9.75
43.57	8.69	5.019	9.86[b]	38.91	9.52
2.262	9.65[b]	9.237	9.68	2.978	10.47[b]
4.764	9.54	15.95	9.50	5.324	10.34
9.011	9.37	25.07	9.30	9.683	10.15
16.31	9.18	37.73	9.09	17.60	9.92
24.50	9.02			27.01	9.71
37.04	8.82			40.07	9.49
$(i\text{-Am})_3BuNBPh_4$		Me_3PhNO_3SPh			
4.061	7.149[a]	1.816	11.44[a]		
7.542	7.025	5.125	11.12		
10.81	6.929	10.00	10.84		
16.88	6.789	17.20	10.51		
25.91	6.634	27.10	10.17		
37.77	6.480	40.88	9.79		
3.410	7.185[b]	1.535	11.49[b]		
7.262	7.041	5.259	11.13		
10.622	6.940	9.481	10.88		
16.84	6.797	16.85	10.54		
25.56	6.644	26.62	10.20		
37.38	6.490	40.48	9.82		

Ph = phenyl; Me = methyl; Et = ethyl; Pr = n-propyl; Bu = n-butyl; Hex = n-hexyl; i-Am = isoamyl.

Table XII. Calculated parameters of the Fuoss-Onsager equation for salts in ADN using weighted data.

Salt	Series	$\sigma\Lambda$	Λ_o	$\underline{a}^o$	K_A	S	E	J^a
NaI	a	0.004	12.52±0.01	3.8±0.1	0	24.81	75.9	181.6
	b	0.004	12.52±0.01	4.0±0.1	0	24.81	75.9	188.8
KI	a	0.004	13.26±0.01	3.5±0.1	0	25.45	81.4	181.1
	b	0.001	13.26±0.004	3.6±0.03	0	25.45	81.4	182.2
KSCN	a	0.004	15.93±0.03	3.4±0.5	24±4	27.75	101.4	211.4
	b	0.002	15.89±0.01	2.9±0.2	18±2	27.71	101.0	182.4
$NaClO_4$	a	0.005	13.15±0.01	2.9±0.1	0	25.35	80.5	153.5
	b	0.005	13.16±0.01	2.9±0.1	0	25.36	80.7	152.4
$NaBPh_4$	a	0.004	9.17±0.01	5.2±0.2	0	21.92	50.8	172.3
	b	0.003	9.15±0.01	5.2±0.1	0	21.90	50.6	173.5
Et_4NBr	a	0.003	13.05±0.007	3.3±0.1	0	25.27	79.8	168.6
	b	0.002	13.06±0.004	3.3±0.1	0	25.27	79.9	167.3
Me_3PhNBr	a	0.003	12.93±0.02	4.0±0.6	27±4	25.16	78.9	197.0
	b	0.002	12.93±0.01	4.2±0.5	28±3	25.16	78.9	202.7
Me_3PhNI	a	0.003	13.27±0.01	2.7±0.1	0	25.46	81.5	145.5
	b	0.004	13.26±0.01	2.8±0.1	0	25.44	81.3	149.8
Pr_4NBr	a	0.003	11.70±0.01	3.9±0.1	0	24.10	69.7	175.8
	b	0.003	11.71±0.01	3.9±0.1	0	24.11	69.7	174.3

continued

Table XII -- Continued

Salt	Series	$\sigma\Lambda$	Λ_o	$\underline{a}^o$	K_A	S	E	J^a
Pr_4NI	a	0.003	12.08±0.01	4.0±0.1	0	24.42	72.5	182.4
	b	0.004	12.08±0.01	3.9±0.1	0	24.43	72.6	180.0
Bu_4NBr	a	0.004	10.94±0.01	4.2±0.1	0	23.44	64.0	171.9
	b	0.002	10.94±0.01	4.2±0.1	0	23.44	64.0	172.3
Bu_4NI	a	0.003	11.30±0.01	4.1±0.1	0	23.75	66.7	173.7
	b	0.005	11.30±0.01	4.2±0.1	0	23.76	66.7	177.2
Hex_4NBr	a	0.004	10.06±0.01	4.4±0.1	0	22.69	57.4	165.8
	b	0.006	10.05±0.02	5.0±0.2	0	22.67	57.4	181.8
Hex_4NI	a	0.002	10.40±0.01	4.4±0.1	0	22.98	60.0	169.8
	b	0.005	10.40±0.01	4.5±0.1	0	22.98	60.0	173.4
$(\underline{i}\text{-Am})_3BuNI$	a	0.005	10.91±0.01	4.2±0.1	0	23.42	63.8	172.6
	b	0.003	10.91±0.01	4.1±0.1	0	23.42	63.8	170.2
$(\underline{i}\text{-Am})_3BuNBPh_4$	a	0.002	7.585±0.006	4.9±0.1	0	20.55	38.9	138.4
	b	0.002	7.578±0.005	4.9±0.1	0	20.55	38.9	138.4
Me_3PhNO_3SPh	a	0.003	11.79±0.02	2.6±0.5	13±4	24.18	70.4	125.7
	b	0.002	11.81±0.01	2.9±0.4	15±3	24.20	70.5	137.7

