

Bulletin 11:
**MULTICOMPONENT MASS TRANSPORT IN AQUEOUS
AND MEMBRANE SYSTEMS**
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MULTICOMPONENT MASS TRANSPORT
" IN AQUEOUS AND MEMBRANE
SYSTEMS

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PREFACE

The term "multicomponent mass transport," as used here refers to those physical processes whereby molecular species in a mixture are caused to move relative to one another. By such processes a change in composition can be brought about.

For example, consider a sample of water containing a pollutant, say a dissolved pesticide. Suppose that a portion of this aqueous solution is forced through a suitable porous membrane by the use of pressure. In general, the membrane is more easily penetrated by the small water molecules than by the larger molecules of pesticide. Thus, the effluent from the low pressure side of the membrane will contain a very much reduced pesticide concentration. Therefore, it is possible to extract potable water from a contaminated source through use of a pressure difference and a suitable membrane. The rate and efficiency of this and similar processes is determined by the rates of mass transfer across a multicomponent system consisting of water, pesticide, and the membrane matrix. It is to the quantitative prediction of the rates and efficiencies of such multicomponent mass transfer operations that this work is addressed.

Processes involving such multicomponent mass transport are found throughout the water resource field. For example, the kinetics and efficiency of membrane desalination processes are governed by rates of mass transport. Similar membrane processes have been proposed for use in contaminate removal from a wide variety of industrial waste disposal streams. Another example are those processes in which rates of oxygen transfer into natural bodies of water is an important parameter in pollution control.

This project has been concerned with mass transport in aqueous and membrane systems. The objective has been to develop the underlying theory and to propose and test practical, quantitative models for the rates of mass transport in such systems. The quantitative information developed should prove invaluable in the engineering and control of pollution control processes.

William R. Walker
Director

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MULTICOMPONENT MASS TRANSPORT IN AQUEOUS AND MEMBRANE SYSTEMS

Project Objectives

The basic objective of this study has been to develop and critically test models for multicomponent mass transport in aqueous and membrane systems. More specifically, this basic aim has been pursued through the following set of sub-objectives:

(1) Selecting a set of aqueous systems for detailed study followed by a comprehensive literature review to collect all pertinent data for the selected systems.

(2) Measuring multicomponent mass transport data in a selected system over a wide range of compositions.

(3) Developing a general mathematical model for multicomponent mass transport

(4) Obtaining optimum parameters for the mass transport models developed in (3).

(5) Determining whether the effective water of hydration of solutes in aqueous solutions can be reasonably determined as that value giving the best fit of the experimental transport data.

Summary of Research Procedures

System Selection and Literature Review

The transport phenomena selected for study were diffusion, electrical conductivity, and transport number. The systems selected for detailed study were those formed from the ions H^+ , Na^+ , Cl^- , NO_3^- , and water, H_2O . The possible binary and ternary systems are as follows:

Binary Systems

NaCl-H₂O
HNO₃-H₂O
NaNO₃-H₂O
HCl-HNO₃

Ternary Systems

HCl-HNO₃-H₂O
HCl-NaCl-H₂O
NaCl-NaNO₃-H₂O
HNO₃-NaNO₃-H₂O
NaCl-HNO₃-H₂O
NaNO₃-HCl-H₂O

A survey of the transport data for such systems is given in Table (1). The numbers in the table are those of the references listed in the bibliography.

Theoretical Considerations and Numerical Procedures

For analysis, the data were divided into binary and ternary systems. A numerical procedure was then developed to extract optimum parameters from the transport data for each system.

Objective Function Selection

The optimum parameters for each binary system were defined as those which minimized the following objective function:

$$\begin{aligned} & \text{Sum Squares of Errors} \\ & = \sum_{\text{all data}} (1-D_e/D_p)^2 + (1-k_e/k_p)^2 + (1-t_e^+/t_p^+)^2 \quad \text{Eq. (1)} \end{aligned}$$

where: D_e = experimental diffusion coefficients

D_p = predicted diffusion coefficients

k_e = experimental electrical conductivity

k_p = predicted electrical conductivity

t_e^+ = experimental cation transport number

t_p^+ = predicted cation transport number

TABLE I
RESULTS OF LITERATURE SURVEY

Data System	Electrolytic Conductance	Diffusivity	Transport Number
NaCl-H ₂ O	7, 12, 22 26, 27, 28, 32, 36, 38, 41	2, 7, 21, 28, 36, 39, 42	1, 6, 12, 13, 18, 21, 27, 29, 30, 43, 44
HCl-H ₂ O	1, 13, 14, 22, 28, 35, 36, 38	2, 7, 28, 36, 39	1, 12, 13, 14, 18, 19, 21, 25
HNO ₃ -H ₂ O	1, 16, 17, 22, 28, 32, 37	2, 23	1, 3, 4, 15, 16, 22, 24, 25, 28, 32, 40
NaNO ₃ -H ₂ O	11, 12, 22, 28, 41	20, 23, 33, 36	4, 32
HCl-HNO ₃ H ₂ O	9	---	---
HCl-NaCl-H ₂ O	5, 10, 21, 31, 34	2, 28	---
NaCl-NaNO ₃ -H ₂ O	8	---	---
HNO ₃ -NaHO ₃ -H ₂ O	---	28	---

The experimental data were points taken at 0.1 eq/l. increments from a smooth curve through the experimentally determined values of D , k , and t^+ in the range of 0 to 1 eq./l. The D_p , k_p , and t_p^+ are complicated functions of the model parameters. It is these parameters which are adjusted to give a minimum in the sum of squares of the errors (as defined in Eq. (1)). Expressions such as $(1-D_e/D_p)$ are used rather than simply (D_p-D_e) , etc., so that each type of transport data has equal weight in determining the optimum coefficients. The goal is to obtain a single set of parameters which will give a good representation of all three types of data over the selected range of concentration.

Optimization Procedure

Because Eq. (1) is a highly non-linear function of the system parameters, considerable difficulty was experienced in finding optimum model parameters. The procedure finally developed was essentially a steepest descent procedure with an acceleration step to speed convergence. Double precision programming was used upon nearing an optimum solution. The acceleration step was a "creep-and-leap" procedure in which a straight-forward steepest ascent was carried out for five iterations using a very small step length. Then the pattern of these small steps was projected using a step length such that if it were doubled, an over-shooting would result (i.e. a worse rather than a better result). In this way the length of the "leap" was nearly the largest permissible, and yet a better result was still guaranteed following the "leap".

Only the numerical procedures for parameter optimization have been outlined. Presumably, this procedure could be used successfully to obtain parameters for a number of models. Here, a particular model was developed and tested.

Model Development

A model for multicomponent mass transport consists of a flux expression for each component in the system. The flux equations must be an explicit expression containing: driving forces, F_i , concentrations, and system parameters. From irreversible thermodynamics, the general form of these flux expressions is known to be linear in the forces. Thus, in a system of n -components, the flux of species i , J_i , must be of the form shown in Eq. (2):

$$J_i = \sum_j^n L_{ij} F_j \quad \text{Eq. (2)}$$

The L_{ij} are the phenomenological coefficients, and these are complex functions of concentration and system parameters, but are independent of the forces, F_j . A model for multicomponent mass transport gives an explicit, algebraic expression for the L_{ij} in terms of the concentrations, C_j , and the system parameters. In the model developed for testing here, the system parameters are given the symbol N_{ij} .

