Prediction of Electrolyte Solution Properties Using a Combined Debye-Hückel, Association, and Solvation Model

by

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Thesis submitted to the Faculty of
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements of the degree of
MASTER OF SCIENCE
In
Geology

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May, 1989
Blacksurg, Virginia

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(ABSTRACT)

This paper presents a semi-theoretical computer model that estimates individual and mean ionic activity coefficients in the NaCl-NaOH-HCl-H_2O system at 25°C. This extrathermodynamic model incorporates long-range electrostatic ion-ion interaction (Debye-Hückel effects), short-range ion-ion interactions (ion association), and short-range ion-solvent interactions (hydration). The activity of water in NaCl, NaOH, and HCl solutions is fit with maximum deviations from experimental values of 0.78%, 0.79%, and 2.09%, respectively. Ion size parameters, å, were modified slightly from literature values. Hydration numbers for individual species were chosen on the basis of best fit. Ion pair dissociation constants of 15.0 were chosen for reactions involving NaCl(aq), NaOH(aq), and HCl(aq) ion pairs. The model predicts individual ionic activity coefficients for ions and ion pairs, and predicts mean molal ionic activity coefficients for NaCl, NaOH, and HCl for solutions up to 6.0 m with maximum deviations from experimental values of 0.73%, 1.77%, and 3.86%, respectively. The estimated degree of dissociation varies widely if the ion pair dissociation constants are varied between 5 and 1000. Calculated values for trace activity coefficients, saturation solubility, and vapor pressure compare favorably to experimental data.

ACKNOWLEDGEMENTS

I express my sincere gratitude to my major advisor, Don Rimstidt, for his cheerful, steadfast support throughout my tenure at Virginia Tech. Thanks also to committee members Robert Bodnar and Norman Gilinsky for their input and review of this manuscript. and proved to be attentive and helpful listeners. My parents, have been very supportive; I thank them for their acceptance of my choice to return to school. My wife, ., has helped me keep body and soul together for this long haul.

This material is based upon work supported under a National Science Foundation Graduate Fellowship.

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LIST OF SYMBOLS

ROMAN

a_w	activity of water
$å$	distance of closest approach for a salt
$å_i$	ion size parameter for the i^{th} solution species
h	hydration number of a salt
h_i	hydration number of i^{th} species (includes ion pairs)
$i....n$	subscripts representing all species in solution (includes ion pairs)
m_i	concentration of i^{th} species in mol/kg (includes ion pairs)
m^o	hypothetical one molal standard state
$m_{w,bound}$	moles of water molecules bound in hydration spheres per kg of water
z_i	charge on i^{th} species
z_M	charge on cation
z_X	charge on anion
A	Debye-Hückel parameter = 0.5092 at 25°C
B	Debye-Hückel parameter = 0.3283 at 25°C
I	conventional ionic strength (equation A.6)
I_t	"true" ionic strength (equation 12)
$K_d(MX)$	equilibrium dissociation constant for the reaction $MX^0 = M^+ + X^-$
K_H	Henry's Law constant (for HCl; $K_H = P_{HCl}/a_{HCl}{}^0$)
M^+	generic cation (aqueous)
MX^0	generic neutral ion pair (aqueous)
$MX(v)$	generic vapor phase species MX
P_{HCl}	partial pressure of HCl over HCl solution
R	ratio of old T_i estimate to $T_{i,init}$ used in continued fraction algorithm (equation 13)
T_i	successive approximation to $T_{i,init}$
$T_{i,init}$	total amount of i^{th} species in solution in all forms; analytical concentration of i^{th} species
W_A	molecular weight of solvent

W_w	molecular weight of water
X^-	generic anion (aqueous)
X_w	mole fraction of water

GREEK

$\gamma_\pm$	stoichiometric mean molal activity coefficient
γ^o	unit activity coefficient for hypothetical ideal solution
$\gamma_{i,\,a}$	individual molal activity coefficient accounting only for association effects
$\gamma_{\pm a}$	mean molal activity coefficient accounting only for association effects
$\gamma_{i,\,DH}$	individual molal activity coefficient accounting only for Debye-Hückel effects
$\gamma_{\pm DH}$	mean molal activity coefficient accounting only for Debye-Hückel effects
$\gamma_{i,\,hyd}$	individual molal activity coefficient accounting only for ion hydration effects
$\gamma_{\pm hyd}$	mean molal activity coefficient accounting only for ion hydration effects
$\gamma_{i,\,st}$	individual molal activity coefficient accounting for association, Debye-Hückel, and ion hydration effects
$\gamma_{i,\,DH\text{-}hyd}$	individual molal activity coefficient accounting only for Debye-Hückel and ion hydration effects
$\gamma_{\pm HCl}$(trace)	stoichiometric mean molal activity coefficient for 0.01 m HCl in NaCl solutions
ϕ	osmotic coefficient
ν	stoichiometric number of ions per mole of solute
ν_M	stoichiometric number of cations per mole of solute
ν_X	stoichiometric number of anions per mole of solute

INTRODUCTION

Many problems in geochemistry require an accurate model of the properties of electrolyte solutions. These problems range from understanding the means of transport of ore minerals or the diagenesis of sediments, to predicting phase behavior in seawater, to predicting the fate of environmental contaminants, to understanding phase behavior in fluid inclusions. To be useful to geochemists, a model of electrolyte solutions must be able to predict, among other properties, the activities of individual ions (needed for kinetic and adsorption studies) and the solubilities of minerals (sparingly soluble to very soluble ones), as well as thermodynamic properties such as heat capacities, vapor pressures, and molar volumes of the solutions. The model should be applicable to mixed electrolyte solutions of complex composition and still be able to predict the activities of trace components. Finally, the model must be valid for temperatures ranging from below 0°C at one bar pressure to the high temperatures and pressures found in metamorphic and magmatic regimes. Ideally such a model should be based on a physically reasonable concept of the nature of electrolyte solutions and should be able to *predict* the behavior of systems for which there are little or no data, as well as to *fit* existing data from well-studied systems. Because electrolyte solutions show such complex behaviors, it is unlikely that a model that meets all of these criteria will be developed soon; however, there are already numerous models that fit some of the criteria, and some of these models are discussed briefly below. This paper presents another approach to developing a model of electrolyte solutions that extends some of the existing models to offer the additional flexibility and predictive capabilities needed by geochemists.

Though many models have been developed, a comprehensive, well-accepted electrolyte solution theory is not yet available for use in the applications mentioned above.

This problem has been approached from thermodynamics, from statistical mechanics, and from experiment. Even with all this attention to experiment and theory, an idea as seemingly simple as the existence of ion pairs in solution is still quite a divisive subject. For example, reported values for ion pair dissociation constants differ by up to seven orders of magnitude for HCl. A brief review of electrolyte models that address one aspect of solution chemistry, namely the prediction of activity coefficients, is presented below.

Previous work

Relationships among ionic activity, activity coefficients, and the activity of water are discussed in Appendix A. The typical variation of activity coefficients with solute concentration is also described in Appendix A.

Most electrolyte solution models utilize some combination of three solution effects to predict activity coefficients: long-range electrostatic interaction (Debye-Hückel effect), ion solvation (here referred to as hydration because this paper deals with water as the solvent), and short-range ion-ion interaction (ion association). Some of the models proposed by previous workers are grouped below according to which of these three effects are used for the model's theoretical basis.

The theoretical Debye-Hückel (DH) limiting law and semi-theoretical extended DH equation (see Appendix A) account for like-ion, long-range effects (Debye and Hückel, 1923; see Bockris and Reddy, 1970 for a clear derivation). Though predictions of mean activity coefficients using the extended version of the DH equation compare very favorably with experiment in very dilute solutions, it is widely recognized that the extended DH equation fails at very low ionic strengths of approximately 0.1 mol/kg (Robinson and Stokes, 1959; Nordstrom and Munoz, 1985). This failure is due to the fact that the DH equation neglects, among other effects, ion association and hydration which significantly influence the activity of aqueous species. A great many electrolyte models that were developed subsequently use the DH equations or similar terms to describe long-range electrostatic interactions; that is, to adjust the DH equation so that it will accurately predict activity coefficients at higher ionic strengths.

Several models use a DH term combined with additional terms to fit deviations from experimental values and values predicted by long-range electrostatic interaction without attributing these deviations to a specific effect such as ion hydration or ion association. Davies (1962) predicts mean activity coefficients by adding a constant to a modified extended DH equation. The National Bureau of Standards model (Lietzke and Stoughton, 1962; Hamer and Wu, 1972; Staples and Nuttall, 1977) employs a power series expansion and an extended DH term to model mean activity coefficients. Helgeson (1969) has fit individual activity coefficients for minor ions in sodium chloride-dominated systems. His method uses a DH term and a "B-dot" term which fits deviations between the DH term and experiment.

The Pitzer approach (Pitzer, 1973; Harvie and Weare, 1980; Pabalan and Pitzer, 1987) uses an extended DH term common to all ions combined with a virial expansion fitting procedure to fit mean activity coefficients or osmotic coefficients and employs a convention to predict internally consistent individual ionic activity coefficients. This model fits the behavior of several electrolytes over a wide range of temperatures and pressures very well, and it shows some promise of being extrapolated to systems more complex than those in which its parameters were determined (Harvie and Weare, 1980). To treat species that are unquestionably strongly associated, the Pitzer approach either employs a second virial coefficient, β_2, or calls upon ion pairs as solution species (Weare, 1987). The rationale for using β_2 or associated species is practical rather than theoretical: the choice is made by picking the method that best fits the experimental data. For example, Harvie and others (1984) give a dissociation constant, K_d, of 0.05 as the critical value below which associated species should be used to model 1-2 electrolytes because below K_d of 0.05, fits using only virial coefficients without associated species are less accurate.

Several models invoke DH effects and ion hydration, without considering ion association, to predict the behavior of strong electrolytes in solution. The role of ion hydration in electrolyte solutions is reviewed in Conway (1981). Stokes and Robinson (1948) add two terms to the DH equation to account for hydration effects. They fit mean activity coefficients for several binary systems from 0.1 to 2.0 m in many cases, and to 4.0 to 5.0 m for some salts. Two modifications of Stokes and Robinson's 1948 work extend this model to higher concentrations (Stokes and Robinson, 1973; Nesbitt, 1982). Bates and others (1970) use the Robinson and Stokes model to predict individual ionic activity coefficients. Jansz (1983) reports individual activity coefficients for H^+ and Cl^- with $\gamma_{H^+} \neq \gamma_{Cl^-}$ using a model with an electrostatic term and hydration terms which vary with concentration. Jacobsen and Skou (1977) model the trace activity coefficient of $ZnCl_2$ in $NaClO_4$ using DH and hydration effects. Bates (1986) predicts individual ionic activity coefficients using a DH term and hydration terms.

Many computer models, developed mostly by geochemists, invoke DH effects coupled with ion association, but no hydration, to model chemical equilibria based on predictions of individual ionic activity coefficients. The phenomenon of ion association is reviewed by Davies (1962). The basis for many of the association models is the work of Garrels and Thompson (1962) who calculated the distribution of species in seawater using equilibrium constants and an iterative mass balance approach. A selection of these models includes GEOCHEM (Mattigod and Sposito, 1979), SOLMNEQ (Kharaka and Barnes, 1973), WATEQ (Truesdell and Jones, 1974), EQUIL (I and Nancollas, 1972), PHREEQE (Parkhurst and others, 1982), EQ3NR (Wolery, 1983). Nordstrom and others (1979) and

Potter (1979) provide reviews of many of the earlier ion association models. Comparison of the predicted saturation index of minerals shows a lack of agreement between models (Nordstrom and others, 1979). Harvie and Weare (1980) found that SOLMNEQ and WATEQF predict solubilities of gypsum with a 19% and 25% error, respectively, at 1.0 m NaCl in the system $NaCl\text{-}CaSO_4\text{-}H_2O$. Harvie and Weare (1980) also found approximately 100% errors for gypsum solubility in the system $Na_2SO_4\text{-}CaSO_4\text{-}H_2O$ at 0.5 and 1.0 m NaCl predicted by SOLMNEQ and WATEQF. Often these models, which can work well for dilute solutions, are used inappropriately at moderate or high concentrations.

Crerar (1973) and Wood and others (1984) present an iterative model that incorporates DH, association, and hydration effects to predict individual and mean ionic activity coefficients. This model uses the MacInnes convention (MacInnes, 1919) that $\gamma_{K^+} = \gamma_{Cl^-} = \gamma_{\pm KCl}$ as a basis to assign values for individual activity coefficients. It also employs hydration numbers for mean salts rather than ions. Crerar's model reproduces the general shape of experimental curves in plots of mean activity coefficient, $\gamma_\pm$, vs. concentration, but $\gamma_\pm$ values are too low at lower concentrations and too high at high concentrations (see Fig. 5, 6, and 7 in Wood and others, 1984).

Brief description of proposed model

The model presented employs many of the concepts from the above methods, especially Stokes and Robinson (1948) and Crerar (1973), but they are combined in a unique fashion. An iterative rather than an analytical approach is used, and it assumed that the activity of solution species can be predicted by accounting for three primary solution effects: DH interactions, ion association, and ion hydration. The DH interactions and ion hydration are accounted for using a variation of the two-parameter equation of Stokes and

Robinson (1948). Ionic strength and species molality used in this equation are adjusted by successive approximations using mass balance and mass action equations as constraints. Ion size parameters and hydration numbers used in water activity and activity coefficient calculations refer to individual solution species rather than salts. The activity of water, which is required to calculate the contribution of hydration to the activity coefficient, is predicted rather than taken from experimental data. Individual ionic activity coefficients are not constrained to be equal. This version of the model predicts 1) the activity of water, 2) speciation in solution, 3) individual ionic activity coefficients, 4) mean ionic activity coefficients, and 5) trace activity coefficients.

Though the three solution effects considered here are clearly not the only types of interactions in aqueous solutions, this model is purposefully simple. Effects due to triple ion formation or other interactions are accounted for in this treatment by adjusting parameters in the DH, ion association, and ion hydration equations.

The main objective of the initial phase of research is to test this model at 25°C against empirical activity coefficient data for the binary systems NaCl-H_2O, HCl-H_2O, NaOH-H_2O and against trace activity coefficients in the system NaCl-HCl-H_2O. Possible expansion of the model to include other components, to predict phase behavior, and to incorporate temperature is discussed later.

THEORETICAL BASIS AND IMPLEMENTATION

Accounting for electrostatic and hydration effects

In the model presented here, DH and hydration effects are accounted for using a modification of Stokes and Robinson's (1948) equation which includes the extended Debye-Hückel equation and two hydration terms

$$\log \gamma\pm = \frac{-A\,|z_M z_X|\sqrt{I}}{1 + å B \sqrt{I}} - \frac{h}{v}\log a_A - \log[1 - 0.001\, W_A\, m\, (h - v)] \qquad (1)$$

where $\gamma\pm$ is the mean activity coefficient for the salt, A and B are temperature-dependent Debye-Hückel parameters, z_M and z_X are the charges on the cations and anions, respectively, I is the stoichiometric ionic strength (see Appendix A), å is the distance of closest approach (or ion size parameter) for the salt of interest, h is the hydration number for the salt, v is the number of moles of ions combined with h moles of solvent ($v = v_M + v_X = 2$ for 1-1 electrolytes), a_A is the activity of the solvent, W_A is the molecular mass of the solvent, m is the molal concentration of a salt. This equation was modified to model the activity coefficient for an individual ionic species

$$\log \gamma_i = \frac{-A\,|z_i^2|\sqrt{I_t}}{1 + å B \sqrt{I_t}} - \frac{h_i}{v_i}\log a_w - \log[1 - 0.018\, m_i\, (h_i - v_i)] \qquad (2)$$

where γ_i is the activity coefficient for the i^{th} ion or ion pair, z_i is the charge on the i^{th} ion or ion pair, I_t is the "true" ionic strength defined below, $å_i$ is the ion size parameter, h_i is the hydration number for the i^{th} ion or ion pair, v_i is the stoichiometric coefficient for the i^{th} ion or ion pair, a_w is the activity of water, $0.001W_A$ is equal to 0.018 for water, and m_i is the molal concentration of the i^{th} ion or ion pair. The DH term in this equation is zero for neutral ion pairs, but the two hydration terms are not zero for neutral ion pairs when solute concentration is greater than zero. The two hydration terms have the effect of raising the activity coefficient except when h_i is less than ν_i. See Appendix A for the relationship between individual and mean activity coefficients.

