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Computer Investigation of the Variation of Conductivity with Concentration

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COMPUTER INVESTIGATION OF THE VARIATION OF CONDUCTIVITY WITH CONCENTRATION

(TITLE)

BY

Larry MacPeers Shadwick

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

MASTER OF SCIENCE, DEPARTMENT OF CHEMISTRY

IN THE GRADUATE SCHOOL, EASTERN ILLINOIS UNIVERSITY
CHARLESTON, ILLINOIS

1973
YEAR

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COMPUTER INVESTIGATION OF THE VARIATION OF CONDUCTIVITY WITH CONCENTRATION

BY

LARRY MACPEERS SHADWICK

M. Sc., Eastern Illinois University, 1973

ABSTRACT OF A THESIS

Submitted in partial fulfillment of the requirements
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ABSTRACT

Title of Thesis: Computer Investigation of the Variation of Conductivity with Concentration

Larry MacPeers Shadwick, Master of Science, 1973

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

Computer programs were developed for the conductance equations of R. M. Fuoss and L. Onsager as well as for the conductance equations of T. J. Murphy and E. G. D. Cohen. These programs were used to calculate values from selected conductance measurements. The resulting values were compared with values produced by other computer programs using the equations of Fuoss and Onsager as well as the equations of E. Pitts. The comparisons demonstrated the equations of Murphy and Cohen to be the equal of or superior to the other equations for the majority of cases. The equations of Pitts were superior for the solutes HCl, NaOH and KI.

Only the equations of Murphy and Cohen are applicable to asymmetric electrolytes. The values computed using those equations for various asymmetric solutes in a variety of solvents indicated fair agreement with accepted values, particularly with the values of the association constant.

The equations of Murphy and Cohen are an extension of and an improvement to the equations of Fuoss and Onsager, which

have been the standard equations used to evaluate conductance measurements. The equations of Murphy and Cohen will most likely achieve that status in the future.

ACKNOWLEDGEMENTS

The author is extremely grateful to Dr. D. W. Ebdon for his encouragement, guidance, and patience. I am particularly indebted to Dr. Ebdon for the many Saturdays spent helping me in this work.

I wish to express appreciation to the members of the chemistry department for their dedication and professionalism.

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GLOSSARY OF SYMBOLS

$\underline{a}$	distance of closest approach of two ions, in Angstroms
C	molar concentration
E	transcendental term in the conductance equation
$\mathcal{F}$	faraday = 96,493 coulombs-equivalent^{-1}
J	coefficient of linear term
J_1	coefficient of linear term in Pitts equation
J_2	coefficient of term in Pitts equation
K_A	ion pair association constant
K_d	ion pair dissociation constant = $K_A{}^{-1}$
S	limiting coefficient in Onsager equation
α	relaxation field coefficient of Onsager equation
β	electrophoretic coefficient of Onsager equation
γ	degree of dissociation
Λ	equivalent conductance in ohm^{-1} cm^2 equivalent^{-1}
Λ_o	limiting equivalent conductance at infinite dilution
Λ_1	term in the conductivity expression for the Murphy-Cohen equation
Λ_2'	term in the conductivity expression for the Murphy-Cohen equation
Λ_2	term in the conductivity expression for the Murphy-Cohen equation
σ	standard deviation of least-squares fit
σ_{K_A}	standard deviation of ion pair association constant

INTRODUCTION

Conductance measurements are among the most precise attainable in electrochemistry. Due to such precision, they have been considered rich sources of data for analyzing the incompletely understood chemistry of electrolytes. The inconsistencies of conductance data with theory have usually led, after periods of confusion, to a better understanding of electrolyte solutions.

Conductance measurements are a direct measure of bulk ionic transport and, if the number of charge carriers is known, can provide an experimental value of the ionic mobility. For electrolytes which do not form ion pairs (unassociated electrolytes) the number of charge carriers can be determined from stoichiometry. However for associated electrolytes one needs a theoretical relationship which describes conductance as a function of concentration so that, with this "baseline" as a guide, the deviations from theory can be interpreted in terms of an ion pair association constant. In order for this constant to be physically meaningful, the theoretical (or empirical) relationship between the measurements and the phenomena must be valid and accurate. The ultimate test of any relationship is how well it works in evaluating accurate conductance measurements for a variety of electrolytes. The criteria used in the evaluation, however, usually are not entirely acceptable from all viewpoints of present thinking in electrochemistry.

Given a mathematical relationship between conductance measurements and electrolyte phenomena, the use of computers makes possible extensive evaluation of these measurements for a great variety of electrolyte-solvent combinations. This evaluation can only be as valid as the criteria used. It is the aim of this thesis to examine a few relationships and some of the evaluation criteria by use of computers and the most accurate conductance data. First, a brief review of the development of conductance theory will be given.

Historical Review

Since the characteristic property of ions is their charge, conductivity became the first method used extensively in the study of ion association. It was conductance measurements which led Arrhenius to postulate in 1883 his theory of electrolytic dissociation, which described electrolytes such as sodium chloride as dissociating into free ions in solution. The mass action law was used to calculate the equilibrium constant, and the degree of dissociation, Υ, was calculated from the ratio of the equivalent conductance at a given concentration to the limiting equivalent conductance at infinite dilution: $\Upsilon = \Lambda/\Lambda_o$. The dissociation constant K_d was then given by

$$K_d = \frac{\Lambda^2 c}{\Lambda_o(\Lambda_o - \Lambda)}$$

The Arrhenius equation predicted that at very low concentrations the equivalent conductance should be linear with concentration. The very precise data of Kohlrausch, however, showed that the variation of equivalent conductance with concentration for salts such as sodium chloride approached a square root dependence at low concentrations. Ostwald, on the other hand, using the Arrhenius hypothesis, stated the Ostwald dilution law

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_o} + \frac{c\Lambda}{K_d\Lambda_o^2}$$

and demonstrated that conductance data for many systems, such as acetic acid in water, conformed to the predictions of the hypothesis.

The confusion was due to a lack of understanding of the fundamental structure of electrolytes. More than a generation elapsed before sufficient evidence was available to resolve the dilemma. Early in the twentieth century, x-ray studies showed that there are no neutral molecules of sodium chloride, only sodium and chloride ions arranged in a periodic crystalline lattice. Acetic acid, on the other hand, exists in the pure form as neutral molecules; it could dissociate into ions as described by the Arrhenius theory. Salts of inorganic acids, such as sodium chloride, could not possibly dissociate since they are inherently ionic species. What, then, leads to the decrease in equivalent conductance of these salts with concentration?

The equivalent conductance Λ for a completely dissociated electrolyte may be written in the form

$$\Lambda = \mathfrak{F} \sum u_i$$

where $\mathfrak{F}$ is the faraday and u_i is the mobility of the ith ion. It is evident that a decrease in Λ is equivalent to a decrease in ionic mobility. (The mobility is defined as the velocity of an ion in an electric potential gradient of one volt per centimeter.) Since it is the charge on the ions which makes electrolytes different from non-ionic solutes, one might expect that such deviations of electrolyte solutions from ideal behavior were due to the coulombic forces between the ions. This fact was definitely established on sound theoretical grounds by Milner,[1] who was able to calculate the thermodynamic properties of electrolytic solutions from theory. His treatment, however, was exceedingly involved and did not yield an entirely satisfactory result.[2]

In 1923 Debye and Hückel,[3] instead of trying to obtain the electrostatic potential energy as a sum of all pairs of ions as Milner had done, considered each ion a discrete site of charge and all ions about the reference ion as a continuous space charge or "ion atmosphere." This concept and the use of Poisson's equation effected a mathematical short cut which leads to relations from which the limiting behaviors of dilute solutions of electrolytes may be quantitatively predicted. They took as their model a completely dissociated electrolyte, the ions of which were rigid, unpolarizable spheres. Interactions between ions were computed by Coulomb's law with the medium assumed uniform hydrodynamically and electrostatically. Thus the viscosity and dielectric constant of the pure solvent were taken as those of the medium. Further, they restricted themselves to very dilute solutions where these approximations were not too drastic.

The first result of the Debye-Hückel theory was to predict that the logarithms of the activity coefficients for dilute solutions of completely dissociated electrolytes should be linear with the square root of the ionic strength, in exact agreement with experiment. Debye and Hückel then obtained a first approximation to the solution of the conductance problem. In their treatment,[4] however, they neglected the thermal motion of the reference ion and made some rather dangerous hydrodynamic approximations. In 1926 Onsager[5] introduced the necessary refinements and published the famous Onsager limiting law of equivalent conductance

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

where α and β are theoretically derivable coefficients for the time of relaxation effect and the electrophoretic effect, respectively. The Onsager equation correctly predicted the limiting slope of a plot of equivalent conductance *versus* the square root of the concentration for completely dissociated electrolytes. Two years later Debye and Falkenhagen[6] extended the Onsager theory to alternating-current conductance.

The main achievement of the Debye-Hückel-Onsager theory was that it showed how to calculate the effects of long-range electrostatic interactions in dilute electrolyte solutions. It demonstrated that many salts in water are completely dissociated. Apparent deviations from the theory would find a physical explanation, it was thought, and would not require a return to the idea of un-ionized salt molecules.[7] But such deviations were not uncommon and at least one possible cause was appreciated. In the mathematical simplifications of the theory it had to be assumed that the electrostatic interaction energy of an ion is small compared with its kinetic energy. This assumption will not be valid for small ions of high charge in media of low dielectric constant.

This complication, the problem of short-range forces, has not been satisfactorily solved even to this day. The first attempt at a solution, however, was made by N. Bjerrum.[8] Using the same model as Debye and Hückel, Bjerrum plotted for dilute solutions the probability of finding an oppositely charged ion at a given distance from a central ion. The distribution curve shows a flat minimum distance where the work of separating the two oppositely charged ions is four times as great as the mean kinetic energy per degree of freedom. Bjerrum regarded a pair of ions within this distance as associated to form an "ion pair." It is evident that the Bjerrum ion pair is a mathematical fiction and that there is an arbitrary element in its definition. It does, however, offer a mathematically simple answer to the complication of short-range effects.

