

## On the use of semiempirical electrolyte theories for the modeling of solution chemical data

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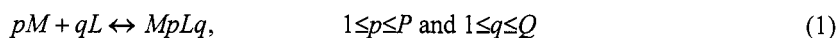
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*Abstract:* In order to compare thermodynamic data on complex formation reactions, protolytic, redox and solubility equilibria determined in ionic media of various types, it is necessary to refer them to a common standard state, usually with pure water as the solvent. This requires estimates of the activity coefficients of reactants and products. We have compared the Brønsted-Guggenheim-Scatchard specific ion interaction (SIT) model and the Pitzer models and shown that they for all practical purposes are equivalent, for the description of the ionic medium/ionic strength dependence of concentration equilibrium constants for ionic strengths up to 3 to 4 m. Equations relating the SIT specific ion interaction coefficients  $\epsilon(i,j)$  and the Pitzer parameters  $\beta^{(0)}$  and  $\beta^{(1)}$  for ionic components, and  $\Delta\beta^{(0)}$  and  $\Delta\beta^{(1)}$ , for reactions are presented.

### Thermodynamic modeling of complex formation reactions

Thermodynamic modeling requires information of both standard state and excess properties. A large number of data of this type is available both for systems of strong (single and mixtures) and weak electrolytes. This communication deals with data of the latter type, mainly for complex formation reactions.

A complex formation reaction in a two-component system M,L in aqueous solution can be described by:



where  $p$  and  $q$  are stoichiometric coefficients with maximum values  $P$  and  $Q$ , respectively. In most systems, except some simple protolytes, there are many complexes present simultaneously, and in comparable concentrations. In order to determine the chemical speciation of such systems it is necessary to vary the total concentrations of the components, while keeping the activity coefficients of reactants/products as constant

as possible. This cannot be achieved in solutions of low ionic strength, but requires the presence of an ionic medium with a concentration much higher than that of the components M and L (ref. 1). For users of thermodynamic data it is essential to have confidence both in the *chemical model* of a certain system, and the *numerical values* of its equilibrium constants. Both require the estimation of activity coefficients referred to a *common* standard state. In the first case one uses the pure ionic medium, in the second a common reference ionic medium, usually the "infinite dilute" solution with pure water as the solvent.

### **The Pitzer and the Brønsted-Guggenheim-Scatchard ion interaction models**

In the *Pitzer model* (refs. 2-4) the excess Gibbs energy of an aqueous solution is expressed as a sum of a Debye-Hückel term and a power (virial) series in the molality of the solute species, c.f. eqn.(2), where  $f'$  and  $g(\alpha\sqrt{I})$  are known functions of the ionic strength,  $I$ . The second virial coefficient is represented as an empirical function of  $I$ , and the third virial coefficient is assumed to be a constant. The virial coefficients account for all binary interactions between anions and cations, binary interactions between ions for the same sign but different charges, and all possible interactions between groups of three ions. Pitzer considered his model as an extension of the simple but general approach, presented by Brønsted (ref.5) as extended by Guggenheim and Scatchard (refs. 6,7). The *SIT-model* describes the long range electrostatic interactions with a slightly different Debye-Hückel term, and a sum of terms describing the short range, non-electrostatic binary interactions between ions of opposite charge, c.f. eqn.(5). The interaction coefficients between ions  $i$  and  $j$ , are denoted  $\epsilon_{ij}$ , and are assumed to be independent of the concentration. This near constancy was recognized long ago (ref.4) at high molality. However,  $\epsilon_{ij}$  is concentration dependent at low molality (refs. 2,8), which from a practical point of view is a minor problem because the term  $(\epsilon_{ij}m)$ , then makes only a small contribution to the calculated activity coefficients. The consideration in explicit form of the ionic strength dependence of the second virial coefficient through  $\beta^{(1)}$ , was one of the principal innovations in the Pitzer model.

The SIT-model has successfully been used for the description of the concentration dependence of complex formation reactions and other chemical equilibria, and the extrapolation of these equilibrium constants to infinite dilution (refs. 6,7,9,10). A large number of ion interaction coefficients have been compiled (refs. 6,7), both for simple ions and complexes, some useful methods of estimation of the unknown interaction coefficients for ion metal complexes have been proposed (ref. 10).

