

# Estimation of the Pitzer Equation Parameters for Aqueous Complexes. A Case Study for Uranium at 298.15 K and 1 atm

Andrey Plyasunov,<sup>a,†</sup> Thomas Fanghänel<sup>b</sup> and Ingmar Grenthe<sup>a,\*</sup>

<sup>a</sup>Inorganic Chemistry, Kungliga Tekniska Högskolan (KTH), S-10044 Stockholm, Sweden and <sup>b</sup>Forschungszentrum Karlsruhe, Institut für Nukleare Entsorgungstechnik, Postfach 3640, D-76021 Karlsruhe, Germany

## Dedicated to Professor Lennart Ebersson on the occasion of his 65th birthday

Plyasunov, A. V., Fanghänel, T. and Grenthe, I., 1998. Estimation of the Pitzer Equation Parameters for Aqueous Complexes. A Case Study for Uranium at 298.15 K and 1 atm. – Acta Chem. Scand. 52: 250–260. © Acta Chemica Scandinavica 1998.

A procedure to estimate the Pitzer parameters for complexes or complex formation reactions from a small number of equilibrium constants ( $\log K$  vs.  $I$ ) obtained in 'constant ionic media' is discussed in some detail. It is then often impossible to determine both  $\log K^\circ$ , the equilibrium constant at  $I=0$ , and all Pitzer parameters, hence some estimations or other simplifications are necessary. Solution coordination chemists have therefore preferred to use the less parameterized Brønsted–Guggenheim–Scatchard (SIT) model. By comparison of analytical statements for the mean activity coefficients and equilibrium constants, for the SIT and Pitzer models we have shown that they are equivalent for ionic strengths less than  $4 \text{ mol kg}^{-1}$ , and have also established relationships between the Pitzer parameter  $\beta^{(1)}$  and the charge type of the interacting ions, and between  $\Delta\beta^{(1)}$  for a complex formation reaction and  $\Delta Z^2$  for the reaction, where  $\Delta Z^2$  is the sum of the squared charges of the reactants/products with the proper stoichiometric coefficients. The first relationship is based on data in single electrolyte systems and the second on equilibrium-constant data determined in ionic media. For reactions involving species of charges one and two in 1–1 electrolyte ionic media we recommend the use of  $\Delta\beta^{(1)}/\Delta Z^2 = 0.337 \pm 0.014 \text{ kg mol}^{-1}$  for the estimation of the  $\Delta\beta^{(1)}$  at 298.15 K and 1 atm. In this way we have used concentration equilibrium constant data to estimate  $\log K^\circ$  and Pitzer parameters  $\beta^{(0)}$  and  $\beta^{(1)}$  for more than 30 uranium complexes with other ions at 298.15 K and 1 atm. The procedure makes it possible to use the information on complex formation, acid/base and redox equilibria obtained in ionic media together with the Pitzer parameters for strong electrolytes for the modeling of complex equilibrium systems over a broad range of ionic strength/ionic medium compositions, up to at least  $4 \text{ mol kg}^{-1}$ .

Many aqueous solution systems are complex multicomponent mixtures, in which the speciation of the solutes is a function of composition, temperature, pressure and master variables such as pH, Eh, the partial pressure of  $\text{CO}_2$ , etc. To perform a thermodynamic modeling of these equilibria one has to know both standard state and excess properties.

Compilations of thermodynamic data always contain information referring to standard state conditions, e.g. defined according to IUPAC.<sup>1</sup> Users of these data must therefore recalculate them for the conditions present in

the system under study. Thermodynamics, in combination with physico-chemical theories, provides the framework for such calculations.

The Pitzer model<sup>2,3</sup> is one of the most comprehensive approaches for describing the excess Gibbs energy of multicomponent strong electrolyte systems, and has been used to describe, for example, the five-component seawater system.<sup>4</sup> The applications to systems where strong complexes are formed are scarce, with the exception of some weak protolytes (e.g. carbonic acid, phosphoric acid, hydrogen sulfate) where experimental data may be obtained at very low ionic strengths. Systems with weak complex formation can be described within the Pitzer framework as strong ion–ion interactions. This is not possible when strong complexes are formed: they must

† Permanent address: Institute of Experimental Mineralogy, Chernogolovka, Moscow District, 142432 Russia.

\* To whom correspondence should be addressed.

be taken into account as such. The only available information for the determination of the interaction parameters of complexes is in general experimentally determined (concentration) equilibrium constants in different ionic media.

The lack of Pitzer parameters for metal complexes makes it difficult to use this formalism to describe the trace metal speciation in ground and surface water systems. Information of this type may be essential, e.g. when estimating the toxicity of trace elements and in safety assessments of waste repositories of different types.