In 1932 Onsager and Fuoss[9] presented a treatise on conductance, diffusion and viscosity, where the limiting laws, valid for electrolytes containing two species of ions, were extended to electrolytes of arbitrary compositions. Their calculations of the electrophoretic term in conductance theory contained a "distance-of-closest-approach" parameter $\underline{a}$ and represented the first attempt to extend the range of the theory by taking into account the finite size of the ions. The next appropriate step seemed to be the incorporation of the ionic diameter into the relaxation term. This was first done by Kaneko[10] and later by Falkenhagen, Leist and Kelbg.[11]

A more complex presentation, incorporating an ion size and resulting in transcendental terms, was given by Pitts in 1953.[12] In his presentation he claimed to have used the complicated potential function of Gronwall, La Mer and Sandved.[13] He actually used the Debye-Hückel solution of the Poisson-Boltzman equation.[14] He also assumed that all perturbation effects on a given ion vanish at the distance of closest ionic approach and at all greater distances. The Pitts equation, although never popular, has been demonstrated by Stokes and his coworkers to be superior to the highly accepted Fuoss-Onsager equation for precise conductance measurements of hydrochloric acid and sodium hydroxide.[15]

Fuoss and Onsager[16] published their well-known conductance equation for symmetrical electrolytes in 1957. Their treatment, like that of Pitts, was quite complex in the basic results. Using suitable mathematical approximations, however, they were able to put their results in a more usable form for the analysis of data. Their resulting equation as later modified by Fuoss and Accascina[17] is

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

The first two terms are those of the Onsager equation, where $S = \alpha\Lambda_0 + \beta$. The remaining two represent higher order terms, mainly in the relaxation field. All three coefficients, S, E, and J, depend on the absolute temperature, the dielectric constant and viscosity of the solvent, the charge type of the electrolyte, and fundamental constants. In addition, J depends upon the ion-size parameter $\underline{a}$.

The success of the Fuoss-Onsager equation in the analysis of a large amount of data for uni-univalent electrolytes[18] demonstrated its essential correctness as far as the form of the equation, in particular the existence of the log term, was concerned. In 1961-63 Atkinson and coworkers[19,20] were able to show that the theory was capable of fitting conductance data for electrolytes of higher charge type.

Prior to the appearance of the Fuoss-Onsager equation, researchers had used empirical extensions[21] of the Onsager equation to analyze conductance data for unassociated symmetrical electrolytes. For those systems which deviated noticeably from these empirical-theoretical equations, association constants were employed to improve the fit. In cases where these constants were not large, they were regarded as little more than adjustable parameters. Now with a theory which seemed to describe precisely the behavior of unassociated electrolytes at low concentrations, many workers showed renewed interest in the determination of ion-association constants from conductance measurements.[7,22] Those systems showing moderate association were re-examined and the association constants derived therefrom were believed to correspond rather closely to physical reality.

The Fuoss-Onsager equation modified for ion association takes the form

$$\Lambda = \Lambda_o - S(C\gamma)^{\frac{1}{2}} + E(C\gamma)\log(C\gamma) + J(C\gamma) - K_A f_{\pm}^{2}(C\gamma)\Lambda$$

and is able to describe observed values of conductance at low concentrations for a variety of systems in media of dielectric constant sometimes as low as 12.[23] Problems arise, however, in the interpretation of the constants. The equation involves three arbitrary constants, Λ_o, J, and K_A, from each of which one can calculate a distance of closest approach or ion diameter <u>a</u>. For an electrolyte which conforms to the behavior theoretically predicted for the model of charged spheres, one might expect the equality

$$a_{\Lambda_o} = a_J = a_{K_A}$$

to hold. This result is not always obtained.[24,25]

In a series of papers with Onsager, Fuoss derived a new equation which depended on two arbitrary parameters, Λ_o and L(a) which purportedly described the conductance behavior of associated electrolytes without the need of an arbitrary association constant. The equation has not been demonstrated successfully.

In 1970 Murphy and Cohen published their improvements and corrections to the Fuoss-Onsager equations.[26] In their derivations they used a different method to solve the differential equation for the nonequilibrium pair distribution function, as well as including a neglected contribution to the conductivity that affects the value of E and J. Moreover, they used a higher order expression for the nonequilibrium pair distribution function so as to extend the applicability of the theory to asymmetric solutes such as $CaCl_2$.

STATEMENT OF PROBLEM

The Murphy-Cohen equation is the result of corrections to and extensions of the Fuoss-Onsager theory of electrolytes. This resulting equation is the first such conductance equation which can be applied to unsymmetric solutes. If the Murphy-Cohen equation accurately describes the conductance relationship for dilute, unassociated, unsymmetric solutes, then accurate association constants can be derived from conductance measurements for associated, unsymmetric solutes.

This thesis will investigate the accuracy of the Murphy-Cohen equation for a variety of solvent-solute combinations.

The first part of the investigation will compare results of the Pitts equation and the Fuoss-Onsager equation obtained by Fernandez-Prini and Prue against results of the Fuoss-Onsager equation and Murphy-Cohen equation obtained by the author for identical data. These data are for unassociated, symmetric solutes in a variety of solvents.

The second part of the investigation will compare association constants obtained by the author using the Murphy-Cohen equation in the associated electrolyte form against association constants obtained by methods other than conductance.

COMPARISON OF CONDUCTANCE EQUATIONS

The Murphy-Cohen equation is the first conductance equation which can be applied to asymmetrical solutes. It uses the same model as the Fuoss-Onsager equation--a hard-core ion of a non-zero radius moving through an incompressible fluid characterized only by a dielectric constant and a viscosity. This equation also uses some of the derivations as used for the Fuoss-Onsager equation and results in the same general form as the Fuoss-Onsager equation.

The Murphy-Cohen equation differs mainly from the Fuoss-Onsager equation due to three general changes being incorporated into the derivations. The first change is the use of a different method to solve the differential equation for the nonequilibrium ion pair distribution function of the ions, which made it possible to derive an expression for the conductivity:

$$\Lambda = \Lambda_o + \Lambda_1 C^{\frac{1}{2}} + \Lambda_{2'} C \ln C + \Lambda_2 C$$

with a more nearly accurate expression for Λ_2.[27,28] The second change is the use of a higher order expression for the extended equilibrium pair distribution function so as to extend the theory to asymmetric solutes.[27] The last change involves the inclusion of a contribution to the conductivity that affects the value of both $\Lambda_{2'}$ and Λ_2. Chen pointed out[29] the neglected term which was the velocity field contribution to the relaxation field. Inclusion of this term, $-E_2$, into the expression for the transcendental term, E, in the Fuoss-Onsager conductance equation gives the transcendental term for the Murphy-Cohen equation

$$E = E_1 \Lambda_o - 2E_2 .$$

This additional term is considerably smaller than E and the function C ln C approximates a linear function over short ranges of concentration, thereby allowing the JC term of the Fuoss-Onsager equation to absorb such differences as caused by the missing $-E_2$ term when the Fuoss-Onsager equation is used on actual data.[30,31] It is interesting to note that the transcendental term for the Pitts equation

$$E = E_1 \Lambda_o - E_2$$

is the same as for the Fuoss-Onsager equation. The similarity is due to Pitts' neglect of the velocity field contribution, which Fuoss-Onsager included. Pitts, however, included the electrophoretic effect contribution, which Fuoss-Onsager neglected.

DEVELOPMENT OF COMPUTER PROGRAMS

The evaluation of the Murphy-Cohen equation was started by first writing programs for the Fuoss-Onsager equation. The Fuoss-Onsager equation has been most successfully and widely-used equation for numerous combinations of symmetric solutes and solvents. The Fuoss-Onsager equation also has the same general form as the Murphy-Cohen equation. Therefore, the Fuoss-Onsager equation is an ideal starting point in the development of programming techniques, test data, and experience in evaluating conductance data. The Fuoss-Onsager equation also offers much simpler relationships for determining various parameters and constants from conductance data.

The FORTRAN IV programming language was used on an IBM 360 model 50 computer for most of the computer programming. The basic method used was that outlined by Kay for the Fuoss-Onsager equation.[32] Kay used differential equations to guide the program in approaching the solution values. This technique proved far superior to overrun methods of hunting for a solution.

The programs used for the Murphy-Cohen equations are given in Appendix 1--for the unassociated electrolyte--and in Appendix 2--for the associated electrolyte. The programs have the following arrangement of instruction blocks:

```
read input data
determine initial values
print input data and initial values
perform least-squares fit
determine distance of closest approach and related terms
perform final calculations
print output
go back to the first instruction block
```

The least-squares fit used in the author's programs does not weight the data as no definite advantage would be gained for evaluation of the results.

COMPARISON OF PROGRAM RESULTS

One particular problem in obtaining conductance data from literature is the tendency of many authors to give conductance data extrapolated to some "even" value of concentration or to give data that has been "rounded" to better fit some graph or empirical equation. Fernandez-Prini and Prue in their paper noted that usually the original unpublished data that they sought for their comparisons had been lost.[14] That paper by Fernandez-Prini and Prue is a well-documented source of conductance data and results for the Fuoss-Onsager equation and particularly the Pitts equation. Table II lists their results from that paper. Table I lists this author's results with the same data using his computer programs for the Fuoss-Onsager equation and the Murphy-Cohen equation.

The differences between Table I and Table II are partly due to the use of the general equation form

$$\Lambda = \Lambda_0 - S C^{1/2} + EC \log C + J_1 C - J_2 C^{3/2}$$

by Fernandez-Prini and Prue. The $- J_2 C^{3/2}$ term is not due to retention of higher order terms in the differential equation, but rather the results of approximations to functions in the complete equations. This $- J_2 C^{3/2}$ term is less of an extension to the Fuoss-Onsager equation and the Pitts equation and more of an empirical addition. It weakens the basic theories while adding to the variability of term values when doing a least-squares fit. Another cause of the differences would be the weighting of the conductance data by the concentration in the treatment by Fernandez-Prini and Prue. Weighting usually creates more questions than answers. For example, would a different weighting factor be better? Another consideration is that many of the solutes Fernandez-Prini and Prue used had already been reported as fitting the Pitts equation better than the Fuoss-Onsager.

Of particular interest in comparing Table I and Table II is the standard deviation of the fit, σ, and the distance of closest ionic approach, a. These show that the author's program for the Fuoss-Onsager equation, which does not have weighted data nor the $- J_2C$ term, has as good or better fit than the program by Fernandez-Prini and Prue for the Fuoss-Onsager equation, and that the author's program gives comparable values for the distance of closest ionic approach. The Pitts equation gives the best overall fit for the data used, with the Murphy-Cohen equation giving the second best. However, if one excepts the solutes of HCl, NaOH, and KI, the Murphy-Cohen equation gives a better fit in every case but one. Comparison of the distance of closest approach values shows that the Murphy-Cohen equation and Pitts equation give similar values in water and ethanol, but give dissimilar values in DMF.

Table III gives the standard deviation of the least-squares fit, the distance of closest ionic approach, the ion association constant, the standard deviation of the ion association constant, and, when available, the ion association constant from a reference source. In most cases this reference value was determined by methods other than those using conductance data. The standard deviation of the least-squares fit, σ , shows fairly good correlation with the exceptions of LaNTS in water at 25°C, and $CaCl_2$ in methanol at 10°C. These exceptions could be due to bad data or could possibly indicate solute, solvent combinations in need of research. The distance of closest approach, a, shows a much larger range of values than one could expect from ionic radii in crystal structures. However, given a tightly held layer of solvent and/or the added bulk of an associated ion, one might expect the distance of closest approach to increase. The association constant, K_A, is susceptable to loss of meaning due to inaccurate data or data of limited accuracy. Therefore, association constants above 50 are usually considered to indicate association. The standard deviation of the association constant can help in evaluating the reasonableness of the association constant. Negative association constants usually indicate no association, bad data, or both. The higher association constant values seem to correlate well with the association values produced from activity coefficient data used in computer modeling of seawater equilibria.[33] The results for $MgCl_2$ in water at 10°C indicate an ion association. The heavier alkaline earth chlorides are generally thought to be unassociated.