The Pitzer model is widely used in geochemistry and chemical engineering to model systems of mixed or single strong electrolytes at high concentrations, e.g. for describing phase equilibria in concentrated aqueous solutions at different temperatures (e.g. refs. 2-4). A survey of the methodology is given by Grenthe *et al.* (ref. 6).

### The ionic strength dependence of equilibrium constants in ionic media

Both the Pitzer and the SIT equations can be simplified at "trace" concentrations of reactants and products. The only binary interactions that have to be taken into account are those between the reactants/products and the ionic medium ions, and those between the ionic medium ions themselves. Triple interactions need to be considered only

### Determination of interaction parameters

The interaction parameters in the two models must be determined from experimental mean activity coefficients, osmotic coefficients and/or concentration equilibrium constants. The accuracy of these data are typically  $\pm 0.005$  in  $\log \gamma_{\pm}$ , or  $\Phi$ , and ten to fifty times lower for concentration equilibrium constants. These constants have usually been determined at fairly few ionic strengths. For the users of thermodynamic data it is essential to be aware of the limitations of the methods used to make activity corrections, and the consequences of approximations in the models. It is useful to find relationships, c.f. eqns.(6,7), between the interaction parameters in the two models, and between the corresponding quantities for reactions. This is practical when one wishes to use the extensive compilations of Pitzer parameters for strong electrolytes together with the compilation of SIT parameters for complexes.

between the reactants/products and the ionic medium ions, not between the reactants/products. The contribution of the third virial coefficient  $C$ , may also be neglected at ionic strengths less than 4 m. Under these assumptions the analytical statements for the concentration dependence of the concentration equilibrium constant for a chemical reaction of the type:

$$\sum_i p_i Q_i + r H_2 O(l) = 0 \quad (2)$$

is given by the following statements for the Pitzer and SIT-models, respectively. This equations have been obtained from the corresponding equations for the activity coefficients using the same notation as in (refs.2-4,6).

The Pitzer model:

$$\begin{aligned} \ln K^o = \ln K + r \ln a_{H_2O} + \sum_i p_i Z_i^2 (f^{\gamma} + m^2 B'_{NX}) + 2m \sum_i p_i B_{ij} + 2m^2 \sum_i p_i C_{ij} + \\ 2m \sum_i p_i \phi_{ii} + m^2 \sum_i p_i \psi_{ij} + m^2 \sum_i p_i |Z_i| C_{NX} = \\ \ln K + r \ln a_{H_2O} + \Delta Z^2 (f^{\gamma} + m B'_{NX}) + m^2 \Delta |Z| C_{NX} + 2m(\Delta B + \Delta \phi) + 2m^2 \left( \Delta C + \frac{\Delta \psi}{2} \right) \end{aligned} \quad (3)$$

where:

$$\Delta B = \Delta\beta^{(0)} + \Delta\beta^{(1)} g(\alpha I^{1/2}) \quad (2), \text{ and } \Delta\beta^{(0)} = \sum_i p_i \beta_i^{(0)} \text{ and } \Delta\beta^{(1)} = \sum_i p_i \beta_i^{(1)}.$$

The unknown parameters have to be determined by a regression analysis of eqn.(3) in the form:

$$\ln K^o = \ln K + r \ln a_{H_2O} + \Delta Z^2 (f^\gamma + m^2 B'_{NX}) + m^2 \Delta |Z| C_{NX} + 2mX_1 + 2mg(\alpha I^{1/2}) X_2 + 2m^2 X_3 \quad (4) \text{ where:}$$

$$X_1 = \Delta\beta^{(0)} + \Delta\phi, X_2 = \Delta\beta^{(1)}, X_3 = \Delta C + 1/2 \Delta\psi.$$

The SIT model

$$\ln K^o = \ln K + r \ln a_{H_2O} - \frac{AI^{1/2}}{1+1.5I^{1/2}} \sum_i p_i Z_i^2 + m \sum_i p_i \varepsilon_\gamma(i, j) = \ln K + r \ln a_{H_2O} - \frac{A\Delta Z^2 I^{1/2}}{1+1.5I^{1/2}} + m\Delta\varepsilon_\gamma \quad (5)$$