For strong electrolytes, either single or mixtures, it is often possible to determine all Pitzer parameters because one has experimental data of high precision, typically better than 0.01 in the osmotic coefficient,  $\Phi$ , or 0.005 in  $\ln \gamma_{\pm}$ . Nevertheless, a statistical analysis of the Pitzer equations<sup>5</sup> has shown that the retrieval of the parameters even from an extensive array of such experimental data is not a trivial exercise. The main problem in the least-squares analysis of the Pitzer model is the correlation between the  $\beta^{(1)}$  and  $C^{\Phi}$  parameters (the notation is the same as that used by Pitzer),<sup>2,3</sup> and therefore the large relative standard errors in their estimates: 'the relative standard error in this ( $\beta^{(1)}$ ) parameter ... is typically at least one order of magnitude greater than the relative standard errors in the other parameters'.<sup>5</sup>

For reasons given below, these problems are aggravated if Pitzer parameters have to be determined from the ionic medium/ionic strength dependence of equilibrium constants. An examination of compilations of stability constants (e.g. Sillén and Martell<sup>6,7</sup> and Högfeldt<sup>8</sup>) reveals the following characteristic features of the data: (i) Often less than ten experimental values of  $\log K$  have been reported for a particular reaction in a certain ionic medium; the ionic strength interval typically ranges between 0.1 and 4 mol kg<sup>-1</sup>. (ii) It is rarely possible to determine equilibrium constants at very low ionic strengths, and theoretically based estimates of  $\log K^{\circ}$ , the equilibrium constant at zero ionic strength, are therefore necessary. (iii) The accuracy of  $\log K$  is often smaller than the precision of individual measurements. As stated by Beck and Nagypal,<sup>9</sup> 'agreement within  $\pm 0.05$  log units is classified as very good agreement, even in systems that can be studied experimentally without difficulty'. This means that  $\log K$  data are at least 10–30 times less accurate than the values of osmotic coefficients.

These facts will strongly complicate the determination of Pitzer parameters from such data using regression analysis, and some simplifications are necessary. Solution coordination chemists<sup>10–12</sup> have therefore used the less parametrized Brønsted–Guggenheim–Scatchard (SIT) model (cf. the following section) to describe the concentration dependence of complex formation reactions and other chemical equilibria, and the extrapolation of these equilibrium constants to zero ionic strength. A large number of ion interaction coefficients have been compiled by Ciavatta<sup>11,13</sup> and Grenthe *et al.*,<sup>12</sup> both for simple

ions and complexes; some useful estimation methods of the unknown interaction coefficients for metal–ion complexes have also been proposed.<sup>13</sup> In this communication we will demonstrate how the available information on SIT interaction parameters for systems where the reactants/products are present in 'trace' concentrations in the presence of an ionic medium, may be transferred to the Pitzer formalism. This will require defensible estimations of the Pitzer parameters  $\beta^{(0)}$  and  $\beta^{(1)}$ , and the corresponding quantities for chemical reactions.

### Development history of the specific ion interaction models

Pitzer<sup>2,3</sup> considered his model as an extension of the simple but general approach, presented by Guggenheim,<sup>14</sup> who proposed the following equation, describing the concentration dependence of the activity coefficient of a cation  $M$  in a mixture:

$$\ln \gamma_M = -\frac{AZ_M^2 I^{1/2}}{1 + I^{1/2}} + \sum_a B_{Ma} m_a \quad (1)$$

where  $A$  is the Debye–Hückel parameter (note that  $A = 3A_{\Phi} = 0.5100 \ln 10 \text{ kg}^{1/2} \text{ mol}^{-1/2}$  at 25 °C, where  $A_{\Phi}$  is the corresponding parameter in the Pitzer model). The summation involves all anions,  $a$ , present in solution.  $B_{Ma}$  is an interaction parameter specific for each cation–anion pair,  $M, a$ . In accordance with the Brønsted<sup>15</sup> postulate on specific interaction between ions, the terms for ions of the same charge sign are equal to zero. The analogous expression for the anion  $L$  is obtained by changing the subscripts  $M$  and  $a$  for  $L$  and  $c$ , respectively, where  $c$  denotes a cation in general. A detailed discussion of the use of the Guggenheim model for describing the concentration dependence of the osmotic coefficient and the mean activity coefficients in both single and mixed electrolyte solutions is given in Pitzer and Brewer.<sup>16</sup>

Scatchard<sup>17,18</sup> suggested that the denominator  $(1 + I^{1/2})$  should be replaced by  $(1 + 1.5I^{1/2})$  to decrease the concentration dependence of the interaction coefficients at low ionic strengths, giving the following expression for the activity coefficient of the reactants in an ionic medium:

$$\ln \gamma_i = -\frac{AZ_i^2 I^{1/2}}{1 + 1.5I^{1/2}} + \sum_j \varepsilon_{\gamma}(i, j) m_j \quad (2)$$

where  $\varepsilon(i, j)$  is the specific ion interaction coefficient for ion  $i$  and the different counter-ions  $j$ . Eqn. (2) is known as the Brønsted–Guggenheim–Scatchard (SIT) model.