[a]No viscosity correction applied.

of Λ and values of Λ weighted by the concentration, C. The weighted data yielded a considerably better fit to the theoretical equations, as evidenced by the smaller values of $\sigma\Lambda$, therefore the final results are reported on that basis. For comparison sake, the same parameters as reported in Table XII are given in Table XIII using unweighted data for six of the systems studied. The detailed results given in Table XII are summarized in Table XIV where the results of the two series of measurements on each salt have been averaged by weighting each parameter inversely by its standard deviation.

The constants α, β, E_1, and E_2 for ADN at 25° have values of 0.8620, 14.01, 7.479, and 17.81, respectively.

The Λ_o values listed in Table XII consistently are 0.01-0.02 unit higher than those in Table XIII as calculated using unweighted data. The Λ_o values of Table XII are about 0.05 unit larger than the corresponding values obtained from preliminary Shedlovsky plots of Λ_o' *vs.* C. The Λ_o values as obtained by the two different methods as well as by the Shedlovsky iteration technique (26) are listed in Table XV. The percentage differences between the Fuoss-Onsager and the two other methods are also included. The average percentage difference between the Fuoss-Onsager and the Λ_o' *vs.* C method is 0.53% for the twelve salts considered, while the average difference is only 0.30% between the Fuoss-Onsager and the Shedlovsky iteration technique. These observations then

Table XIII. Calculated parameters of the Fuoss-Onsager equation for salts in ADN using unweighted data.

Salt	Series	$\sigma\Lambda$	Λ_o	$\underline{a}^o$	K_A	S	E	J^a
NaI	a	0.019	12.50±0.02	4.0±0.2	0	24.79	75.7	189.2
	b	0.011	12.51±0.01	4.1±0.1	0	24.80	75.8	193.8
Me_3PhNBr	a	0.013	12.91±0.02	3.4±0.8	22±5	25.14	78.7	169.5
	b	0.010	12.92±0.01	3.7±0.6	25±4	25.14	78.8	184.3
Pr_4NBr	a	0.010	11.69±0.01	4.0±0.1	0	24.09	69.6	176.5
	b	0.008	11.70±0.01	4.0±0.1	0	24.10	69.7	177.0
Bu_4NBr	a	0.013	10.93±0.01	4.3±0.1	0	23.43	63.9	176.2
	b	0.009	10.93±0.01	4.3±0.1	0	23.43	63.9	175.4
Hex_4NI	a	0.005	10.40±0.01	4.4±0.1	0	22.98	60.0	170.4
	b	0.011	10.39±0.01	4.6±0.2	0	22.97	59.9	176.6
$(\underline{i}\text{-Am})_3BuNBPh_4$	a	0.008	7.571±0.006	4.9±0.1	0	20.54	38.8	140.9
	b	0.009	7.576±0.007	5.0±0.2	0	20.54	38.9	141.5

[a]No viscosity correction applied.

Table XIV. Averaged conductance parameters for adiponitrile solutions.

Salt	Λ_o	$\underline{a}^o$	K_A
NaI	12.52	3.9	0
KI	13.26	3.6	0
KSCN	15.91	3.1	20
$NaClO_4$	13.16	2.9	0
$NaBPh_4$	9.16	5.2	0
Et_4NBr	13.06	3.3	0
Me_3PhNBr	12.93	4.2	28
Me_3PhNI	13.27	2.7	0
Pr_4NBr	11.71	3.9	0
Pr_4NI	12.08	4.0	0
Bu_4NBr	10.94	4.2	0
Bu_4NI	11.30	4.2	0
Hex_4NBr	10.06	4.6	0
Hex_4NI	10.40	4.4	0
$(\underline{i}\text{-Am})_3BuNI$	10.91	4.1	0
$(\underline{i}\text{-Am})_3BuNBPh_4$	7.58	4.9	0
Me_3PhNO_3SPh	11.80	2.8	14

Table XV. Comparison of Λ_o values as given by various conductance treatments.[a]

Salt	Λ_o A	Λ_o B	Λ_o C	% Diff. A and B	% Diff. A and C
NaI	12.52	12.48	12.49	0.32	0.24
KSCN	15.91	15.76	15.90	0.95	0.06
Me_3PhNBr	12.93	12.80	12.90	1.01	0.23
Me_3PhNI	13.27	13.23	13.26	0.34	0.08
Pr_4NBr	11.71	11.66	11.66	0.42	0.42
Pr_4NI	12.08	12.03	12.04	0.42	0.33
Bu_4NBr	10.94	10.89	10.90	0.46	0.37
Bu_4NI	11.30	11.25	11.26	0.44	0.36
Hex_4NBr	10.06	10.00	10.00	0.60	0.60
$(\underline{i}\text{-Am})_3BuNI$	10.91	10.86	10.87	0.46	0.37
$(\underline{i}\text{-Am})_3BuNBPh_4$	7.58	7.55	7.55	0.40	0.40
Me_3PhNO_3SPh	11.80	11.74	11.81	0.51	0.08