TABLE I CALCULATIONS BY AUTHOR FOR UNASSOCIATED SYMMETRIC ELECTROLYTES

FUOSS-ONSAGER

SOLVENT	ELECTROLYTE	N	10^4 C	Λ_o	J	$\underline{a}$	σ
H_2O	HCl (15a)	10	3-150	426.67	526.7	3.49	0.125
	HCl (34)	11	2-150	426.41	546.8	3.62	0.179
	HCl (35)	6	20-150	426.87	504.6	3.35	0.105
	NaOH (15c)	13	10-160	249.47	298.7	3.16	0.080
	KCl (36)	7	5-100	149.94	208.0	3.27	0.029
	KCl (37)	6	5-130	149.97	197.4	3.11	0.013
	KI (37)	11	10-160	150.53	222.2	3.48	0.043
DMF	KI (38)	11	4-40	83.11	1067.5	4.85	0.095
	$CsClO_4$ (38)	14	1-50	86.96	1000.7	4.24	0.039
CH_3OH	KCl (39)	25	0.7-50	104.92	1352.8	3.25	0.045
	NaCl (39)	23	0.4-40	97.26	1430.3	3.81	0.042

MURPHY-COHEN

SOLVENT	ELECTROLYTE	N	10^4 C	Λ_o	J	$\underline{a}$	σ
H_2O	HCl (15a)	10	3-150	426.63	490.2	3.39	0.108
	HCl (34)	11	2-150	426.38	509.7	3.52	0.162
	HCl (35)	6	20-150	426.81	470.3	3.25	0.098
	NaOH (15c)	13	10-160	249.41	264.1	2.98	0.068
	KCl (36)	7	5-100	149.91	168.4	3.06	0.018
	KCl (37)	6	5-130	149.94	159.9	2.91	0.013
	KI (37)	11	10-160	150.48	187.2	3.35	0.030
DMF	KI (38)	11	4-40	83.03	830.4	2.98	0.080
	$CsClO_4$ (38)	14	1-50	86.91	757.9	2.49	0.020
CH_3OH	KCl (39)	25	0.7-50	104.84	900.6	2.94	0.079
	NaCl (39)	23	0.4-40	97.19	970.7	3.37	0.046

TABLE II CALCULATIONS BY FERNANDEZ-PRINI AND PRUE[14] FOR UNASSOCIATED SYMMETRIC ELECTROLYTES USING THE SAME DATA AS TABLE I

FUOSS-ONSAGER

SOLVENT	ELECTROLYTE	Λ_0	J_1	J_2	a	σ
H_2O	HCl (15a)	426.83	521.4	98.2	3.46	0.148
	HCl (34)	426.92	532.9	106.8	3.54	0.238
	HCl (35)	426.90	510.6	90.4	3.40	0.087
	NaOH (15c)	249.53	300.2	66.8	3.18	0.082
	KCl (36)	149.93	210.9	75.8	3.32	0.028
	KCl (37)	149.97	205.0	69.8	3.23	0.008
	KI (37)	150.55	230.5	96.7	3.61	0.038
DMF	KI (38)	83.18	1059.	313.2	4.80	0.097
	$CsClO_4$ (38)	87.01	993.6	153.3	4.21	0.047
CH_3OH	KCl (39)	104.90	1353.	-98.8	3.25	0.046
	NaCl (39)	97.29	1424.	75.3	3.79	0.046

PITTS

SOLVENT	ELECTROLYTE	Λ_0	J_1	J_2	a	σ
H_2O	HCl (15a)	426.44	683.7	1257.	3.88	0.016
	HCl (34)	426.54	701.3	1321.	4.03	0.070
	HCl (35)	426.50	670.3	1209.	3.77	0.068
	NaOH (15c)	249.32	380.6	614.9	3.26	0.034
	KCl (36)	149.87	245.6	375.5	3.10	0.009
	KCl (37)	149.88	244.8	373.0	3.09	0.031
	KI (37)	150.38	294.4	538.0	3.99	0.016
DMF	KI (38)	83.00	1319.	3784.	4.54	0.056
	$CsClO_4$ (38)	86.87	1197.	2848.	3.52	0.024
CH_3OH	KCl (39)	104.76	1573.	2858.	2.16	0.107
	NaCl (39)	97.15	1679.	3595.	2.78	0.065

TABLE III CALCULATION RESULTS FOR ASSOCIATED ELECTROLYTES USING MURPHY-COHEN EQUATION COMPARED WITH ASSOCIATION CONSTANT VALUES FROM REFERENCES

							REFERENCE
SOLVENT*	ELECTROLYTE**		σ	<u>a</u>	K_A	K_A	K_{A_σ}***
H_2O	Na_2SO_4	(40)	0.022	7.70	11.1	3.5	5.0 (7)
H_2O	Na_2SO_4	(40)	0.018	8.41	12.9	1.5	5.0 (7)
H_2O	MgBDS	(41)	0.090	3.22	34.2	3.1	
H_2O	KCl	(17)	0.015	5.37	1.2	0.3	NONE (7)
H_2O	K_2SO_4	(40)	0.040	8.82	14.8	1.4	10.0 (7)
H_2O	(40)$K_3Fe(CN)_6$		0.061	3.95	27.9	2.8	20.0 (7)
H_2O	K_2BDS	(40)	0.043	11.27	17.6	2.2	
H_2O	$CaCl_2$	(40)	0.100	5.92	-2.7	3.1	NONE (7)
H_2O	$CaCl_2$	(40)	0.077	7.27	1.9	1.8	NONE (7)
H_2O	$CaCl_2$	(40)	0.019	6.99	1.0	0.6	NONE (7)
H_2O	CaBDS	(41)	0.031	6.42	104.3	9.6	
H_2O	CaBDS	(41)	0.019	6.07	98.8	6.8	
H_2O	CaBDS	(41)	0.038	3.06	36.5	2.9	
H_2O	$MnCl_2$	(40)	0.049	8.43	6.9	2.1	1.0 (7)
H_2O	$MnSO_4$	(40)	0.022	2.73	223.8	2.6	190.5 (7)
H_2O	$MnSO_4$	(40)	0.147	2.72	210.0	4.7	190.5 (7)
H_2O	MnBDS	(19)	0.128	7.50	44.1	0.2	
H_2O	CuBDS	(19)	0.428	6.31	67.9	19.6	
H_2O	$SrCl_2$	(40)	0.023	7.27	2.9	0.5	NONE (7)
H_2O	SrBDS	(41)	0.087	7.81	57.2	6.6	

TABLE III (continued)

SOLVENT*	ELECTROLYTE**		σ	a	K_A	K_A	$K_{A\sigma}$***
H_2O	SrBDS	(41)	0.052	5.53	39.6	3.7	
H_2O	$BaCl_2$	(40)	0.045	7.93	6.3	1.1	
H_2O	BaBDS	(41)	0.049	6.23	102.4	19.9	
H_2O	BaBDS	(41)	0.039	4.76	47.2	2.8	
H_2O	LaNTS	(19)	1.043	18.20	2894.7	226.6	
H_2O 10°C	$MgCl_2$	(40)	0.076	13.84	23.9	14.0	
H_2O 10°C	K_2SO_4	(40)	0.128	1.82	22.8	4.6	
H_2O 10°C	K_2BDS	(40)	0.062	10.48	14.6	3.3	
H_2O 10°C	$CaCl_2$	(40)	0.059	7.87	4.9	2.0	
H_2O 10°C	$MnCl_2$	(40)	0.038	7.11	2.3	1.1	
H_2O 10°C	$MnSO_4$	(40)	0.103	2.69	174.7	6.4	
H_2O 10°C	$SrCl_2$	(40)	0.017	6.37	-1.6	0.7	
H_2O 10°C	$BaCl_2$	(40)	0.039	7.77	5.4	1.2	
D_2O	K_2SO_4	(40)	0.083	9.06	16.2	2.5	
D_2O	(40)$K_3Fe(CN)_6$		0.043	3.98	27.4	1.3	
D_2O	K_2BDS	(40)	0.066	11.08	17.2	3.0	
D_2O	$CaCl_2$	(40)	0.052	7.39	3.4	1.4	
D_2O	$MnCl_2$	(40)	0.096	2.80	-16.0	3.9	
D_2O	$MnSO_4$	(40)	0.139	2.74	212.3	6.7	
D_2O	$SrCl_2$	(40)	0.054	7.97	5.6	1.7	
D_2O	$BaCl_2$	(40)	0.056	6.88	1.9	2.1	
MeOH	$MgCl_2$	(40)	0.150	4.18	278.6	14.5	
MeOH	K_2BDS	(40)	0.062	4.11	460.8	12.7	

TABLE III (continued)

SOLVENT*	ELECTROLYTE**		σ	<u>a</u>	K_A	K_A	$K_{A\sigma}$***
MeOH	$CaCl_2$	(40)	0.101	4.40	374.0	13.6	
MeOH	$SrCl_2$	(40)	0.148	4.17	-78.6	108.8	
MeOH	$BaCl_2$	(40)	0.089	4.23	357.1	30.0	
MeOH10°C	$MgCl_2$	(40)	0.121	4.68	152.3	17.0	
MeOH10°C	$CaCl_2$	(40)	0.235	4.51	43.1	83.5	
MeOH10°C	$SrCl_2$	(40)	0.142	4.57	180.3	19.2	

* All solutions are at 25°C unless otherwise noted.
D_2O represents deuterium oxide.
MeOH represents methanol

** BDS represents <u>m</u>-benzenedisulfonate.
NTS represents 1,3,5-naphthalenetrisulfonate

*** NONE indicates no evidence of ion-pairs has been found.

SUMMARY

The Murphy-Cohen equation is an extension of and an improvement over the Fuoss-Onsager equation. The Pitts equation is superior for only a few symmetric solutes. The Murphy-Cohen equation gives fairly good results for associated solutes, but the possibilities have only been touched. Of particular importance is that the Murphy-Cohen equation has the same general form as the Fuoss-Onsager equation, therefore, even if the Murphy-Cohen equation supplants the Fuoss-Onsager, those publications of the past which used the Fuoss-Onsager equations to determine the validity of their data would still be pertinent to the Murphy-Cohen equation.

It should be noted that the models used in the equations discussed in this thesis limit the theories therein derived to low concentrations and moderately high dielectric constants where the long-range forces are dominant and calculable. Further work to specify more realistic models plus the creative energy to transform these improved models into applicable equations is needed for the future growth of conductance measurements as a science.