While the same general model is used for mass transport in both membranes and aqueous solutions, there are differences. These differences arise because of an immobilized species present in the membrane--the membrane matrix. Because of this special feature, the basic set of flux equations governing mass transport in membranes form an independent set. While very similar flux expressions govern mass transport in aqueous solutions, the appropriate set of flux expressions is not independent. One of the significant advantages of the model developed here is that it is equally applicable to both the membrane and solution cases. However, in determining the range of convergence of the model developed here it is necessary to consider the membrane and solution cases separately.

Model for Membranes

In the model developed here, there are postulated frictional forces between species i and j . These forces are taken proportional to the product of the concentration of species j , C_j , and the relative velocity of species i with respect to species j . The total frictional force, f_i , is set equal to the negative of the total external force on species i , F_i , taken to be the negative of the gradient of the total potential. These assumptions lead to a set of equations of the following form. Similar expressions have been obtained by others.

$$F_i = \sum_j C_j N_{ij} (u_i - u_j) \quad j \neq i \quad \text{Eq. (3)}$$

There are n -mobile components, and one fixed component, m , the membrane being treated as a completely homogeneous phase in which the matrix material is included as a component. Membrane swelling is allowed for by including a concentration term, C_m , for the matrix material.

If the set of linear equations of the form of (3) are solved for the species velocities u_i , the flux equations J_i can be calculated as follows:

$$J_i = C_i u_i \quad \text{Eq. (4)}$$

Solution of (3) for the u_i is straightforward, but even for a single 1-1 electrolyte, the results are fairly complex, for solution (3) is rewritten so that each species velocity appears but once:

$$F_i = u_i \sum_j C_j N_{ij} - \sum_j C_j N_{ij} u_j \quad j \neq i \quad \text{Eq. (5)}$$

For a system of $n + 1$ components, the set of equations given by (5) can be written in matrix notations, a bracket indicating that the enclosed array is a matrix:

$$\begin{bmatrix} F_1 \\ F_2 \\ \cdot \\ \cdot \\ F_n \end{bmatrix} = \begin{bmatrix} A_{11} & A_{12} & \cdot & \cdot & \cdot & A_{1n} \\ A_{21} & A_{22} & \cdot & \cdot & \cdot & A_{2n} \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ A_{n1} & \cdot & \cdot & \cdot & \cdot & A_{nn} \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ \cdot \\ \cdot \\ u_n \end{bmatrix} \quad \text{Eq. (6)}$$

The A_{ij} have been introduced for convenience and are related to the C_j and N_{ij} as follows:

$$A_{ii} = \sum_j C_j N_{ij} \quad j \neq i \quad \text{Eq. (7)}$$

$$A_{ij} = -N_{ij} C_j \quad \text{Eq. (8)}$$

Equation (6) can be abbreviated if it is understood that F , A , and u represent the appropriate matrices:

$$[F] = [A] [u] \quad \text{Eq. (9)}$$

The solution of (9) leads to a similar matrix equation where A^{-1} is now the inverse matrix of A .

$$[u] = [A^{-1}] [F] \quad \text{Eq. (10)}$$

Since matrix A is of order n and there are $n + 1$ components in the system, matrix A is non-singular in the model given here. Thus, the inverse matrix can be found by standard means. However, this holds only for the case where the matrix material is considered as a component so that there are a total of $n+1$ components in the system.

The flux equations are found by multiplying the u 's in (10) by the appropriate concentrations. In matrix notation this can be written as follows:

$$[J] = [C] [I] [A^{-1}] [F] \quad \text{Eq. (11)}$$

Results of the form shown by (11) are such that for a four component system there are four external forces and each is multiplied by a term involving a third order determinant divided by a fourth order determinant. It is thus evident that the algebra is rapidly becoming complicated. Nonetheless, if the N_{ij} is known, direct matrix inversion would remain a reasonable procedure since well-known numerical methods are available. However, the N_{ij} must in general be determined from experiments involving the flux equations or quantities derivable from them. This is where difficulty is encountered. The purpose here is to show how the exact flux equations can be approximated to give expressions of greatly reduced complexity. In this way, the task of extracting the N_{ij} 's from experimental data is greatly facilitated.

First, it will be noted that the diagonal terms in the matrix in (6) are the major elements. The off-diagonal terms would be expected to be significantly smaller than the diagonal terms. This

suggests a procedure for obtaining an approximate inverse. In particular, a first approximation is obtained by setting the off-diagonal terms equal to zero. The first approximate inverse to matrix A is then A_1^{-1} .

$$\left[A_1^{-1} \right] = \begin{bmatrix} 1/A_{11} & 0 & \cdot & \cdot & \cdot \\ 0 & 1/A_{22} & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{bmatrix} \quad \text{Eq. (12)}$$

This approximate inverse corresponds to fluxes in a hypothetical case where each species moves through the membrane with the other species held fixed. With this first approximation, a more realistic inverse results from use of a second order iteration formula which is reported to converge rapidly. This is as follows:

$$\left[A_2^{-1} \right] = \left[A_1^{-1} \right] \left[2I - AA_1^{-1} \right] \quad \text{Eq. (13)}$$

Here A_1^{-1} is the first approximate inverse, A_2^{-1} is a second approximation to the true inverse of A, and I is a unit matrix. Applying this to (12), one obtains the following approximate inverse:

$$\left[A_2^{-1} \right] = \begin{bmatrix} 1/A_{11} & -A_{12}/A_{11}A_{22} & -A_{13}/A_{11}A_{33} & \cdot & \cdot \\ -A_{21}/A_{22}A_{11} & 1/A_{22} & \cdot & \cdot & \cdot \\ -A_{31}/A_{33}A_{11} & \cdot & 1/A_{33} & \cdot & \cdot \\ -A_{31}/A_{33}A_{11} & \cdot & \cdot & \cdot & \cdot \end{bmatrix} \quad \text{Eq. (14)}$$

The iteration formula could be again applied to A_2^{-1} but this would result in a significantly more complicated approximate inverse. No further refinement of the approximate inverse will be sought here.

The condition for convergence of (13) is that the off-diagonal terms in the matrix A (given in (6)) be less than the diagonal terms. The diagonal terms are A_{ii} , while the off-diagonal terms

are of the form A_{ij} . Thus, one needs to show that A_{ij}/A_{ii} is less than one. Since the A_{ii} terms are sums of the form $\sum_{j \neq i} C_j N_{ij}$, while the A_{ij} are single terms of the form $C_j N_{ij}$, this condition will usually be satisfied, particularly since the large term $C_m N_m$ will always appear in the A_{ii} term and never as an A_{ij} term.