Estimating the activity of water

In the original formulation of their combined DH-hydration model, Stokes and Robinson (1948) used experimentally determined values of a_A in equation (1). In the model developed here, the activity of water, a_w, used in equation (2) is derived as follows. There are 55.51 moles of water per kilogram, and the number of moles of all solute species in solution with these 55.51 moles of water is $\sum_i^n m_i$ so the mole fraction of water, X_w, is

$$X_w = \frac{55.51}{55.51 + \sum_i^n m_i} \tag{3}$$

If aqueous solutions were ideal mixtures, the activity of water, a_w, would equal X_w. In NaCl-H_2O mixtures, the activity of water deviates from that predicted by ideal mixing as shown in figure (1). The deviation from ideal behavior seen in figure (1) is probably related to the fact that some of the water molecules in the solutions are closely associated with solute species as part of their hydration spheres. The present model adjusts for this non-ideal behavior by including a term that accounts for the number of moles of water bound in the hydration spheres of all of the solute species, both free ions and ion pairs

$$m_{w,\,bound} = \sum_i^n h_i m_i$$

The activity of water is estimated as the mole fraction of water not involved in hydration

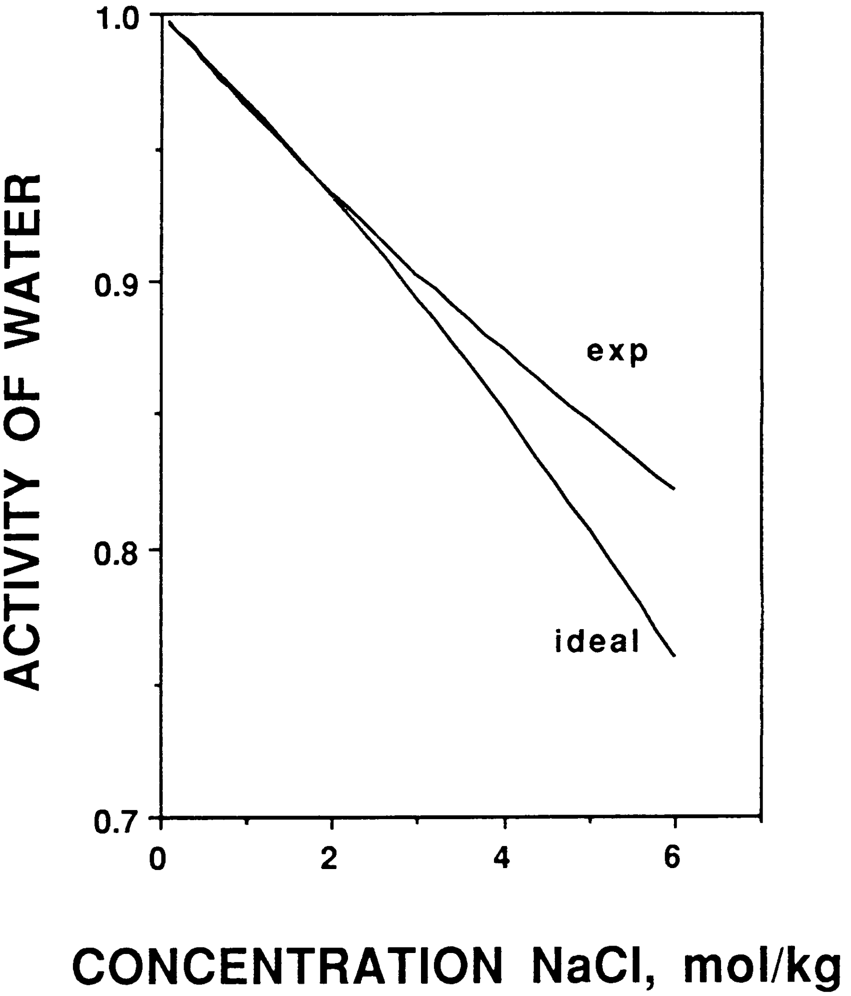

Figure 1. Activity of water *versus* concentration of NaCl. The curve marked **ideal** is calculated from equation (3). The curve marked **exp** is smoothed experimental data reported in Robinson and Stokes (1959).

$$a_w = \frac{55.51 - \sum_i^n h_i m_i}{55.51 - \sum_i^n h_i m_i + \sum_i^n m_i} \tag{4}$$

which is equivalent to

$$a_w = 1 - \frac{\sum_i^n m_i}{55.51 - \sum_i^n h_i m_i + \sum_i^n m_i} \tag{5}$$

This approach for estimating the activity of water is similar to that of Jacobsen and Skou (1977) and Jansz (1983).

Accounting for Ion Association

Debye-Hückel theory assumes that when a solute dissolves in a solvent, the ions are completely dissociated into cations and anions with no association (ion pairing or complexing); i.e., the reaction

$$MX^0 = M^+ + X^- \tag{6}$$

proceeds completely to the right. This assumption has been employed in many treatments of electrolyte solutions (Stokes and Robinson, 1948), even though there are cases where ion association is clearly significant (Pitzer, 1987). The present model assumes that experimentally derived dissociation constants, K_d, for reactions involving ion pairs accurately indicate the extent of association/dissociation of ions in electrolyte solutions. In this model, ion association is accounted for by using dissociation constant and mass balance constraints. For the reaction in equation (6), the dissociation constant is

$$K_d(MX) = \frac{\gamma_{M^+} m_{M^+} \gamma_{X^-} m_{X^-}}{\gamma_{MX^0} m_{MX^0}} \tag{7}$$

where γ_{M^+}, γ_{X^-}, and γ_{MX^0} are molal activity coefficients for the unassociated cation, unassociated anion, and associated ion pair, respectively. Values for the activity coefficients for both the individual ions and the ion pairs in equation (7) come from equation (2). Equation (7) can be be rearranged to give

$$m_{MX^0} = \frac{\gamma_{M^+} m_{M^+} \gamma_{X^-} m_{X^-}}{\gamma_{MX^0} K_d(MX)} \tag{8}$$

which is the estimated concentration of the ion pair, m_{MX^0}.

In even simple electrolyte solutions such as NaCl dissolved in water, there are several ion association/dissociation equilibrium relationships that must be tallied to account for all ionic interactions. A good way to visualize all of these possible interactions is to prepare a diagram (figure 2) listing all possible species containing a particular cation in a row and all possible species containing a particular anion in a column. The dissociation equilibria involving all of the species in the shaded area of figure 2 are accounted for by determining the concentration of the associated species using equation (8) which describes the equilibrium distribution of ion pairs and "free" ions. "Free" ions are, of course, electrostatically associated with waters of hydration. In addition, the distribution of all aqueous species is constrained by mass balance such that the sum of the species listed in each row and each column of figure 2 must equal the analytical concentration, T_i, of these species

$$T_{Na} = m_{Na^+} + m_{NaCl^0} + m_{NaOH^0} \tag{9a}$$

$$T_H = m_{H^+} + m_{H_2O} + m_{HCl^0} \tag{9b}$$

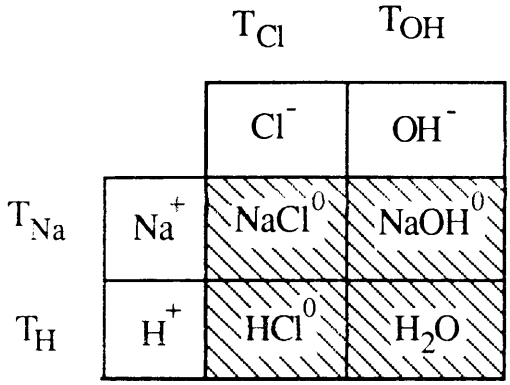

Figure 2. A diagram representing all of the possible species (neglecting triple ions) present in a solution of NaCl in water. The concentrations of the species in the shaded area are calculated using the mass action constraints in equation (17). Mass balance relationships are given in equations (18a-d).

$$T_{Cl} = m_{Cl^-} + m_{NaCl^0} + m_{HCl^0} \tag{9c}$$

$$T_{OH} = m_{OH^-} + m_{NaOH^0} + m_{H_2O} \tag{9d}$$

The mass balance and mass action constraints are combined to give

$$T_{Na} = m_{Na^+} + \frac{\gamma_{Na^+} m_{Na^+} \gamma_{Cl^-} m_{Cl^-}}{\gamma_{NaCl^0} K_d\,(NaCl)} + \frac{\gamma_{Na^+} m_{Na^+} \gamma_{OH^-} m_{OH^-}}{\gamma_{NaOH^0} K_d\,(NaOH)} \tag{10a}$$

$$T_H = m_{H^+} + \frac{\gamma_{H^+} m_{H^+} \gamma_{Cl^-} m_{Cl^-}}{\gamma_{HCl^0} K_d(HCl)} \tag{10b}$$

$$T_{Cl} = m_{Cl^-} + \frac{\gamma_{Na^+} m_{Na^+} \gamma_{Cl^-} m_{Cl^-}}{\gamma_{NaCl^0} K_d(NaCl)} + \frac{\gamma_{H^+} m_{H^+} \gamma_{Cl^-} m_{Cl^-}}{\gamma_{HCl^0} K_d(HCl)} \tag{10c}$$

$$T_{OH} = m_{OH^-} + \frac{\gamma_{Na^+} m_{Na^+} \gamma_{OH^-} m_{OH^-}}{\gamma_{NaOH^0} K_d\,(NaOH)} \tag{10d}$$

Note that m_{H2O} is omitted from equations (10b) and (10d) due to the numerical difficulty of handling the equilibrium constant for the ionization of water. Neglecting the dissociation of water in this model does not affect the calculation of activity coefficients.

Combining the three solution effects

The modified Robinson and Stokes equation (2) accounts for the effect of electrostatic interaction and ion hydration, and the mass balance and mass action constraints (equations 10a-d) account for the effect of ion association on the activity coefficient. One can consider the individual stoichiometric activity coefficients as a composite of three activity coefficients, $\gamma_{i,\,DH}$, $\gamma_{i,\,hyd}$, and $\gamma_{i,\,a}$, where these separate activity coefficients account for DH, hydration, and association interactions, respectively. Equation (2) combines the electrostatic interaction and ion hydration effects into $\gamma_{i,\,DH\text{-}hyd}$, which is equal to the product of $\gamma_{i,\,DH}$ times $\gamma_{i,\,hyd}$. The quantity $\gamma_{i,\,a}$ is numerically equivalent to the degree of dissociation, α_i

$$\gamma_{i,\,a} = \alpha_i = \frac{m_{i,\,\text{free ion}}}{T_{i,\,\text{init}}} \qquad (11)$$

and the relationship between the three activity coefficients is

$$\gamma_{i,\,st} = (\gamma_{i,\,DH})(\gamma_{i,\,hyd})(\gamma_{i,\,a}) \qquad (12)$$

where $\gamma_{i,\,st}$ is the individual stoichiometric activity coefficient which is multiplied times the analytical concentration, T_i, to obtain the activity, a_i, of an ion or ion pair. Similarly, the mean activity coefficient, $\gamma\pm$, is composed of three mean activity coefficients, and figure 3 schematically shows the relationships among $\gamma\pm_{DH}$, $\gamma\pm_{hyd}$, and $\gamma\pm_{a}$, and $\gamma\pm$ for NaCl in water. This separation into components provides an intuitive way of looking at the relative contribution of the three solution interactions to the stoichiometric mean activity coefficient. See Crerar (1973) for a more extensive discussion of the relationships between these activity coefficients.

To solve the above system of non-linear equations, a numerical approach is necessary. The program developed to carry out this computation is entitled SALTY DOG 1.0 : A Solvation, Association, and Debye-Hückel Model for the Prediction of Individual and Mean Ionic Activity Coefficients in Electrolyte Solutions and is written in Pascal using the Turbo™ Pascal Version 1.00A compiler on the Apple MacIntosh™ computer. The computer code is presented in Appendix B. The algorithm for this model is outlined briefly

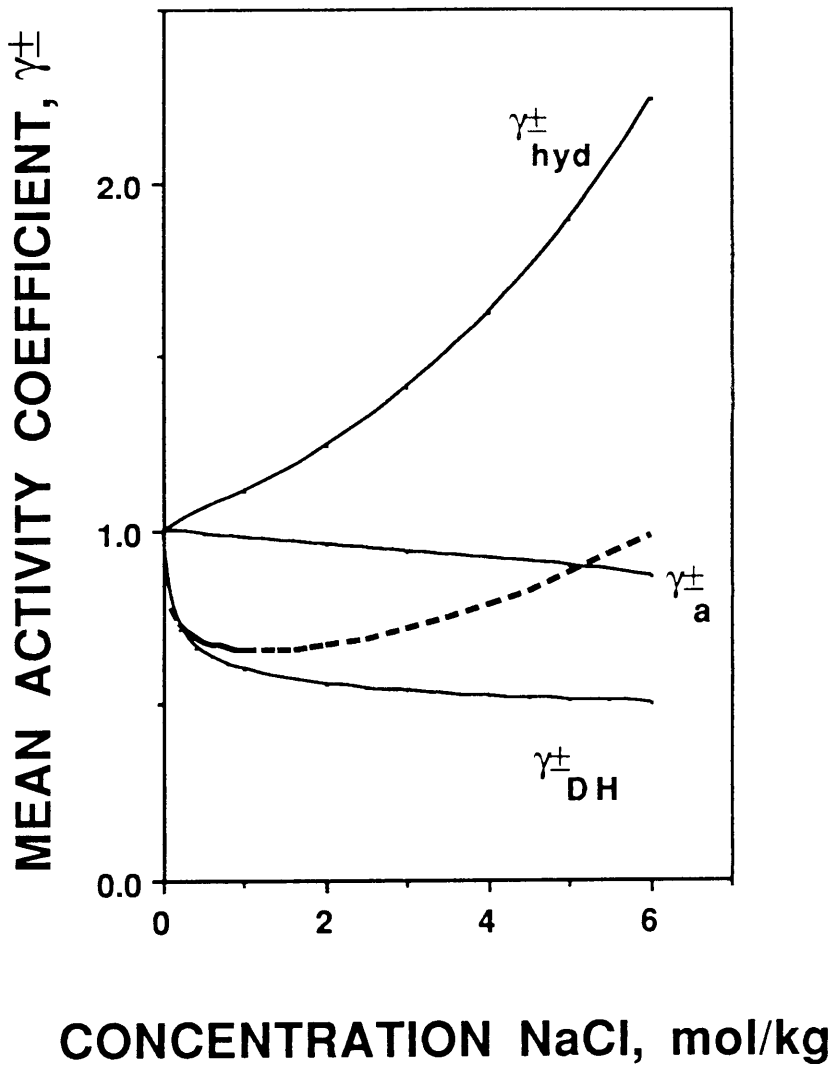

Figure 3. Mean activity coefficient, γ±, *versus* concentration in NaCl solution. Curves labelled **DH**, **a**, and **hyd** show the calculated relative contributions of electrostatic interaction, ion association, and ion hydration, respectively, to the stoichiometric mean activity coefficient (dashed curve).

here, and figure 4 shows a simplified flow chart for SALTY DOG. The calculations are carried in the following steps:

1) The analytical concentrations of the species H, OH, Na, and Cl are read into the subroutine <u>batchinput</u>.
2) The subroutine <u>chargearray</u> assigns charges to each species.
3) The subroutine <u>ionstr</u> calculates the "true" ionic strength of the solution. Helgeson (1969) introduced the concept of "true" ionic strength, I_t ($\bar{I}$ in Helgeson's symbolism); neutral ion pairs do not contribute to true ionic strength according to this definition. The equation for "true" ionic strength is

   $$I_t = \frac{1}{2}\sum_i^n m_i z_i^2 \qquad (13)$$

   where m_i is the molal concentration of the i^{th} species, and z_i is the charge on the i^{th} species. For the first iteration, the concentrations of the ions are assumed to equal the analytical concentrations for H, OH, Na, and Cl. Subsequently, the values for m_i approach the value for the concentration of "free" ions or ion pairs in solution. For example, if NaCl is 95 percent dissociated in a 1.0 m NaCl solution ($T_{Na} = 1.0$), the calculated value for the concentration of "free" Na ions should converge to 0.95 m_{Na} and the value for the concentration of NaCl ion pairs should converge to 0.05 m_{NaCl^0}. The "true" ionic strength of this solution would be 0.95.
4) The activity of water is calculated within the subroutine <u>DHequation</u>; equation (5), with the modifications mentioned in the text, is used for this calculation.

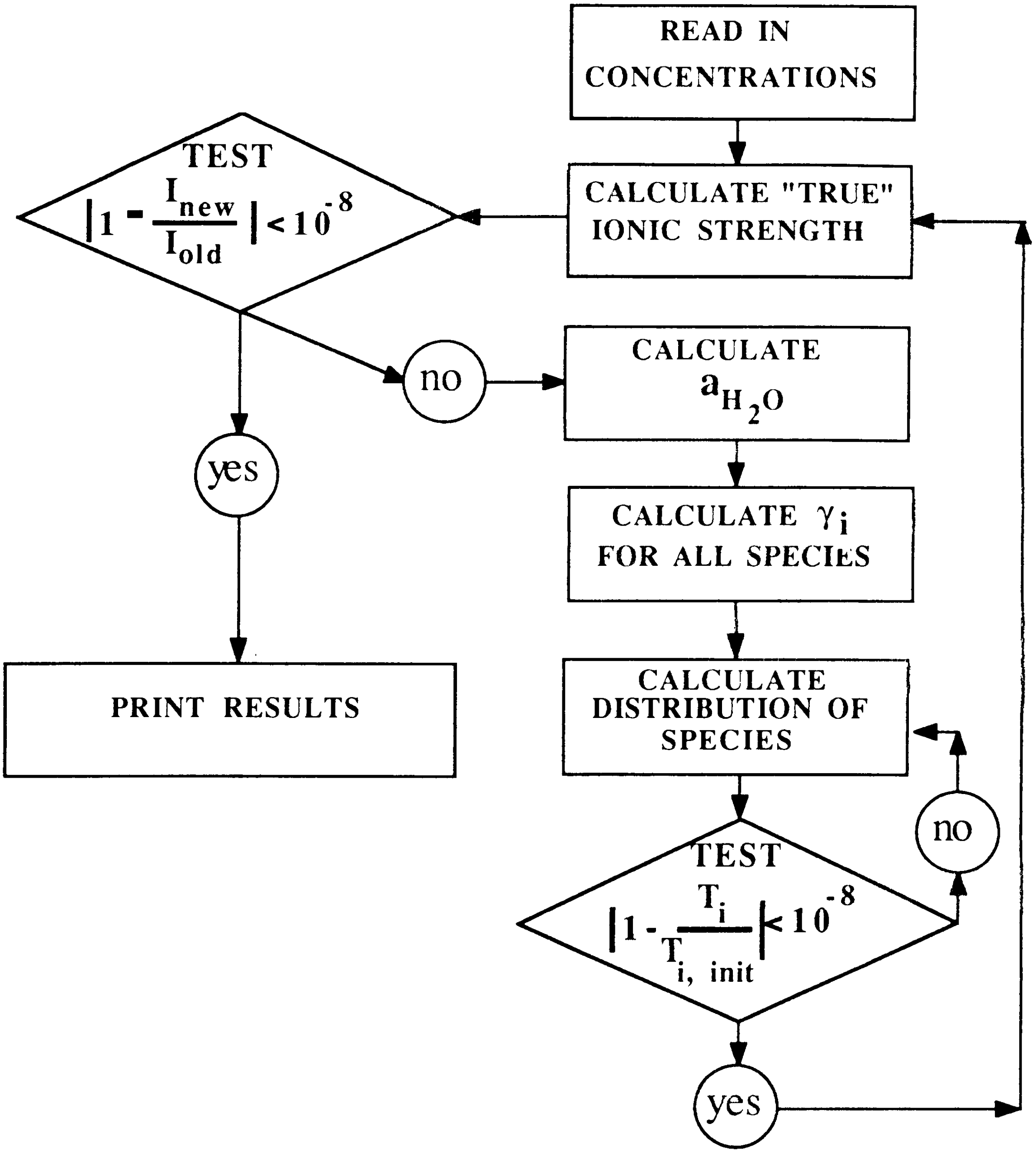

Figure 4. Simplified flow chart for SALTY DOG 1.0.