APPENDIX 1

COMPUTER PROGRAM USING THE MURPHY-COHEN EQUATION FOR UNASSOCIATED ELECTROLYTES

```
C      PROGRAM FOUR   -- A LEAST-SQUARES FIT OF CONDUCTANCE DATA FOR
C          UNASSOCIATED ELECTROLYTES OF ANY CHARGE TYPE USING THE MURPHY
C          AND COHEN EQUATION.
C
C          THE GENERAL MURPHY-COHEN EQUATION IS:
C
C          LAMBDA(I)=LAMZRO-S*SQRT(C(I))+EP*C(I)*ALOG(C(I))+JMC*C(I)
C          WHERE  I  IS A POSITIVE INTEGER DEFINING A DATA TABLE POSITION
C
C          SIMILARLY THE *PLOTTING RELATIONSHIPS* ARE:
C
C          LMSTAR(I)=(LAMBDA(I)-LAMZRO+S*SQRT(C(I)))/(C(I))
C          LMSTAR(I)=EP*ALOG(C(I))+JMC
C
C          LMPRIM(I)=LAMBDA(I)+S*SQRT(C(I))-EP*C(I)*ALOG(C(I))
C          LMPRIM(I)=LAMZRO+JMC*C(I)
C
C
C      THE FOLLOWING NAMES ARE USED IN THE PROGRAM:
C
C       N           -- NUMBER OF DATA POINTS IN A DATA GROUP
C       AN          -- FLOATING POINT VALUE OF  N
C       AM(I)       -- ALPHAMERIC WORD CONTAINING TITLE CARD DESCRIPTION
C       D           -- DIELECTRIC CONSTANT
C       ETA         -- SOLVENT VISCOSITY
C       T           -- ABSOLUTE TEMPERATURE
C       Z1          -- UNSIGNED CHARGE NUMBER ON THE POSITIVE ION
C       Z2          -- UNSIGNED CHARGE NUMBER ON THE NEGATIVE ION
C       LAMZR1      -- IONIC EQUIVALENT CONDUCTANCE AT INF DIL OF POS ION
C       LAMZR2      -- IONIC EQUIVALENT CONDUCTANCE AT INF DIL OF NEG ION
C       LAMZRO      -- EQUIVALENT CONDUCTANCE OF SOLUTION AT INF DIL
C       AZR         -- DISTANCE OF CLOSEST APPROACH OF TWO IONS
C       C(I)        -- MOLAR CONCENTRATION
C       LAMBDA(I)   -- EQUIVALENT CONDUCTANCE
C       ALPHA       -- RELAXATION FIELD COEFFICIENT OF ONSAGER EQUATION
C       BETA        -- ELECTROPHORETIC COEFFICIENT OF ONSAGER EQUATION
C       EP          -- COEFFICIENT OF THE TRANSCENDENTAL TERM
C       EP1         -- COEFFICIENT OF THE TRANSCENDENTAL TERM
C       EP2         -- COEFFICIENT OF THE TRANSCENDENTAL TERM
C       S           -- LIMITING COEFFICIENT IN ONSAGER EQUATION
C       JMC         -- COEFFICIENT OF THE LINEAR TERM
C       LMPRIM(I)   -- *MODIFIED* EQUIVALENT CONDUCTANCE
C       Y           --
C       B           -- BJERRUM PARAMETER
C       SIGMC1      -- COEFFICIENT OF LINEAR TERM
C       SIGMC2      -- COEFFICIENT OF LINEAR TERM
C       SUMDIF      -- SUMMATION OF THE SQUARES OF DELTLM(I)
C       PHI         --
C       STDLM       -- STANDARD DEVIATION OF LAMBDA(I) VERSUS LMCALC(I)
C    A11 THRU A23   -- DETERMINANT VALUES FOR A LEAST SQUARES FIT
C       A11         -- FLOATING POINT VALUE OF N
C       LMPRIM(I)   --
C       LMSTAR(I)   --
C       LMCALC(I)   --
C       STDKA       --
C       STDKA       --
C       STDAZR      --
C       STDLZO      --
C       DELTLM(I)   --
```

```
C        KAPPA(I)  --
C        KAPAA(I)  --
C        KAPAAB(I) --
C
C
C
                   REAL LAMBDA(30),LMPRIM(30),LMCALC(30),KAPAA(30),KAPAAB(3
     10),LOGC(30),KAPPA(30),LMSTAR(30)
      DIMENSION C(30),DELTLM(30),AM(20)
      REAL LAMZRO,LAMZR1,LAMZR2,KA,JMC,NU1,NU2,KAP,LL1,L1,LL2,L2,JMCALC
C      DATA DECK SHOULD CONTAIN A TITLE CARD, A SOLVENT CARD, A SOLUTE
C          CARD, CONCENTRATION DATA CARD(S), AND A CONDUCTANCE DATA
C          CARD(S) FOR EACH DATA GROUP.   A-BLANK CARD INDICATES NO
C          FURTHER DATA GROUPS.
C     TITLE CARD CONTAINS  N  AND TITLE OF DATA GROUP
   10 READ(5,100)N,(AM(I),I=1,19)
  100 FORMAT(I2,19A4)
      WRITE(6,900)
  900 FORMAT(1H1,'PROGRAM 4  -- A LEAST-SQUARES FIT OF CONDUCTANCE DATA
     1FOR UNASSOCIATED ELECTROLYTES OF ANY CHARGE TYPE',/,20X,'USING THE
     2 MURPHY AND COHEN EQUATION.',/,20X,'LARRY M. SHADWICK  BOX 112   C
     3HEM DEPT GRAD RESEARCH')
      AN=N
C     CHECK FOR BLANK CARD
      IF(N)1000,1000,105
C     SOLVENT CARD CONTAINS  D, ETA, AND T
  105 READ(5,110)D,ETA,T
  110 FORMAT(F6.2,F6.6,F6.2)
C     SOLUTE CARD CONTAINS Z1, Z2, LAMZR1, LAMZR2, LAMZRO*EST*, AZR*EST*
      READ(5,115)Z1,Z2,LAMZR1,LAMZR2,LAMZRO,AZR
  115 FORMAT(2F1.0,3F6.3,F4.2)
C     CONCENTRATION DATA CARD(S) CONTAIN  C(I)
      READ(5,120)(C(I),I=1,N)
  120 FORMAT(12F6.4)
C     CONCENTRATION DATA CHANGED TO MOLE /LITER  VALUES
          DO 125 I=1,N
  125     C(I)=C(I)*1.E-4
C     CONDUCTANCE DATA CARD(S) CONTAINS  LAMBDA(I)
      READ(5,130)(LAMBDA(I),I=1,N)
  130 FORMAT(12F6.3)
C     INPUT OF DATA COMPLETE; NOW PRINT INITIAL OUTPUT
      WRITE(6,905)(AM(I),I=1,19)
  905 FORMAT(1H0,19A4,/)
      WRITE(6,910)D,ETA,T
  9100FORMAT(' SOLVENT DATA'7X'--'8X'D ='5X,F7.3,8X'ETA ='6X,F9.6,7X'T =
     1'5X,F6.2)
      WRITE(6,915)Z1,Z2,LAMZR1,LAMZR2
  915 FORMAT(' SOLUTE DATA'8X'--'7X'Z1 ='7X,F2.0,12X'Z2 ='7X,F2.0,8X,
     1'LAMZR1 ='5X,F7.3,5X'LAMZR2 ='5X,F7.3)
      IF(AZR.EQ.0.0)   AZR=3.0
      WRITE(6,920)LAMZRO,AZR
  920 FORMAT(' INITIAL ESTIMATES  --'3X'LAMZRO ='5X,F7.3,8X'AZR ='6X,
     1F5.2)
C     AZR CHANGED TO CENTIMETERS
      AZR=AZR*1.E-8
      WRITE(6,925)N
  925 FORMAT(' MISCELLANEOUS'6X'--'8X'N ='6X,I2)
C     PRINTING OF INITIAL DATA COMPLETED; CALCULATE BASIC CONSTANTS
  200 IF(Z1-Z2) 205,210,205
  205 NU1=Z2
```

```
      NU2=Z1
      GO TO 215
  210 NU1=1.0
      NU2=1.0
  215 IF(LAMZR2) 225,220,225
  220 LMZRSW=1
      GO TO 235
  225 IF(LAMZR1) 235,230,235
  230 LMZRSW=2
      GO TO 235
  235 SQRTW=SQRT(0.5*(NU1*Z1*Z1+NU2*Z2*Z2))
      PHI=16.7098E-4*Z1*Z2/(D*T)
      KAP=0.502915E10*SQRTW/SQRT(D*T)
      A11=N
C
  300     DO 350 L=1,20
          IF(LMZRSW-1) 310,305,310
  305     LAMZR2=LAMZRO-LAMZR1
          GO TO 320
  310     IF(LMZRSW-2) 320,315,320
  315     LAMZR1=LAMZRO-LAMZR2
          GO TO 320
  320     Q=SQRT((Z1*Z2)*(LAMZR1+LAMZR2)/((Z1+Z2)*(Z2*LAMZR1+LAMZR2*Z1))
     1)
          ALPHA=2.8012E6*Z1*Z2*SQRTW*Q*Q/((1.0+Q)*((D*T)**1.5))
          BETA=41.243*(Z1+Z2)*SQRTW/(ETA*(SQRT(D*T)))
          S=ALPHA*LAMZRO+BETA
          EP1=((Q*KAP*PHI)**2)/12.0
          EP2=(KAP*PHI*BETA)/16.0
          EP=EP1*LAMZRO-4.0*EP2*(Q*Q+((Z1-Z2)**2)/(Z1*Z2))
          TMPLMO=LAMZRO
C         RESET DETERMINANT VALUES TO ZERO, PRIOR TO LEAST-SQUARES APPL.
          A12=0.0
          A13=0.0
          A22=0.0
          A23=0.0
               DO 330 I=1,N
               LMPRIM(I)=LAMBDA(I)+S*SQRT(C(I))-EP*C(I)*ALOG(C(I))
               A12=A12+C(I)
               A13=A13+LMPRIM(I)
               A22=A22+C(I)*C(I)
  330          A23=A23+C(I)*LMPRIM(I)
          DETD=A11*A22-A12*A12
          LAMZRO=(A13*A22-A12*A23)/DETD
          JMC=(A11*A23-A12*A13)/DETD
          IF(ABS(LAMZRO-TMPLMO)-0.001) 400,350,350
  350     CONTINUE
C     CALCULATION OF ION SIZE, AZR, BY M-C EQUATION USING DIFFERENTIAL
C         APPROXIMATION.
  400 DO 480 II=1,50,1
          DD = 1. + 4./2.**II
          B=PHI/AZR
C