At this point, it is convenient to introduce generalized mobilities, U_i , which are defined by (15).

$$U_i = 1/A_{ii} = (\sum_j N_{ij} C_j)^{-1} \quad j \neq i \quad \text{Eq. (15)}$$

With this definition, the approximate flux expressions can be written in simple form:

$$J_i = U_i C_i F_i + C_i U_i \sum_j N_{ij} U_j C_j F_j \quad j \neq i \quad \text{Eq. (16)}$$

Neglecting the explicit N_{ij} in (16) a form results which is similar to the Nernst-Planck Equations, namely:

$$J_i = C_i U_i F_i \quad \text{Eq. (17)}$$

By comparison with Eq. (2), one obtains the following predictive expressions for the L_{ij} . These predictive expressions for the L_{ij} then constitute the model for mass transport in membranes:

$$L_{ii} = C_i U_i \quad \text{Eq. (18)}$$

$$L_{ij} = N_{ij} C_i U_i C_j U_j \quad \text{Eq. (19)}$$

$$i \neq j$$

where:
$$U_i = (\sum_j C_j N_{ij})^{-1} \quad \text{Eq. (20)}$$

$$j \neq i$$

From the predictive expressions for the L_{ij} , it is possible to predict the theoretical expressions for the transport coefficients D_p , k_p and t_p^+ (for the binary solutions) and this will be given after the model for mass transport in aqueous solutions is developed.

Interestingly enough, the solution model is identical to the result for the membrane, although the method of obtaining it is quite different and the conditions for convergence are different. It will, of course, be realized that the matrix iteration formula used to develop the membrane model can not be applied directly to the singular set of solution flux expressions, and hence a difference in approach is needed in the solution case.

Model for Aqueous Solutions

As in the membrane case, Eq. (2) is the starting point, but in the solution case there are simply N -mobile components. This set of flux expressions can also be written in the matrix form given by Eq. (9). There is the complication here that the coefficient matrix formed from the set of equations given by Eq. (3) is singular. Hence, before an exact matrix inversion can be carried out, certain operations must be carried out; ordinarily, the N -th flux is algebraically eliminated and the N -th force expression is dropped. But in doing this, a great deal of the simplicity of Eq. (3) is lost.

Because the approximation procedure to be used here involves only algebraic rearrangement of the singular set, the procedure can be used without first converting the singular set into a non-singular set. Thus, the approximate procedures used here have the property of transforming a singular set of force expressions into a singular set of flux expressions.

In the case considered here, each element in the matrix (to be inverted) is already a moderately complex function. The further complication introduced by the inversion yields functions of the concentrations and the parameters (i.e. the N_{ij}) that are so complex that the task of extracting the parameters from experimental data is impractical. In such a case, two possible alternatives are: (1) to assume the highly non-linear functions of concentrations to be sensibly constant over the range of concentrations of interest or (2) to approximate the inversion process so that simpler functions result. The latter approach has been used here. Approach (1) can be used providing one is simply interested in correlating a single type of experimental data over a small range of concentrations.

For reasons that will become apparent later, Eq. (3) is rewritten so that each species velocity appears but once:

$$F_i = u_i \sum_j C_j N_{ij} - \sum_j C_j N_{ij} u_j \quad j \neq i \quad \text{Eq. (21)}$$

The first sum in Eq. (21) is defined to be a generalized mobility, U_i , and an ideal flux, J_i^* , is introduced and defined by Eq. (23).

$$U_i = 1 / \sum_j C_j N_{ij} \quad j \neq i \quad \text{Eq. (22)}$$

$$J_i^* = C_i U_i F_i \quad \text{Eq. (23)}$$

With these definitions, Eq. (21) can be recast as follows:

$$J_i = J_i^* + C_i U_i \sum_j N_{ij} J_j \quad j \neq i \quad \text{Eq. (24)}$$

Equation (24) is simply Eq. (21) with the definitions in Eqs. (22) and (23) introduced. No approximations have been made, and only the form of Eq. (21) has been changed.

Why the J_i^* are called ideal fluxes and why the U_i are termed generalized mobilities can be seen from Eq. (24). Suppose that all of the fluxes were zero except for a particular one, J_i . Then J_i would be equal to J_i^* . Thus, J_i would be directly proportional to F_i . The proportionality constant would be equal to the product of the generalized mobility and the concentration of species i . This will, of course, be recognized as being in the form of the so-called "Nernst-Planck" flux equations.

From the foregoing discussion, one apparent method of approximating the inversion of Eq. (21) is to neglect the second term on the right hand side of Eq. (24). Then using Eq. (23), a Nernst-Planck expression is obtained in which the generalized mobilities, U_i , have a particular concentration dependence. Hence, as a first order approximation, one obtains the following inverted form:

$$J_i = J_i^* = C_i U_i F_i \quad \text{Eq. (25)}$$

where: $U_i = 1/\sum_j C_j N_{ij}$ $j \neq i$

Higher order approximations can be obtained in the following way: starting with the form of Eq. (24) one writes a general expression for the flux of a species j and introduces another index k .

$$J_j = J_j^* + C_j U_j \sum_k N_{jk} J_k \quad k \neq j \quad \text{Eq. (26)}$$

This expression for N_j is then substituted into Eq. (24) to give:

$$J_i = J_i^* + C_i U_i \sum_j N_{ij} J_j^* + C_i U_i \sum_j N_{ij} C_j U_j \sum_k N_{jk} J_k \quad j \neq i, k \neq j$$

Eq. (27)

This process of substituting Eq. (24) into itself yields a new expression with three terms on the right hand side; the first containing no explicit N_{ij} 's, a second term which is linear in the N_{ij} 's, and a third term which is quadratic in the N_{ij} 's. This substitution process can be continued by eliminating J_k from Eq. (27) to give a term which is third order in the N_{ij} 's. Further substitution gives a term which is fourth order in the N_{ij} 's, etc. At each stage, only the last term contains J_j 's; the other terms contain only J_j^* 's. The general approximation scheme, then, is to expand Eq. (24) by substituting it into itself until the terminal factor becomes negligible. With neglect of the last term in Eq. (27), for example, one obtains the following form:

$$J_i = J_i^* + C_i U_i \sum_j N_{ij} J_j^* \quad j \neq i \quad \text{Eq. (28)}$$

With Eq. (23) this is cast in the desired, inverted form as follows:

$$J_i = C_i U_i F_i + C_i U_i \sum_j N_{ij} C_j U_j F_j \quad j \neq i \quad \text{Eq. (29)}$$

This is exactly the result obtained for the membrane case, Eq. (16). Thus, the predictive expressions for the L_{ij} are also given by Eqs. (18) and (19).

It remains to be shown that each succeeding term in a form such as Eq. (27) is smaller than its predecessor, since this is not evident upon casual inspection. One method of demonstrating this is to suppose that all of the N_{ij} 's are identical. This might be the case, for example, if one had several isotopes of the same parent compound.

With the velocities in Eq. (21) with respect to the molar average, the fluxes sum to zero:

$$\sum_{j=1}^n J_j = 0 \quad \text{Eq. (30)}$$

Combining Eqs. (29) and (30), one obtains:

$$J_i = J_i^* + C_i U_i N_{ij} (-J_j) \quad \text{Eq. (31)}$$

Solving for the ratio of J_i^* to J_i and introducing a new symbol a_i , results in the following:

$$J_i^*/J_i = 1 + C_i U_i N_{ij} = 1 + a_i \quad \text{Eq. (32)}$$

The symbol a_i has been introduced and one should remember that the term $C_i U_i N_{ij}$ will be equal to a_i only for the special case of equal N_{ij} 's. Rearranging Eq. (32) and expanding in an appropriate series form, one obtains:

$$J_i = \begin{array}{l} J_i^* (1 - a_i + a_i^2 \dots) \quad \text{If } a_i \leq 1 \\ \text{or} \\ J_i^* (1/a_k - 1/a_k^2 + 1/a_k^3 \dots) \quad \text{If } a_k \geq 1 \end{array} \quad \text{Eq. (33)}$$

From substitution of the definition of U_i into Eq. (32), it is seen that the a_i are simply related to the concentrations expressed as mole fractions, X_i :

$$a_i = X_i/(1-X_i) \quad \text{Eq. (34)}$$

However, this simple result applies only for the special case of equal N_{ij} . Also, only one a , denoted as a_k , can be greater than unity (i.e. $X_k > 0.5$). In the general multicomponent case, there need be no a greater than unity. Frequently, however, the solvent species mole fraction will be nearly unity, in which case the a for the solvent species will be quite large.