The SIT model ignores both binary interactions between species of the same charge, and the contribution of ternary interactions to the activity coefficients. The constancy of the ion interaction coefficients in the SIT model at high molality was recognized long ago. However, the parameter is concentration dependent at low molality.<sup>2,16</sup> These variations give only a small contribution to the accuracy of the calculated activity coefficients, because the product  $\varepsilon(i, j) m_j$  makes only a

small contribution at low molality, cf. eqn. (2). The concentration dependence of the interaction parameters reflects the concentration dependence of the sum of the radial distribution functions for like-charged and unlike-charged ions; see Pitzer.<sup>2,3,17</sup>

In the Pitzer formalism the concentration dependence of the activity coefficient of a cation  $M$  (the corresponding equation for an anion  $L$  is obtained by interchanging  $L$  for  $M$ ,  $a$  for  $c$ , and  $c$  for  $a$  throughout, where  $a$  and  $c$  stand for anion and cation in general) in a mixed solution containing a number of different ions and neutral species [for notation cf. Pitzer,<sup>3</sup> eqn. (63)] is:

$$\begin{aligned} \ln \gamma_M = & Z_M^2 F + \sum_a m_a (2B_{Ma} + ZC_{Ma}) \\ & + \sum_c m_c \left( 2\phi_{Mc} + \sum_a m_a \psi_{Mca} \right) + \sum_a \sum_{a'} m_a m_{a'} \psi_{Maa'} \\ & + |Z_M| \sum_c \sum_a m_c m_a C_{Ca} + 2 \sum_n m_n \lambda_{nM} \end{aligned} \quad (3)$$

The subscript  $n$  denotes neutral species;  $B_{Ma}$  is the virial coefficient describing the interactions between a cation,  $M$ , and an anion,  $a$ ;  $C_{Ma}$  and  $C_{Ca}$ , abbreviated  $C_{ca}$  are defined by eqn. (9),  $\phi_{Mc}$  is the virial coefficient arising from binary interaction between a specific cation and the other cations;  $\lambda_{nM}$  is the virial coefficient representing the interactions between a specific cation and neutral species;  $\Psi_{ijk}$  is the virial coefficient representing interactions between ions  $i, j, k$  (where  $i$  and  $j$  are different anions and  $k$  is a cation or when  $i$  and  $j$  are different cations and  $k$  is an anion). The parameters  $\psi$  and  $\lambda$  are assumed to be independent of ionic strength. The quantity  $F$  includes the Debye-Hückel,  $f^\gamma$ , and other terms as follows:

$$\begin{aligned} F = & f^\gamma + \sum_c \sum_a m_c m_a B'_{ac} + \sum_c \sum_{c'} m_c m_{c'} \phi'_{cc'} \\ & + \sum_a \sum_{a'} m_a m_{a'} \phi'_{aa'} \end{aligned} \quad (4)$$

where

$$f^\gamma = -A_\phi \left\{ \frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right\} \quad (5)$$

and  $\phi'$  and  $B'$  are the ionic strength derivatives of  $\phi$  and  $B$ , respectively (see below).  $Z$ ,  $B$  and  $B'$  are equal to

$$Z = \sum_i m_i |Z_i| \quad (6)$$

$$\begin{aligned} B_{Ma} = & \beta_{Ma}^{(0)} + \frac{2\beta_{Ma}^{(1)}}{\alpha^2 I} \{1 - (1 + \alpha I^{1/2}) \exp(-\alpha I^{1/2})\} \\ = & \beta_{Ma}^{(0)} + \beta_{Ma}^{(1)} g(\alpha I^{1/2}) \end{aligned} \quad (7)$$

and

$$\begin{aligned} B'_{Ma} = & -\frac{2\beta_{Ma}^{(1)}}{\alpha^2 I^2} \left[ 1 - \left( 1 + \alpha I^{1/2} + \frac{\alpha^2 I}{2} \right) \exp(-\alpha I^{1/2}) \right] \\ = & \beta_{Ma}^{(1)} \frac{g'(\alpha I^{1/2})}{I} \end{aligned} \quad (8)$$