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C THE CALCULATIONS THAT FOLLOW DETERMINE, BY THE M-C EQUATION, WHAT THE
C    VALUE OF JMC; JMCALC IS THE NAME USED, WOULD BE FOR A GIVEN VALUE
C     OF AZR; AS WELL AS THE DIFFERENTIAL OF JMCALC WITH RESPECT TO THE
C     GIVEN AZR, DJMCDA IS THE NAME USED.
C
C     DETERMINATION OF EI AND DEIDB
```

```
  500 BFAC=1.0
      EI=0.5772157+ALOG(B)
      DEIDB=1./B
          DO 510 I=1,50,1
          AI=I
          IF((BFAC*B).GT.1.E70) GO TO 510
          BFAC=BFAC*B/AI
          TMPEI=BFAC/AI
          EI=EI+TMPEI
          DEIDB=DEIDB+BFAC/B
          IF(ABS(EI*1.E-4)-ABS(TMPEI)) 510,510,520
  510     CONTINUE
  520 CONTINUE
C
C     DETERMINATION OF SSTAR AND DSTRDB
  600 SSTAR=0.0
      DSTRDB=0.0
      PART1=1.0
      PART2=Z1*Z1
      PART3=Z2*Z2
      FAC=2.0
          DO 610 I=3,50,1
          IF(PART1.GT.1.E70) GO TO 610
          PART1=PART1*(-B/(Z1*Z2))
          PART2=PART2*Z1
          PART3=PART3*(-Z2)
          AI=I
          FAC=FAC*AI
          TMPSTR=(PART1/(FAC*(AI-2.0)))*(((PART2-PART3)/(Z1+Z2))**2)
          SSTAR=SSTAR+TMPSTR
          DSTRDB=DSTRDB+(AI-2.0)*TMPSTR/B
          IF(ABS(SSTAR*1.E-4)-ABS(TMPSTR)) 610,610,620
  610     CONTINUE
  620 CONTINUE
C
C     DETERMINATION OF L2
       L2   =   (1./(Q*Q*B)+EI/2.+(EXP(B)*(-5.*(B**5)-36.*(B**4)
     1    +30.*(B**3)+30.*(B**2)-18.*(B)-36.)+6.*(B**4)+45.*(B**3)
     2    +6.*(B**2)+54.*(B)+36.)/(108.*(B**5))+SSTAR/(Q*Q*Z1*Z2)
     3    -(((Z1-Z2)**2)/(2.*Q*Q*Z1*Z2))*(0.5772157+ALOG(3.0)
     4    +0.1666667-ALOG(B)))
       L2   =   L2            -(((Q*Q*EP2)/(9.*EP1*LAMZRO*(B**4)))
     1    *(EXP(B)*((B**4)+5.*(B**3)+3.*(B**2)-12.*(B)+6.)
     2    -4.5*(B**4)-3.*(B**3)+6.*(B**2)+6.*(B)-6.))
C
C     DETERMINATION OF DL2DB
       DL2DB  =  (-1./(Q*Q*B*B)+DEIDB/2.+(EXP(B)*(-5.*(B**6)-36.*(B**5)
     1    +66.*(B**4)-30.*(B**3)-108.*(B**2)+36.*(B)+180.)-6.*(B**4)
     2    -90.*(B**3)-18.*(B**2)-216.*(B)-108.)/(108.*(B**6))
     3    +DSTRDB/(Q*Q*Z1*Z2)+(((Z1-Z2)**2)/(2.*Q*Q*Z1*Z2*B)))
       DL2DB  =   DL2DB   -(((Q*Q*EP2)/(9.*EP1*LAMZRO*(B**5)))
     1    *(EXP(B)*((B**5)+5.*(B**4)-2.*(B**3)-18.*(B**2)+42.*(B)-24.)
     2    +3.*(B**3)-12.*(B**2)-18.*(B)+24.))
C
C     DETERMINATION OF LL2
       LL2 = (((18.*(Q)+61.*(Q**2)+21.*(Q**3)-6.*(Q**4))/(48.*(Q**2)
     1    *(1.+Q)))+((1.-2.*(Q)+1.*(Q**2)+1.*(Q**3)-(Q**5))
     2    *ALOG(1.+Q)-1.*(1.+Q*Q)*(1.-Q)*ALOG(1.-Q)-(2.+1.*(Q)
     3    +2.*(Q**2)+5.*(Q**3)-(Q**5))*ALOG(2.+Q)+1.*(1.+Q*Q)
     4    *(2.-Q)*ALOG(2.-Q))/(8.*(Q**3))-0.5772157)
```

```
C
C     DETERMINATION OF SIGMC2
      SIGMC2  =16.*EP2*(-0.5*(((Z1-Z2)**2)/(Z1*Z2)+Q*Q)*ALOG(PHI*KAP)
     1    +Q*Q*(LL2+L2))
C
C     DETERMINATION OF DSG2DA
      DSG2DA =  (-B/AZR)*(16.*EP2*Q*Q*DL2DB)
C
C     DETERMINATION OF L1
      L1   =  ((EXP(B)*(23.*(B**2)+9.*(B)+12.)-6.*(B**3)-8.*(B**2)
     1    -9.*(B)-12.)/(18.*(B**3))-EI)
C
C     DETERMINATION OF DL1DB
      DL1DB   =   ((EXP(B)*(23.*(B**3)-14.*(B**2)-6.*(B)-36.)
     1    +8.*(B**2)+18.*(B)+36.)/(18.*(B**4))-DEIDB)
C
C     DETERMINATION OF LL1
      LL1   =   (1.1544314-(6.*(Q)+15.*(Q**2)+21.*(Q**3)-13.*(Q**4)
     1    -35.*(Q**5)+6.*(Q**6))/(12.*(Q**2)*(1.+Q)*(1.-Q*Q))
     2    +(2.-Q*Q*(1.-Q*Q))*(ALOG(2.+Q))/(2.*(1.-Q*Q))
     3    +(1.-2.*Q*Q)*(ALOG(1.+2.*Q))/(1.-Q*Q)
     4    +((1.-Q*Q)**2)*(ALOG(1.+Q))/(2.*Q*Q))
      LL1   =   LL1-(((Z1-Z2)**2)*((1./3.)-(2.*Q*Q*(ALOG(3./(2.+Q)))
     1    /(1.-Q*Q)))/(2.*Z1*Z2*(1.-Q*Q)))
C
C     DETERMINATION OF SIGMC1
      SIGMC1   =   2.*EP1*(ALOG(PHI*KAP)+LL1+L1)
C
C     DETERMINATION OF DSG1DA
      DSG1DA =  (-B/AZR)*(2.*EP1*DL1DB)
C
C     DETERMINATION OF JMCALC
      JMCALC = SIGMC1*LAMZRO +SIGMC2
C
C     DETERMINATION OF DJMCDA
      DJMCDA = DSG1DA*LAMZRO+DSG2DA
C
C     THE CALCULATIONS ABOVE DETERMINE JMCALC AND DJMCDA FOR A GIVEN AZR
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
         DELAZR=(JMC-JMCALC)/DJMCDA
         AZR=AZR+DELAZR/DD
      IF(AZR.LE.1.E-8) AZR = 0.5*(AZR-DELAZR/DD)+1.E-8
      IF(AZR.GT.20.E-8) AZR = 20.E-8/DD
         IF(ABS(DELAZR)-.5E-12) 700,480,480
  480    CONTINUE
C
C     CALCULATION OF LMCALC(I) AND STANDARD DEVIATION OF
C        LAMBRA(I) -- STDLM, JMC -- STDJMC, LAMZRO -- STDLZO,
C        AZR -- STDAZR.
  700 SUMDIF=0.0
         DO 710 I=1,N
         LMCALC(I)=LAMZRO-S*SQRT(C(I))+EP*C(I)*ALOG(C(I))+JMC*C(I)
         DELTLM(I)=LAMBDA(I)-LMCALC(I)
         LMSTAR(I)=(LAMBDA(I)-LAMZRO+S*SQRT(C(I)))/(C(I))
         LMPRIM(I)=LAMBDA(I)+S*SQRT(C(I))-EP*C(I)*ALOG(C(I))
  710    SUMDIF=SUMDIF+(DELTLM(I)**2)
      STDLM=SQRT(SUMDIF/(A11-2.0))
      STDJMC=STDLM*SQRT(A11/DETD)
      STDLZO=STDLM*SQRT(A22/DETD)
```

```
      STDAZR=ABS(STDJMC/DJMCDA)
C
C
C
C     CALCULATION BLOCK COMPLETED; CALCULATED OUTPUT BLOCK BEGINS.
      WRITE(6,930)LAMZRO,STDLZO
  930 FORMAT(1X/'0LAMZRO ='4X,F8.3,4X'STDLZO ='4X,F8.3)
      WRITE(6,935)S,ALPHA,BETA
  935 FORMAT(6X'S =‘4X,F8.3,5X,'ALPHA ='6X,F8.5,4X,'BETA ='5X,F8.4)
      WRITE(6,940)EP,EP1,EP2
  940 FORMAT(5X'EP =',F12.3,7X,'EP1 ='5X,F9.5,5X,'EP2 ='4X,F9.4)
      WRITE(6,942)SIGMC1,LL1,L1
  942 FORMAT(' SIGMC1 =',F13.4,6X,'LL1 =',5X,F9.5,6X,'L1 = ',F12.4)
      WRITE(6,944)SIGMC2,LL2,L2
  944 FORMAT(' SIGMC2 =',F13.4,6X,'LL2 =',5X,F9.5,6X,'L2 = ',F12.4)
      WRITE(6,945)JMC,STDJMC,JMCALC
  945 FORMAT(4X'JMC =',F11.2,5X'STDJMC =  'F9.2,5X'JMCALC ='F11.2)
C     AZR  AND  STDAZR  CHANGED TO ANGSTROMS
      AZR=AZR*1.E8
      STDAZR=STDAZR*1.E8
      WRITE(6,950)AZR,STDAZR,II
  950 FORMAT(4X'AZR ='6X,F7.4,3X,'STDAZR ='6X,F7.4,7X,'II =',6X,I2)
C     AZR CHANGED BACK TO ANGSTROMS
      AZR=AZR*1.E-8
C     PHI CHANGED TO ANGSTROMS
      PHI = 1.E8*PHI
      WRITE(6,960)B,PHI,Q
  960 FORMAT(6X,'B =',5X,F8.4,4X,'AZR*B =',5X,F8.4,8X,'Q =',6X,F8.5)
      WRITE(6,965)L,STDLM
  965 FORMAT('0THIS RUN CONVERGED AFTER 'I3,' ITERATIONS WITH A STANDA',
     1'RD DEVATION OF 'F8.3)
      WRITE(6,970)
  970 FORMAT(1X/' I      C(I)     LAMBDA(I) LMCALC(I) DELTLM(I) LMPRIM(I)'
     1,' KAPPA(I) KAPPA(I)*A KAPPA(I)*A*B    LMSTAR(I)    LMPRIM(I) ALOG(
     2C(I))          ',/1X)
C     C(I)  CHANGED TO  MOLES/(LITERS*10**4)
          DO 990 I=1,N
          KAPPA(I)=KAP*SQRT(C(I))
          KAPAA(I)=KAPPA(I)*AZR
          KAPAAB(I)=KAPPA(I)*AZR*B
          LOGC(I)=ALOG(C(I))
          C(I)=C(I)*1.E4
      KAPPA(I)=1.E-8*KAPPA(I)
          WRITE(6,980)I,C(I),LAMBDA(I),LMCALC(I),DELTLM(I),LMPRIM(I),KAP
     1PA(I),KAPAA(I),KAPAAB(I),LMSTAR(I),LMPRIM(I),LOGC(I)
  980     FORMAT(1X,I2,3X,F8.4,3X,F7.3,3X,F7.3,3X,F7.3,3X,F7.3,3X,F7.5,3
     1X,F7.5,3X,F7.5,8X,F9.2,4X,F7.3,2X,F8.4,11X)
  990     CONTINUE
      GO TO 10
 1000 CONTINUE
      RETURN
      END
```