Substitution of Eq. (32) into Eq. (29) gives:

$$J_i = J_i^* + a_i \left[\sum_j (1 - a_j + a_j^2 \dots) J_j^* + (1/a_k - 1/a_k^2 \dots) J_k^* \right] \quad \text{Eq. (35)}$$

$$= C_i U_i F_i + a_i \left[\sum_j (1 - a_j + a_j^2 \dots) U_j C_j F_j + (1/a_k - 1/a_k^2 + 1/a_k^3) U_k C_k F_k \right] \quad \text{Eq. (35)}_a$$

where: $j \neq i, k$ $a_j \leq 1$

$k \neq i, j$ $a_k \geq 1$

Equation (35) gives a result that can be compared with the successive approximation scheme for the special case of equal N_{ij} . In this form, the requirements for rapid convergence can be seen, namely, the a_j should be small, and the a_k , if any, should be large.

For example, by neglecting terms of order $a_i a_j$ and higher, and terms of order a_i/a_k and higher, one obtains the following approximate expression:

$$J_i = J_i^* + a_i \sum_j J_j^* \quad j \neq i, k \quad \text{Eq. (36)}$$

$$= C_i U_i F_i + a_i \sum_j C_j U_j F_j$$

This same expression results from neglecting the last term in Eq. (27).

For very small concentrations of solute, the corresponding a_i becomes very small, and J_i might be taken as J_i^* for the solutes.

However, note that using a similar expression for the solvent would be quite invalid since a_k would be very large, and thus Eq. (36) could not be further simplified.

The general form in which the N_{ij} 's are not necessarily equal, and where no particular reference is specified, can be written as follows:

$$\begin{aligned}
 J_i &= J_i^* + C_i U_i \left[\sum_j N_{ij} (1 - a_j + a_j^2 - a_j^3 \dots) N_j^* \right. \\
 &\quad \left. + N_{ik} (1/a_k - 1/a_k^2 \dots) N_k^* \right] \\
 &= C_i U_i F_i + C_i U_i \left[\sum_j N_{ij} (1 - a_j + a_j^2 \dots) C_j U_j F_j \right. \\
 &\quad \left. + N_{ik} (1/a_k - 1/a_k^2 \dots) N_k \right] \quad \text{Eq. (37)} \\
 &\quad j \neq i, k
 \end{aligned}$$

Again, clearly, the method will converge if the a_i 's and a_j 's are small, and the a_k large. However, the simple interpretation that the a_j 's are equal to $C_i U_i N_{ij}$ is no longer valid.

Predictive Expressions

From the basic model, given by Eqs. (18) through (20), the expressions can be derived for the transport coefficients of interest in binary aqueous solutions, that is: the diffusion coefficient D_p , the electrical conductivity k_p , and the cation transport number t_p^+ . The model in this case can be used to predict the concentration dependence of these transport coefficients in terms of concentrations and model parameters. These derivations will not be given here since the detail can be found elsewhere. Here, only the resulting predicted expressions for the transport coefficients will be given. These are as follows:

$$D_p = (2RT/F) (U_1 U_2 - C^2 N_{12}^2 U_1^2 U_2^2) / (U_1 + U_2 - 2CN_{12} U_1 U_2)$$

Eq. (38)

$$k_p = C (U_1 + U_2 - 2CN_{12}U_1U_2) \quad \text{Eq. (39)}$$

$$t_p^+ = (U_1 - CN_{12}U_1U_2)/(k/C) \quad \text{Eq. (40)}$$

where: R = gas const.

F = Faraday

The parameter U_i is introduced for convenience and is termed a generalized mobility. It is easily expressed in terms of C_i 's and N_{ij} 's (see Eq. (20)), but its use allows simplifications in writing mathematical expressions. This mobility also has the physical significance of a true mobility.

For ternary and more complex mixtures, only electrical conductivity data have been obtained. The expression for conductivities of these 1-1 electrolyte mixtures is as follows:

$$k_p = RT/F (\sum_{+ions} L_{ij} - \sum_{-ions} L_{ij}) \quad \text{Eq. (41)}$$

Results

Experimental Data

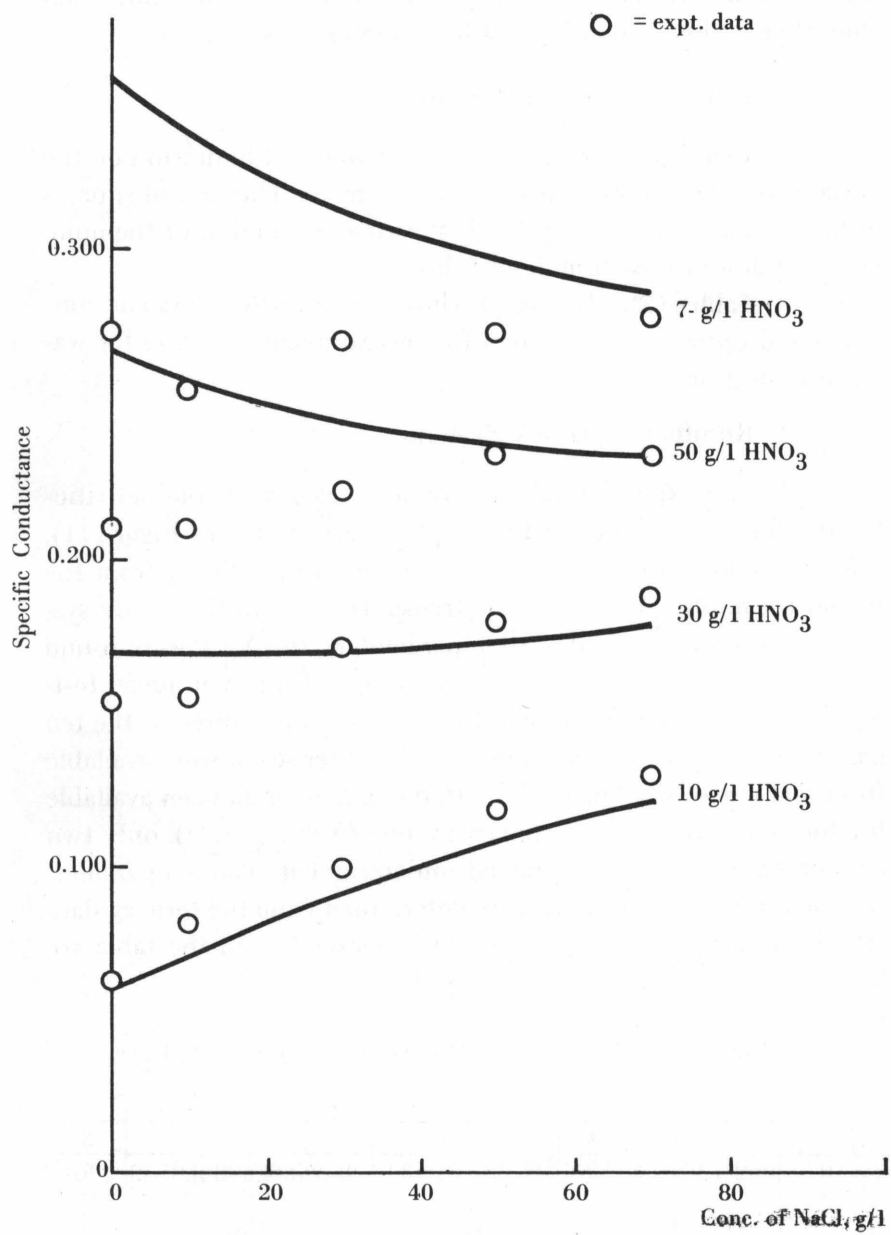
Because of the scanty data available for ternary systems, a complete set of electrical conductivity data for the system NaCl-HNO₃-H₂O was determined for the concentration range of 0-1.0N. The determinations were made with a null bridge using a 60 cycle A. C. oscillator. All determinations were made at 25° C. These data are shown as points in Figure (1). Correlations of these data are shown as curves and these theoretical results will be discussed presently.