5) The individual activity coefficient, $\gamma_{i,\,DH\text{-}hyd}$, which accounts for DH and hydration effects but not association effects, is calculated using the modified Robinson and Stokes equation (2) for ions and ion pairs, in the subroutine <u>DHequation</u>.

6) The distribution of species is calculated in the subroutine <u>speciesdistribution</u> using the mass action constraints in equations (10a-d).

7) Mass balance is checked in the subroutine <u>testagainstanalyticalvalues</u>. For example, in a 1.0 m NaCl solution, on the first iteration the value of m_{Na} is 1.0 and the values of $m_{NaCl}{}^0$ and $m_{NaOH}{}^0$ are greater than zero, and because the total analytical concentration of sodium in equation (10a), T_{Na}, is equal to 1.0, these values must be adjusted. This correction is accomplished using the continued fraction method (Wigley, 1977). The ratio, R, of the current approximation for T_i over the initial (analytical) concentration,

$T_{i,\,init}$,

$$\frac{T_i}{T_{i,\,init}} = R \qquad (14)$$

is multiplied by the old approximation for the concentration of free ions

$$R\,m_{i,\,old} = m_{i,\,new} \qquad (15)$$

to obtain the new estimation for the concentration of free ions. Iteration continues within <u>testagainstanalyticalvalues</u> and <u>speciesdistribution</u> until the absolute value of unity minus the ratio of the initial concentration divided by the calculated total concentrations of Na and Cl are less than 10^{-8},

$$\left| 1 - \frac{T_{Na}}{T_{Na,\ init}} \right| < 10^{-8} \qquad (16)$$

$$\left| 1 - \frac{T_{Cl}}{T_{Cl,\ init}} \right| < 10^{-8} \qquad (17)$$

which indicates that the mass balance calculation has effectively converged.

8) Upon convergence, the last step in speciesdistribution is to multiply $\gamma_{i,\ DH\text{-}hyd}$ times $\gamma_{i,\ a}$ to obtain the stoichiometric activity coefficient, $\gamma_{i,\ st}$.

9) The new values for m_i are then returned to the equation for "true" ionic strength (equation 12) and the cycle starts again, and iteration continues until the ionic strength converges as shown below

$$\left| 1 - \frac{I_{t,\ new}}{I_{t,\ old}} \right| < 10^{-8} \qquad (18)$$

If the relationship in equation (18) is true, then the entire calculation has converged.

10) The subroutine meangamma calculates the mean activity coefficients using the individual ionic activity coefficients (see Appendix A.).

11) The results are sent to a data file by the subroutine reporttodatafile.

RESULTS AND DISCUSSION

In order to establish the numerical stability of the model, a wide range of parameters were tested. In addition, existing methods of estimating K_d, å, and h were reviewed. The following sections discuss the selection of parameters, give the results obtained, and discuss various tests of this model.

PARAMETERS AND CALIBRATION OF THE MODEL

Distance of closest approach, å

The distance of closest approach or ion size parameter, å, is used in the extended Debye-Hückel equation to account for the fact that ions are not point charges; thus this value assigns a finite size to individual ions. According to Bockris and Reddy (1970), å is best considered an adjustable parameter because although its magnitude can be determined from theory, its absolute value thus far is determined from experiment. See Bockris and Reddy (1970) for a discussion of the derivation of the ion size parameter. Kielland (1937) reports rounded values for å of individual ions with no clear justification for the method of rounding; these values for å are probably the ones most often used with the Debye-Hückel equation and its extensions. Kielland (1937) also reports å values calculated from two ion mobility methods. Pitzer (1973) accounts for the distance of closest approach in two terms: one term does not vary with individual ions, while the second term corrects for variation in size between different ions. The å values chosen for the present model are very close to Kielland's (1937) rounded values. A range of å values were tested in the model (see section on selection of parameters below) to insure the stability of the numerics and to identify those values that gave the best fit for the binary systems NaCl-H_2O, NaOH-H_2O, and HCl-H_2O. Tables 1 and Table C.1 show the best fits obtained during this testing.

Dissociation constants, K_d

Davies (1962) acknowledges a significant problem facing the worker who wishes to use K_d

> The experimental attack on these problems meets the fundamental difficulty of the assumption that we can have an exact knowledge of the behavior of free ions before we can assess the amount of ion-pairing. In very dilute solutions the number of ion-pairs will be very small, and to calculate this number at all demands a high degree of reliance on the accuracy of the limiting equations. At higher concentrations ion-pairs will be more plentiful, but the criterion of complete dissociation may be correspondingly more uncertain.

The problem of extrapolating high concentration data back to infinite dilution, extrapolating high temperature data to 25°C, and the fact that experimental equilibrium constant determinations are model-dependent lead to disagreement over the "correct" value for a particular equilibrium constant. As an extreme example, Robinson (1936) gives 1.3×10^6 as the K_d(HCl) at 25°C, whereas Ruaya and Seward (1987) favor a value of 5.1 ± 0.9. Figures 5 and 6 show published values of log K_d *versus* temperature for NaCl, NaOH, and HCl. In this model, K_d values of 1.0, 5.0, 15.0, 100.0, and 1000.0 were tested for NaCl, NaOH, and HCl. These K_d values were chosen to span the published values and thereby test the ability of the model to fit activity coefficient data regardless of the degree of ion pairing predicted by the equilibrium constant. The model did not converge for $K_d(MX) = 1.0$; for $K_d(MX)$ greater than or equal to 5.0, the model

Table 1. Parameters chosen for use in this model. Choices are discussed in the text. The values of h are used in the modified Robinson and Stokes equation (2); the h' values are used in equation (5) in the calculation of the activity of water.

	species						
parameters	H^+	Na^+	OH^-	Cl^-	HCl^0	$NaCl^0$	$NaOH^0$
å	8.7	4.6	3.6	3.3	—	—	—
h	7.0	2.4	3.1	2.4	5.1	3.9	5.1
h'	6.0	1.7	2.4	1.4	4.1	3.2	4.4
K_d	—	—	—	—	15.0	15.0	15.0

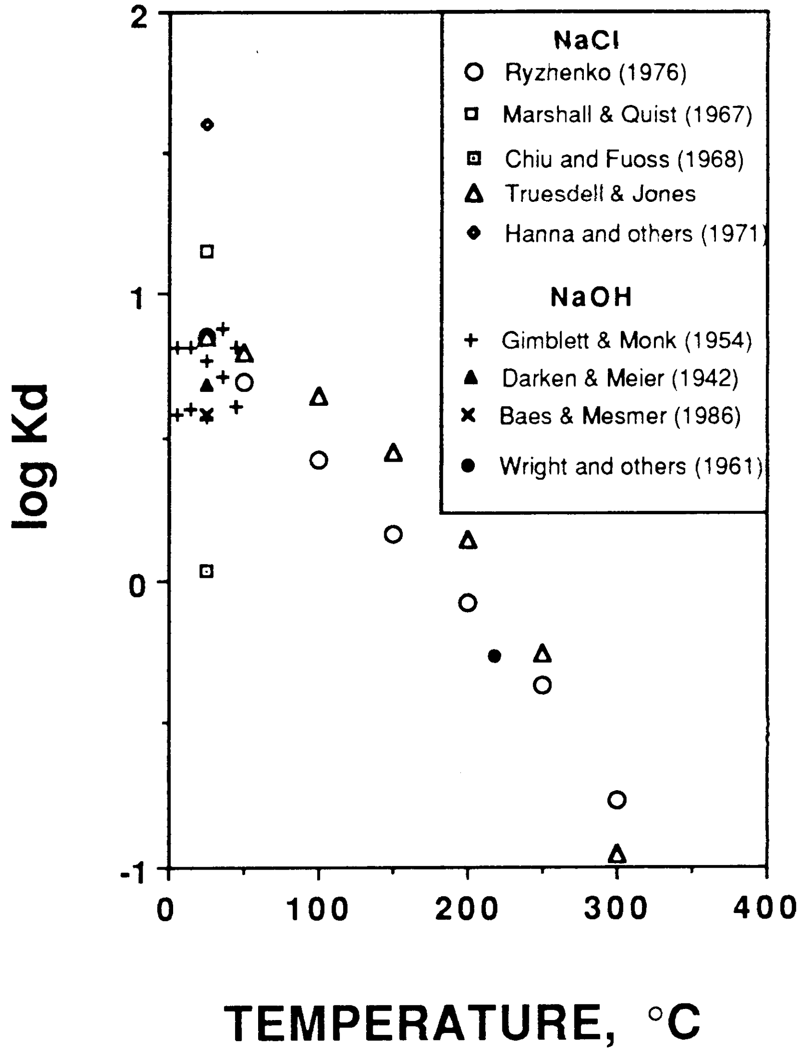

Figure 5. Reported values of log K_d(NaCl) and log K_d(NaOH) *versus* temperature for conditions along the liquid-vapor curve. Data from Truesdell and Jones is unpublished and is referenced in Helgeson (1969). Datum from Marshall and Quist (1967) is extrapolated from dioxane-water mixtures.

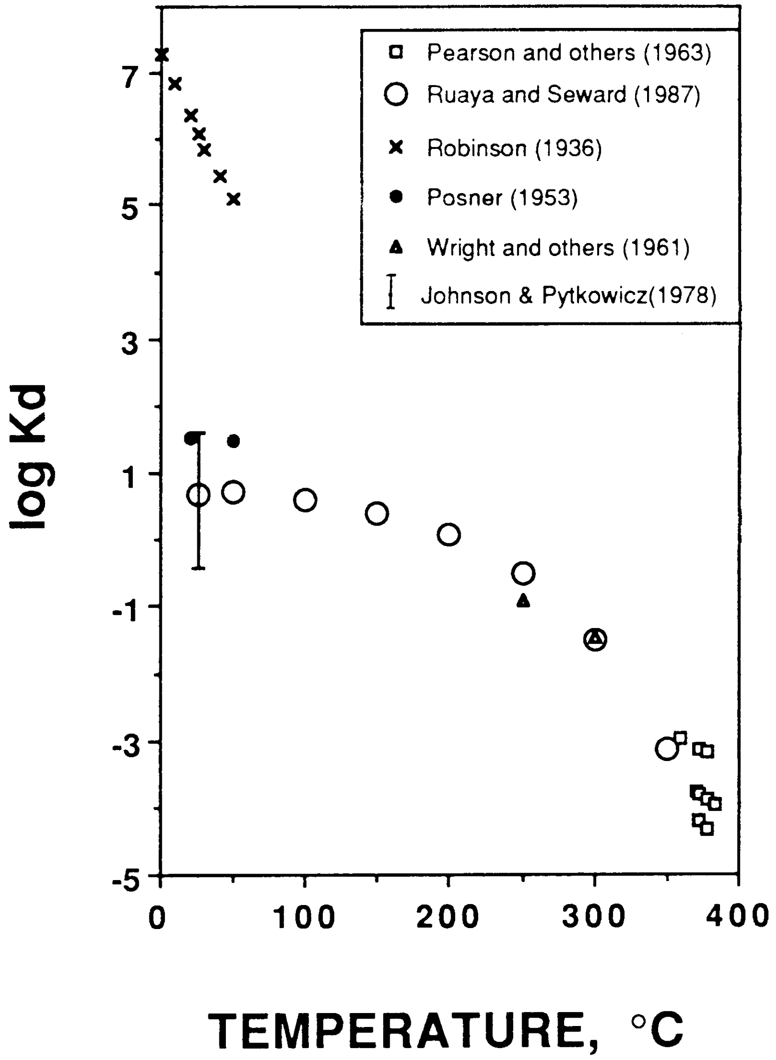

Figure 6. Reported values of log K_d(HCl) *versus* temperature for conditions along the liquid-vapor curve. Error bars represent extrapolation of Johnson and Pytkowicz (1978) to zero ionic strength.

fits the experimental data as shown in Table C.2. The choice of parameters recommended for use with this model is given in Table 1. K_d values of 15.0 for NaCl, NaOH, and HCl were chosen based on inspection of plots of log K_d *versus* temperature shown in figures 5 and 6, and on the basis of goodness of fit to binary activity coefficient and activity of water data. Alternative choices of parameters corresponding to higher and lower degrees of dissociation are listed in Table C.1.

Hydration number

The hydration number, h, represents a quantity of water molecules that reside for a period of time in the vicinity of solute species. This interaction occurs because water is a polar molecule and is electrostatically attracted to charged cations, anions, and ion pairs. Water molecules are not permanently associated with a particular ion, so the hydration number is best envisioned as a statistical quantity. There are numerous methods to evaluate and define hydration numbers. Conway (1981) states

> The hydration number is conventionally defined as the number, n, of water (or solvent) molecules that are "associated" with the ion in solution. The problem of defining n arises from the question of how "association" of water with an ion can be meaningfully and quantitatively defined. In particular, it is necessary to distinguish those water molecules that are simply geometrically coordinated as inevitable neighbors of the ions and those that, in the time average, are in some way physically or chemically associated with the ions.

Hinton and Amis (1971) state that, "the field is in a state of confusion" concerning hydration numbers for two reasons. First, the value of the hydration number depends strongly on the method of measurement. Second, there is no standard reference ion for determining hydration numbers.

Among the methods for determining hydration numbers reviewed by Hinton and Amis (1971) are transference, conductance, electromotive force, thermodynamic, diffusion, isotopic equilibrium, spectroscopic, sound velocity, effective volume, dielectric properties, X-ray, and nuclear magnetic resonance. Molecular dynamics and Monte Carlo simulations (Andaloro and others, 1988; see Enderby and Neilson, 1981 for a review) have also been used to arrive at hydration numbers. Recently, X-ray and neutron diffraction have provided some results that may be less ambiguous than other methods (Enderby and others, 1987; Powell and others, 1988). These diffraction studies suggest that cation and anion hydration numbers are approximately equal. Using a molecular dynamics approach, Belch and others (1986) determined that ion pairs are hydrated, and in the present model the ion pairs are treated as hydrated. Stokes and Robinson (1948) suggested a convention of treating anions as unhydrated. Bates and others (1970) and Bates (1986) employ this convention in an electrolyte solution model that employs hydration and electrostatic effects. Hydration numbers used in the present model are fit parameters obtained after setting the dissociation constant and ion size parameters; Table 1 and Table C.1 list these parameter choices. The best fit hydration numbers for Na^+ and Cl^- are approximately equal; however the model is much more sensitive to the sum ($h_{Na^+} + h_{Cl^-}$) than to variation of individual hydration numbers h_{Na^+} and h_{Cl^-} with the sum ($h_{Na^+} + h_{Cl^-}$) held constant. Hydration numbers for Na^+ are based upon two binary systems, $NaCl$-H_2O and $NaOH$-H_2O. Hydration numbers for Cl^- were chosen to give best fits for the systems $NaCl$-H_2O and HCl-H_2O. Hydration numbers for H^+ and OH^- were chosen to give best fits for the systems HCl-H_2O and $NaOH$-H_2O, respectively. The h values used in this model probably do not represent an exact number of water molecules associated with ions or ion pairs. However, if upon expansion to a larger data base a consistent trend in h values can indeed be correlated to a physical measurement, such a trend should prove sufficient to allow this model to be a reliable predictive tool.

Selection of parameters

The choices for dissociation constants have been discussed above. For a particular choice of K_d, the parameters å and h must be adjusted. The equations used in this model combine to represent a complicated functional, and in order to determine more about the nature of this functional, the model was tested by comparing the sums of squares of the residuals (experimental - calculated) for the activity of water and mean activity coefficients calculated using systematic combinations of å and h values. The å values were varied up to ± 4.0 in 0.25 increments about Kielland's (1937) values. The individual ion hydration numbers were varied from 0.0 to 12.0 in 0.25 increments. The binary systems NaCl-H_2O, NaOH-H_2O, and HCl-H_2O were examined separately, thus a five-dimensional space was investigated for each binary system; for example in NaCl-H_2O, values of $å_{Na}$, $å_{Cl}$, h_{Na}, h_{Cl}, and h_{NaCl^0} were simultaneously varied. This testing established that the functional behaves in a predictable fashion, and that å values close to Kielland's (1937) work best in this model. In addition, this testing established that the model converges for a wide range of parameter choices, but that there appears to be a unique minimum in the 5-dimensional space examined for each solute (binary system). The parameter choices in Table 1 and Table C.1 do not represent unique minima, but rather the choices are compromise best fits that take some information from two binary systems into account, such as the use of the two binary systems, NaCl-H_2O and NaOH-H_2O, for determination of the value for h_{Na^+}.

Also, å and h values were limited by the arbitrary choice of 0.1 as the smallest increment of variation used in selecting best fits.

When hydration numbers that produced acceptable mean activity coefficients were used in equation (5) to calculate the activity of water, the activity of water that was consistently too low. To adjust for this result, $(h_i - 0.7)$ for all species except H^+ and HCl^0 were used in equation (5) instead of h_i alone. For species involving HCl, the values $(h_{HCl^0} - 1.0)$ and $(h_H - 1.0)$ were substituted for h_i. These substitutions are listed as h' in Tables 1 and C.1.

TESTING THE MODEL

The results of this study for K_d equal to 15.0 for $NaCl^0$, $NaOH^0$, and HCl^0 are presented in graphical form in this section; numerical values, results for values of K_d other than 15.0, and residuals are tabulated in Appendix C. In all of the graphs in this section, model-predicted values at concentrations of 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0 m are shown as discrete points.

Thermodynamic quantities

The predicted values for the stoichiometric mean molal activity coefficient, $\gamma_\pm$, in solutions of pure NaCl, NaOH, and HCl *versus* concentration are illustrated in figure 7a. For comparison, Robinson and Stokes' (1959) smoothed data are shown as solid curves in figure 7a. Figure 7b shows the residuals for $\gamma_\pm$, where residuals are equal to $\gamma_{\pm(\text{Robinson \& Stokes})} - \gamma_{\pm(\text{calculated})}$ as shown in figure 7b. The maximum deviations from experimental activity coefficients are 0.73%, 1.77%, and 3.86% for NaCl, NaOH, and HCl, respectively.