APPENDIX 2

COMPUTER PROGRAM USING THE MURPHY-COHEN EQUATION FOR ASSOCIATED ELECTROLYTES

```
C      PROGRAM SIX  --  A LEAST-SQUARES FIT OF CONDUCTANCE DATA FOR
C         ASSOCIATED ELECTROLYTES OF ANY CHARGE TYPE USING THE
C         MURPHY AND COHEN EQUATION.
C
C         THE GENERAL FORM OF THE MURPHY-COHEN EQUATION IS:
C
C         LAMBDA(I)=LAMZR0-S*SQRT(C(I)*G(I))
C                  +EP*C(I)*G(I)*ALOG(C(I)*G(I))+JMC*C(I)*G(I)
C                  -KA*DLMDKA(I)
C              WHERE
C                  DLMDKA(I)=-F(I)*(P*LAMBDA(I)+Z3*(LAMZR0-LAMZRN
C                            -LAMZR3-(S-SN)*SQRT(C(I)*G(I))))*C(I)*G(I)
C
C         WHERE  I  IS A POSITIVE INTEGER DEFINING A DATA TABLE POSITION
C
C
C
C      THE FOLLOWING NAMES ARE USED IN THE PROGRAM:
C
C       N          -- NUMBER OF DATA POINTS IN A DATA GROUP
C       AN         -- FLOATING POINT VALUE OF  N
C       AM(I)      -- ALPHAMERIC WORD CONTAINING TITLE CARD DESCRIPTION
C       D          -- DIELECTRIC CONSTANT
C       ETA        -- SOLVENT VISCOSITY
C       T          -- ABSOLUTE TEMPERATURE
C       Z1         -- UNSIGNED CHARGE NUMBER ON THE POSITIVE ION
C       Z2         -- UNSIGNED CHARGE NUMBER ON THE NEGATIVE ION
C       LAMZR1     -- IONIC EQUIVALENT CONDUCTANCE AT INF DIL OF POS ION
C       LAMZR2     -- IONIC EQUIVALENT CONDUCTANCE AT INF DIL OF NEG ION
C       LAMZR0     -- EQUIVALENT CONDUCTANCE OF SOLUTION AT INF DIL
C       AZR        -- DISTANCE OF CLOSEST APPROACH OF TWO IONS
C       C(I)       -- MOLAR CONCENTRATION
C       LAMBDA(I)  -- EQUIVALENT CONDUCTANCE
C       ALPHA      -- RELAXATION FIELD COEFFICIENT OF ONSAGER EQUATION
C       BETA       -- ELECTROPHORETIC COEFFICIENT OF ONSAGER EQUATION
C       EP         -- COEFFICIENT OF THE TRANSCENDENTAL TERM
C       EP1        -- COEFFICIENT OF THE TRANSCENDENTAL TERM
C       EP2        -- COEFFICIENT OF THE TRANSCENDENTAL TERM
C       S          -- LIMITING COEFFICIENT IN ONSAGER EQUATION
C       JMC        -- COEFFICIENT OF THE LINEAR TERM
C       LMPRIM(I)  -- *MODIFIED* EQUIVALENT CONDUCTANCE
C       Y          --
C       B          -- BJERRUM PARAMETER
C       SIGMC1     -- COEFFICIENT OF LINEAR TERM
C       SIGMC2     -- COEFFICIENT OF LINEAR TERM
C       SUMDIF     -- SUMMATION OF THE SQUARES OF DELTLM(I)
C       PHI        --
C       STDLM      -- STANDARD DEVIATION OF LAMBDA(I) VERSUS LMCALC(I)
C    A11 THRU A23  -- DETERMINANT VALUES FOR A LEAST SQUARES FIT
C       A11        -- FLOATING POINT VALUE OF N
C       LMPRIM(I)  --
C       LMSTAR(I)  --
C       LMCALC(I)  --
C       STDKA      --
C       STDKA      --
C       STDAZR     --
C       STDLZ0     --
C       DELTLM(I)  --
C       KAPPA(I)   --
```

```
C       KAPAA(I)  --
C       KAPAAB(I) --
C      AACT        -- DISTANCE OF CLOSEST APPROACH FOR ACTIVITY COEFFICENTS
C       KA -- ION PAIR ASSOCIATION CONSTANT
C       FCTR -- FACTOR FOR DETERMINATING LAMZR3
C
C
C
                 REAL LAMBDA(30),LMPRIM(30),LMCALC(30),KAPAA(30),KAPAAB(3
     10),LOGC(30),KAPPA(30),LMSTAR(30),LMIONC(30)
      DIMENSION C(30),DELTLM(30),AM(20),G(30),GSTAR(30),WPRIM(30),CG(30)
     1,DLMDKA(30),F(30)
      REAL LAMZRO,LAMZR1,LAMZR2,LAMZR3,KA,JMC,NU1,NU2,KAP,LL1,L1,LL2,L2,
     1JMCALC
C       DATA DECK SHOULD CONTAIN A TITLE CARD, A SOLVENT CARD, A SOLUTE
C           CARD, CONCENTRATION DATA CARD(S), AND A CONDUCTANCE DATA
C           CARD(S) FOR EACH DATA GROUP.   A BLANK CARD INDICATES NO
C           FURTHER DATA GROUPS.
C      TITLE CARD CONTAINS  N  AND TITLE OF DATA GROUP
   10 READ(5,100)N,(AM(I),I=1,19)
  100 FORMAT(I2,19A4)
      WRITE(6,900)
  900 FORMAT(1H1,'PROGRAM 6  --  A LEAST-SQUARES FIT OF CONDUCTANCE DATA
     1 FOR ASSOCIATED ELECTROLYTES OF ANY CHARGE TYPE',/,21X,'USING THE
     2MURPHY AND COHEN EQUATION.',/,21X,'LARRY M. SHADWICK   BOX 112   C
     3HEM DEPT GRAD RESEARCH')
      AN=N
C      CHECK FOR BLANK CARD
      IF(N)1000,1000,105
C      SOLVENT CARD CONTAINS  D, ETA, AND T
  105 READ(5,110)D,ETA,T
  110 FORMAT(F6.2,F6.6,F6.2)
C      SOLUTE CARD CONTAINS Z1, Z2, LAMZR1, LAMZR2, LAMZRO*EST*, KA*EST*,
C          LAMZR3*EST*, AACT
      READ(5,115)Z1,Z2,LAMZR1,LAMZR2,LAMZRO,AZR,KA,LAMZR3,AACT
  115 FORMAT(2F1.0,3F6.3,F4.2,F6.0,F6.3,F4.2)
C      CONCENTRATION DATA CARD(S) CONTAIN  C(I)
      READ(5,120)(C(I),I=1,N)
  120 FORMAT(12F6.4)
C      CONCENTRATION DATA CHANGED TO MOLE /LITER  VALUES
          DO 125 I=1,N
          G(I)=1.
          GSTAR(I)=1.
          C(I)=C(I)*1.E-4
  125     CG(I)=C(I)*G(I)
C      CONDUCTANCE DATA CARD(S) CONTAINS  LAMBDA(I)
      READ(5,130)(LAMBDA(I),I=1,N)
  130 FORMAT(12F6.3)
C      INPUT OF DATA COMPLETE; NOW PRINT INITIAL OUTPUT
      WRITE(6,905)(AM(I),I=1,19)
  905 FORMAT(1H0,19A4,/)
      WRITE(6,910)D,ETA,T
  910 FORMAT(' SOLVENT DATA          --                D =        ',F7.3,
     1'         ETA =         ',F9.6,'         T =         ',F6.2)
      WRITE(6,915)Z1,Z2,LAMZR1,LAMZR2
  915 FORMAT(' SOLUTE DATA           --                Z1 =          ',F2.0,
     1'              Z2 =         ',F2.0,'          LAMZR1 =        ',
     2F7.3,'        LAMZR2 =       ',F7.3)
      IF(AZR.EQ.0.0)   AZR=3.0
      KA=AMAX1(KA,5.0)
```

```
      WRITE(6,920)LAMZRO,AZR,KA,LAMZR3
  920 FORMAT(' INITIAL ESTIMATES    --       LAMZRO =        ',F7.3,
     1'           AZR =           ',F5.2,'              KA =     ',F8.1,
     2'          LAMZR3 =       ',F7.3)
C     AZR CHANGED TO CENTIMETERS
      AZR=AZR*1.E-8
      WRITE(6,925)N,AACT
  925 FORMAT(' MISCELLANEOUS         --              N =         ',I2,
     1'                AACT =          ',F5.2)
C     PRINTING OF INITIAL DATA COMPLETED; CALCULATE BASIC CONSTANTS
      LMZ3SW=0
      IF(LAMZR3.NE.0)  LMZ3SW=1
  200 IF(Z1-Z2) 205,210,205
  205 NU1=Z2
      NU2=Z1
      P=AMIN1(NU1,NU2)
      GO TO 215
  210 NU1=1.0
      NU2=1.0
      P=1.0
  215 IF(LAMZR2) 225,220,225
  220 LMZRSW=1
      GO TO 235
  225 IF(LAMZR1) 235,230,235
  230 LMZRSW=2
      GO TO 235
  235 SQRTW=SQRT(0.5*(NU1*Z1*Z1+NU2*Z2*Z2))
      PHI=16.7098E-4*Z1*Z2/(D*T)
      KAP=0.502915E10*SQRTW/SQRT(D*T)
      Z3=ABS(Z1-Z2)
      ZN=AMIN1(Z1,Z2)
      VALFAC=Z3/AMAX1(Z1,Z2)
      ZDIF=AMAX1(1.,Z3)
      JMC=(Z1*Z2)**3*160.-Z3**3*700.
      A11=N
C
  300       DO 350 L=1,20
            IF(LMZRSW-1) 310,305,310
  305       LAMZR2=LAMZRO-LAMZR1
            GO TO 320
  310       IF(LMZRSW-2) 320,315,320
  315       LAMZR1=LAMZRO-LAMZR2
            GO TO 320
  320       IF(LMZ3SW.EQ.1) GO TO 325
            LAMZR3=Z3/AMAX1(Z1,Z2)*(((Z1-P)/ZDIF)*LAMZR1
     1           +((Z2-P)/ZDIF)*LAMZR2)
  325       LAMZRN=((Z2-P)/ZDIF)*LAMZR1+((Z1-P)/ZDIF)*LAMZR2
            Q=SQRT((Z1*Z2)*(LAMZR1+LAMZR2)/((Z1+Z2)*(Z2*LAMZR1+LAMZR2*Z1))
     1)
            QN=0.0
            IF(Z1.NE.Z2)  QN=SQRT((ZN*Z3)*(LAMZRN+LAMZR3)/((Z3+ZN)
     1         *(ZN*LAMZR3+Z3*LAMZRN)))
            ALPHA=2.8012E6*Z1*Z2*SQRTW*Q*Q/((1.0+Q)*((D*T)**1.5))
            ALPHAN=2.8012E6*Z3*ZN*SQRTW*QN*QN/((1.0+QN)*((D*T)**1.5))
            BETA=41.243*(Z1+Z2)*SQRTW/(ETA*(SQRT(D*T)))
            BETAN=41.243*(Z3+ZN)*SQRTW/(ETA*(SQRT(D*T)))
            S=ALPHA*LAMZRO+BETA
            SN=ALPHAN*(LAMZR3+LAMZRN)+BETAN
            EP1=((Q*KAP*PHI)**2)/12.0
            EP2=(KAP*PHI*BETA)/16.0
```

```
          EP=EP1*LAMZRO-4.0*EP2*(Q*Q+((Z1-Z2)**2)/(Z1*Z2))
          TMPLMO=LAMZRO
C         RESET DETERMINANT VALUES TO ZERO, PRIOR TO LEAST-SQUARES APPL.
          A12=0.0
          A13=0.0
          A14=0.0
          A22=0.0
          A23=0.0
          A24=0.0
          A33=0.0
          A34=0.0
          SUMDIF=0.0
               DO 340 I=1,N
                    TEMPGS=GSTAR(I)
                    DO 330 II=1,10
                    LMIONC(I)=LAMZRO-S*SQRT(CG(I))+EP*CG(I)*ALOG(CG(2))
     1                   +JMC*CG(I)
                    GSTAR(I)=(LAMBDA(I)-VALFAC*((LAMZR3+LAMZRN)
     1                   -SN*SQRT(CG(I))))/(LMIONC(I)-VALFAC
     2                   *((LAMZR3+LAMZRN)-SN*SQRT(CG(I))))
                    IF(GSTAR(I).GT.1.) GSTAR(I) = 1.0
                    IF(GSTAR(I).LT.0.) GSTAR(I) = 0.1
                    G(I)=1.-(Z1*Z2*P*(1.-GSTAR(I))/(SQRTW*SQRTW))
                    CG(I)=C(I)*G(I)
                    IF(ABS(GSTAR(I)-TEMPGS).LT.0.00005) GO TO 337