Results of Numerical Analysis

Results for Binary Systems:

The literature data and the predicted data for the binary

FIG. (1) SPECIFIC CONDUCTANCE FOR NaCl-HCl-H₂O SYSTEM AT 25° C



systems NaCl-H₂O, HNO₃-H₂O, and HCl-H₂O are shown in Figures (2), (3), and (4). In all cases, the effective water of hydration of the solute has been taken to be 3.5 moles of H₂O/mole of solute. Complete data for the system NaNO₃-H₂O was not available. Hence, this system has not been analyzed as yet.

Effect of Water of Hydration:

Figure (5) shows the effect of water of hydration on the deviations between prediction and experiment. The sum of squares of the errors, defined in Eq. (1), is shown as a function of the number of hydrate for each mole of solute.

Tables (2), (3), and (4) show the predicted data and the associated optimum parameters for several assumed values for water of hydration.

Results for Ternary Systems:

The experimental and predicted electrical conductivities for the ternary system NaCl-HNO₃-H₂O are shown in Figure (1). The data points are shown and the curves are predicted from the model for multicomponent mass transport. As with the binary systems, an optimum set of system parameters, the N_{ij}'s, were found by the numerical search technique developed for use in model testing. However, it was necessary to determine only three of the ten parameters involved since values for the other seven were available from analysis of the binary data. Had complete data been available for the remaining possible binary system (NaNO₃-H₂O), only two parameters would have remained undetermined. The ten parameters, including the three that were determined from the ternary data, are given in Table (5). The first three parameters in the table are those determined from the ternary data.

TABLE V OPTIMUM N_{ij} FOR SYSTEM NaCl-HNO₃-H₂O

i	2	1	1	1	2	1	2	3	3	4
j	4	3	4	5	3	2	5	4	5	5
N _{ij} × 10 ³	.8962	1.9361	6.3798	.4139	.7732	3.8128	.2560	.6982	.0538	.3361