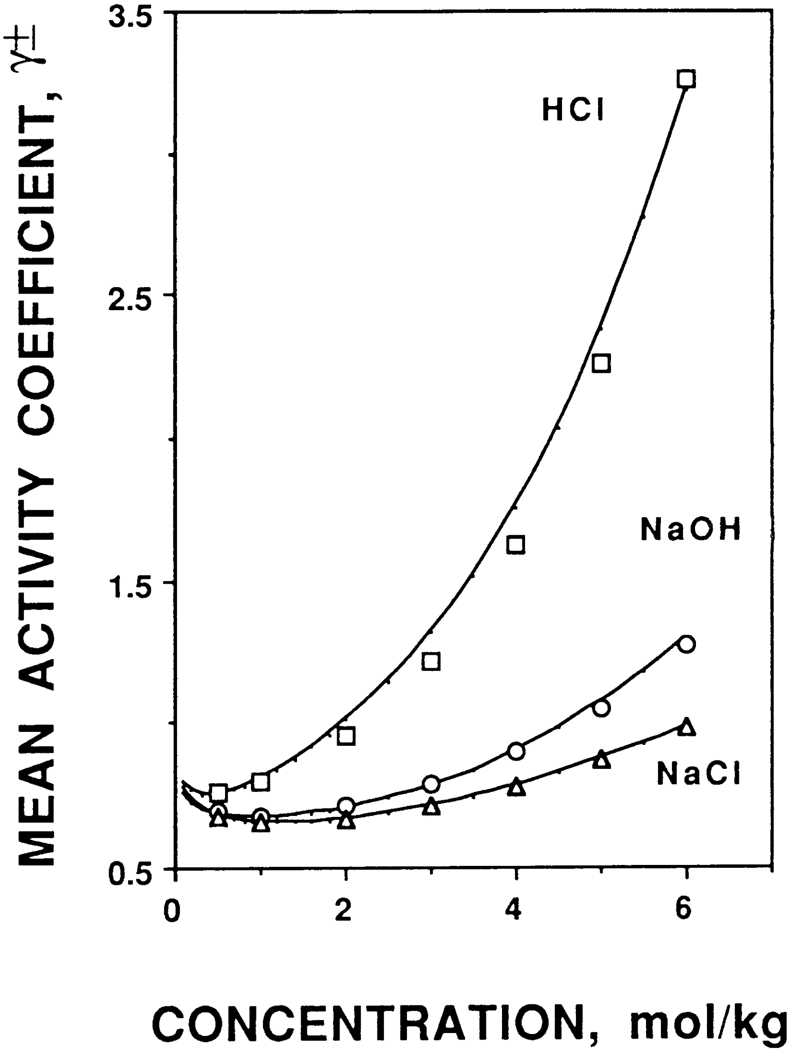

Figure 7a. Calculated mean activity coefficient, γ±, *versus* concentration in binary solutions of NaCl, NaOH, and HCl. The curves follow the smoothed experimental data reported by Robinson and Stokes (1959). K_d(NaCl) = K_d(NaOH) = K_d(HCl) = 15.0.

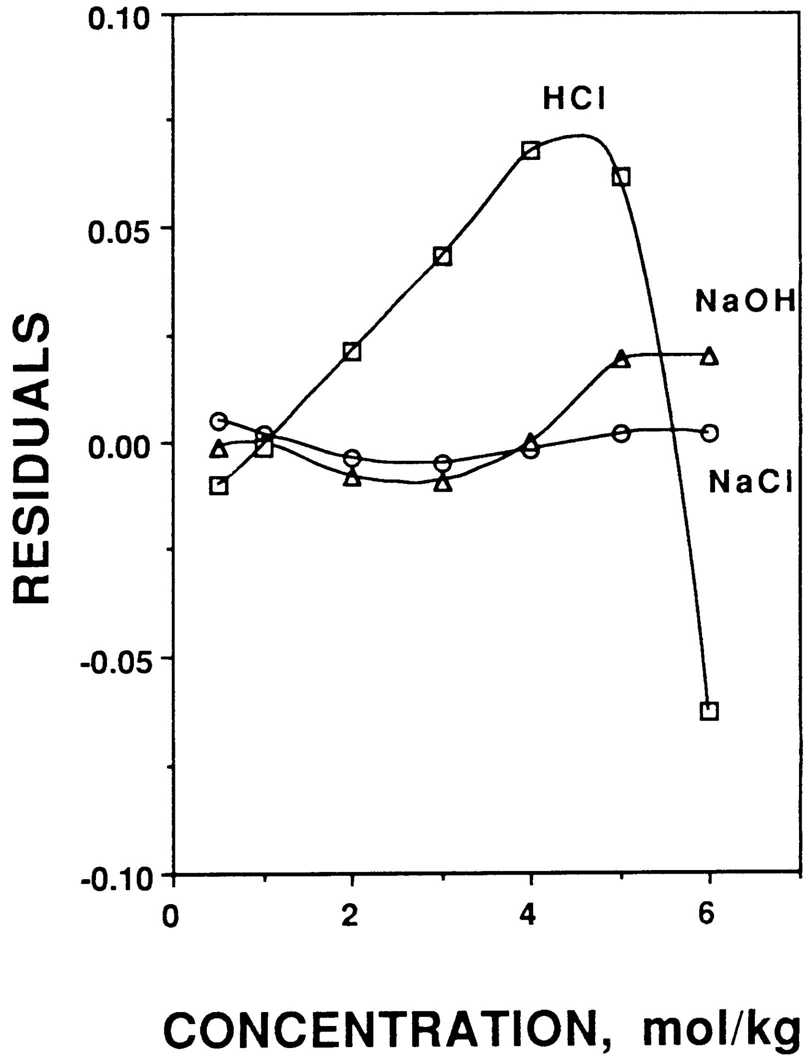

Figure 7b. Residuals ($\gamma\pm$Robinson and Stokes,1959 minus $\gamma\pm$calculated) for mean activity coefficient*versus* concentration for figure 8a. K_d(NaCl) = K_d(NaOH) = K_d(HCl) = 15.0.

Predicted values for the activity of water *versus* concentration in pure NaCl, NaOH, and HCl solutions are compared against smoothed experimental values (Robinson and Stokes, 1959) in Figure 8. The maximum deviations from experimental values are 0.78%, 0.79%, and 2.09% for NaCl, NaOH, and HCl, respectively.

Individual ionic activity coefficients

Individual stoichiometric molal ionic activity coefficients, γ_i, are plotted *versus* concentration of NaCl in figure 9. H^+ and OH^- are present in trace amounts in such a solution, and, for example, the value of γ_{H^+} in an HCl solution would be higher than those shown in figure 9. Solid lines are interpolations between calculated points. For comparison, the mean activity coefficient for NaCl reported by Robinson and Stokes (1959) lies along essentially the same curve as the γ_{OH^-} curve in figure 9.

Trace activity coefficients

One test of predictive ability is to compare trace activity coefficients calculated by the model against experimental trace activity coefficients (Harvie and others, 1984; see Robinson and Stokes, 1959 and Harned and Owen, 1958 for a discussion of trace activity coefficients). Prediction of trace activity coefficients gives an indication of how well the model deals with mixed electrolytes. In figure 10, calculated values of $\gamma_{\pm HCl}$ (trace) in an NaCl solution containing 0.01 m HCl are compared to experimental values of $\gamma_{\pm HCl}$ (trace) determined by electromotive force methods reported in Harned and Owen (1958), and γ_{NaCl} (pure solution) and γ_{HCl} (pure solution) reported in Robinson and Stokes (1959). The maximum deviation from experimental values is 0.07 (6.48%) at 3.0 m NaCl. No experimental data were found for concentrations of NaCl higher than 3.0 m.

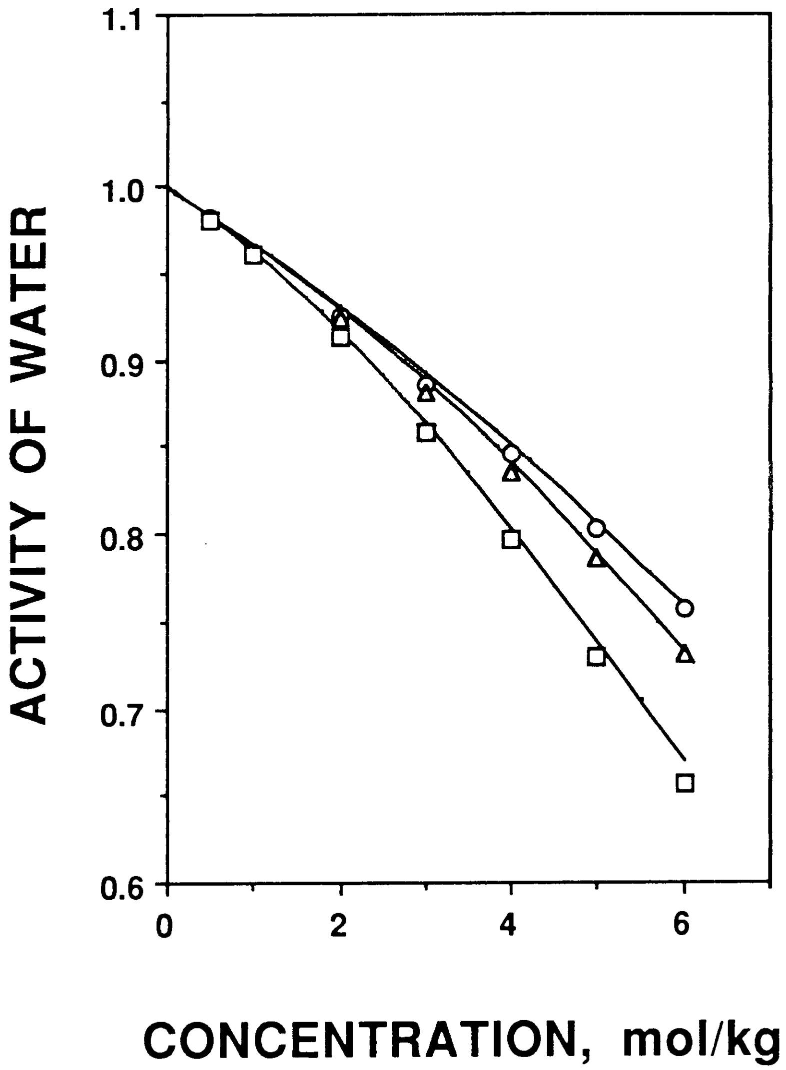

Figure 8. Calculated activity of water *versus* concentration in binary solutions of NaCl, NaOH, and HCl. The curves are smoothed experimental data from Robinson and Stokes (1959). Circles are for NaCl solutions; triangles are for NaOH solutions; squares are for HCl solutions. $K_d(NaCl) = K_d(NaOH) = K_d(HCl) = 15.0$.

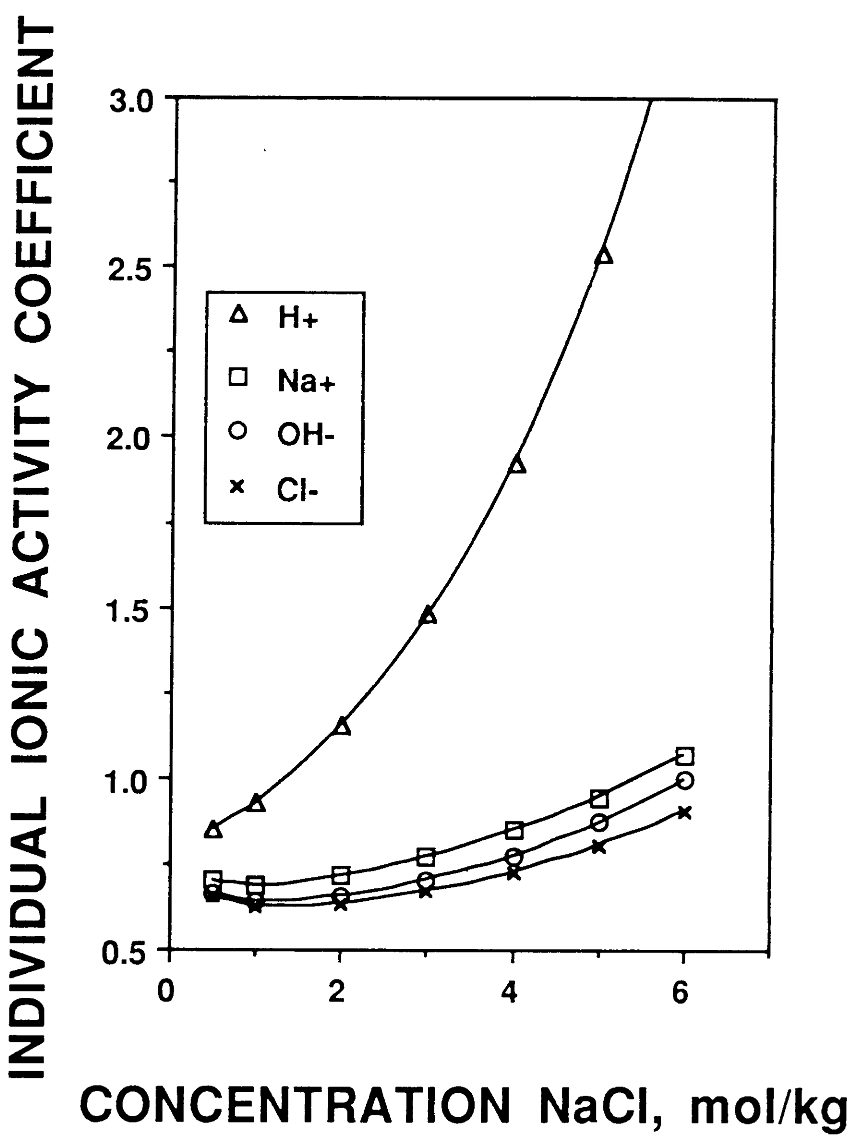

Figure 9. Stoichiometric individual activity coefficient, $\gamma_{i,st}$, *versus* concentration in a binary solutions of NaCl. The mean activity coefficient for NaCl (Robinson and Stokes, 1959) lies under the curve for γ_{OH^-}. The γ_{OH^-} and γ_{H^+} values are trace activity coefficients in an NaCl solution. $K_d(NaCl) = K_d(NaOH) = K_d(HCl) = 15.0$.

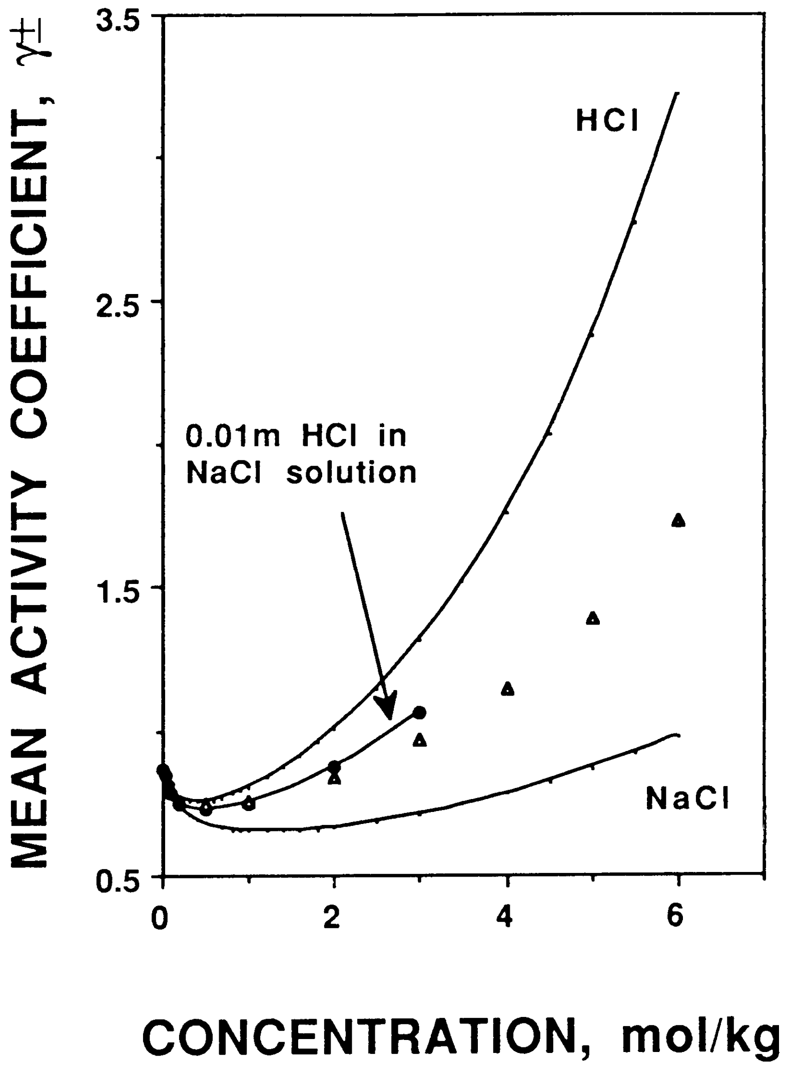

Figure 10. Mean activity coefficient *versus* concentration. Curves labelled NaCl and HCl are for pure binary systems from Robinson and Stokes (1959). Circles are data reported in Harned and Owen (1958) for the trace activity of 0.01M HCl in NaCl solutions; a solid line is interpolated between these data points. Triangles are predicted values for 0.01M HCl in NaCl solutions with $K_d(NaCl) = K_d(NaOH) = K_d(HCl) = 15.0$.

Ion pair activity coefficients

Harvie (1981) criticizes the ion pairing approach because the curve for the activity coefficient for an ion pair, γ_{MX°, *versus* concentration must take a form similar to that in figure 11, which shows model values calculated for γ_{NaCl^0} using $K_d(NaCl) = 15.0$. Harvie (1981) says that "This dependence [on ionic strength] more resembles that for an ionic species subject to the electrostatic forces rather than that characteristic of the weak forces associated with the salting out effect." However, the ionic strength dependence of γ_{MX^0} observed in figure 11 for NaCl is also reported by Helgeson (1969) for the neutral solution species CO_2, who uses $\gamma_{CO_2{}^0}$ to approximate the γ_{MX^0} for the neutral molecule NaCl.