[a]A represents the Fuoss-Onsager treatment; B represents the Λ_o' *vs.* C treatment; C represents the Shedlovsky iteration technique.

point out that although the modern conductance theory is considerably more complex in both derivation and application than the earlier methods, the refinements are relatively small. This observance is in accord with findings of Harkness and Daggett in their acetonitrile study (48). Figure 14 illustrates the Λ_o' vs. C plots obtained by least squares analysis. Calculation of the conductance differences at infinite dilution between corresponding bromides and iodides and between corresponding sodium and triisoamyl-n-butylammonium salts indicates an uncertainty in Λ_o values of 0.03 units or about 0.3%. This apparent level of accuracy is quite satisfactory in comparison to the results for most other nonaqueous systems and reflects the general consistency of the overall results.

Single ion limiting conductances were obtained on the basis of the assumption of Coplan and Fuoss (29) that the limiting conductance of the triisoamyl-n-butylammonium ion is equal to that of the tetraphenylborate ion in all solvents. That is

$$\lambda_o(\text{i-Am})_3\text{BuN}^+ = \lambda_o(\text{BPh}_4)^- = \frac{1}{2}\Lambda_o(\text{i-Am})_3\text{BuNBPh}_4 \qquad 12.$$

From the Λ_o values for salts with a common ion, limiting equivalent ionic conductances of fourteen ions in ADN have been calculated; the results are summarized in Table XVI. These data will reproduce the experimentally determined Λ_o value for each of the salts within 0.01 unit. For example the Λ_o value for Me_3PhNI as obtained from Table XIV is 13.27, whereas the

Figure 14. Λ_o' as a function of C for A, NaI, B, Me_3PhNI, D, Bu_4NI, and E, Hex_4NI.

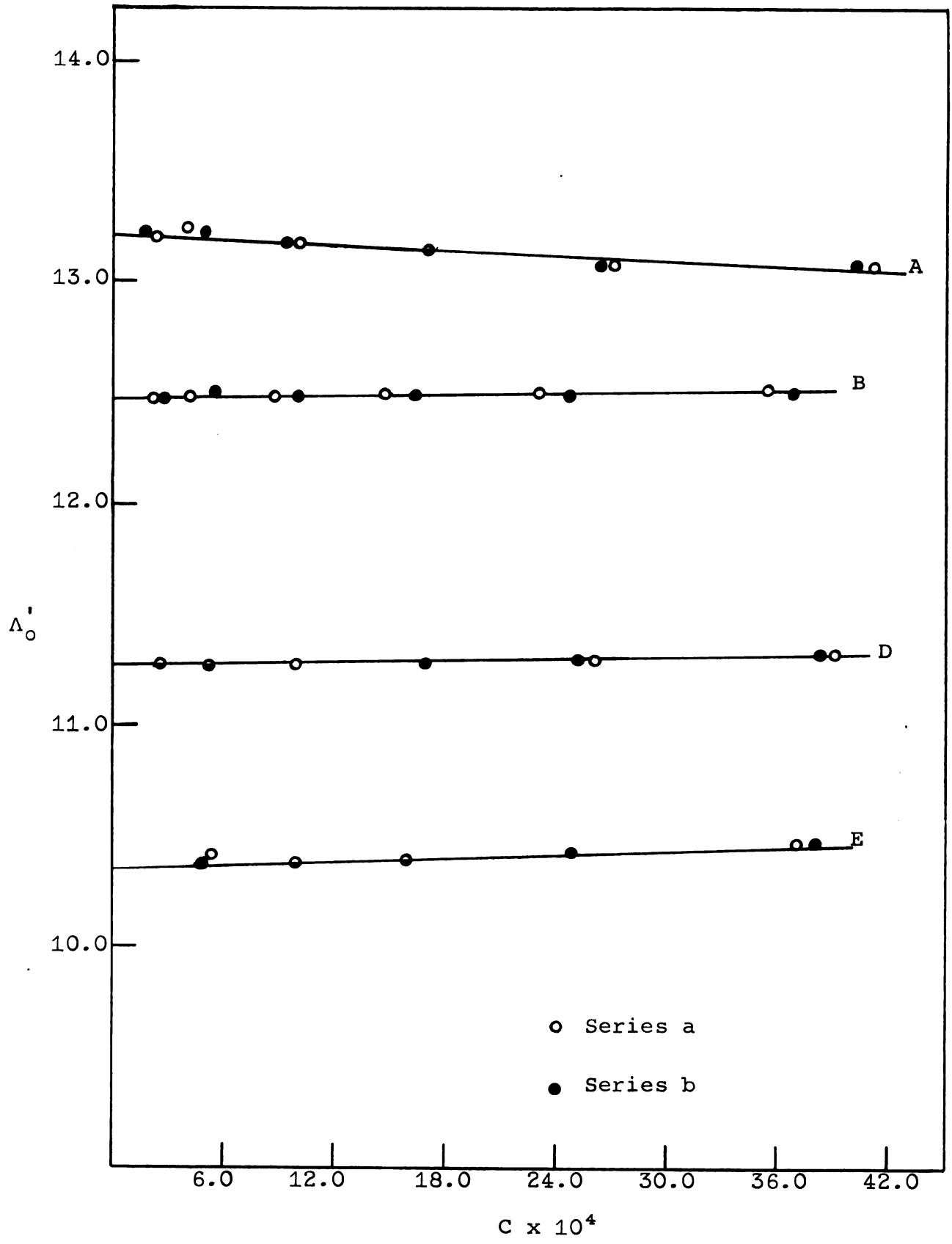
14.0
13.0
12.0
11.0
10.0
Λ_o'
A
B
D
E
Series a
Series b
6.0
12.0
18.0
24.0
30.0
36.0
42.0
C x 10^4