(1) = Na⁺ (2) = Cl⁻ (3) = H⁺ (4) = NO₃ (5) = H₂O

FIG. (2) DIFFUSION COEFFICIENTS FOR BINARY SYSTEMS AT 25° C

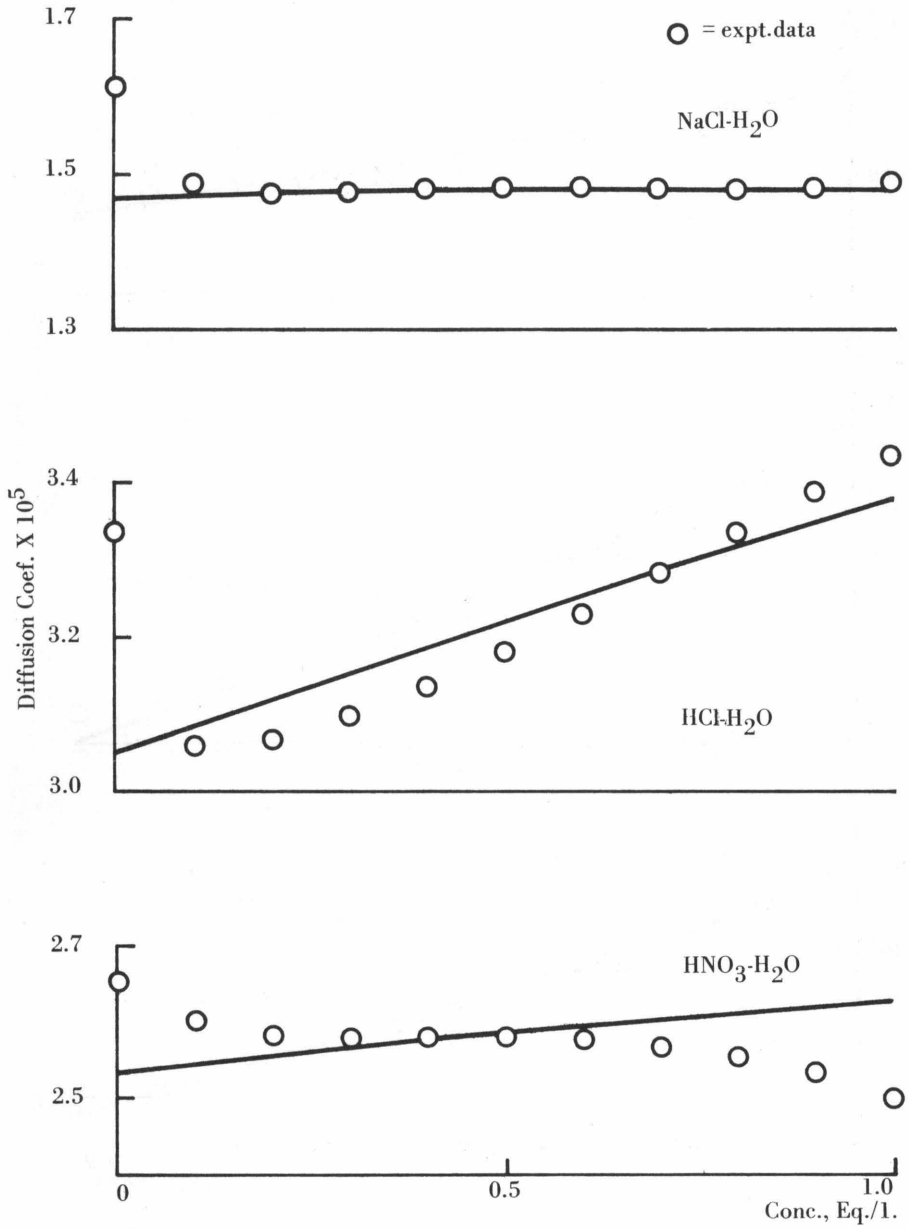


FIG. (3) EQUIVALENT CONDUCTIVITY FOR BINARY SYSTEMS AT 25° C

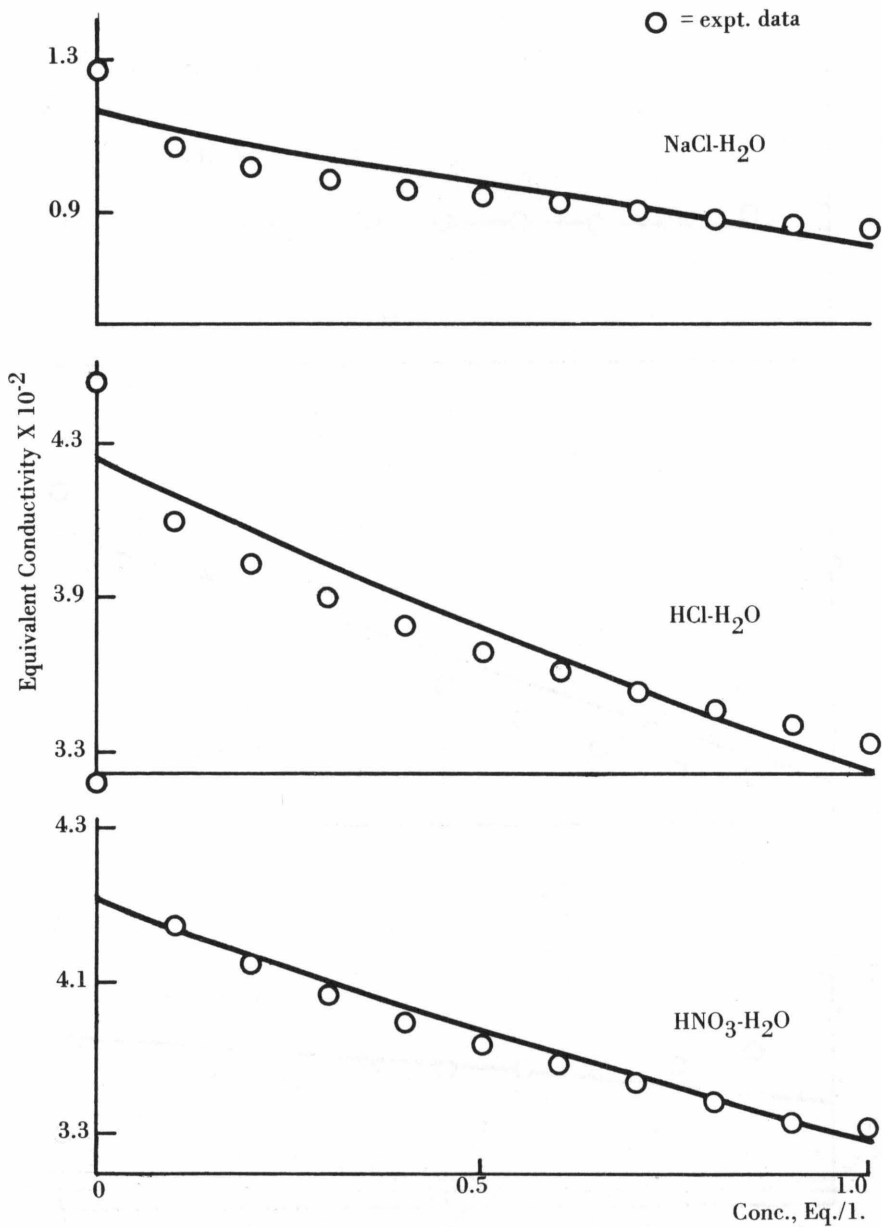


FIG. (4) CATION TRANSPORT NUMBERS FOR BINARY SYSTEMS AT 25° C

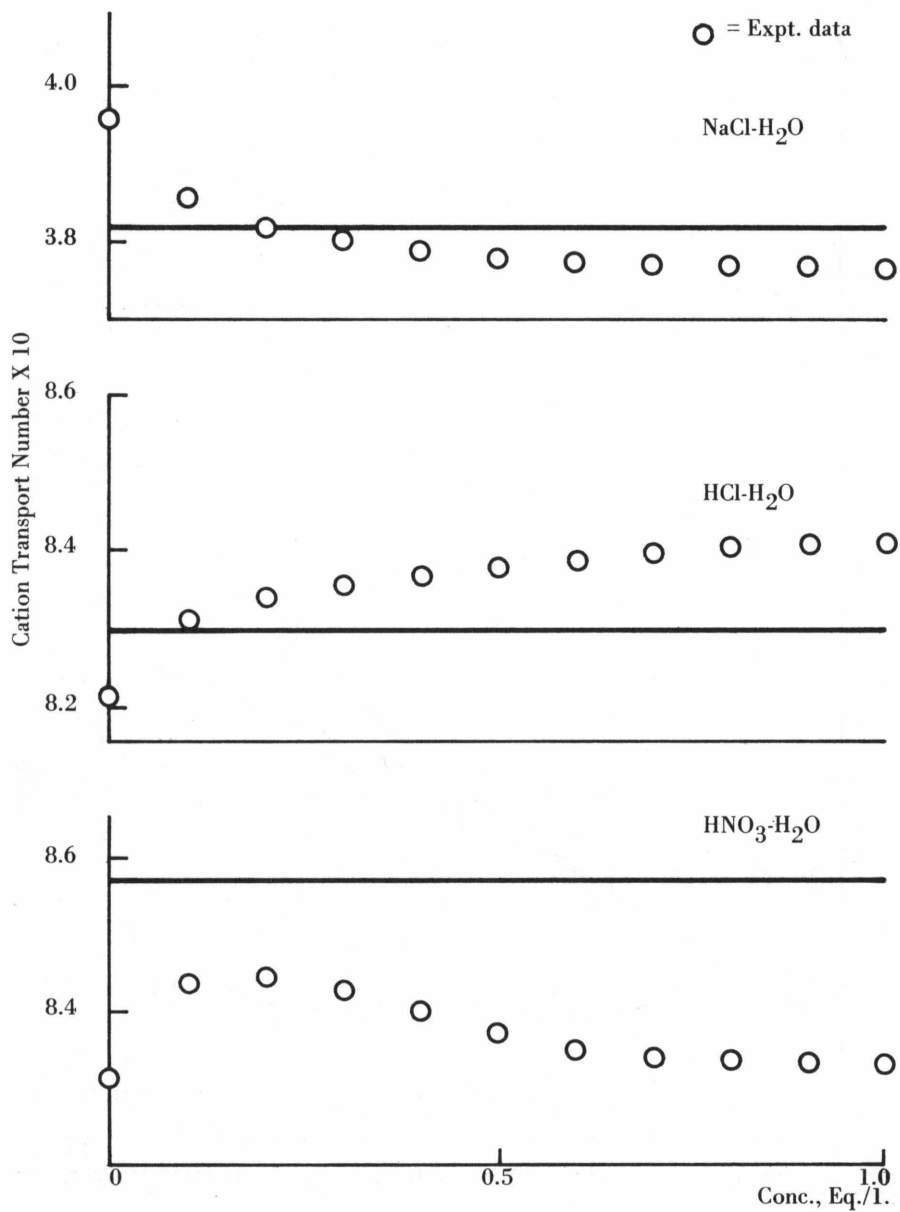


FIG. (5) SUM OF SQUARES OF ERRORS VS. WATER OF HYDRATION

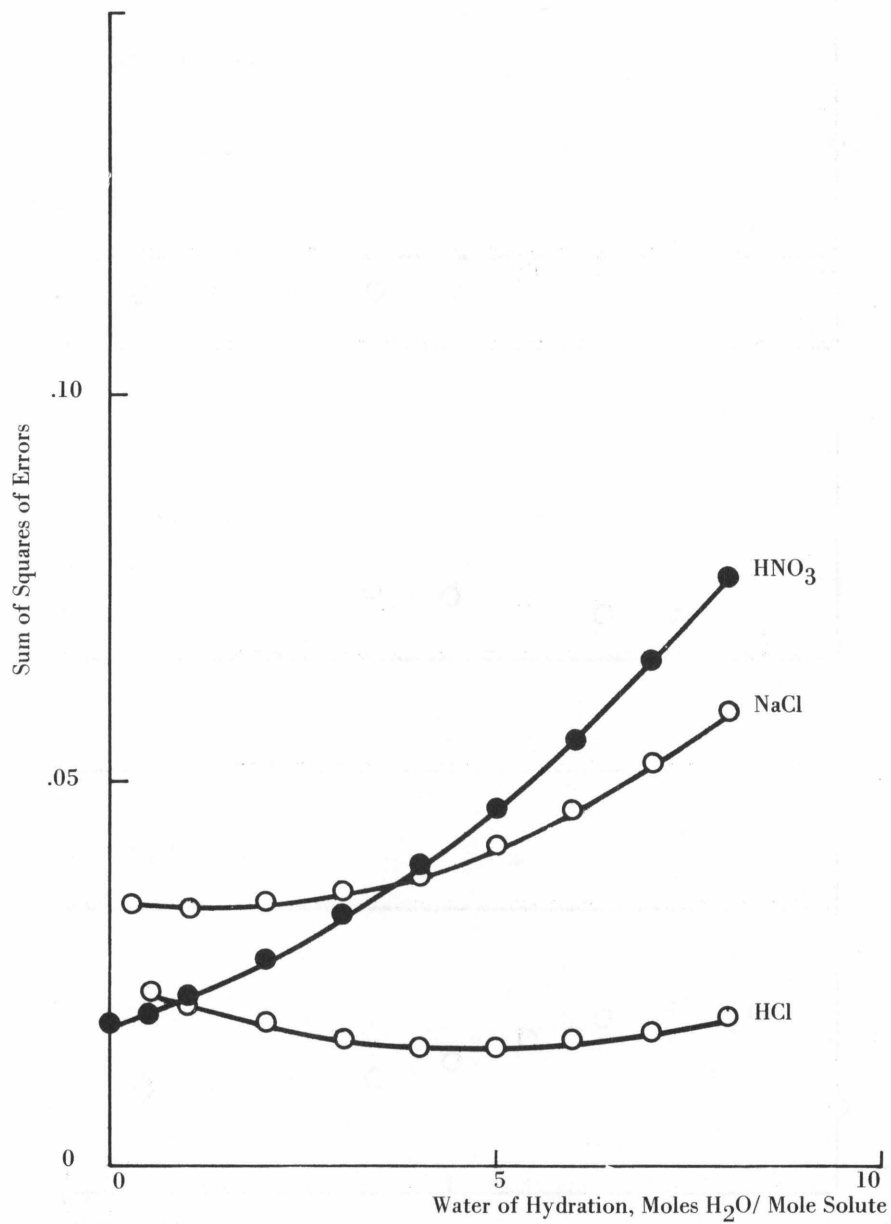


TABLE II
Optimum Parameters and Calculated Data for NaCl-H₂O System for Various Waters of Hydration

Conc. eq./l.	1 mole H ₂ O/mole solute			3.5 moles H ₂ O/mole solute			8.0 moles H ₂ O/mole solute			Experimental data		
	Dx10 ⁵	k/C	t ⁺	D	k/C	t ⁺	D	k/C	t ⁺	D	k/C	t ⁺
0	1.464	116.5	.3819	1.438	114.6	.3811	1.389	110.9	.3796	1.612	126.5	.3962
.1	1.468	112.1	.3819	1.449	110.6	.3811	1.412	107.7	.3796	1.484	106.7	.3853
.2	1.472	108.0	.3819	1.460	106.8	.3811	1.434	104.5	.3796	1.478	101.7	.3821
.3	1.675	104.0	.3819	1.469	103.2	.3811	1.455	101.5	.3796	1.476	98.8	.3810
.4	1.476	100.3	.3819	1.477	99.7	.3811	1.475	98.5	.3796	1.475	96.1	.3800
.5	1.477	96.7	.3819	1.484	96.3	.3811	1.495	95.6	.3796	1.474	93.6	.3778
.6	1.477	93.3	.3819	1.491	93.1	.3811	1.514	92.7	.3796	1.475	91.8	.3775
.7	1.477	90.1	.3819	1.497	90.1	.3811	1.534	90.0	.3796	1.476	90.0	.3773
.8	1.475	87.0	.3819	1.502	87.1	.3811	1.552	87.3	.3796	1.477	88.3	.3770
.9	1.474	84.1	.3819	1.507	84.3	.3811	1.570	884.6	.3796	1.480	86.9	.3765
1.0	1.472	81.3	.3819	1.511	81.6	.3811	1.588	82.0	.3796	1.483	85.8	.3762