 330                TEMPGS=GSTAR(I)
 337           F(I)=EXP(-KAP*PHI*SQRT(CG(I))/
     1              (1.+1.E-8*KAP*AACT*SQRT(CG(I))))
               DLMDKA(I)=-F(I)*(P*LAMBDA(I)+Z3*(LAMZRO-LAMZRN-LAMZR3
     1              -(S-SN)*SQRT(CG(I))))*CG(I)
               LMCALC(I)=LMIONC(I)+KA*DLMDKA(I)
               DELTLM(I)=LAMBDA(I)-LMCALC(I)
               A12=A12+CG(I)
               A13=A13+DLMDKA(I)
               A22=A22+CG(I)*CG(I)
               A23=A23+CG(I)*DLMDKA(I)
               A33=A33+DLMDKA(I)*DLMDKA(I)
               A14=A14+DELTLM(I)
               A24=A24+CG(I)*DELTLM(I)
               A34=A34+DLMDKA(I)*DELTLM(I)
 340           SUMDIF=SUMDIF+DELTLM(I)*DELTLM(I)
      DETLMZ=(A13*(A24*A23))+(A14*(A22*A33))+(A12*(A23*A34))
     1    -(A12*(A24*A33))-(A13*(A22*A34))-(A14*(A23*A23))
      DETJMC=(A13*(A12*A34))+(A11*(A24*A33))+(A14*(A22*A13))
     1    -(A14*(A12*A33))-(A13*(A24*A13))-(A11*(A23*A34))
      DETKA=(A14*(A12*A23))+(A11*(A22*A34))+(A12*(A24*A13))
     1    -(A12*(A12*A34))-(A14*(A22*A13))-(A11*(A24*A23))
      DETD=(A13*(A12*A23))+(A11*(A22*A33))+(A12*(A23*A13))
     1    -(A12*(A12*A33))-(A13*(A22*A13))-(A11*(A23*A23))
      LAMZRO=LAMZRO+DETLMZ/DETD
      JMC=JMC+DETJMC/DETD
      KA=KA+DETKA/DETD
          IF(ABS(LAMZRO-TMPLMO)-0.0005) 400,350,350
 350      CONTINUE
C     CALCULATION OF ION SIZE, AZR, BY M-C EQUATION USING DIFFERENTIAL
C         APPROXIMATION.
 400  DO 480 II=1,50,1
          DD = 1. + 4./2.**II
          B=PHI/AZR
C
```

```
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C THE CALCULATIONS THAT FOLLOW DETERMINE, BY THE M-C EQUATION, WHAT THE
C    VALUE OF JMC, JMCALC IS THE NAME USED, WOULD BE FOR A GIVEN VALUE
C      OF AZR; AS WELL AS THE DIFFERENTIAL OF JMCALC WITH RESPECT TO THE
C      GIVEN AZR, DJMCDA IS THE NAME USED.
C
C      DETERMINATION OF EI AND DEIDB
  500 BFAC=1.0
      EI=0.5772157+ALOG(B)
      DEIDB=1./B
          DO 510 I=1,50,1
          AI=I
          IF((BFAC*B).GT.1.E70) GO TO 510
          BFAC=BFAC*B/AI
          TMPEI=BFAC/AI
          EI=EI+TMPEI
          DEIDB=DEIDB+BFAC/B
          IF(ABS(EI*1.E-4)-ABS(TMPEI)) 510,510,520
  510     CONTINUE
  520 CONTINUE
C
C      DETERMINATION OF SSTAR AND DSTRDB
  600 SSTAR=0.0
      DSTRDB=0.0
      PART1=1.0
      PART2=Z1*Z1
      PART3=Z2*Z2
      FAC=2.0
          DO 610 I=3,50,1
          IF(PART1.GT.1.E70) GO TO 610
          PART1=PART1*(-B/(Z1*Z2))
          PART2=PART2*Z1
          PART3=PART3*(-Z2)
          AI=I
          FAC=FAC*AI
          TMPSTR=(PART1/(FAC*(AI-2.0)))*(((PART2-PART3)/(Z1+Z2))**2)
          SSTAR=SSTAR+TMPSTR
          DSTRDB=DSTRDB+(AI-2.0)*TMPSTR/B
          IF(ABS(SSTAR*1.E-4)-ABS(TMPSTR)) 610,610,620
  610     CONTINUE
  620 CONTINUE
C
C      DETERMINATION OF L2
      L2   =   (1./(Q*Q*B)+EI/2.+(EXP(B)*(-5.*(B**5)-36.*(B**4)
     1     +30.*(B**3)+30.*(B**2)-18.*(B)-36.)+6.*(B**4)+45.*(B**3)
     2     +6.*(B**2)+54.*(B)+36.)/(108.*(B**5))+SSTAR/(Q*Q*Z1*Z2)
     3     -(((Z1-Z2)**2)/(2.*Q*Q*Z1*Z2))*(0.5772157+ALOG(3.0)
     4     +0.1666667-ALOG(B)))
      L2   =   L2             -(((Q*Q*EP2)/(9.*EP1*LAMZRO*(B**4)))
     1     *(EXP(B)*((B**4)+5.*(B**3)+3.*(B**2)-12.*(B)+6.)
     2     -4.5*(B**4)-3.*(B**3)+6.*(B**2)+6.*(B)-6.))
C
C      DETERMINATION OF DL2DB
      DL2DB   =   (-1./(Q*Q*B*B)+DEIDB/2.+(EXP(B)*(-5.*(B**6)-36.*(B**5)
     1     +66.*(B**4)-30.*(B**3)-108.*(B**2)+36.*(B)+180.)-6.*(B**4)
     2     -90.*(B**3)-18.*(B**2)-216.*(B)-108.)/(108.*(B**6))
     3     +DSTRDB/(Q*Q*Z1*Z2)+(((Z1-Z2)**2)/(2.*Q*Q*Z1*Z2*B)))
      DL2DB   =   DL2DB   -(((Q*Q*EP2)/(9.*EP1*LAMZRO*(B**5)))
     1     *(EXP(B)*((B**5)+5.*(B**4)-2.*(B**3)-18.*(B**2)+42.*(B)-24.)
     2     +3.*(B**3)-12.*(B**2)-18.*(B)+24.))
```

```
C
C     DETERMINATION OF LL2
      LL2 = (((18.*(Q)+61.*(Q**2)+21.*(Q**3)-6.*(Q**4))/(48.*(Q**2)
     1    *(1.+Q)))+((1.-2.*(Q)+1.*(Q**2)+1.*(Q**3)-(Q**5))
     2    *ALOG(1.+Q)-1.*(1.+Q*Q)*(1.-Q)*ALOG(1.-Q)-(2.+1.*(Q)
     3    +2.*(Q**2)+5.*(Q**3)-(Q**5))*ALOG(2.+Q)+1.*(1.+Q*Q)
     4    *(2.-Q)*ALOG(2.-Q))/(8.*(Q**3))-0.5772157)
C
C     DETERMINATION OF SIGMC2
      SIGMC2  =16.*EP2*(-0.5*(((Z1-Z2)**2)/(Z1*Z2)+Q*Q)*ALOG(PHI*KAP)
     1    +Q*Q*(LL2+L2))
C
C     DETERMINATION OF DSG2DA
      DSG2DA =  (-B/AZR)*(16.*EP2*Q*Q*DL2DB)
C
C     DETERMINATION OF L1
      L1   =  ((EXP(B)*(23.*(B**2)+9.*(B)+12.)-6.*(B**3)-8.*(B**2)
     1    -9.*(B)-12.)/(18.*(B**3))-EI)
C
C     DETERMINATION OF DL1DB
      DL1DB  =   ((EXP(B)*(23.*(B**3)-14.*(B**2)-6.*(B)-36.)
     1    +8.*(B**2)+18.*(B)+36.)/(18.*(B**4))-DEIDB)
C
C     DETERMINATION OF LL1
      LL1  =   (1.1544314-(6.*(Q)+15.*(Q**2)+21.*(Q**3)-13.*(Q**4)
     1    -35.*(Q**5)+6.*(Q**6))/(12.*(Q**2)*(1.+Q)*(1.-Q*Q))
     2    +(2.-Q*Q*(1.-Q*Q))*(ALOG(2.+Q))/(2.*(1.-Q*Q))
     3    +(1.-2.*Q*Q)*(ALOG(1.+2.*Q))/(1.-Q*Q)
     4    +((1.-Q*Q)**2)*(ALOG(1.+Q))/(2.*Q*Q))
      LL1  =   LL1-(((Z1-Z2)**2)*((1./3.)-(2.*Q*Q*(ALOG(3./(2.+Q)))
     1    /(1.-Q*Q)))/(2.*Z1*Z2*(1.-Q*Q)))
C
C     DETERMINATION OF SIGMC1
      SIGMC1   =  2.*EP1*(ALOG(PHI*KAP)+LL1+L1)
C
C     DETERMINATION OF DSG1DA
      DSG1DA =   (-B/AZR)*(2.*EP1*DL1DB)
C
C     DETERMINATION OF JMCALC
      JMCALC = SIGMC1*LAMZRO +SIGMC2
C
C     DETERMINATION OF DJMCDA
      DJMCDA = DSG1DA*LAMZRO+DSG2DA
C
C     THE CALCULATIONS ABOVE DETERMINE JMCALC AND DJMCDA FOR A GIVEN AZR
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
C
          DELAZR=(JMC-JMCALC)/DJMCDA
          AZR=AZR+DELAZR/DD
      IF(AZR.LE.1.E-8) AZR = 0.5*(AZR-DELAZR/DD)+1.E-8
      IF(AZR.GT.20.E-8) AZR = 20.E-8/DD
          IF(ABS(DELAZR)-.5E-12) 700,480,480
  480     CONTINUE
C
C     CALCULATION OF LMCALC(I) AND STANDARD DEVIATION OF
C         LAMBRA(I) -- STDLM, JMC -- STDJMC, LAMZRO -- STDLZO,
C         AZR -- STDAZR.
  700 STDLM = SQRT(SUMDIF/(A11-3.0))
      STDLZO = STDLM*SQRT(ABS((A22*A33-A23*A23)/DETD))
      STDJMC = STDLM*SQRT(ABS((A11*A33-A13*A13)/DETD))
```

```
      STDKA = STDLM*SQRT(ABS((A11*A22-A12*A12)/DETD))
      STDAZR=ABS(STDJMC/DJMCDA)
C
C
C
C     CALCULATION BLOCK COMPLETED; CALCULATED OUTPUT BLOCK BEGINS.
      WRITE(6,930)LAMZRO,STDLZO
  930 FORMAT(1X/'0LAMZRO =      ',F8.3,'       STDLZO =      ',F8.3)
      WRITE(6,935)S,ALPHA,BETA
  935 FORMAT('      S =    ',F8.3,'         ALPHA =        ',F8.5,
     1'      BETA =        ',F8.4)
      WRITE(6,940)EP,EP1,EP2
  940 FORMAT('     EP =',F14.3,'          EP1 =       ',F9.5,
     1'       EP2 =     ',F9.4)
      WRITE(6,942)SIGMC1,LL1,L1
  942 FORMAT(' SIGMC1 =',F15.4,'          LL1 =       ',F9.5,
     1'         L1 =',F15.4)
      WRITE(6,944)SIGMC2,LL2,L2
  944 FORMAT(' SIGMC2=',F16.4,'          LL2 =       ',F9.5,
     1'         L2 =',F15.4)
      WRITE(6,945)JMC,STDJMC,JMCALC
  945 FORMAT('    JMC =',F13.2,'       STDJMC =    ',F9.2,
     1'       JMCALC =',F13.2)
C     AZR  AND  STDAZR  CHANGED TO ANGSTROMS
      AZR=AZR*1.E8
      STDAZR=STDAZR*1.E8
      WRITE(6,950)AZR,STDAZR,II
  950 FORMAT('    AZR =        ',F7.4,'     STDAZR =        ',F7.4,
     1'         II =        ',I2)
C     AZR CHANGED BACK TO ANGSTROMS
      AZR=AZR*1.E-8
      WRITE(6,955)KA,STDKA
  955 FORMAT('      KA =  ',F10.1,'          STDKA =    ',F8.1)
C     PHI CHANGED TO ANGSTROMS
      PHI = 1.E8*PHI
      WRITE(6,960)B,PHI,Q
  960 FORMAT('      B =       ',F8.4,'      AZR*B =       'F8.4,
     1'          Q =      ',F8.5)
      WRITE(6,965)L,STDLM
  965 FORMAT('0THIS RUN CONVERGED AFTER 'I3,' ITERATIONS WITH A STANDA',
     1'RD DEVATION OF 'F8.3)
      WRITE(6,970)
  970 FORMAT(1X/'  I        C(I) LAMBDA(I) LMCALC(I) DELTLM(I)    ',
     1'GAMMA(I)  GAMSTR(I) ACTCOEF(I)   KAPPA(I) KAPPA(I)*A ',
     2'KAPPA(I)*A*B',/1X)
C     C(I)  CHANGED TO  MOLES/(LITERS*10**4)
          DO 990 I=1,N
          KAPPA(I)=KAP*SQRT(C(I))
          KAPAA(I)*KAPPA(I)*AZR
          KAPAAB(I)=KAPPA(I)*AZR*B
          LOGC(I)=ALOG(C(I))
          C(I)=C(I)*1.E4
          KAPPA(I)=1.E-8*KAPPA(I)
          WRITE(6,980)I,C(I),LAMBDA(I),LMCALC(I),DELTLM(I),G(I),
     1    GSTAR(I),F(I),KAPPA(I),KAPAA(I),KAPAAB(I)
  980     FORMAT(1X,I2,2X,F9.4,3X,F7.3,3X,F7.3,3X,F7.3,3X,F8.5,3X,F8.5,
     1    3X,F8.5,4X,F7.5,3X,F7.5,3X,F7.5)
  990     CONTINUE
      GO TO 10
 1000 CONTINUE
      RETURN
      END
```