We have tested the two models using concentration equilibrium constants for a simple protolytic reaction,  $H^+ + SO_4^{2-} \leftrightarrow HSO_4^-$ , studied in  $NaClO_4$  media. 18 potentiometric determinations reported in "Stability Constants" (refs. 11-13) and by Sapijesko *et al.* (ref. 14) have been used. They were recalculated into molality units and to 298.15 K where necessary, and cover an ionic strength range from 0.1 to 3.5 m. The ionic strength dependence of the higher-order electrostatic unsymmetrical mixing term  $E_{ClO_4, SO_4}(I)$  was taken into account as recommended in (ref. 3). Independent data of the Pitzer interaction coefficients for all reactants and products are known for this reaction. In general equilibrium constant data are much less precise than in the example and all Pitzer parameters are rarely available. It is straight forward to use the SIT-model, this is not the case for the Pitzer model. The following methods to estimate  $\log K^o$ , and the Pitzer parameters were tested:

- I. the determination of the whole set of parameters  $\log K^o, X_1, X_2, X_3$ ;
- II. the determination of  $\log K^o, X_1, X_2$ , *i.e.* neglecting the contribution of all ternary interactions;
- III. the determination of  $\log K^o, X_1, X_3$ , *i.e.* assuming  $\beta^{(1)}=0$  for all reaction participants as suggested by (ref. 15);
- IV. the determination of  $\log K^o, X_1$ , *i.e.* using the smallest possible number of parameters in the Pitzer model.
- V. the determination of  $X_1, X_2$  and  $X_3$  using the CODATA value of  $\log K^o$  (or the value determined from the SIT-model) as a fixed parameter.

The symbol (0) in Table 1 means that the corresponding parameter was set equal to zero in the data fitting. All uncertainties are given as  $\pm 3\sigma$ , where  $\sigma$  is the mean square error of an unknown. The "true" value of  $\log K^o$  was that recommended by CODATA (ref. 16). The "Tabulated" values of the Pitzer parameters were calculated from the values of

$\beta^{(0)}$ ,  $\beta^{(1)}$ , C for NaHSO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, and HClO<sub>4</sub> (ref. 3). The parameters for binary and ternary interactions of ClO<sub>4</sub><sup>-</sup> with HSO<sub>4</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup> are unknown, but the possible effect of neglecting them is probably within proposed uncertainties of the "Tabulated" values.

Table 1. Regression results for data of log *K* for the reaction H<sup>+</sup>+SO<sub>4</sub><sup>2-</sup>⇌HSO<sub>4</sub><sup>-</sup> in NaClO<sub>4</sub> ionic media at 298.15 K. All uncertainties are given as 3σ. values within parenthesis in column V were obtained with X<sub>3</sub>=0.

The model	SIT	Parameters in the Pitzer model	I	II	III	IV	V	Tabulated values
log <i>K</i> <sup>o</sup> =1.989 ±0.084		log <i>K</i> <sup>o</sup>	2.10 ±0.27	2.04 ±0.20	2.13 ±0.13	2.23 ±0.11	1.989	1.987 ±0.0009
Δε=0.003 ±0.051		X <sub>1</sub>	-0.45 ±0.88	-0.19 ±0.16	-0.56 ±0.21	-0.34 ±0.21	-0.18±0.60 (-0.16±0.11)	-0.15 ±0.05
		X <sub>2</sub>	-0.46 ±3.40	-1.39 ±1.34	(0)	(0)	-1.67±1.67 (-1.73±0.57)	-0.995
		X <sub>3</sub>	0.05 ±1.02	(0)	0.07 ±0.07	(0)	0.005 ±0.128 (0)	-0.006 ±0.010

From the example we draw the following conclusions: The simple one-parameter SIT-model reproduces the experimental data very well, it also results in a reliable determination of log *K*<sup>o</sup>, with a small uncertainty and in an excellent agreement with the CODATA recommendation. In the Pitzer model there is a very strong correlation between the parameters, which makes it difficult to obtain precise values. Hence the estimates of log *K*<sup>o</sup> and the values of the coefficients X<sub>1</sub> differ fairly much between the different models, and from the CODATA value. As expected, the determination of the complete set of constants results in very large uncertainties (model I). Models III (assuming X<sub>2</sub>=Δβ<sup>(1)</sup>=0) and IV give unreliable estimations of the parameters and should be avoided. Only II which includes X<sub>1</sub> (≈Δβ<sup>(0)</sup>) and X<sub>2</sub> (Δβ<sup>(1)</sup>) can be recommended with precaution. Model V gives an estimate of the uncertainty of the Pitzer parameters, and shows that it is not possible to determine a precise value of the parameters, even from these very precise log *K* data and with a known value of log *K*<sup>o</sup>.