$C_{ca}$  and the virial coefficient  $\phi_{ij}$  are defined as follows:

$$C_{ca} = \frac{C_{ca}^\Phi}{2|Z_c Z_a|^{1/2}} \quad (9)$$

$$\phi_{ij} = \theta_{ij} + {}^E\theta_{ij}(I) \quad (10)$$

$C_{ca}^\Phi$  are tabulated quantities for each cation-anion pair.<sup>3</sup>  ${}^E\theta_{ij}(I)$  is a function of the ionic strength only; it is zero except for unsymmetrical mixing of ions of the same sign, i.e. when the charges of  $i$  and  $j$  are of the same sign but different magnitude. (This term is given by theory and its values can be calculated numerically as described in Pitzer,<sup>3</sup> Appendix B.)  $g(\alpha I^{1/2})$  and  $g'(\alpha I^{1/2})$  are known functions of  $I$ , and  $\alpha$  is an empirical parameter equal to  $2.0 \text{ kg}^{1/2} \text{ mol}^{-1/2}$ .

The features of the Pitzer and the SIT models given above provide the rationale for the simplification of the Pitzer equations presented below.

### Comparison of the SIT and Pitzer models: evaluation of the Pitzer parameters based on correlation with the charge type of the interacting ions

The most common simplification of the Pitzer model is to neglect the contribution of third virial coefficient. Indeed, a check of the typical values of  $C^\Phi$  from the available compilation<sup>3</sup> shows that this contribution is significant only at high ionic strength, typically above  $5\text{--}6 \text{ mol kg}^{-1}$ ; cf. the results for LiOH, LiBrO<sub>3</sub>, NaF, NaClO<sub>4</sub>, NaNO<sub>3</sub>, etc. listed in Table 1 of Marshall *et al.*<sup>5</sup> Hence,  $C^\Phi = 0$  is a reasonable assumption when the concentrations of reactants/products are small, in comparison with the ionic medium concentration. Another simplification of the Pitzer model was proposed by Millero,<sup>20</sup> who suggested the estimate  $\beta^{(1)} = 0$  for complexes. This simplified one-parameter Pitzer equation looks identical with the SIT model:

$$\ln \gamma_i = Z^2(\text{DH-term}) + \sum_j \varepsilon_\gamma(i, j) m_j \quad (11)$$

$$\ln \gamma_M = Z^2(\text{DH-term}) + 2 \sum_a \beta_{Ma}^{(0)} m_a \quad (12)$$

However, the Debye-Hückel limiting law terms (DH-term) in the two models are different: the denominators are  $(1 + 1.5I^{1/2})$  and  $(1 + 1.2I^{1/2})$ , respectively. Hence, the interaction coefficient  $B_{Ma}$ , cf. eqn. (7), has a larger variation with the ionic strength than the SIT interaction parameters. (The factor 1.5 in the denominator of the SIT model was selected to minimise the ionic strength dependence of the interaction parameters.) Figure 1 illustrates how  $B_{Ma}$  varies with the ionic strength for 1-1, 2-1 and 3-1 electrolytes. The vertical bar indicates an uncertainty of  $\pm 0.15$  in  $\log K$ , and illustrates that it is impossible to determine  $B_{Ma}$  for 1-1 and 2-1 electrolytes from equilibrium constant data unless these are very precise.  $\beta^{(1)} = 0$  is not a satisfactory approximation. To illustrate this, the experimental and fitted mean activity coefficients of NaCl, MgCl<sub>2</sub> and NdCl<sub>3</sub>

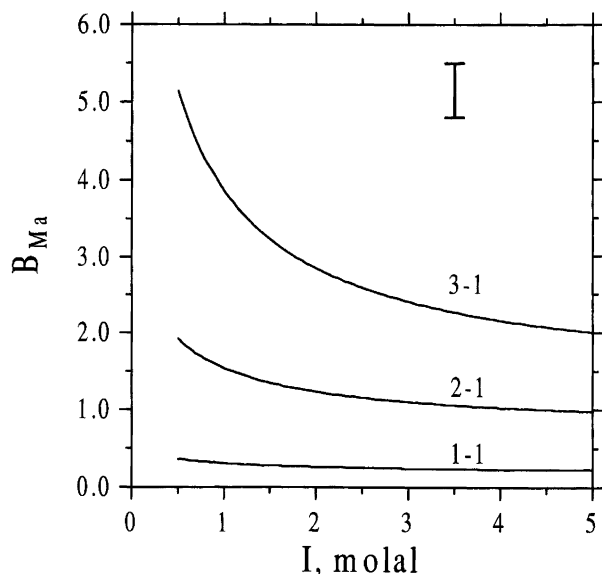


Fig. 1. The ionic strength dependence of the Pitzer parameter  $B_{Ma}$  for 1-1, 2-1 and 3-1 ions combinations obtained using some typical values of  $\beta^{(0)}$  and  $\beta^{(1)}$ , see text. The vertical bar shows the effect on  $B_{Ma}$  of an uncertainty  $\pm 0.15$  units in  $\log K$ .