Figure 14

Table XVI. Single ion limiting equivalent conductances in adiponitrile based on triisoamyl-n-butylammonium tetraphenylborate as reference electrolyte.

Ion	λ_o^+	Ion	λ_o^-
Et_4N^+	6.29	SCN^-	9.79
Me_3PhN^+	6.15	ClO_4^-	7.77
K^+	6.12	I^-	7.13
Na^+	5.38	Br^-	6.77
Pr_4N^+	4.94	$PhSO_3^-$	5.65
Bu_4N^+	4.17	BPh_4^-	3.79
$(i\text{-Am})_3BuN^+$	3.79		
Hex_4N^+	3.28		

value obtained from adding the ionic conductances of Me_3PhN^+ and I^- as given in Table XVI is 13.28. The potassium and sodium ions have limiting conductances between those of the trimethylphenylammonium and tetra-n-propylammonium ions; all other ionic conductances occur in the expected sequences.

CONCLUSIONS

The above results indicate that adiponitrile is a good dissociating solvent, since only three of the seventeen salts studied show any ion-pair association in the concentration range of $\backsim 10^{-4}$ to 5 x 10^{-3} M. The relatively high viscosity is reflected in the low values obtained for the limiting conductance (e.g., Λ_o value for Bu_4NI is 11.30 as compared with 164.6 for the same salt in acetonitrile (47) and 101.72 in methanol (66)). On the other hand it is interesting to note that although dielectric constants of acetonitrile and methanol are very close to that of adiponitrile (36.02 and 32.63 as opposed to 32.45 at 25° respectively). The latter seems to have a greater dissociating power, since, in general, it has been shown that tetraalkylammonium salts are slightly associated both in acetonitrile (47) and methanol (66). Despite its high viscosity, therefore, adiponitrile should be a very useful solvent for the study of inorganic reactions.

RECOMMENDATIONS FOR FUTURE STUDIES

Additional research which might be performed on 1,1,3,3-tetramethylguanidine could include:

1. Determining Λ_o and K_{HX} values for a series of tetraalkylammonium salts and in conjunction with this the determination of limiting ionic conductances. This could in turn reflect on the nature of solvation in TMG.

2. Development of a more suitable proton sensitive electrode in TMG to be used in conjunction with a reference electrode of known behavior such as aqueous SCE.

3. Formation of the lyate ion, TMG^-, and as a result determining the autoprotolysis constant, K_s.

4. Spectrophotometric study of acid-base indicators in TMG alone or in conjunction with electrochemical studies.

5. Polarography in TMG.

In as much as adiponitrile is the first of the dinitriles to be studied, some of the following might be attempted:

1. Conductance studies of a series of dinitriles such as malononitrile, glutaronitrile, and succinonitrile to determine Λ_o values and limiting ionic conductances.

2. Potentiometric studies in ADN using some of the electrode systems already characterized for acetonitrile.

3. Acid-base equilibrium studies by electrochemical or spectroscopic techniques.

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APPENDICES

APPENDIX I

COMPUTER PROGRAMS

A. General Introduction

The numerical calculations given in this thesis were performed on a Control Data 3600 digital computer with the programs written in Fortran. Since this system is widely used and compatible with most modern computers, Fortran programs are listed below for evaluating both conductance and potentiometric data.