We have tested many more examples with the same conclusions as for the reaction discussed above: it is impossible to get a statistically significant value of the ternary interaction parameter X<sub>3</sub>; the value of log *K*<sup>o</sup> has a larger uncertainty than the corresponding SIT estimate; the estimate of X<sub>2</sub> (Δβ<sup>(1)</sup>) is very uncertain. These

conclusions are similar to those of (ref. 17) for osmotic coefficients data for 1-1 electrolytes, even though the typical errors in the parameter estimates are at least two orders of magnitude smaller than for complex formation reactions.

For chemical equilibria studied in the presence of an ionic medium ( $I < 4$  m) one can neglect all parameters accounting for triple ion interactions and binary higher-order electrostatic mixing terms for the reactants/products. For reactions in 1-1 ionic media we can equate eqns. (4) and (5), which after elementary transformations gives:

$$Y = \left\{ A_{\Phi} \left[ \frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) - \frac{3I^{1/2}}{1 + 1.5I^{1/2}} \right] - m^2 B'_{NX} \right\} / 2m = \frac{1}{\Delta Z^2} (X_1 - \frac{\Delta \epsilon_{\gamma}}{2}) + \frac{X_2}{\Delta Z^2} g(\alpha I^{1/2}) \quad (6)$$

*i.e.*  $Y$  is a linear function of  $g(\alpha I^{1/2})$ , with the slope  $X_2/\Delta Z^2$  and the intercept  $(X_1 - \Delta \epsilon_{\gamma}/2)/\Delta Z^2$ . The values of  $Y$  can be calculated from the Debye-Hückel parameter  $A_{\Phi}$  and  $B'_{NX}$ , *i.e.*  $\beta^{(1)}$  for the 1-1 ionic medium electrolyte, these data are available.

In Fig.1 we have plotted the values of  $Y$  for some common 1-1 ionic media. The linearity is good for all electrolytes considered, and the values of the quantities  $(X_1 - \Delta \epsilon_{\gamma}/2)/\Delta Z^2$  and  $X_2/\Delta Z^2$  can be determined for each electrolyte. As the values, especially the slope, do not vary much with the nature of electrolyte, one unique set of parameters,  $(X_1 - \Delta \epsilon_{\gamma}/2)/\Delta Z^2 = 0.029 \pm 0.005$ , and  $X_2/\Delta Z^2 = 0.337 \pm 0.014$  can be used for all these ionic media. The uncertainties are given as  $3\sigma$ . This finding is very convenient for the estimation of the Pitzer parameter  $\Delta\beta^{(1)}$  for reactions, because it only requires the value of the sum of squared charges of the ions participating in the reaction,  $\Delta Z^2$ . One can also show that for iso-coulombic reactions, where  $\Delta Z^2 = 0$ , eqn.(6) is consistent with  $\Delta\beta_{\gamma}^{(1)} = 0$ . If values of the Pitzer parameters  $\beta_{\gamma}^{(1)}$  are known for the single ion participants in the reaction, then the value of  $\beta^{(1)}$  accounting for the interaction of the complex with the ionic medium ion of opposite charge may be estimated.

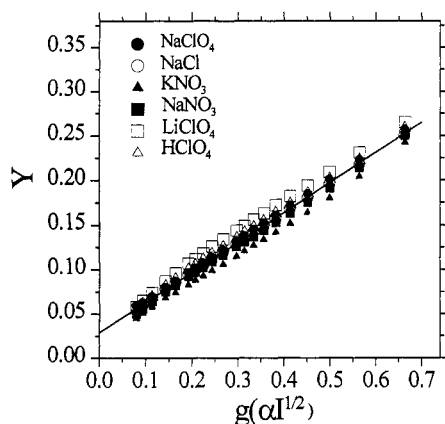


Fig. 1. The relationship between  $\Delta \epsilon_{\gamma}$ , and  $\Delta\beta_{\gamma}^{(0)}$  and  $\Delta\beta_{\gamma}^{(1)}$  in 1:1 ionic media, c.f. eqn. (6).