The utility of the activity coefficient calculated by the model for a neutral ion pair may also be examined via the Henry's Law constant, K_H,

$$K_H = \frac{P_{MX}}{a_{MX^0}} \qquad (19)$$

where P_{MX} is the partial pressure of MX over a solution of MX and a_{MX^0} is the activity of an aqueous ion pair in equilibrium with MX in the vapor phase. In order to estimate a Henry's Law constant for the reaction $HCl^0 = HCl(v)$, experimental vapor pressure data (Gokcen, 1980) and model-derived values for a_{HCl^0} were used in equation (19) and plotted *versus* concentration in figure 12a. Choosing $K_H = 0.005$ from figure 12a as a reasonable value, using model values for a_{HCl^0}, and solving equation (19) for P_{HCl} allows one to estimate the partial pressure of HCl over an HCl solution. In figure 12b, $K_H = 0.005$ and model values for a_{HCl^0} were used to estimate this partial pressure. The points represented

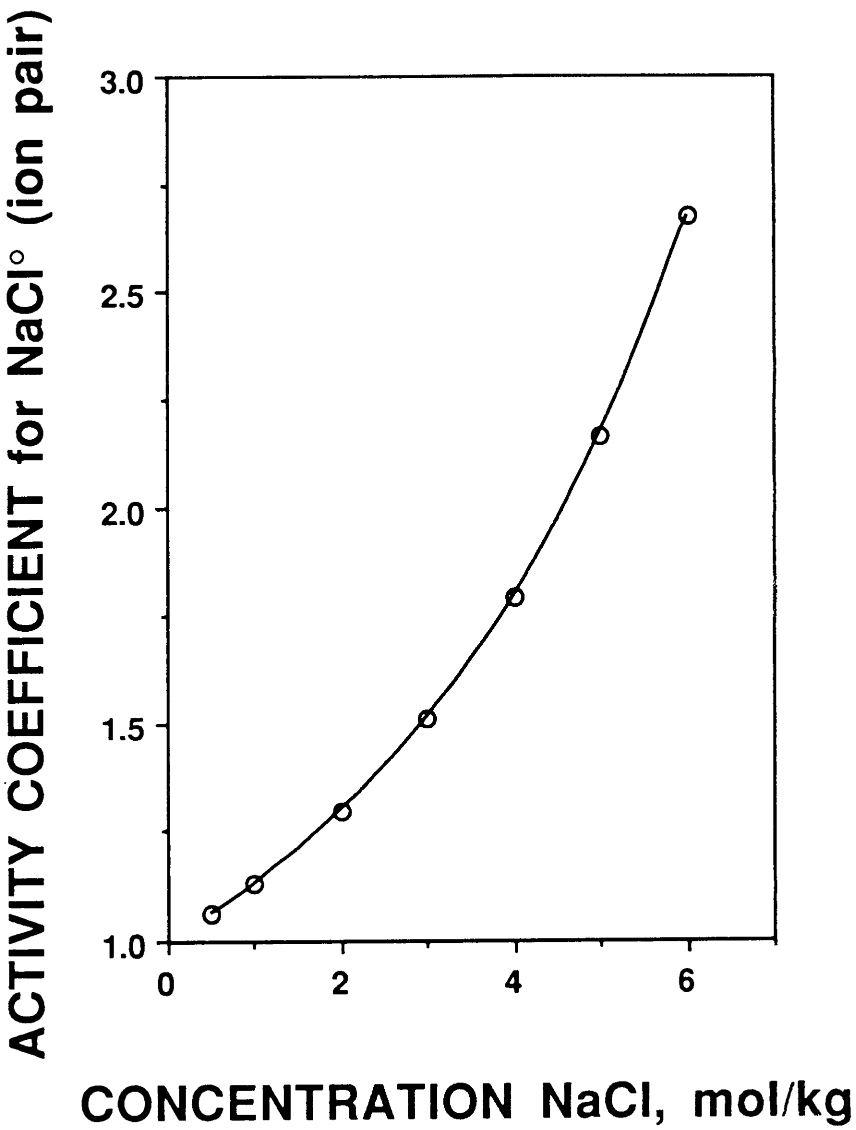

Figure 11. Activity coefficient for the ion pair HCl°, $\gamma_{HCl°}$, *versus* concentration in solutions of HCl-H_2O. $\gamma_{HCl°}$ is calculated from equations (2) and (11). $K_d(HCl) = 15.0$.

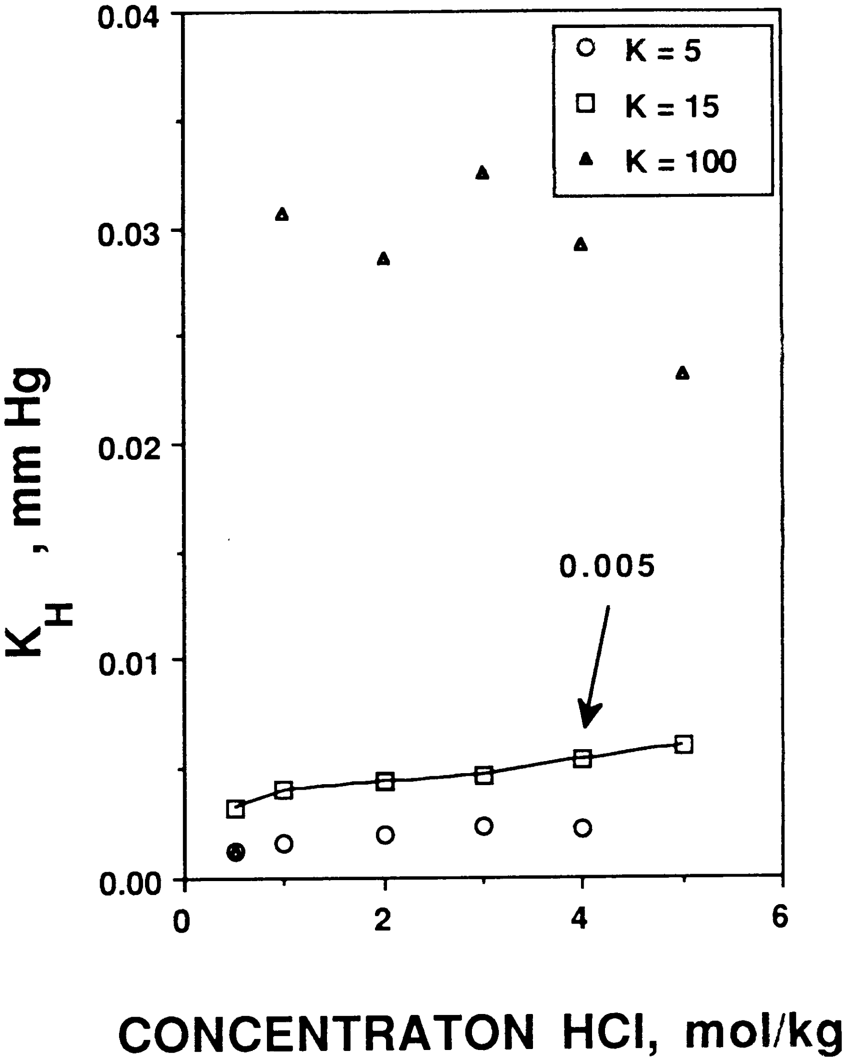

Figure 12a. Henry's Law constant, K_H, *versus* concentration of HCl.
For the reaction HCl° = HCl(vapor), K_H is estimated by dividing the experimental partial pressure of HCl over HCl solutions by the model-derived value of $a_{HCl°}$ using three different values for K_d(HCl). The value 0.005 for K_H is used to predict partial pressure shown in figure 13b. The partial pressure of HCl in millimeters of mercury is from Gokcen (1980).

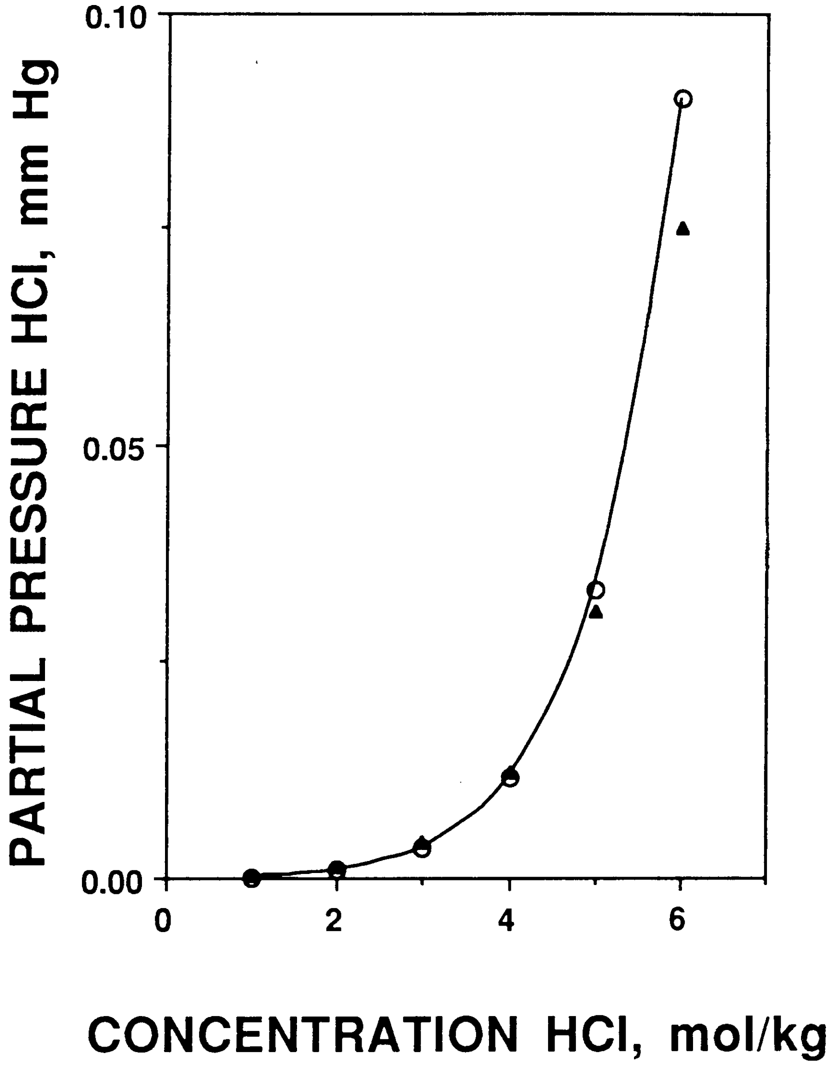

Figure 12b. Predicted partial pressure of HCl over HCl solutions *versus* concentration of HCl. The curve through the circles is from Gokcen (1980). The triangles are estimated from the present model using $K_H = 0.005$.

by triangles were calculated using $a_{HCl}{}^0$ from the present model with $K_d(HCl) = 15.0$. The curve labelled **exp** is an interpolation of the vapor pressure data of Gokcen (1980). Using $a_{HCl}{}^0$ from the present model and a Henry's Law constant based on this model allows calculation of a good estimate of the partial pressure of HCl over HCl solutions in this concentration range.

Distribution of species

The degree of dissociation, α, which is the ratio of the concentration of "free" ion to the total analytical solute concentration (equation 11), for NaCl, NaOH, and HCl in pure NaCl, NaOH, and HCl solutions, respectively, is plotted *versus* concentration in figures 13a-c for model calculations using different K_d values. Note that the solid lines are interpolations between calculated points. No experimental data are available for direct comparison so the predicted distribution of species must be treated as somewhat speculative. However, I favor K_d values near 15.0 as being most likely, and therefore expect that the bold curves labelled as 15 are nearest correct. This choice is based upon inspection of experimental data (figures 5 and 6), the behavior of the model (values of K_d lower than 15.0 require significant changes in parameters), and the calculation of the Henry's Law constant. The Henry's Law constant in figure 12a is more nearly a constant for $K_d(HCl) = 5.0$ or 15.0 than for $K_d(HCl) = 100.0$; this suggests that the distribution of species using $K_d(HCl)$ of approximately 15.0 is more accurate than the distribution predicted using $K_d(HCl) = 100.0$. However, the amount of ion pairing in solution (indicated by decreased *dissociation*) almost certainly increases as concentration increases. As yet, there seems to be no unambiguous method for determining the distribution of species in these strong electrolyte solutions. At any rate, the effect of changing the equilibrium constant upon the predicted degree of dissociation is most significant when

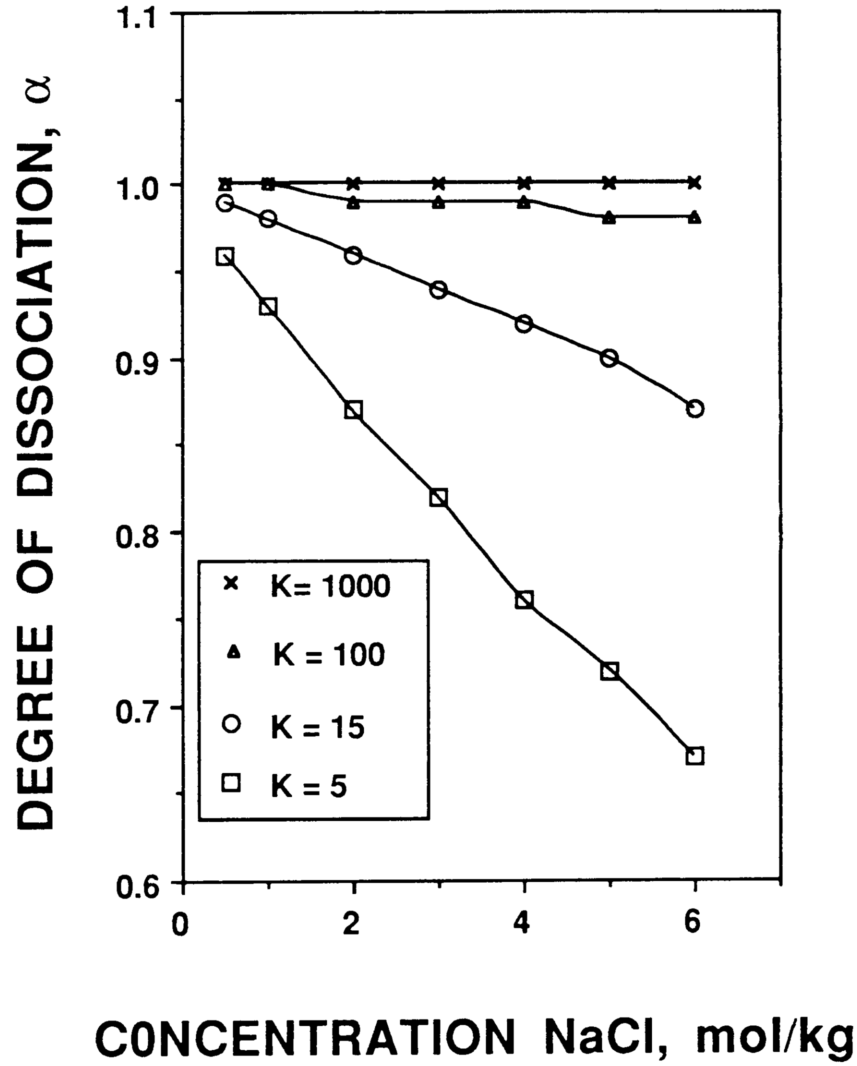

Figure 13a. Degree of dissociation, α, *versus* concentration in a binary solution of NaCl for K_d(NaCl) = 5.0, 15.0, 100.0,and 1000.0. Degree of dissociation is defined here as moles of "free" cations divided by moles of solute.

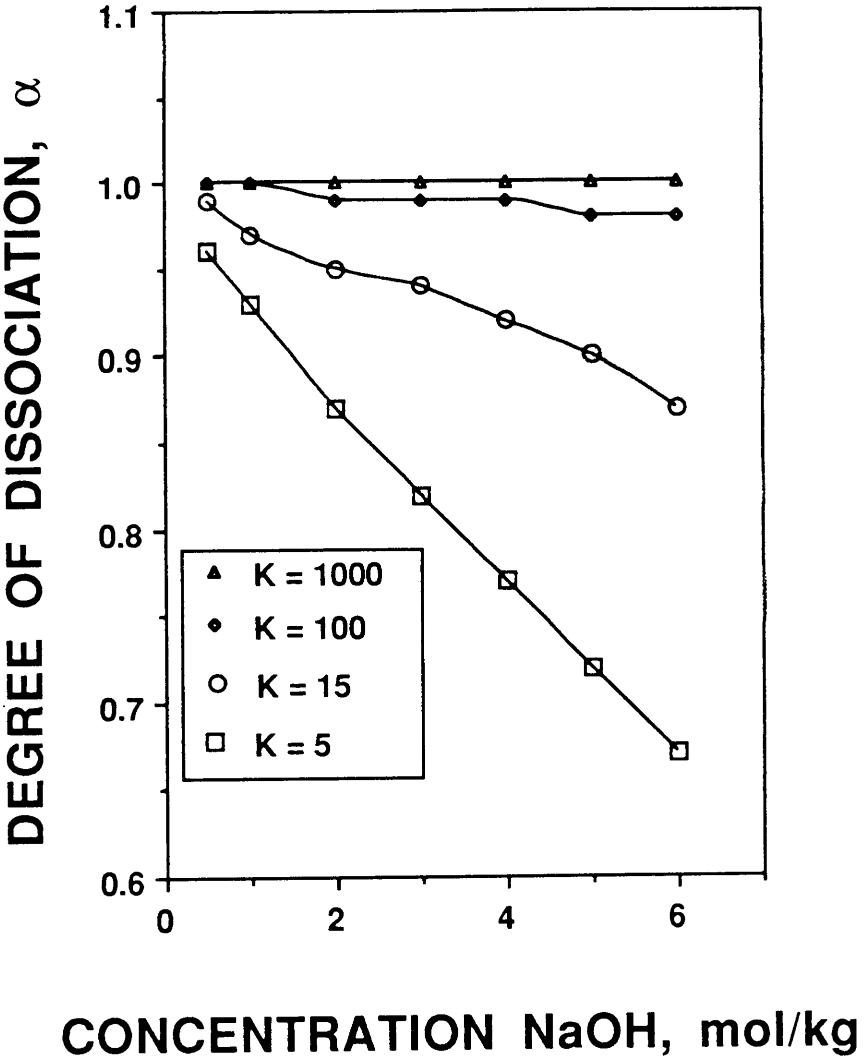

Figure 13b. Degree of dissociation, α, *versus* concentration in a binary solution of NaOH for K_d(NaOH) = 5.0, 15.0, 100.0,and 1000.0.