For the conductance program the following data are read in: ID, which is the identification; ETA, which is the viscosity in poise; DIELEC, which is the dielectric constant; TEMP, which is the absolute temperature; ZERO, which is a first assumption to Λ_o; IAM, which is an integer controlling the input with respect to accepting literature or laboratory data; N, the number of data sets read in; IAC, an integer which controls the extent to which the program is executed; RHO, which is the density in g./ml.; KONST, the cell constant; LSOLV, the specific conductance of the solvent; M2, the molecular weight of the solute; SOLV, which is the original weight of the solvent; RATIO1 which is the g. solute/g. stock solution; RATIO2, which is the g. solvent/g. stock solution; R, which is the resistance

in ohms; WTSS, the weight of stock solution; IJ, which is END OF D always placed in column 21 of the last data card; LAMBDA, the equivalent conductance; and C, the molar concentration. It should be pointed out, however, that not all of the above are read in for one data set. The read in data are governed by the input of laboratory or literature data. Examination of the comment, C, and the READ statements will clarify this matter. The output consists of printing the values above plus Λ_o values as obtained by three methods, the overall acidity constants KS and KF as obtained by the Fuoss-Shedlovsky and by the Fuoss-Kraus methods, respectively, and the value of K_{HX} obtained by the Ostwald dilution technique; X, which is the notation for $C\Lambda S_z f_{\pm}^2$; Y, the symbol for $1/\Lambda S_z$; and YCALC,T,DEVIATION, which are parameters evaluated in the statistical section of the program concerned with the rejection of points. The other output data are clearly labeled and should be familiar to the conductance experimenter and are consistent with the notation used in the text above. The statistical routine is only incorporated with the Fuoss-Shedlovsky treatment.

For the e.m.f. program the following data are read in: L, which is always the integer 1; Q, the value of $E_H^{o'}$; ID, the identification; E, the e.m.f. value in volts; C, which is the molar concentration corresponding to a given E value; and IJ, which is END OF D always placed in column 21 of the

last data card. The output consists of printing the above plus K, the value for K_{HX}; LOG K, which is $-pK_{HX}$; ACTIVITY which is a_{H^+}; ARG, which is $[(C_{HX})_t - a_{H^+}]$; and LOG ARG, which is $\log_{10}$ of ARG. The other output parameters are clearly labeled such that there should be no ambiguity when referring to the text.

B. Conductance Program

```
      PROGRAM SHEDLOV
      TYPE REAL LAMBDA,M,K,LSOLN,LSOLV,KONST    ,M2,KS
      DIMENSION ID(7),X(50),C(50),LAMBDA(50),LSOLN(50),R(50),
     1WTSOLT  (50),WTSOLV(50),WTSS(50),PRIME(50),SQRTC(50),YCALC(50),
     2T(50),DEV(50),XX(50),YY(50)
      CALL Q8Q ERSET (0)
   14 READ 8,ID
    8 FORMAT(7A8)
      PRINT 9,ID
    9 FORMAT(1H1,20X,7A8)
      IF(ID.EQ.8HEND OF R)STOP
      READ 247,ETA,DIELEC,TEMP,ZERO
  247 FORMAT(4F10.0)
      PRINT 248,ETA,DIELEC,TEMP
  248 FORMAT(/10X*VISCOSITY =*F8.6,5X*DIELECTRIC CONST. =*F6.3,5X*TEMPER
     1ATURE =*F7.3)
      A=1.825E6/((DIELEC*TEMP)**1.5)
      B1=8.203E5/((DIELEC*TEMP)**1.5)
      B2=82.43/(ETA*SQRTF(DIELEC*TEMP))
      PRINT 249,A,B1,B2
  249 FORMAT(/10X*DEBYE HUCKEL CONSTANT =*F7.3,/10X*ONSAGER CONSTANT ALP
     1HA =*F8.4,/10X*ONSAGER CONSTANT BETA=*F8.4)
C     IAM =0 FOR LAB DATA, IAM = 1 FOR LIT DATA
C     IF IAC IS BLANK THEN THE PROGRAM IS EXECUTED COMPLETELY.  IF IAC
C     = 1, THEN THE PROGRAM IS TERMINATED AT THE SHEDLOVSKY LAMBDA ZERO
C     PRIME CALCULATION.
      READ 501,IAM,N,IAC
  501 FORMAT(3I5)
      IF (IAM.EQ. 1)503,502
  502 READ1,RHO, KONST,LSOLV,M2,SOLV,RATIO1,RATIO2
    1 FORMAT(7F10)
      PRINT2,KONST,LSOLV,M2,SOLV,RATIO1,RATIO2 $ I=1
    2 FORMAT(/10X*KONST=*F10.8,5X*LSOLV=*F14.12,5X*M.W.=*F6.2,5X*WT. SOL
     1VENT ORIGINALLY =*F6.2,/10X*RATIO1=*F12.9,5X*RATIO2=*F8.6)
      PRINT 639,RHO
```