using  $\beta^{(1)}=0$  have been plotted as a function of the ionic strength (Fig. 2). We consider only data up to  $I=3 \text{ mol kg}^{-1}$ , where the contribution of the terms accounting for triple ion interactions may be neglected. The thick full-drawn curves represent the experimental data, the dotted curve the mean activity coefficients calculated using the Pitzer model with  $\beta^{(0)}$  as the only fitting parameter and  $\beta^{(1)}=0$ . The dashed curves are calculated

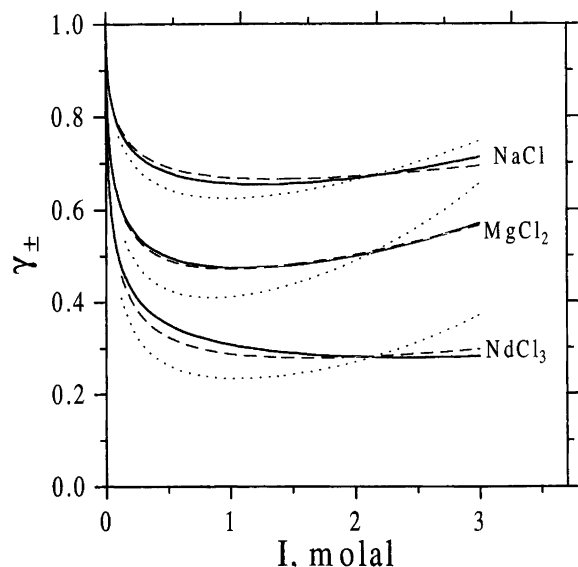


Fig. 2. Mean activity coefficients of NaCl, MgCl<sub>2</sub> and NdCl<sub>3</sub> as a function of ionic strength at 298.15 K and 1 atm. Thick solid lines, experimental data. There is no significant deviation between the complete Pitzer model and the experimental data. Dashed lines, SIT model. Dotted lines, the Pitzer model with  $\beta^{(1)}=0$ .

using the SIT model with a fitted value of  $\varepsilon_\gamma$ . From Fig. 2 it is apparent that the one-parameter Pitzer model is inferior to the SIT model. Another important observation is that the values of  $\beta^{(0)}$  obtained using  $\beta^{(1)}=0$  always differ from the tabulated ones, for NaCl  $\beta^{(0)}=0.110$  (0.0765), for MgCl<sub>2</sub>  $\beta^{(0)}=0.557$  (0.352) and for NdCl<sub>3</sub>  $\beta^{(0)}=1.247$  (0.568), the tabulated values from Pitzer<sup>3</sup> are given in parentheses. The difference between the two sets of  $\beta^{(0)}$  is a consequence of neglecting the contribution of the  $\beta^{(1)}$  term. The higher the valence type of the electrolyte, the larger the error. Hence, the approximation  $\beta^{(1)}=0$ , results in an erroneous estimation of the  $\beta^{(0)}$  term and in an unnecessary loss of accuracy, as compared to the one-parameter SIT model. The Pitzer equations must be used with both the  $\beta^{(0)}$  and  $\beta^{(1)}$  terms.

An examination of the values of  $\beta^{(1)}$  at 298.15 K from Pitzer<sup>3</sup> shows that they are correlated with the charge type of the electrolyte: for most 1-1 electrolytes the values of  $\beta^{(1)}$  fall in a range  $0.20 \pm 0.20$ , for most 2-1 electrolytes in the range  $1.4 \pm 0.6$ , and for most 3-1 electrolytes in the range  $5.2 \pm 1.2$ . The averages may then be used as 'fixed' values of  $\beta^{(1)}$  in the Pitzer equations, thus reducing the number of unknown parameters. We prefer the method outlined as follows: Using the analytical statements for the mean activity coefficients in the SIT model, and in the Pitzer model without the  $C^\Phi$  term, we may demonstrate the concentration range in which the two models are equivalent, and also a method to estimate  $\beta^{(1)}$ . The Pitzer equation is then equal to:

$$\ln \gamma_{\pm} = -|Z_M Z_L| A_{\Phi} \left( \frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right) + m \frac{2\nu_M \nu_L}{\nu} (2\beta_{ML}^{(0)} + 2\beta_{ML}^{(1)} X) \quad (13)$$

where

$$X = \frac{1}{\alpha^2 I} \left[ 1 - \left( 1 + \alpha I^{1/2} - \frac{\alpha^2 I}{2} \right) \exp(-\alpha I^{1/2}) \right] \quad (14)$$

and the SIT model:

$$\ln \gamma_{\pm} = -\frac{A|Z_M Z_L| I^{1/2}}{1 + 1.5I^{1/2}} + m \frac{2\nu_M \nu_L}{\nu} \varepsilon_\gamma(M, L) \quad (15)$$

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

$$Y = -\frac{A_{\Phi}|Z_M Z_L|\nu}{4\nu_M \nu_L m} \left( \frac{3I^{1/2}}{1 + 1.5I^{1/2}} - \frac{I^{1/2}}{1 + bI^{1/2}} - \frac{2}{b} \ln(1 + bI^{1/2}) \right) = \left( \beta_{ML}^{(0)} - \frac{\varepsilon_\gamma(M, L)}{2} \right) + \beta_{ML}^{(1)} X \quad (16)$$

$X$  and  $Y$  are known quantities which depend only on the charge type of the electrolyte, the ionic strength/molality and  $A_{\Phi}$ . The linear function  $Y(X)$  has the intercept  $[\beta_{ML}^{(0)} - \varepsilon_\gamma(M, L)/2]$  and the slope  $\beta_{ML}^{(1)}$ . The functions  $Y(X)$

are plotted in Fig. 3 for 1-1, 2-1 and 3-1 ion combinations. The linearity is very good, indicating that the SIT model is approximately equivalent to the Pitzer model without the  $C^\Phi$  term and with a constant value of  $\beta^{(1)}$  for each charge type. The relationships between the two sets of parameters given in Table 1 for different ion combinations, may be used to convert the large set of  $\varepsilon_\gamma$  values already available<sup>11,12</sup> for complexes, into  $\beta^{(0)}$  and  $\beta^{(1)}$  values. Note that  $\varepsilon$  values, not  $\varepsilon_\gamma$ , are tabulated in Refs. 11 and 12; the relationship between them is  $\varepsilon_\gamma = \varepsilon \ln(10)$ .

The estimated values of  $\beta^{(1)}$  for 3-1 and 4-1 interactions ( $\beta^{(1)} = 4.3$  for 3-1 and 1-3, and  $\beta^{(1)} = 8.9$  for 4-1 and 1-4 interactions) seem to be slightly lower than the 'averaged' values from Pitzer,<sup>4</sup>  $\beta^{(1)} = 5.2 \pm 1.2$  and  $\beta^{(1)} = 11 \pm 2$ , respectively. However, Fig. 1 indicates that  $\beta^{(1)}$  for these electrolytes may be determined experimentally, provided sufficiently precise experimental data are available, *vide infra* Table 4.

Complex formation equilibria are in general described using concentration equilibrium constants, these are 'true thermodynamic' quantities because concentrations and

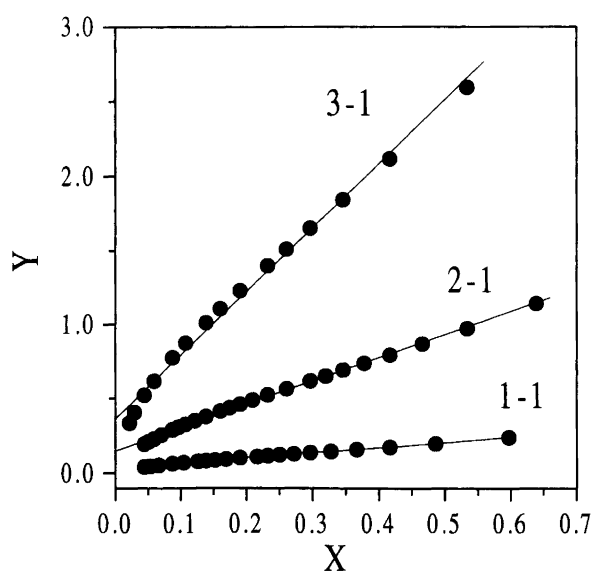


Fig. 3. The determination of relationship between the parameter  $\varepsilon_\gamma$  in the SIT model and the parameters  $\beta^{(0)}$  and  $\beta^{(1)}$  in the Pitzer model at 298.15 K and 1 atm for completely dissociated 1-1 (a), 2-1 (b) and 3-1 (c) electrolytes, see text for details. The filled circles have been calculated using eqn. (15), and the line represents a least-squares fit. The two models are equivalent up to an ionic strength of about 5-6 mol kg<sup>-1</sup>.