Optimum Parameters												
N ₁₂	= 3.644 x 10 ⁻³			= 3.813 x 10 ⁻³				= 4.112 x 10 ⁻³				
N ₁₃	= 0.4062 x 10 ⁻³			= 0.4139 x 10 ⁻³				= 0.4294 x 10 ⁻³				
N ₂₃	= 0.2509 x 10 ⁻³			= 0.2549 x 10 ⁻³				= 0.2628 x 10 ⁻³				
Sum Sq. Errors	= 0.03363			= 0.03658				= 0.05931				

(1) = Na⁺ (2) = Cl⁻ (3) = H₂O D = cm²/sec. k/C = cm²/ohm-eq.

TABLE III
Optimum Parameters and Calculated Data for HNO₃-H₂O System for Various Waters of Hydration

Conc. eq./l.	0.2 moles H ₂ O/mole solute		0.5 moles H ₂ O/mole solute		3.5 moles H ₂ O/mole solute		experimental data		
	Dx10 ⁵	k/C	Dx10 ⁵	t ⁺	Dx10 ⁵	t ⁺	Dx10 ⁵	k/C	t ⁺
0	2.544	390.1	2.538	.8569	2.466	.8577	2.650	421.0	.8303
.1	2.552	383.0	2.547	.8569	2.489	.8577	2.600	384.2	.8440
.2	2.561	376.2	2.557	.8569	2.512	.8577	2.585	374.4	.8450
.3	2.569	369.5	2.566	.8569	2.536	.8577	2.580	366.0	.8430
.4	2.579	363.1	2.575	.8569	2.558	.8577	2.580	359.0	.8410
.5	2.584	356.8	2.584	.8569	2.581	.8577	2.580	356.6	.8380
.6	2.591	350.8	2.593	.8569	2.605	.8577	2.579	347.5	.8350
.7	2.598	344.8	2.601	.8569	2.627	.8577	2.565	347.0	.8340
.8	2.605	339.1	2.610	.8569	2.651	.8577	2.550	338.3	.8336
.9	2.612	333.5	2.618	.8569	2.674	.8577	2.530	335.0	.8333
1.0	2.618	328.0	2.629	.8569	2.697	.8577	2.500	333.2	.8330
<u>Optimum Parameters</u>									
N ₁₂	= 5545 x 10 ⁻³		= .5721 x 10 ⁻³		= .6982 x 10 ⁻³				
N ₁₃	= .05409 x 10 ⁻³		= .05394 x 10 ⁻³		= .05386 x 10 ⁻³				
N ₂₃	= .3240 x 10 ⁻³		= .3250 x 10 ⁻³		= .3361 x 10 ⁻³				
Sum Sq. Errors	= .01856		= .01973		= .03570				

(1) = H⁺ (2) = NO₃ (3) = H₂O D = cm²/sec. k/C = cm²/ohm-eq.