continued

```
  639 FORMAT( 10X*DENSITY =*F7.5)
      PRINT 67
   67 FORMAT(8X*CHECK OF INPUT DATA*//12X*R           WT. STOCK SOLN.*)
   10 READ 4,R(I),WTSS(I),IJ
    4 FORMAT(2F10,A8)
      PRINT 66,R(I),WTSS(I)
   66 FORMAT(10X,F12.4,F12.6)
      IF(IJ.EQ.8HEND OF D)125,12
   12 I=I+1  $GO TO 10
  125 DO 113 J=1,I
      WTSOLT(J)=RATIO1*WTSS(J)
      WTSOLV(J)=RATIO2*WTSS(J) +SOLV
      C(J)=1000.*RHO*WTSOLT(J)/(M2*(WTSOLV(J)))
      LSOLN(J)=KONST   /R(J)
  113 LAMBDA(J)=1000.*(LSOLN(J)-LSOLV)/C(J)
      GO TO 551
  503 I=1
  504 READ 561,LAMBDA(I),C(I),IJ
  561 FORMAT(2F10,A8)
      IF (IJ.EQ.8HEND OF D)551,581
  581 I=I+1
      GO TO 504
  551 PRINT 19
   19 FORMAT (/10X*LAMBDA ZERO PRIME        C          LAMBDA        SQRT
     1C*)
      DO 511 J=1,I
      SQRT C(J)=SQRTF(C(J))
      PRIME(J)=(LAMBDA(J)*B2)SQRTF(C(J)))/(1.-B1*SQRTF(C(J)))
  511 PRINT 16,PRIME(J),C(J),LAMBDA(J),SQRT C(J)
   16 FORMAT(14X,F8.4,5X,3F13.8)
      CALL LNLSTSQ(C,PRIME,I,CEPT,SLOPE)
C     CEPT IS THE INTERCEPT LAMBDA ZERO
      PRINT 18,CEPT,SLOPE
   18 FORMAT(/10X*LAMBDA ZERO FROM LAMBDA ZERO PRIME PLOT =*F8.4,/10X*SL
     1OPE =*F20.10)
      IF(IAC.EQ. 1)14,21
C     BEGIN LOOP WHICH FIGURES X AND Y FOR EACH LAMBDA AND C
C     THE VARIABLE ZERO IS LAMBDA ZERO.
```

continued

```
 21 PRINT 3
  3 FORMAT(/10X*LAMBDA ZERO          M*12X*C            LAMBDA        SQRT
    1 C            X             Y              Z             SZ*)
 22 DO 13 J=1,I
    Z = (B2+B1*ZERO)*SQRTF(LAMBDA(J)*C(J))/(ZERO**1.5  )
    SZ = 1. + Z + .5*Z**2 + .333*Z**3 + .25*Z**4
    F=10.**(-A*SQRTF(SZ*LAMBDA(J)*C(J)/ZERO))
    Y(J)=1./(LAMBDA(J)*SZ)
    X(J)=C(J)*LAMBDA(J)*SZ*F**2
 13 PRINT 200,C(J) ,LAMBDA(J),SQRT C(J),X(J),Y(J),Z,SZ
200 FORMAT(37X7F13.8)
    SUMX=0.0
    SUMX2=0.0
    SUMXY=0.0
    SUMY=0.0
    SUMY2=0.0
    DO 201J=1,I
    SUMX=SUMX+X(J)
    SUMX2=X(J)*X(J)+SUMX2
    SUMY=SUMY+Y(J)
    SUMY2=Y(J)*Y(J)+SUMY2
201 SUMXY=X(J)*Y(J)+SUMXY
    W=N
    FND=(SUMX2*W)-(SUMX*SUMX)
    FCDE=(SUMX2*SUMY)-(SUMX*SUMXY)
    B=FCDE/FND
    M=(SUMXY-SUMX*B)/SUMX2
    PRINT 5,ZERO,M
  5 FORMAT(10XF11.6,F12.6)
    ZERO2=ABSF(1./B)
    DIFF = ABSF(ZERO2-ZERO)
    IF(DIFF.LE. .0001*ZERO)25,15
 15 ZERO=ZERO2 $ GO TO 22
 25 KS=1./(M*(ZERO2**2))
    PRINT 7,KS
  7 FORMAT (/8X*KS = *F15.10)
    K=1./((1./KS)-((B2*B1*ZERO)**2/ZERO**2))
    PRINT 6,K
  6 FORMAT(/8X*KF=*F15.10)
```