Table 1. The relationship between the Pitzer parameters  $\beta^{(0)}$  and  $\beta^{(1)}$  in kg mol<sup>-1</sup>, and the SIT  $\varepsilon_\gamma$  parameter for different ion combinations at 298.15 K.

Ion combination	$(\beta^{(0)} - \varepsilon_\gamma/2)$	$\beta^{(1)}$
M <sup>+</sup> , X <sup>-</sup>	0.035	0.34
M <sup>2+</sup> , X <sup>-</sup> and M <sup>+</sup> , X <sup>2-</sup>	0.150	1.56
M <sup>3+</sup> , X <sup>-</sup> and M <sup>+</sup> , X <sup>3-</sup>	0.366	4.29
M <sup>4+</sup> , X <sup>2-</sup> and M <sup>+</sup> , X <sup>4-</sup>	0.754	8.89

activities for reactants/products are proportional to one another in ionic media. Each ionic medium may thus be considered as a particular solvent, and a comparison of equilibrium constants obtained in different ionic media must be made by using one reference medium, usually pure water. A simplified Pitzer model for the concentration/ionic medium dependence of equilibrium constants in ionic media is described in the following section.

### Evaluation of the Pitzer parameter $\beta^{(1)}$ for complexes (or $\Delta\beta^{(1)}$ for a reaction) based on the charge type of the reaction

For a chemical reaction in the general form

$$\sum_i p_i Q_i + r \text{H}_2\text{O}(l) = 0 \quad (17)$$

we have

$$\begin{aligned} \ln K^\circ &= \sum_i p_i \ln m_i + \sum_i p_i \ln \gamma_i + r \ln a_{\text{H}_2\text{O}} \\ &= \ln K + \sum_i p_i \ln \gamma_i + r \ln a_{\text{H}_2\text{O}} \end{aligned} \quad (18)$$

Most experimental studies of complex formation reactions have been performed in ionic media,<sup>9,21</sup> with a concentration that is much higher than that of the reactants/products. In this way the 'trace' activity coefficients of reactants/products remain very near constant, even if their total concentrations are varied. At 'trace' concentrations of reactants and products, all summations in eqns. (2) and (3) reduce to terms which include only the molality of the ionic medium electrolyte: the others are negligible. Hence, the Pitzer model in a 1:1 electrolyte ionic medium, NX, results in the following analytical statement:

$$\begin{aligned} \ln K^\circ &= \ln K + r \ln a_{\text{H}_2\text{O}} + \sum_i p_i Z_i^2 (f^\gamma + m^2 B'_{\text{NX}}) \\ &\quad + 2m \sum_i p_i B_{ij} + 2m^2 \sum_i p_i C_{ij} + 2m \sum_i p_i \phi_{ii'} \\ &\quad + m^2 \sum_i p_i \psi_{ii'j} + m^2 \sum_i p_i |Z_i| C_{\text{NX}} \\ &= \ln K + r \ln a_{\text{H}_2\text{O}} + \Delta Z^2 (f^\gamma + m^2 B'_{\text{NX}}) + m^2 \Delta |Z| C_{\text{NX}} \\ &\quad + 2m(\Delta B + \Delta \phi) + 2m^2 \left( \Delta C + \frac{\Delta \psi}{2} \right) \end{aligned} \quad (19)$$

where the index  $i$  refers to species  $i$ , and  $i'$  and  $j$  stand for ionic medium ions, having the same and opposite charge signs, respectively, as  $i$ . The definitions of  $\Delta Z^2$ ,  $\Delta B$ , etc. are clear from eqn. (19),  $m$  is the molality of ionic medium 1-1 electrolyte. The ionic strength dependence of parameter  $\Delta B$  is

$$\Delta B = \Delta\beta^{(0)} + \Delta\beta^{(1)} g(\alpha I^{1/2}) \quad (20)$$

where

$$\Delta\beta^{(0)} = \sum_i p_i \beta_i^{(0)} \quad \text{and} \quad \Delta\beta^{(1)} = \sum_i p_i \beta_i^{(1)}$$