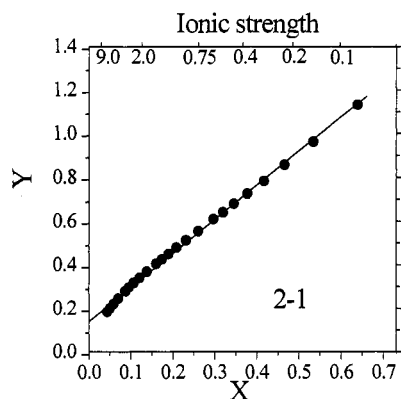


Fig. 2. The relationship between  $\epsilon_{\gamma}$ , and  $\beta_{\gamma}^{(0)}$  and  $\beta_{\gamma}^{(1)}$  for strong 1:2 and 2:1 electrolytes, c.f. eqn. (10)

Examination of tabulated Pitzer coefficients reveal that there is a correlation between  $\beta^{(1)}$  and the charge type for single electrolytes. This can be demonstrated using the same approximations as in eqn.(6) to derive the following expression relating the Pitzer and SIT parameters for single electrolytes:

$$\ln \gamma_{\pm} = -|Z_M Z_L| A_{\Phi} \left\{ \frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right\} + m \frac{2\nu_M \nu_L}{\nu} (2\beta_{ML}^{(0)} + 2\beta_{ML}^{(1)} X) \quad (7)$$

where

$$X = \frac{1}{\alpha^2 I} \left\{ 1 + (1 + \alpha I^{1/2} - \frac{\alpha^2 I}{2}) \exp(-\alpha I^{1/2}) \right\} \quad (8)$$

the mean activity coefficient in the BGS-model is equal to:

$$\ln \gamma_{\pm} = -\frac{A|Z_M Z_L| I^{1/2}}{1 + 1.5I^{1/2}} + m \frac{2\nu_M \nu_L}{\nu} \varepsilon_{\gamma}(M, L) \quad (9)$$

Taking into account that  $A=3A_{\Phi}$  and making elementary transformations we obtain:

$$Y = -\frac{A_{\Phi}|Z_M Z_L| \nu}{4\nu_M \nu_L m} \left\{ \frac{3I^{1/2}}{1 + 1.5I^{1/2}} - \frac{I^{1/2}}{1 + bI^{1/2}} - \frac{2}{b} \ln(1 + bI^{1/2}) \right\} = (\beta_{ML}^{(0)} - \frac{\varepsilon_{\gamma}(M, L)}{2}) + \beta_{ML}^{(1)} X \quad (10)$$

Eqns.(6) and (10) were obtained by neglecting the contribution of the terms for higher-order electrostatic unsymmetrical mixing.  $X$  and  $Y$  are known functions of the ionic strength. In regions where the Pitzer and SIT models are equivalent we expect a linear relationship between  $X$  and  $Y$ , for each charge type, c.f. Fig. (2) for 1:2 and 2:1 electrolytes. By including these terms the slope of the function  $Y$  is changed somewhat, particularly for ions of charge 3, or higher. However, for higher-charged ions it is possible to determine the relative contributions of  $\beta^{(0)}$  and  $\beta^{(1)}$ , provided a sufficiently large number of precise  $\log K$  data are available. This is because the parameter  $B$  depends much stronger on ionic strength for the higher charge type electrolytes, which have large absolute values of  $\beta^{(1)}$ .

## Conclusions

We have demonstrated that the determination of the Pitzer parameters from  $\log K$  data is an ill-conditioned problem which requires some model simplifications. From our experience,  $\log K$  data for complex formation reactions rarely permit the determination of more than one interaction parameter. Therefore, we suggest the following strategy:

- use the SIT equation to obtain  $\log K^{\circ}$ ,
- use all the Pitzer parameters for single ions, the known values of binary and ternary mixing terms for interactions involving single ion reactants/products and the ions of the ionic medium, and  $\log K^{\circ}$  value as fixed parameters in the regression analysis to obtain  $\beta^{(0)}$  and  $\beta^{(1)}$  for the complex species. If the charge of the complex does not exceed 2,

estimate  $X_2$  from the  $\Delta Z^2$  value, and use this as a fixed parameter in the regression. All terms, including  $m^2 \Delta |Z| C_{NX}$  (see Eq.(3)) and higher-order electrostatic unsymmetrical mixing terms for all ions, including the complexes, should be taken into account in the regression procedure.

- in order to describe equilibrium data at higher ionic strengths or mixed electrolyte systems, it may be necessary to determine additional interaction parameters, as described by Könneke *et al* at this conference. This can only be achieved by additional equilibrium constant measurements under these conditions.

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