continued

```
C     K IS FUOSS AND KRAUS CONSTANT AND KS IS SHEDLOVSKY CONSTANT
      FN=W
      FRACT=((SUMXY-SUMX*SUMY/FN)**2)/(SUMX2-SUMX**2/FN)
      E=SUMY2-(SUMY**2/FN)-FRACT
      S2=E/(FN-2.)
      S=SQRTF(S2)
      SA2=S2/(SUMX2-(SUMX**2/FN))
      SA=SQRTF(SA2)
      SB2=S2*SUMX2/(FN*SUMX2-SUMX**2)
      SB=SQRTF(SB2)
      THEOS=(B2+B1*ZERO2)
      PRINT 613,THEOS
  613 FORMAT(/10X*THEORETICAL SLOPE =*F20.10)
      PRINT 901,S,SA,SB
  901 FORMAT(/10X*STD. DEV. OF A SINGLE Y =*F14.10,5X*STD. DEV. OF SLOP
     1E =*F14.10,/10X*STD. DEV. OF INTERCEPT =*F14.10,/)
      STDZ=SB/B**2
      STDK=SQRTF((B**4)*(SA**2)/(M**4)+4*(B**2)*(SB**2)/(M**2))
      PRINT 623,STDZ,STDK
  623 FORMAT(/10X*STD. DEV. OF LAMBDA ZERO =*F14.10,/10X*STD. DEV. OF KS
     1=*F14.10)
      PRINT 902
  902 FORMAT(/15X*Y              YCALC          T              DEVIATION*
     1/)
  949 FORMAT(10X,4F14.10)
      DO 911J=1,I
      YCALC(J)=M*X(J)+B
      T(J)=ABSF(Y(J)-YCALC(J))
      DEV(J)=T(J)-3.*S
      PRINT949,Y(J),YCALC(J),T(J),DEV(J)
      IF(DEV(J),LT.0.)911,912
  911 CONTINUE
      PRINT 706
  706 FORMAT(/10X*RECIPROCAL LAMBDA     C X LAMBDA*/)
      DO 707 J=1,I
      YY(J)=1./LAMBDA(J)
      XX(J)=C(J)*LAMBDA(J)
  707 PRINT 708,YY(J),XX(J)
  708 FORMAT(15X,F12.9,F20.7)
      CALL LNLSTSQ(XX,YY,I,CE,SL)                                    continued
```

```
      PRINT 710,SL,CE
  710 FORMAT(/10X*OSTWALD SLOPE =*F12.9,5X*OSTWALD INTERCEPT =*F12.9)
      Q=1./CE
      OS=CF/SL
      PRINT 711,Q,OS
  711 FORMAT(/10X*OSTWALD LAMBDA ZERO =*F8.4,5X*OSTWALD DISS. CONST. =*F
     112.9)
      GO TO 14
  912 PRINT 921,Y(J)
  921 FORMAT(/10X*REJECTED POINT =*F14.10)
      L=J
      DO 631 J=L,I
      C(J)=C(J+1)
  631 LAMBDA(J)=LAMBDA(J+1)
      N=FN
      I=N-1
      N=N-1
      GO TO 21
      END


      SUBROUTINE LNLSTSQ(X,Y,N,A,B)
      DIMENSION Y(50),X(50)
      SUMX=0.0
      SUMX2=0.0
      SUMXY=0.0
      SUMY=0.0
      SUMY2=0.0
      DO201 I=1,N
      SUMX=SUMX+X(I)
      SUMX2=X(I)*X(I) +SUMX2
      SUMY=SUMY+Y(I)
      SUMY2=SUMY2+Y(I)*Y(I)
  201 SUMXY=SUMXY    +X(I)*Y(I)
      Z=N
      FND=(SUMX2*Z)-(SUMX*SUMX)
      FCDE=(SUMX2*SUMY)-(SUMX*SUMXY)
      A=FCDE/FND
      B=(SUMXY-SUMX*A)/SUMX2
      END
```

C. E.M.F. Program

```
      PROGRAM EMFCALC
      TYPE REAL K,INT,M,K1
      DIMENSION ID(7),C(50),E(50),AH(50), ARG(50),X(50),Y(50)
      CALL Q8QERSET(0)
101   READ 1,L,Q,ID
  1   FORMAT(I1,F9.0,7A8)
      PRINT2,ID
  2   FORMAT(1H1,20X,7A8)
      IF(ID.EQ.8HEND OF R)STOP
      I=1
100   READ 3,E(I),C(I),IJ
  3   FORMAT(2F10,A8)
      IF(IJ.EQ.8HEND OF D)22,21
 21   I=I+1    $ GO TO 100
 22   PRINT 4,Q
  4   FORMAT(/10X*Q = *F10.5)
      DO 200 J=1,I
      Y(J)=E(J)
200   X(J)=LOGF(C(J))/2.303
300   SUMX=0.0
      SUMX2=0.0
      SUMXY=0.0
      SUMY=0.0
      SUMY2=0.0
      DO 201J=1,I
      SUMX=SUMX+X(J)
      SUMX2=X(J)*X(J)+SUMX2
      SUMY=SUMY+Y(J)
      SUMY2=Y(J)*Y(J)+SUMY2
201   SUMXY=X(J)*Y(J)+SUMXY
      W=I
      FND=(SUMX2*W)-(SUMX*SUMX)
      FCDE=(SUMX2*SUMY)-(SUMX*SUMXY)
      B=FCDE/FND
      M=(SUMXY-SUMX*B)/SUMX2
      INT=B
      IF(L.EQ.1)400,401
```