APPENDIX 3

THE MURPHY-COHEN EQUATION FOR UNSYMMETRICAL, N-M, ELECTROLYTES

The equation is:

$$\Lambda = \Lambda^\circ - S\sqrt{C} + E'C\ln C + J'C$$

where $S = \alpha\Lambda^\circ + \beta$:

$$\alpha = \frac{q^2 \kappa/\sqrt{C}\ ab}{3(1+q)} = \frac{2.8012 \times 10^6 |Z_1 Z_2| \omega^{1/2} q^2}{(1+q)(DT^{3/2})}$$

$$\beta = \frac{F\varepsilon\ \kappa/\sqrt{C}\ (|Z_1| + |Z_2|)}{1{,}798.755\pi\eta}$$

$$\beta = \frac{41.234(|Z_1| + |Z_2|)\omega^{1/2}}{\eta(DT)^{1/2}}$$

$$q^2 = \frac{|Z_1|.|Z_2|}{(|Z_1|+|Z_2|)} \times \frac{(\lambda_1^\circ + \lambda^\circ)}{(|Z_1|\lambda_1^\circ + |Z_2|\lambda_2^\circ)}$$

$$ab = \frac{|Z_1||Z_2|\varepsilon^2}{DkT} = \frac{16.7098 \times 10^{-4}|Z_1 Z_2|}{(DT)}$$

$$\kappa/\sqrt{C} = \frac{0.502915 \times 10^{10}\sqrt{\omega}}{(DT)^{1/2}}$$

$$\omega = (\nu_1 Z_1^2 + \nu_2 Z_2^2)$$

$$E' = E_1'\Lambda^\circ - 4E_2'[q^2 + \frac{(|Z_1| - |Z_2|)^2}{|Z_1 Z_2|}]$$

$$E_1' = \frac{(q\kappa ab)^2}{12C}$$

$$E_2' = \frac{\kappa ab\beta}{16\sqrt{C}}$$

$$J' = \sigma_1'\Lambda^\circ + \sigma_2'$$

$$\sigma_1' = 2E_i'[\ln\frac{\kappa ab}{\sqrt{C}} + f(q) + I_1(b)]$$

$$f_1(q) = 1.1544314 - \frac{6q + 15q^2 + 21q^3 - 13q^4 - 35q^5 + 6q^6}{12q^2(1+q)(1-q^2)}$$

$$+ \frac{2-q^2(1-q^2)}{2(1-q^2)}\ln(2+q) + \frac{1-2q^2}{1-q^2}\ln(1+2q) + \frac{(1-q^2)^2}{2q^2}\ln(1+q)$$

$$- \frac{(|Z_1|-|Z_2|)^2}{2|Z_1Z_2|(1-q^2)}[\frac{1}{3} - \frac{2q^2}{1-q^2}\ln\frac{3}{2+q}]$$

$$I_1(b) = [[e^b(23b^2 + 9b + 12) - 6b^3 - 8b^2 - 9b - 12]/18b^3 - E_i(b)]$$

$$\sigma_2' = 16E'[-\tfrac{1}{2}[\frac{(|Z_1|-|Z_2|)^2}{|Z_1Z_2|} + q^2]\ln\frac{\kappa ab}{\sqrt{C}} + q^2[f_2(q) + I_2(b)]]$$

$$f_2(q) = \frac{18q + 61q^2 + 21q^3 - 6q^4}{48q^2(1+q)} + [(1 - 2q + q^2 + q^3 - q^5)\ln(1+q)$$

$$- (1+q^2)(1-q)\ln(1-q) - (2 + q + 2q^2 + 5q^3 - q^5)\ln(2+q)$$

$$+ (1+q^2)(2-q)\ln(2-q)]/8q^3 - 0.5772157]$$

$$I_2(b) = [\frac{1}{q^2b} + \tfrac{1}{2}E_i(b) + [e^b(-5b^2 - 36b^4 + 30b^3 + 30b^2 - 18b - 36) + 6b^4$$

$$+ 45b^3 + 6b^2 + 54b + 36]/108b^5 + \frac{1}{q^2|Z_1Z_2|}\xi_s^*(b)$$

$$- \frac{(|Z_1|-|Z_2|)}{2q^2|Z_1Z_2|}(0.5772157 + \ln 3 + 0.16666667 - \ln b)$$

$$- \frac{q^2E_2'}{9E_1'\Lambda^\circ b^4}[e^b(b^4 + 5b^3 + 3b^2 - 12b + 6) - \frac{9b^4}{2} - 3b^3 + 6b^2 +$$

$$6b - 6]]$$

$$\xi_s^*(b) = \sum_{n=3}^{\infty}\frac{(-b/|Z_1Z_2|)^{n-2}}{n!(n-2)}[\frac{|Z_1|^n - (-|Z_2|)^n}{|Z_1| + |Z_2|}]$$

$$E_i(b) = 0.5772157 + \ln b + \sum_{n=1}^{\infty}\frac{b^n}{n!n}$$

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