TABLE IV

Optimum Parameters and Calculated Data for HCl-H₂O System for Various Waters of Hydration

Conc. eq./l	1.0 moles H ₂ O/mole solute			3.5 moles H ₂ O/mole solute			5.0 moles H ₂ O/mole solute			Experimental Data		
	Dx10 ⁵	k/C	t ⁺	Dx10 ⁵	k/C	t ⁺	Dx10 ⁵	k/C	t ⁺	Dx10 ⁵	k/C	t ⁺
0	3.156	408.2	.8236	3.091	406.6	.8273	3.051	405.5	.8295	333.6	426.0	.8209
.1	3.168	398.6	.8236	3.117	397.3	.8273	3.085	396.5	.8295	305.0	389.8	.8314
.2	3.179	389.3	.8236	3.142	388.4	.8273	3.118	387.7	.8295	306.4	379.6	.8337
.3	3.188	380.3	.8236	3.165	379.6	.8273	3.150	379.1	.8295	309.3	371.0	.8360
.4	3.198	371.7	.8236	3.189	371.2	.8273	3.183	370.9	.8295	313.0	362.5	.8370
.5	3.208	363.4	.8236	3.213	363.1	.8273	3.216	362.9	.8295	318.4	359.2	.8380
.6	3.216	355.3	.8236	3.237	355.2	.8273	3.248	355.1	.8295	322.5	350.0	.8390
.7	3.224	347.6	.8236	3.259	347.5	.8273	3.280	347.5	.8295	328.6	348.5	.8400
.8	3.232	340.1	.8236	3.282	340.1	.8273	3.312	340.1	.8295	330.0	341.0	.8403
.9	3.240	332.9	.8236	3.305	332.9	.8273	3.345	332.9	.8295	338.3	337.0	.8406
1.0	3.247	325.9	.8236	3.327	325.9	.8273	3.377	325.9	.8295	343.6	332.8	.8410
<u>Optimum Parameters</u>												
N ₁₂	= .6812 x 10 ⁻³			= .7732 x 10 ⁻³				= .8281 x 10 ⁻³				
N ₁₃	= .05376 x 10 ⁻³			= .05373 x 10 ⁻³				= .05374 x 10 ⁻³				
N ₂₃	= .2510 x 10 ⁻³			= .2574 x 10 ⁻³				= .2615 x 10 ⁻³				
Sum Sq. Errors	= .02098			= .01591				= .01513				
(1) = H ⁺	(2) = Cl ⁻	(3) = H ₂ O		D = cm ² /sec.		k/C = cm ² /ohm-ec.						

Discussion of Results

For the system HCl-H₂O and NaCl-H₂O, the plots of the sum of squares of errors versus water of hydration show a definite minimum at a reasonable value of this parameter: about 5 moles H₂O/mole HCl and about 1 mole H₂O/mole NaCl. For the HNO₃-H₂O system, no minimum was found. A value of zero for this parameter gave the best fit of the data, negative values of this parameter being considered inadmissible on physical grounds. Another anomaly in the HNO₃-H₂O data is that (see Figure (4)) the theoretical fit of the transport data for this system appears inconsistent with the other results. It is quite possible that this data is in error and this may account for an unrealistic value indicated for the water of hydration in this system. It also appears that the NaCl-H₂O result is low, but almost equally good results were obtained at a more realistic value of this parameter (see Table (2)).

As can be seen from Tables (2), (3), and (4), the effective water of hydration has only a small effect on the fit between the experimental and predicted data so long as a value not too far removed from the optimum is chosen. Furthermore, when the same parameter (N_{ij}) is compared for two binary systems (say the N_{ij} coefficient for the Cl⁻ and H₂O interaction), the value should be the same for the model. This was approximately true for the N_{ij} when the optimum waters of hydration were used, but an even closer agreement was achieved when the same value of the water of hydration was used for all of the systems.

Finally, there is the main point of how well the derived model fits the experimental data. It is quite easy to calculate an average percentage deviation from the sum of squares of the errors reported in Tables (2), (3), and (4). The figure shows the sum of squares of the percentage error for 33 points. The square root of this quantity divided by 33 is then approximately the average deviation between theory and experiment. Thus, for the system NaCl-H₂O at a water of hydration of 3.5, the sum of the squares of the errors is 0.03658. The square root of this quantity divided by 33

gives an average fractional deviation of about .033 or 3.3 percent. For the system HCl-H₂O at water of hydration of 5.0, a corresponding calculation gives an average deviation of about 2.1 percent. Thus, it can be seen that, typically, the model fits the data with an average deviation of 2 to 3 percent, and that all three types of data are about equally represented.

The largest deviations are in the concentration range .0-0.1 eq./l., a region in which the experimental transport coefficients undergo an anomalously large change also. This implies that the N_{ij} 's, assumed constant in the model, are moderately concentration dependent in the region of low concentrations, and that perhaps the data should be divided into a low concentration group (i.e. 0 to 0.1 eq./l) and into a moderate to high concentration group (i.e. 0.1 to 1.0 eq./l.). This would undoubtedly lead to a very close agreement between theory and experiment, but would have the disadvantage of producing two sets of N_{ij} rather than one. In any event, the comparison between theory and experiment for binary systems is well within the accuracy needed for engineering work, and the model can be used with confidence in this context.

The comparison of the theory with the ternary data is less satisfactory. At very low NaCl but at high HNO₃ concentrations, the deviations are as large as 25 percent. At moderate or low HNO₃ concentrations, the agreement is fairly good throughout the range of NaCl concentrations and high NaCl and high HNO₃ concentrations, the agreement is satisfactory. It is thought that some of the data is perhaps in error, and it is planned to recheck these experimental results before proceeding with further analysis.

Summary and Conclusions

A general model for multicomponent mass transport was developed. A numerical procedure was developed for determining the optimum parameters for mass transport models, and this was used to establish the optimum parameters for several systems for the particular model derived here. The mass transport model developed was shown to reproduce experimental transport data of several types over an extended range of concentrations with an average accuracy of about 2 - 3 percent.

Water of hydration was shown to be an important parameter in the determination of the average deviation between experimental and predicted data. In two cases studied (NaCl, HCl), an optimum water of hydration was found, corresponding to a physically reasonable value for this parameter. In a third case (HNO₃) the optimum parameter was found to be zero, but there appear to be other anomalies in this same data.

Experimental electrical conductivities were measured in the system NaCl-HNO₃-H₂O, and optimum model parameters were extracted from this data. The comparison between experimental and theoretical results was less satisfactory for this ternary system than for the binary system in certain ranges of concentration and this was thought due to experimental errors.

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