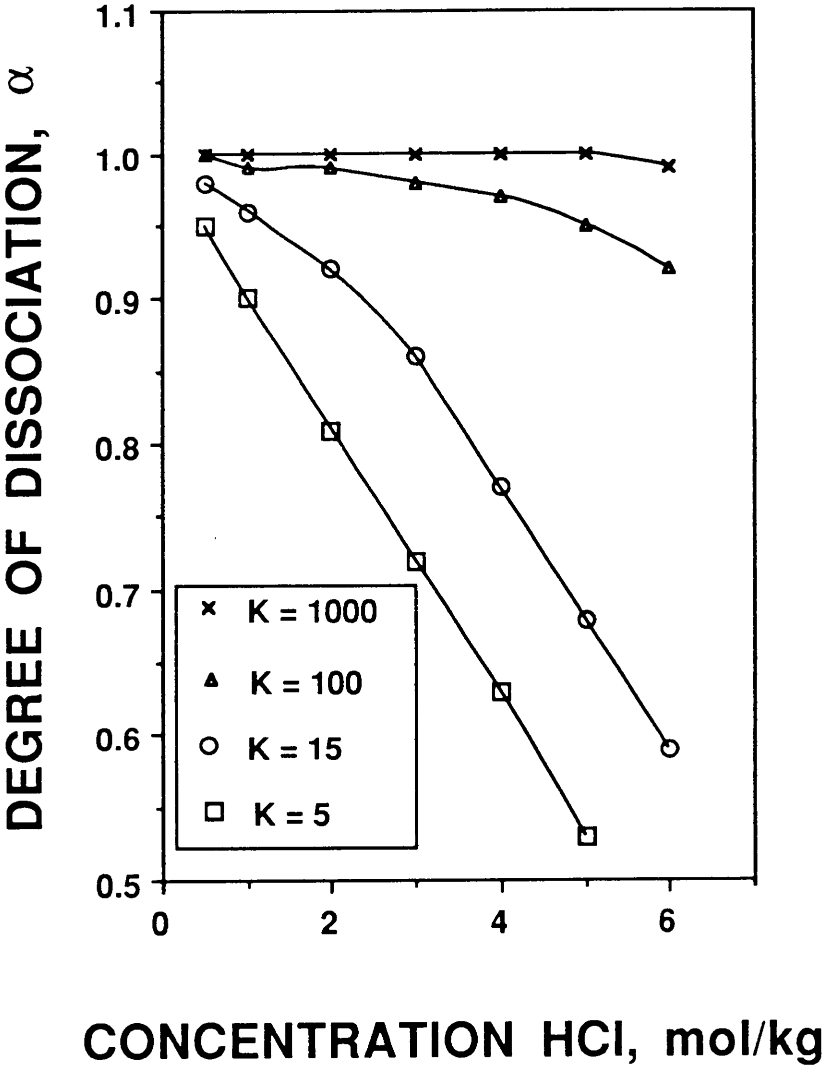

Figure 13c. Degree of dissociation, α, *versus* concentration in a binary solution of HCl for K_d(HCl) = 5.0, 15.0, 100.0,and 1000.0.

the equilibrium constant is relatively small. As shown in figure 13a, the difference in dissociation for NaCl changes more upon changing K_d from 5.0 to 15.0 than upon changing from 100.0 to 1000.0. This effect is due to the fact that when K_d gets large, the solution is treated as completely or nearly completely dissociated and increasing K_d further cannot increase the amount of dissociation significantly. The flexibility of this model is demonstrated by the fact that it can effectively fit thermodynamic properties using dissociation constants which indicate extensive ion pairing or complete dissociation for the same solute.

Solubility

The individual ionic activity coefficients predicted by this model can be combined with a solubility product of NaCl calculated from reported free energies for Na^+, Cl^-, and NaCl (solid) to estimate NaCl solubility. One method is demonstrated in figure 14 which is a plot of $(a_{Na^+})(a_{Cl^-})$ *versus* concentration of NaCl. The solubility product for the reaction $NaCl(solid) = Na^+(aq) + Cl^-(aq)$ was calculated as 37.1 from the free energies reported in Robie and others (1979). The dashed lines correspond to the reported uncertainty resulting from the uncertainties in the reported free energy data. A second order polynomial was fit to the calculated points at $m_{NaCl} = 4.0, 5.0, 6.0$, and 7.0. The value of m_{NaCl} , 6.1 m, where the K = 37.1 line intercepts the fitted curve represents the model's prediction of the saturation for NaCl in H_2O at 25 °C. Linke (1965) reports the saturation of NaCl as 6.12 m NaCl at 25°C. The same approach to the prediction of solubility in more complex systems has yet to be tested.

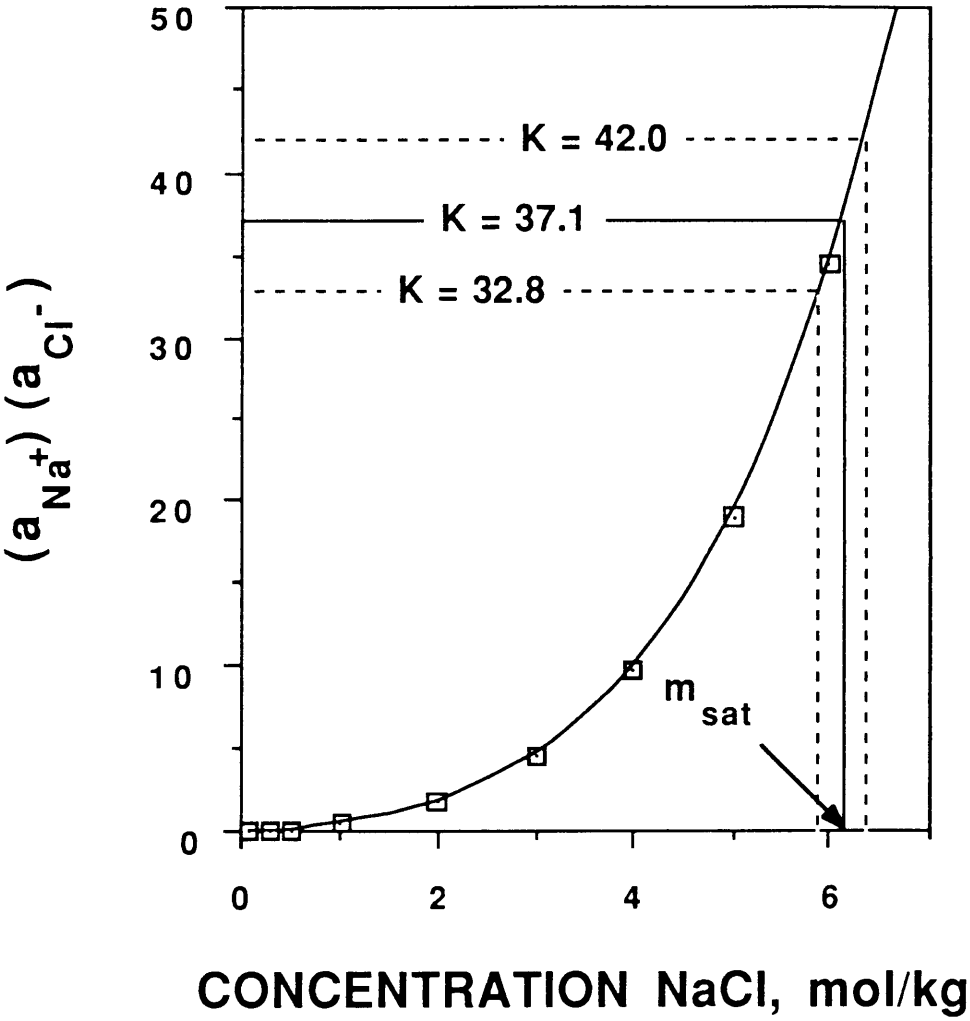

Figure 14. Solubility product, $[(a_{Na^+})(a_{Cl^-})]$, *versus* concentration of NaCl. Values of K are calculated from $\ln K = -\Delta G_r^o/RT$ using data from Robie and others (1979) with K = 42.0 and K = 32.8 bracketing uncertainties in Gibbs free energy data. The point labelled m_{sat} corresponds to 6.1 mol/kg NaCl and is the predicted value for saturation concentration of NaCl in NaCl-H_2O mixtures at 25°C. Linke (1965) gives 6.12 m as the saturation solubility for NaCl in water at 25°C.

Future directions

This model was envisioned for use in complex mixed electrolyte solutions such as those found in geological systems. The next logical steps in the development of this approach are expansion to include other 1-1 electrolytes, nonsymmetrical electrolytes, and to consider higher temperatures and pressures. The inclusion of other 1-1 electrolytes should involve only the addition of the dissociation constants for the reactions involved, though as pointed out above, the selection of these K_d values may be far from straightforward. The addition of nonsymmetrical electrolytes may prove a problem, for the Debye-Hückel theory has difficulty modeling the behavior of nonsymmetrical electrolytes. Adding temperature as a variable will involve treating the Debye-Hückel A and B parameters as functions of temperature; these values have been tabulated to 370°C along the liquid-vapor curve (Naumov and others, 1974). The å and h values will also likely need to be made functions of temperature. Helgeson (1969) discusses the lack of information about å values at temperatures other than 25°C. Crerar (1973) varies h values with temperature in his model which used the same three effects as the present model.

Any expansion of this model will have to be thoroughly tested against binary data ($MX-H_2O$) to fully establish the applicability to other systems and other temperatures. In addition, more rigorous testing will involve the comparison of activity coefficient and solubility data from ternary and more complex systems against model predictions. A word of caution is in order to anyone who might modify this model. The testing of parameters is absolutely essential to the production of reasonable estimates for activity coefficients by this model. It would be desirable if consistent patterns in parameter selection should emerge upon development of a larger data base. For example, a particular experimental method may provide hydration numbers which work well in this model, or one may be able to choose hydration numbers using the periodic table of the elements as a guide. If such choose hydration numbers using the periodic table of the elements as a guide. If such consistency can be found, another element of generality will be afforded to this approach which will allow extrapolation into systems where data are sparse or absent. Ideally, the method presented here could be incorporated into a generalized computer program for the estimation of activities, solubilities, and distribution of species which the geochemist would find accurate and easy to use. The possibility of predicting the phase behavior of complex mixed electrolytes and the solubility of sparingly soluble salts using this model is encouraging.

CONCLUSION

The model presented here offers a promising, physically reasonable approach to the prediction of individual and mean activity coefficients in electrolyte solutions. It treats the dissociation of species as a continuum and is conceptually simple. This approach incorporates three physical effects, DH interactions, ion association, and ion hydration, in a novel way. The demonstrated ability to effectively deal with solutes as significantly associated or completely dissociated suggests that this model has considerable flexibility. The prediction of vapor pressure over an HCl solution as well as the solubility of NaCl provides an independent check on the internal consistency of the model. In addition, the prediction of trace activity coefficients shows that this approach is effective in mixed electrolytes. Though the model covers only the system Na-Cl-OH-H, the results presented suggest that this model warrants expansion to account for additional electrolytes (symmetrical and nonsymmetrical), mixtures of electrolytes, and pressure and temperature.

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APPENDIX A

Definitions

The mean molal ionic activity, $a\pm$, of a component is a measureable thermodynamic quantity which is related to individual ionic activities a_M and a_X by the following definition

$$a\pm_{MX} = \left(a_M^{(\nu_m)} a_X^{(\nu_X)}\right)^{1/(a_M + a_X)} \tag{A.1}$$

where M and X refer to cation and anion, respectively, and ν is the stoichiometric coefficient for each ion. For 1-1 electrolytes, equation (A.1) simplifies to $a\pm = \sqrt{a_M\, a_X}$. The individual activities are not uniquely measureable but may be established by convention provided that equation (1) is satisfied. The quantity $a\pm$ can be calculated using a Gibbs-Duhem relationship and using data for the activity of water in an MX-water solution in the following relationships

$$\ln a_w = -\frac{\nu\, m\, W_w}{1000}\,\phi \tag{A.2}$$

$$\phi - 1 = \frac{1}{m}\int_0^m m\, d\ln\gamma \tag{A.3}$$

where a_W is the activity of water, ν is the sum of the stoichiometric coefficients for the electrolyte, m is concentration of the electrolyte in mol/kg, W_W is the molecular mass of water, and ϕ is the osmotic coefficient. The activity of water can be determined from vapor pressure or electromotive force measurements of the electrolyte solution.

The mean molal ionic activity coefficient, $\gamma\pm$, is related to $a\pm$ by

$$a\pm = \frac{\gamma\pm \ m}{\gamma^{o}\pm \ m^{o}} \tag{A.4}$$

where superscript ^{o} refers to a hypothetical one molal standard state such that $\gamma^{o}\pm$ and m^{o} are both unity, m is the concentration of an electrolyte in mol/kg, and $\gamma\pm$ is defined as

$$\gamma\pm_{MX} = \left(\gamma_M^{(\nu_m)}\gamma_X^{(\nu_X)}\right)^{1/(\gamma_M + \gamma_X)} \tag{A.5}$$

such that if γ_M and γ_M are known, $\gamma\pm$ can be calculated. For 1-1 electrolytes, equation (A.1) simplifies to $\gamma\pm = \sqrt{\gamma_M \gamma_X}$.

The stoichiometric ionic strength is defined as

$$I = \frac{1}{2}\sum_i m_i z_i^2 \tag{A.6}$$

where m_i is the total concentration of the i^{th} ion and z_i is the charge on the i^{th} species; this definition assumes complete dissociation.

Behavior of activity coefficients with concentration

The experimentally determined activity coefficients of many electrolytes change with concentration in a fashion similar to that of NaCl which is illustrated in figure A.1. The experimental $\gamma\pm_{NaCl}$ reported by Robinson and Stokes (1959) is shown along with the $\gamma\pm_{NaCl}$ calculated using the extended Debye-Hückel equation

$$\log \gamma\pm = \frac{-A\left|z_M z_X\right|\sqrt{I}}{1 + \mathring{a}B\sqrt{I}} \tag{A.8}$$

with $\mathring{a}_{NaCl} = 4.0$ (Bockris and Reddy, 1970) to illustrate the fact that this equation fails at ionic strengths of approximately 0.1. The Debye-Hückel equation accounts for long-range electrostatic repulsion between like-charged ions. Though this effect is significant even at

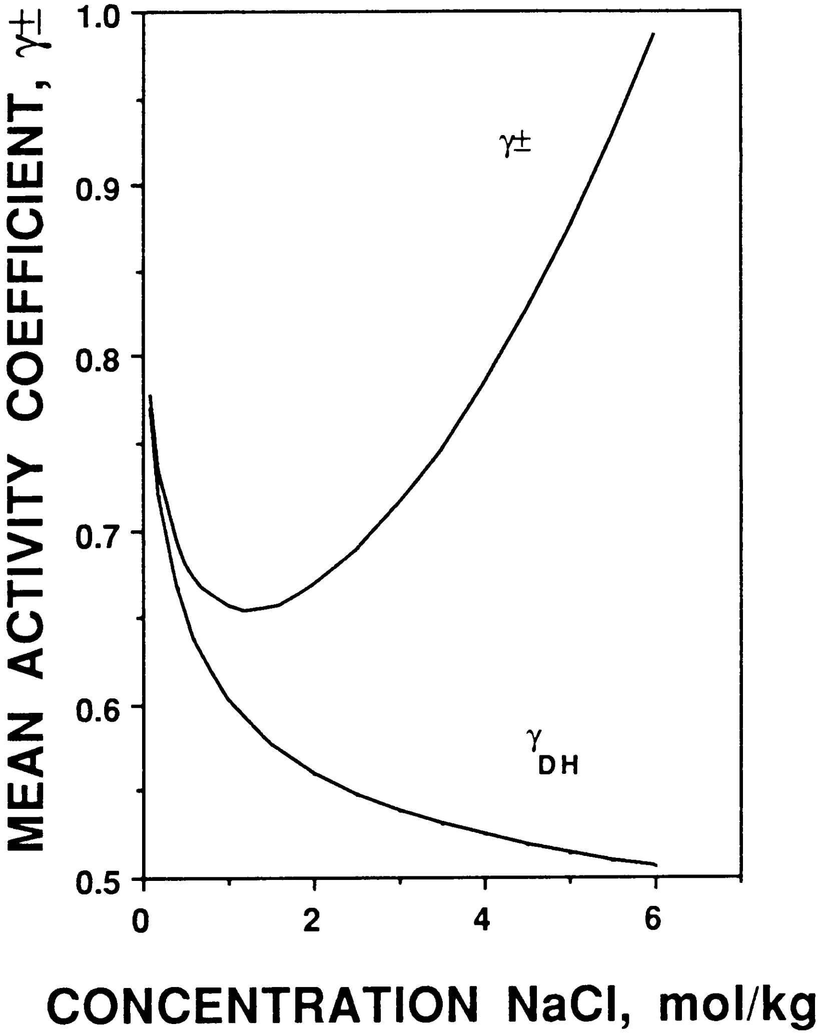

Figure A.1. Mean activity coefficient for NaCl, $\gamma_{\pm NaCl}$, *versus* concentration of NaCl at 25°C. The curve marked $\gamma_{\pm}$ shows smoothed experimental data reported in Robinson and Stokes (1959). The curve marked γ_{DH} was calculated using the extended Debye-Hückel equation (A.8) with $å_{NaCl} = 4.0$.

high concentrations, it is obvious by comparing the $\gamma_\pm$ curve to the γ_{DH} curve in figure A.1 that Debye-Hückel long-range effects alone are insufficient to account for experimentally observed behavior at even moderate ionic strengths. Figure 2 illustrates the effect of electrostatic interactions upon the mean activity coefficient of NaCl.

Ion association effectively decreases activity coefficients with increasing concentration. This effect is due to the "loss" of free ions to the formation of ion pairs, effectively reducing the concentration of free ions. The effect of ion association is often more pronounced in solutions which contain di- and trivalent ions, and in high temperature solutions. Figure 2 shows the calculated effect of association upon the mean activity coefficient of NaCl.

Ion hydration involves the association of water molecules with solution species due to short-range electrostatic attraction between the dipolar water molecules and charged cations and anions or dipolar ion pairs. Hydration effectively "binds" water to solute particles, making it less active (reducing its activity) than it would be if it did not hydrate ions. When the activity of water decreases, the activity of ions increases. The hydration effect on activity coefficients is most significant at moderate to high concentrations, and hydration contributes to the mean activity of NaCl as shown in figure 2.