continued

```
400 K=10.**((INT-Q)/.02958)
    GO TO 500
401 K1=10.**(( INT-Q)/.02958)
    DIFF=ABSF(K1-K)
    IF(DIFF.LE. .0001*K)101,501
501 K=K1
500 ALNK=(INT-Q)/.02958
    PRINT 12
 12 FORMAT(////20X*NEW ITERATION BEGINS*//)
    PRINT 7,M,INT,K,ALNK
  7 FORMAT (//10X*SLOPE =*F10.6,5X*INTERCEPT=*F10.6,5X*K =*F13.10,
   15X*LOG K =*F9.5)
    FN=W
    FRACT=((SUMXY-SUMX*SUMY/FN)**2)/(SUMX2-SUMX**2/FN)
    E=SUMY2-(SUMY**2/FN)-FRACT
    S2=ABSF(E/(FN-2.))
    S=SQRTF(S2)
    SA2=S2/(SUMX2-(SUMX**2/FN))
    SA=SQRTF(SA2)
    SB2=S2*SUMX2/(FN*SUMX2-SUMX**2)
    SB=SQRTF(SB2)
    PRINT 901,S,SA,SB
901 FORMAT(/10X*STD. DEV. OF A SINGLE Y =*F14.10,5X*STD. DEV. OF SLOP
   1E =*F14.10,/10X*STD. DEV. OF INTERCEPT =*F14.10,/)
    SQ2=0.0011**2
    SLOGK=(.4343/(INT-Q))*SQRTF(SB**2 + SQ2)
    PRINT10,SLOGK
 10 FORMAT(/10X*STD. DEV. OF LOG K =*F10.6)
    I=FN
    PRINT 9
  9 FORMAT(//10X*ACTIVITY          ARG          LOG ARG          EMF
   1        TOTAL CONC.*/)
    DO 25 J=1,I
    AH(J)=(SQRTF(K**2 + 4. *K*C (J))-K)/2.
    ARG(J)=C(J)-AH(J)
    X(J)=LOGF(ARG(J))/2.303
 25 PRINT 8,AH(J),ARG(J),X(J),Y(J),C(J)
  8 FORMAT(10X,F12.10,5X,F10.8,5X,F9.5,5X,F9.5,5X,F10.8)
    L=2
    GO TO 300
    END
```

APPENDIX II

Derivation of the Equations for the Standard Deviations of Λ_o and K_{HX}

If the probable error is known for two independent variables x,y from which the function u is calculated, the probable error in u may be computed according to the technique illustrated by Daniels et al. (67). That is

$$Pu = \left[\left(\frac{\partial u}{\partial x}\right)_y^2 P_x^2 + \left(\frac{\partial u}{\partial y}\right)_x^2 P_y^2 \right]^{\frac{1}{2}} \qquad 1.$$

where Pu, Px, and Py represent the probable errors associated with u, x, and y. Since

$$\sigma i = \frac{Pi}{0.6745} \qquad 2.$$

where σi represents the standard deviation of any variable, i, Equation 1 may be written in terms of the standard deviations σu, σx, and σy associated with u, x, and y, respectively.

$$\sigma u = \left[\left(\frac{\partial u}{\partial x}\right)_y^2 \sigma_x^2 + \left(\frac{\partial u}{\partial y}\right)_x^2 \sigma_y^2 \right]^{\frac{1}{2}} \qquad 3.$$

For the case where u is a function of only one variable, x, Equation 3 reduces to

$$\sigma u = \frac{du}{dx} \quad \sigma x \qquad 4.$$

Since $\Lambda_o = 1/b$ and the standard deviation, σb, of the intercept, b, is known from least squares analysis, Equation 4 may be solved for the standard deviation, $\sigma\Lambda_o$ associated with Λ_o.

$$\sigma\Lambda_o = \frac{d\Lambda_o}{db} \quad \sigma b \qquad 5.$$

Differentiating Λ_o with respect to b yields

$$\sigma\Lambda_o = - \frac{\sigma b}{b^2} \qquad 6.$$

or in statistical terms

$$\sigma\Lambda_o = \pm \left| - \frac{\sigma b}{b^2} \right| \qquad 7.$$

For calculating the standard deviation of K_{HX}, σK_{HX}, where $K_{HX} = b^2/m$ and σm, the standard deviation of the slope, m, and σb are known Equation 3 becomes

$$\sigma K_{HX} = \left[\left(\frac{\partial K_{HX}}{\partial m}\right)_b^2 \cdot \sigma_m^2 + \left(\frac{\partial K_{HX}}{\partial b}\right)_m^2 \cdot \sigma_b^2 \right]^{\frac{1}{2}} \qquad 8.$$

The following equation results after taking the indicated derivatives

$$\sigma K_{HX} = \left[\frac{b^4}{m^4} \sigma_m^2 + \frac{4b^2}{m^2} \sigma b^2 \right]^{\frac{1}{2}} \qquad 9.$$

which may also be written as

$$\sigma K_{HX} = \pm \left| \left[\frac{b^4}{m^4} \sigma m^2 + \frac{4b^2}{m^2} \sigma b^2 \right]^{\frac{1}{2}} \right| \qquad 10.$$