APPENDIX B

SOURCE CODE FOR SALTY DOG 1.0

```
{*****************************************************************************************************
*   program:  SALTY DOG V 1.0              June 6, 1989                                              *
*                                                                                                    *
*   written by:  Carl S. Kirby                                                                       *
*                Dept. of Geological Sciences                                                        *
*                Virginia Tech                                                                       *
*                Blacksburg, Virginia 25061-0796                                                     *
*                                                                                                    *
*   Turbo™ Pascal version 1.00A                                                                      *
*                                                                                                    *
*   purpose: This program calculates individual and mean ionic                                       *
*         activity coefficients, the activity of water, and                                          *
*         the distribution of species for solutions of                                               *
*         NaCl, NaOH, HCl, and mixtures of these 1-1 electrolytes                                    *
*        in water.                                                                                   *
*                                                                                                    *
*****************************************************************************************************}
program SALTYDOG (input, output);

uses SANE;  { Standard Apple Numeric Environment library which is required
         to allow operations such as log x}

type
  name = (H, NA, OH, CL, NACL, NAOH, HCL); {defines a data type which is
    used as the subscript for several arrays; this data type cannot be I/Oed}
  molalconc = array[H..HCL] of real;{stores molal concentrations from analyses;
    corresponds to mi in text}
  zARRAY = array[H..HCL] of integer;   {defines data type for ion charges}
  gamARRAY = array[H..HCL] of extended; {defines data type for activity coefficients}
  azeroARRAY = array[H..HCL] of real;  {defines data type for ion size parameters}
  hydARRAY = array[H..HCL] of real;    {defines data type for hydration numbers}
  alphaARRAY = array[CL..HCL] of real;  {defines data type for degree of dissociation}

label 20,100;

var
  report : text;   {creates a text file, runnmuber, where results are sent}
  runnumber : string[50];  {name of output text file}
  concentration :  molalconc; {estimate of concentration of ions and ion  pairs in mol/kg}
  charge : zARRAY;       {stores ion charges}
  i : name;  {subscripts for  ions and ion  pairs H, NA, OH, CL, NACL, NAOH, HCL }
  ionicstrength : real;   {"true" ionic strength; molal}
  gamma : gamARRAY;      {molal activity coefficient}
  iterationcounter : integer;{counter to prevent infinite loops in procedure distributionofspecies}
  analyticalNA, analyticalCL, analyticalH, analyticalOH : real;
    {analytical concentration in mol/kg; =Ti, init}
  actvtycoefNACL, actvtycoefNAOH, actvtycoefHCL : real; { activity coefficient for an ion pair}
```

```
  activityofwater : real; {activity of water calculated by model}
  alpha : alphaARRAY; {degree of dissociation array}
  end_this_run : boolean;  {flag for convergence of "true" ionicstrength}
  oldionicstrength : real; {stores old ionic strength for
                            comparison with next iteration to determine convergence}
  inputfile : text; {name of text file where data is entered to use SALTY DOG;
                     format is concentration H (tab) OH (tab) NA (tab) CL in mol/kg;
                     enter a small number such as 1.0e-10 instead of zero for undetectable
                     concentrations}
  AZERO : azeroARRAY; {ion size parameter for individual ion}
  hyd : hydARRAY;     {hydration number for individual ion or ion pair}
  KNACL, KNAOH, KHCL : real; {dissociation constant for ion pair}
  awflag : boolean;  { a flag to indicate lack of convergence }
  ionstrcounter : integer; {counter to avoid infinite outer loop found in procedure ionstr}

{*********************************************************************************************
*   subroutine  BATCH INPUT     V 1.0      June 6, 1989                                      *
*                                                                                             *
*   written by:  Carl S. Kirby                                                                *
*                Dept. of Geological Sciences                                                 *
*                Virginia Tech                                                                *
*                Blacksburg, Virginia 25061-0796                                              *
*                                                                                             *
*  Turbo™ Pascal version 1.00A                                                                *
*                                                                                             *
*    purpose: This subroutine allows the user to enter several analyses                       *
*  at once.  Concentration units are mol/kg.  Format for data entry                           *
*  is  H (tab) OH (tab) NA (tab) CL.  For undetectable concentrations                         *
*  enter a small number such as 1.0e-10 instead of zero.                                      *
*********************************************************************************************}
procedure batchinput(var concentration :  molalconc);

begin

read(inputfile, analyticalH);          {this block reads in concentrations        }
read(inputfile, analyticalOH);        {from the file "inputdata"                  }
read(inputfile, analyticalNA);         {analyticalH corresponds to TH in text     }
read(inputfile, analyticalCL);

concentration[NA] := analyticalNA; { analytical = T; does not change through}
concentration[CL] := analyticalCL; { calculations performed on one analysis }
concentration[H] := analyticalH;
concentration[OH] := analyticalOH;
concentration[NACL] := 0.0;          {Initializes mNACL outside of iteration loop.    }
concentration[NAOH] := 0.0;          {This value will change if ion pairs are present. }
concentration[HCL] := 0.0;

end; {subroutine batchinput}
{*********************************************************************************************}
```

```
{*****************************************************************************************
*     subroutine: CHARGE ARRAY SUBROUTINE    V 1.0  June 6, 1989                          *
*                                                                                         *
*    written by:  Carl S. Kirby                                                           *
*                  Dept. of Geological Sciences                                           *
*                 Virginia Tech                                                           *
*                  Blacksburg, Virginia 25061-0796                                        *
*                                                                                         *
*     Turbo™ Pascal version 1.00A                                                         *
*                                                                                         *
*     purpose: This subroutine was used to assign the correct charge to                   *
* ions and to assign a charge of zero to ions not in the analysis                         *
* This subroutine does not as yet handle divalent or trivalent ions.                      *
*****************************************************************************************}
procedure chargearray( concentration :  molalconc; var charge : zARRAY);
begin

for i := H to HCL do                   {initializes charge to zero so that          }
begin                                     {elements not analyzed for will not be  }
  charge[i] := 0;                       {included in ionic strength calculation   }
end; {for}

for i := H to NA do                       {change charge of monovalent      }
begin                                     {cations from zero to 1 if            }
  if (concentration[i] > 0.0) then    {any of that ion is present            }
  charge[i] := 1;
end; {for}

for i := OH to CL do                     { change charge of monovalent  }
begin                                     { anions from zero to -1 if          }
  if (concentration[i] > 0.0) then    {any of that ion is present            }
  charge[i] := -1;
end; {for}


end; {procedure chrgarray}
{****************************************************************************************}
{*****************************************************************************************
*    subroutine IONIC STRENGTH     V 1.0       June 10, 1989                              *
*                                                                                         *
*    written by:  Carl S. Kirby                                                           *
*                  Dept. of Geological Sciences                                           *
*                 Virginia Tech                                                           *
*                  Blacksburg, Virginia 25061-0796                                        *
*                                                                                         *
*    Turbo™ Pascal version 1.00A                                                          *
*                                                                                         *
*     purpose: This subroutine calculates the "true" ionic strength of                    *
*           the solution using molalities corrected for                                   *
*           ion association (no correction on the first iteration).                       *
*            It also compares the calculated ionic strength to the                        *
*           analytical (initial) ionic strength to determine if                           *
*          the entire program has converged.                                              *
*                                                                                         *
*****************************************************************************************}
```

```
procedure ionstr(concentration : molalconc;  charge : zARRAY;
          var ionicstrength : real; var end_this_run : boolean);

var

  part : real;  {used to sum concentrations of ions & ion pairs}

begin {procedure ionstr}
part := 0.0;
if (ionstrcounter = 25) then {indicates no convergence}
  awflag := true;

for i := H to HCL do begin
 part := concentration[i]*sqr(charge[i]) + part;
end; {for}     {this loop sums the concentrations & squared charges}

ionicstrength := 1/2*(part);
if (abs(1.0 - oldionicstrength/ionicstrength) < 10e-7)
  then                          { this if clause tests for convergence based }
    end_this_run := true  { on the difference between the last two       }
  else begin              { values for the "true" ionic strength         }
    end_this_run := false;
    oldionicstrength := ionicstrength;
  end; {else}
ionstrcounter := ionstrcounter + 1;
end; {procedure ionicstrength}
{*****************************************************************************************}
{*****************************************************************************************
*   subroutine  D-H     V 1.0      September 14, 1988                                    *
*                                                                                        *
*   written by:  Carl S. Kirby                                                           *
*                Dept. of Geological Sciences                                            *
*                Virginia Tech                                                           *
*                Blacksburg, Virginia 25061-0796                                         *
*                                                                                        *
*   Turbo™ Pascal version 1.00A                                                          *
*                                                                                        *
*   purpose: This subroutine calculates the activity of water,                           *
*      individual ionic activity coefficients for ions and ion pairs.                    *
*      The equation for activity coefficients is a modification                          *
*      of the 1948 Stokes & Robinson equation which accounts for                         *
*      electrostatic and ion hydration effects.  The concentration                       *
*      used is corrected for ion association as is the ionic strength.                   *
*****************************************************************************************}
procedure DHequation( concentration : molalconc; charge : zARRAY;
  ionicstrength : real; var gamma : gamARRAY; var activityofwater :real);
label 20; {end of procedure DHequation}

var
  logGAMMA : extended;    {log base 10 of individual activity coefficient}
  A, B : real;       {Debye-Hückel parameters for 25°C}

begin
A := 0.5092;
B := 0.3283;
```

```
if (((55.51    {this if clause prevents the denominator in the activity of }
               {water calculation from going below 0                       }
  -((hyd[NA]-0.7)*concentration[NA] + (hyd[H]-1.0)*concentration[H]
  + (hyd[OH]-0.7)*concentration[OH] + (hyd[CL]-0.7)*concentration[CL]
  + (hyd[NACL]-0.7)*concentration[NACL] +(hyd[NAOH]-0.7)*concentration[NAOH]
  + (hyd[HCL]-1.0)*concentration[HCL])
  + (concentration[NA] + concentration[H]
  + concentration[OH] + concentration[CL] + concentration[NACL]
   + concentration[NAOH] +concentration[HCL]) )
  ) <= 0.0) then
begin
  writeln('aw failed');
  awflag := true;
  goto 20; {end of procedure DHequation}
end; {if}

activityofwater := 1 -
  ((concentration[NA] + concentration[H]
  + concentration[OH] + concentration[CL] +
  concentration[NACL] + concentration[NAOH] +concentration[HCL])/
  (55.51
  -((hyd[NA]-0.7)*concentration[NA] + (hyd[H]-1.0)*concentration[H]
  + (hyd[OH]-0.7)*concentration[OH] + (hyd[CL]-0.7)*concentration[CL]
  + (hyd[NACL]-0.7)*concentration[NACL] +(hyd[NAOH]-0.7)*concentration[NAOH]
  + (hyd[HCL]-1.0)*concentration[HCL])
  + (concentration[NA] + concentration[H]
  + concentration[OH] + concentration[CL] + concentration[NACL]
  + concentration[NAOH] +concentration[HCL])));

  {above equation is equation 5 in text with h values modified as shown in}
  {tables 1 and B.1                                                       }

if (activityofwater <= 0.0) then
begin
  writeln('aw failed');
  awflag := true;
  goto 20; {end of procedure DHequation}
end; {if}
for i := H to HCL do
begin
  logGAMMA := -(A *  sqr(charge[i])* sqrt(ionicstrength)) /
  ( 1.0 + B * AZERO[i] * sqrt(ionicstrength)) -
  ((hyd[i]) * ln(activityofwater))/ln(10.0) -
  ln(1.0 + (0.001 * 18.0 *(1.0 - hyd[i]) * concentration[i]))/ln(10.0);
     {above is modified from Stokes & Robinson (1948)  }
     {This loop estimates an individual activity        }
     {for ions & ion pairs which accounts for hydration }
     {and electrostatic effects, but not association.   }
     {gamma[i] is equal to gammaDH-hyd in text.         }

  gamma[i] := XpwrY(10.0, logGAMMA); {takes antilog of gamma[i]}
end; {for}
20 : end; {procedure DHequation}
{*****************************************************************************************************}
```

```
******************************************************************************************
*   subroutine TEST AGAINST ANALYTICAL VALUES    V 1.0                                    *
*                      June 10, 1989                                                      *
*   written by: Carl S. Kirby                                                             *
*               Dept. of Geological Sciences                                              *
*               Virginia Tech                                                             *
*               Blacksburg, Virginia 25061-0796                                           *
*                                                                                         *
*   Turbo™ Pascal version 1.00A                                                           *
*                                                                                         *
*    purpose: This subroutine tests for convergence of the mass balance                   *
*      calculations by looking at Na and Cl, then if convergence                          *
*      has not been achieved, it uses the continued fraction method                       *
*      to get a better approximation of the concentration                                 *
*      of the free ions.                                                                  *
*****************************************************************************************}

procedure test_against_analytical_values(sumSODIUM,sumCHLORINE, sumHYDROGEN,
   sumHYDROXL : real; var endroutine : boolean);

var
     ratioNA, ratioCL, ratioH, ratioOH : real; {R in equation 14}
begin
if ( abs((analyticalNA - sumSODIUM)/analyticalNA) < 10e-7 )
   or (abs((analyticalCL - sumCHLORINE)/analyticalCL) < 10e-7 )
   then
     endroutine := true {tells program that mass balance has converged}
   else begin
     ratioNA := analyticalNA / sumSODIUM;       {continued fraction method }
     ratioCL := analyticalCL / sumCHLORINE;  {for adjusting free ion          }
     ratioH := analyticalH / sumHYDROGEN;     {concentrations                 }
     ratioOH := analyticalOH / sumHYDROXL;
     concentration[NA] := ratioNA * concentration[NA];
     concentration[CL] := ratioCL * concentration[CL];
     concentration[H] := ratioH * concentration[H];
     concentration[OH] := ratioOH * concentration[OH];

     iterationcounter := iterationcounter + 1;
   end; {else}
end; {subroutine test_against_analytical_values)
{****************************************************************************************}
```

```
{****************************************************************************************************
*   subroutine DISTRIBUTION OF SPECIES      V 1.0                                                  *
*                          June 12, 1989                                                            *
*   written by: Carl S. Kirby                                                                       *
*               Dept. of Geological Sciences                                                        *
*               Virginia Tech                                                                       *
*               Blacksburg, Virginia 25061-0796                                                     *
*                                                                                                   *
*   Turbo™ Pascal version 1.00A                                                                     *
*                                                                                                   *
*    purpose: This subroutine calculates the concentration of ion pairs                             *
*      in solution, sums the total estimated concentration for                                      *
*      all components in solution, calls the subroutine test_against_                              *
*      analytical_values. and assigns new values to ion pair                                        *
*      concentrations after adjusting for mass balance and mass action.                             *
****************************************************************************************************}
procedure distributionofspecies;

label 30;{end of distributionofspecies}
var
   mNACL, mNAOH, mHCL, NAfree, CLfree, OHfree, Hfree : real;
      { calculated concentrations of ion pairs and ions in mol/kg}
   sumSODIUM, sumCHLORINE, sumHYDROXL, sumHYDROGEN : real;
      {sum of concentrations of species containing a component; }
     {should converge to T                                       }
   ratioNA, ratioH, ratioOH, ratioCL : real;{R in continued fraction method}
   endroutine : boolean; {flag to stop iteration}

begin
endroutine := false;   {initializes endroutine (see procedure test_against_}
                       {analytical_values)                                  }
repeat {until endroutine = true which signifies that the mass action/mass }
          {balance calculation has converged                               }

   mNACL := (concentration[NA] * concentration[CL] * gamma[NA] * gamma[CL])/
      (gamma[NACL]*KNACL);
      {this calculates the amount of NA tied up as NACL ion pair}
   mNAOH := (concentration[NA] * concentration[OH] * gamma[NA] * gamma[OH])/
     ( gamma[NAOH]*KNAOH);
      {this calculates the amount of NA tied up as NAOH ion pair}
   mHCL := (concentration[H] * concentration[CL] * gamma[H] * gamma[CL])/
     ( gamma[HCL] * KHCL);
      {this calculates the amount of CL tied up as HCL ion pair}
   NAfree := concentration[NA]; {amount of the NA as free ion}
   CLfree := concentration[CL]; {amount of the CL as free ion}
   Hfree := concentration[H];  {amount of the H as free ion}
   OHfree := concentration[OH]; {amount of the OH as free ion}

   sumSODIUM := mNACL + mNAOH + NAfree; {= total calculated Na}
   sumCHLORINE := mHCL + mNACL + CLfree;{= total calculated Cl}
   sumHYDROXL := mNAOH + OHfree;       {= total calculated OH}
   sumHYDROGEN := mHCL + Hfree;       {= total calculated H }
  if (iterationcounter >= 1000) then  {this if clause prevents infinite     }
  begin                               {loops in mass balance section       }
    awflag := true;
```

```
      goto 30; {end of distributionofspecies}
   end; {if}

    test_against_analytical_values (sumSODIUM, sumCHLORINE,sumHYDROGEN,
       sumHYDROXL, endroutine);
       {calls procedure test_against_analytical_values}

    concentration[NACL] := mNACL; {assigns association-adjusted value  }
    concentration[NAOH] := mNAOH; {to ion pair concentrations          }
    concentration[HCL] := mHCL;

    until (endroutine = true);

alpha[NACL] := concentration[NA]/analyticalNA;{degree of diss. for NA & OH ion}
alpha[HCL] := concentration[H]/analyticalH;{degree of diss. for H ion   }
alpha[CL] := concentration[CL]/analyticalCL;{degree of diss. for CL ion }
   {alpha's are equal to gamma sub a or alpha in text; the three lines }
   {immediately above multiply the association adjusted gamma times the }
   {DH&hydration-adjusted gamma to get the stoichiometric gamma        }
gamma[NA] := gamma[NA]*alpha[NACL];
gamma[OH] := gamma[OH]*alpha[NACL];    {stoichiometric gamma's}
gamma[H] := gamma[H]*alpha[HCL];
gamma[CL] := gamma[CL]*alpha[CL];
gamma[HCL] := gamma[HCL]*alpha[HCL];
gamma[NACL] := gamma[NACL]*alpha[NACL];
gamma[NAOH] := gamma[NAOH]*alpha[NACL];

30 : end; {procedure distributionofspecies}
{**********************************************************************************************}
{**********************************************************************************************
*    subroutine MEAN GAMMA          V 1.0                                                     *
*                       June 10, 1989                                                         *
*    written by: Carl S. Kirby                                                                *
*                 Dept. of Geological Sciences                                                *
*                Virginia Tech                                                                *
*                 Blacksburg, Virginia 25061-0796                                             *
*                                                                                             *
*     Turbo Pascal version 1.00A                                                              *
*                                                                                             *
*     purpose: This subroutine takes individual ionic activity                                *
*   coefficients and uses them to calculate the mean ionic activity                           *
*   coefficient for a salt.                                                                   *
***********************************************************************************************}

procedure meangamma;

var
  gammaNACL, gammaHCL, gammaNAOH : real;

begin

gammaNACL := sqrt(gamma[NA]*gamma[CL]);
gammaHCL := sqrt(gamma[H]*gamma[CL]);
gammaNAOH := sqrt(gamma[NA]*gamma[OH]);
```

```
actvtycoefNACL := gammaNACL;  {this block renames gammaMX to pass back to  }
actvtycoefNAOH := gammaNAOH;  {the main program                            }
actvtycoefHCL := gammaHCL;

end; {procedure meangamma}
{*******************************************************************************************}
*********************************************************************************************
*    subroutine  REPORT TO DATA FILE      V 1.0       June 10, 1989                         *
*                                                                                           *
*    written by:  Carl S. Kirby                                                             *
*                 Dept. of Geological Sciences                                              *
*                 Virginia Tech                                                             *
*                 Blacksburg, Virginia 25061-0796                                           *
*                                                                                           *
*     Turbo Pascal version 1.00A                                                            *
*                                                                                           *
*    purpose: This subroutine sends a report to a data file named                           *
*   "runnumber" and also sends the results to the screen.                                   *
********************************************************************************************}
procedure reporttodatafile;

begin

writeln(' gH   gNA  gOH    gCL   gNACL  gNAOH  gHCL');
if (awflag = true) then
   writeln(' invalid data immediately below');
writeln(gamma[H]:5:3, chr(9),'  ', gamma[NA]:5:3, chr(9),'  ', gamma[OH]:5:3,
 chr(9),'  ', gamma[Cl]:5:3, chr(9),'   ', actvtycoefNACL:5:3, chr(9),'  '
 ,actvtycoefNAOH:5:3, chr(9),'   ', actvtycoefHCL:5:3, chr(9));

if (awflag = true) then
   writeln(report, ' invalid data immediately below');

writeln(report, analyticalH:3:2, chr(9),' ',analyticalNA:3:2, chr(9),' ',
   analyticalOH:3:2, chr(9),' ',analyticalCL:3:2, chr(9),' ',
   ionicstrength:5:3, chr(9),'  ',
   activityofwater:5:3, chr(9),' ', gamma[H]:5:3
   , chr(9),' ', gamma[NA]:5:3, chr(9),' ', gamma[OH]:5:3
   , chr(9),' ', gamma[CL]:5:3, chr(9),'  ', actvtycoefNACL:5:3
   , chr(9),' ',actvtycoefNAOH:5:3, chr(9),' ', actvtycoefHCL:5:3
   , chr(9),'  ', alpha[NACL]:3:2,chr(9),'    ', alpha[HCL]:3:2
   , chr(9),' ',gamma[NACL]:5:3, chr(9),' ', gamma[NAOH]:5:3
   , chr(9),' ', gamma[HCL]:5:3);

end; {subroutine reporttodatafile}
{*******************************************************************************************}
{*******************************************************************************************}
begin {main program}

reset (inputfile, 'inputdata'); {scrolls the input file named "inputdata" to  }
                                {the beginning of the file                    }
rewrite(report, 'runnumber'); {creates the output text file named "runnumber";}
                              { any line w/ "report" goes to this file        }
writeln('You must have an input file named "inputdata" in Turbo Pascal to run' );
writeln('this version of SALTY DOG.  The format for input is as follows.' );
```

```
writeln('mH   mOH   mNa   mCl ');
writeln('mH   mOH   mNa   mCl ');
writeln('.     .     .     . ');
writeln('.     .     .     . ');
writeln('-1    1     1      1   [this line signals end of file]');
writeln('Concentration must be in mol/kg.  If any component, H, OH, Na, or Cl');
writeln('is not included in the analysis, you must still enter a very small');
writeln('number (1.0e-10) for such a component.');
writeln('Press return to continue.');
readln;

writeln(report,'The parameters for this run are:');{this statement goes to "runnumber"}

AZERO[H] := 8.7;   {This block contains the parameters used in SALTY DOG}
AZERO[NA] := 4.6;
AZERO[OH] := 3.6;
AZERO[CL] := 3.3;
hyd[H] := 7.0;
hyd[NA] := 2.4;
hyd[OH] := 3.1;
hyd[CL] := 2.4;
hyd[NACL] :=  3.9;
hyd[NAOH] :=  5.1;
hyd[HCL] :=  5.1;
KNACL := 15.0;
KNAOH := 15.0;
KHCL := 15.0;

writeln(report, 'for H,NA,OH,CL,NACL,NAOH,HCL');   {This block sends a record of              }
writeln(report, 'respectively');                                   {the parameters used to "runnumber}
writeln(report, 'å =',AZERO[H]:3:2 ,', ',AZERO[NA]:3:2 ,', ',
   AZERO[OH]:3:2,', ',AZERO[CL]:3:2);
writeln(report, 'h = ',hyd[H]:2:1,', ',hyd[NA]:2:1,', ',
   hyd[OH]:2:1,', ',hyd[CL]:2:1,', ',hyd[NACL]:2:1,', ',
   hyd[NAOH]:2:1 ,', ',hyd[HCL]:2:1);
writeln(report, 'for NACL,NAOH,HCL');
writeln(report, 'respectively');
writeln(report, 'K=',KNACL:2:1,',',KNAOH:2:1,',',KHCL:2:1);
writeln(report, 'T=25°C');
writeln(report);

writeln(report,'The abbreviations below stand for the following quantities:');
writeln(report,'molal analytical concentrations, "true" ionic strength, ');
writeln(report,'activity of water, individual molal ionic activity coefficients, ');
writeln(report,'mean molal ionic activity coefficients, degree of dissociation for ');
writeln(report,'sodium and hydrogen, and molal activity coefficients for ion pairs.');
writeln(report,'N.B., alphaNA refers to NaCl in NaCl solutions and ');
writeln(report,'refers to NaOH in NaOH solutions, alphaH refers to HCl in HCl solutions.');
writeln(report,'As yet, this program does not report alpha for mixed solutions.');
writeln(report);
writeln(report,' mH', chr(9),'  mNa',chr(9),'   mOH',chr(9),'  mCl',chr(9),'   I',chr(9),'     aw, ',chr(9),'
gH',
chr(9),'   gNA',chr(9),'   gOH',chr(9),'   gCL',chr(9),'  g±NACL',chr(9),'g±NAOH',chr(9),'g±HCL',
chr(9),'alphaNA',chr(9),' alphaH',chr(9),' gnacl ',chr(9),'gnaoh',chr(9),'  ghcl');
     {above are the data sent to "runnumber"; see "runnumber for meaning of symbols}
```

```
repeat  {until (analyticalH < 0.0) which indicates end of file}
        {this will cause an infinite loop if user doesn't enter a -1 for the last analysis}

 awflag := false;   {initializes flag within outside loop}

 batchinput(concentration);
 if (analyticalH < 0.0) then begin
   writeln('You must open the file named "runnumber" to be able to copy ');
   writeln(' the results in order to export data to another program for ');
   writeln('graphics, statistics, etc.');
   writeln ('Press return to get back to source code');
   readln;                           {This blocks prints message at end of program}
   goto 100;   {end of program}
 end {if}
 else;

 chargearray(concentration, charge);  {calls subroutine chargearray}

 iterationcounter := 0; {initializes counter in proc distributionofspecies}
 oldionicstrength := 0.0; {initialize}
 ionstrcounter := 0;  {initialize}

 end_this_run := false;

repeat  {until (end_this_run = true); this loop processes one analysis}
    ionstr(concentration, charge,ionicstrength,
    end_this_run); {calls subroutine ionstr}

   if (analyticalNA = 0.0) and (analyticalCL = 0.0) then
   begin                        {This if clause tells the program to quit  }
     end_this_run := true;  {if there is no Na or Cl in the input           }
     goto 20; {end of this repeat loop}
   end; {if}


   if (awflag = true) then
   begin                        {This if clause tells the program to quit  }
     end_this_run := true;  {if there is a lack of convergence.           }
     goto 20; {end of this repeat loop}
   end; {if}

    DHequation(concentration, charge, ionicstrength,
     gamma, activityofwater);     {calls subroutine DHequation}

   if (awflag = true) then
   begin                        {This if clause tells the program to quit  }
     end_this_run := true;  {if there is a lack of convergence.           }
     goto 20; {end of this repeat loop}
   end; {if}

    distributionofspecies;   {calls subroutine distributionofspecies}

   if (awflag = true) then
   begin                        {This if clause tells the program to quit  }
```

```
      end_this_run := true;  {if there is a lack of convergence.            }
      goto 20; {end of this repeat loop}
    end; {if}

20 : until (end_this_run = true);

  meangamma;   {calls subroutine meangamma}

  reporttodatafile; {calls subroutine reporttodatafile}

until (analyticalH < 0.0);

100: close(report);
close (inputfile);

end. {program SALTY DOG 1.0}
*****************************************************************************************************************
```

Sample output from SALTY DOG 1.0.

```
The conditions and results for the run named example A are:

for H,NA,OH,CL,NACL,NAOH,HCL
respectively
a =8.70, 4.60, 3.60, 3.30
h = 7.0, 2.4, 3.1, 2.4, 3.9, 5.1, 5.1
for NACL,NAOH,HCL
respectively
K=15.0,15.0,15.0
T=25°C

The abbreviations below stand for the following quantities:
molal analytical concentrations, "true" ionic strength,
activity of water, individual molal ionic activity coefficients,
mean molal ionic activity coefficients, degree of dissociation for
sodium and hydrogen, and molal activity coefficients for ion pairs.
N.B., alphaNA refers to NaCl in NaCl solutions and
refers to NaOH in NaOH solutions, alphaH refers to HCl in HCl solutions.
As yet, this program does not report alpha for mixed solutions.

mH    mNa   mOH   mCl   I     aw    gH    gNA   gOH   gCL   g±NACL g±NAOH g±HCL alphaNA alphaH gnacl gnaoh ghcl
0.00  6.00  0.00  6.00  5.241 0.758 3.402 1.071 0.998 0.904 0.984  1.034  1.754 0.87    0.70   2.676 3.583 2.871
1.00  0.00  0.00  1.00  0.964 0.961 1.054 0.676 0.649 0.623 0.649  0.662  0.810 0.98    0.96   1.141 1.198 1.187
3.00  0.00  0.00  3.00  2.566 0.859 2.444 0.783 0.788 0.663 0.720  0.786  1.273 0.94    0.86   1.703 2.044 1.916
5.00  0.00  0.00  5.00  3.414 0.730 6.951 1.103 1.233 0.773 0.923  1.166  2.318 0.92    0.68   3.133 4.572 3.857
```

APPENDIX C

PARAMETERS AND DATA TABLES

Though a value for K_d of 15.0 was chosen for NaCl, NaOH, and HCl, other values of K_d were investigated. The combinations of parameters for all values of K_d used in this study are shown in Table C.1. Tables C. 2 and C. 3 list the smoothed experimental activity of water and activity coefficient data, respectively, from Robinson and Stokes (1959) and the values for these quantities calculated by the model using four different values for K_d. The residuals for the activity of water and mean activity coefficient are shown in Table C. 4.

Table C.1. Choice of parameters for various values of the dissociation constant, K_d. The values of h are used in the modified Robinson and Stokes equation (2); the h' values are used in equation (5) in the calculation of the activity of water.

				species						
K_d(HCl)	K_d(NaCl)	K_d(NaOH)	parameter	H^+	Na^+	OH^-	Cl^-	HCl^0	$NaCl^0$	$NaOH^0$
5.0	5.0	5.0	å	9.8	4.8	3.8	3.5	-	-	-
			h	7.4	3.1	3.7	3.1	6.7	4.1	5.2
			h'	6.4	2.2	2.8	2.2	5.7	3.1	4.3
15.0	15.0	15.0	å	8.7	4.6	3.6	3.3	-	-	-
			h	7.0	2.4	3.1	2.4	5.1	3.9	5.1
			h'	6.0	1.7	2.4	1.7	4.1	3.2	4.4
100.0	100.0	100.0	å	8.7	4.6	3.5	3.3	-	-	-
			h	5.3	2.2	2.9	2.1	5.1	3.9	5.1
			h'	4.3	1.5	2.2	1.5	4.1	3.2	4.4
1000.0	1000.0	1000.0	å	8.7	4.6	3.5	3.3	-	-	-
			h	5.0	2.2	2.8	2.0	5.1	3.9	5.1
			h'	4.0	1.5	2.1	1.3	4.1	3.2	4.4

Table C.2 Estimated values of the activity of water, a_w, for different values of the dissociation constant, K_d, and concentration, m (mol/kg), for binary systems. Also given are the smoothed values (exp) from Robinson and Stokes (1959).

			K_d			
	m	$a_{w,exp}$	5	15	100	1000
a_w, $NaCl$-H_2O	0.5	0.984	0.982	0.982	0.982	0.982
	1.0	0.967	0.964	0.963	0.963	0.963
	2.0	0.932	0.927	0.926	0.926	0.926
	3.0	0.893	0.888	0.886	0.887	0.887
	4.0	0.852	0.848	0.846	0.847	0.847
	5.0	0.807	0.806	0.803	0.805	0.806
	6.0	0.760	0.761	0.758	0.762	0.764
a_w, $NaOH$-H_2O	0.5	0.984	0.982	0.982	0.982	0.982
	1.0	0.967	0.963	0.963	0.963	0.963
	2.0	0.930	0.924	0.924	0.923	0.924
	3.0	0.888	0.882	0.881	0.881	0.882
	4.0	0.841	0.837	0.836	0.837	0.837
	5.0	0.790	0.786	0.786	0.788	0.790
	6.0	0.734	0.728	0.732	0.737	0.739
a_w, HCl-H_2O	0.5	0.983	0.981	0.981	0.981	0.981
	1.0	0.963	0.961	0.961	0.961	0.962
	2.0	0.918	0.916	0.914	0.917	0.918
	3.0	0.864	0.863	0.859	0.866	0.869
	4.0	0.804	0.798	0.797	0.807	0.811
	5.0	0.739	0.718	0.730	0.738	0.744
	6.0	0.671	-	0.657	0.657	0.665

Table C.3 Estimated values of the mean molal activity coefficient, $\gamma\pm$, for different values of the dissociation constant, K_d, for binary systems. Also given are the smoothed values (exp) from Robinson and Stokes (1959).

			K_d			
	m	$a_{w,exp}$	5	15	100	1000
	0.5	0.681	0.678	0.676	0.679	0.679
	1.0	0.657	0.658	0.655	0.659	0.659
	2.0	0.668	0.674	0.672	0.677	0.677
$\gamma\pm_{NaCl}$	3.0	0.714	0.718	0.719	0.725	0.725
in NaCl-H_2O	4.0	0.783	0.781	0.785	0.794	0.793
	5.0	0.874	0.864	0.872	0.883	0.881
	6.0	0.986	0.974	0.984	0.996	0.992
	0.5	0.688	0.689	0.689	0.691	0.691
	1.0	0.677	0.677	0.677	0.680	0.681
	2.0	0.707	0.712	0.715	0.722	0.721
$\gamma\pm_{NaOH}$	3.0	0.782	0.785	0.791	0.802	0.801
in NaOH-H_2O	4.0	0.901	0.893	0.901	0.916	0.914
	5.0	1.074	1.051	1.055	1.074	1.070
	6.0	1.296	1.291	1.276	1.294	1.284
0.5	0.757	0.765	0.767	0.756	0.753	
	1.0	0.809	0.798	0.810	0.784	0.778
	2.0	1.009	0.939	0.988	0.923	0.906
$\gamma\pm_{HCl}$	3.0	1.316	1.175	1.273	1.160	1.124
in HCl-H_2O	4.0	1.762	1.581	1.694	1.548	1.479
	5.0	2.380	2.373	2.318	2.215	2.090
	6.0	3.220	-	3.283	3.447	3.260

Table C.4. Residuals for the activity of water, a_w, and the mean activity coefficient, $\gamma\pm$, for NaCl, NaOH, and HCl using various values of the dissociation constant, K_d. The residuals are calculated as Robinson and Stokes' (1959) reported value minus the value calculated by the present model.

		$K_d = 5.0$		$K_d = 15.0$		$K_d = 100.0$		$K_d = 1000.0$	
	mol/kg	a_w	$\gamma\pm$	a_w	$\gamma\pm$	a_w	$\gamma\pm$	a_w	$\gamma\pm$
NaCl	0.5	0.0016	0.003	0.001	0.005	0.0016	0.002	0.0016	0.002
	1.0	0.0029	-0.001	0.004	0.002	0.0039	-0.002	0.0039	-0.002
	2.0	0.0046	-0.006	0.006	-0.004	0.0056	-0.009	0.0056	-0.009
	3.0	0.0052	-0.004	0.007	-0.005	0.0062	-0.011	0.0062	-0.011
	4.0	0.0035	0.002	0.006	-0.002	0.0045	-0.011	0.0045	-0.01
	5.0	0.0008	0.01	0.004	0.002	0.0018	-0.009	0.0008	-0.007
	6.0	-0.0012	0.012	0.002	0.002	-0.0022	-0.01	-0.0042	-0.006
NaOH	0.5	0.002	-0.001	0.002	-0.001	0.002	-0.003	0.002	-0.003
	1.0	0.0043	0.000	0.004	0.000	0.0043	-0.003	0.0043	-0.004
	2.0	0.006	-0.005	0.006	-0.008	0.007	-0.015	0.006	-0.014
	3.0	0.006	-0.003	0.007	-0.009	0.007	-0.02	0.006	-0.019
	4.0	0.0042	0.008	0.005	0.000	0.0042	-0.015	0.0042	-0.013
	5.0	0.0038	0.023	0.004	0.019	0.0018	0.000	-0.0002	0.004
	6.0	0.0056	0.005	0.002	0.02	-0.0034	0.002	-0.0054	0.012
HCl	0.5	0.002	-0.008	0.002	-0.01	0.002	0.001	0.002	0.004
	1.0	0.002	0.011	0.002	-0.001	0.002	0.025	0.001	0.031
	2.0	0.002	0.07	0.004	0.021	0.001	0.086	0.000	0.103
	3.0	0.001	0.141	0.005	0.043	-0.002	0.156	0.005	0.192
	4.0	0.006	0.181	0.007	0.068	-0.003	0.214	0.007	0.283
	5.0	0.021	0.007	0.009	0.062	0.001	0.165	0.005	0.29