Eqn. (19) shows that the coefficients for the terms in  $m$

and  $m^2$  contain  $\Delta\beta^{(0)}$  and  $\Delta\phi$ , and  $\Delta C$  and  $\Delta\psi$ , respectively. Hence, it is not possible to obtain the individual Pitzer parameters  $\Delta\beta^{(0)}$  and  $\Delta C$  from this equation alone. When using eqn. (19) in a regression analysis it is convenient to rewrite it as

$$\ln K^\circ = \ln K + r \ln a_{\text{H}_2\text{O}} + \Delta Z^2 (f^\gamma + m^2 B'_{\text{NX}}) + m^2 \Delta |Z| C_{\text{NX}} + 2mX_1 + 2mg(\alpha I^{1/2})X_2 + 2m^2 X_3 \quad (21)$$

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

Using the SIT formalism, the concentration dependence of the equilibrium constant for reaction (17), studied at trace concentration of the reaction participants in a constant ionic medium, is equal to

$$\begin{aligned} \ln K^\circ &= \ln K + r \ln a_{\text{H}_2\text{O}} - \frac{AI^{1/2}}{1 + 1.5I^{1/2}} \sum_i p_i Z_i^2 \\ &\quad + m \sum_i p_i \varepsilon_\gamma(i, j) \\ &= \ln K + r \ln a_{\text{H}_2\text{O}} - \frac{A\Delta Z^2 I^{1/2}}{1 + 1.5I^{1/2}} + m\Delta\varepsilon_\gamma \end{aligned} \quad (22)$$

where  $m$  is the molality of the ionic medium electrolyte. The definitions of  $\Delta Z^2$  and  $\Delta\varepsilon_\gamma$  are clear from eqn. (22).

In order to illustrate the problems with a regression analysis of equilibrium constant data using the Pitzer model, we have chosen a simple protolytic reaction, the first protonation constant of sulfate  $\text{H}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{HSO}_4^-$  studied in a  $\text{NaClO}_4$  medium. Only potentiometric data from Refs. 6–8 and from Sapienko *et al.*<sup>22</sup> have been used. These have been recalculated into molality units and to 298.15 K where necessary; see Ref. 12 for details. For this reaction the Pitzer interaction coefficients for all reactants and products are known from activity and osmotic coefficient data. The value of  $\log K^\circ$  is a CODATA key value, evaluated from different experimental data at low ionic strength. In general, equilibrium constant data are much less precise than in this example, and Pitzer parameters are rarely available for all reactants and products. In the example, 18 experimental determinations have been reported over a wide range of ionic strengths, down to 0.10 mol kg<sup>-1</sup>, which facilitates the regression analysis; the data have been obtained in different laboratories, allowing a good estimate of the accuracy of  $\log K$ .

The ionic strength dependence of the higher-order electrostatic unsymmetrical mixing term  ${}^E\theta_{\text{ClO}_4, \text{SO}_4}(I)$  was taken into account as recommended in Ref. 3. The results of the regression are given in Table 2 and in Fig. 4. The following methods to estimate the Pitzer parameters from these data are discussed: (I) the determination of the whole set of parameters  $\log K^\circ$ ,  $X_1$ ,  $X_2$ ,  $X_3$ ; (II) the determination of  $\log K^\circ$ ,  $X_1$ ,  $X_2$ , i.e. neglecting the contribution of all ternary interactions; (III) the determination of  $\log K^\circ$ ,  $X_1$ ,  $X_3$ , i.e. assuming  $\beta^{(1)} = 0$  for all reactants/products as suggested by Millero;<sup>20</sup> (IV) the determination of  $\log K^\circ$ ,  $X_1$ , 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  $\log K^\circ$  as a fixed parameter.

The symbol (0) in Table 2 is used when 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.<sup>23</sup> The ‘Tabulated’ value of  $\log K^\circ$  was that recommended by CODATA,<sup>24</sup> while those for the Pitzer parameters were calculated from the values of  $\beta^{(0)}$ ,  $\beta^{(1)}$  and  $C$  for  $\text{NaHSO}_4$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{HClO}_4$  (Pitzer).<sup>3</sup> The parameters for binary and ternary interactions of  $\text{ClO}_4^-$  with  $\text{HSO}_4^-$  and  $\text{SO}_4^{2-}$  are unknown, but the possible effect of neglecting them is probably within proposed uncertainties of the ‘Tabulated’ values.

The example allows us to draw the following conclusions: The simple one-parameter SIT model reproduces the experimental data fairly well, it also results in a reliable determination of  $\log K^\circ$  with a small uncertainty (the value of  $\log K^\circ$  is in an excellent agreement with the CODATA recommendation). The problems with the Pitzer model are also clearly demonstrated. All refinement models allow accurate data interpolation, however, the estimates of  $\log K^\circ$  and the values of the coefficients  $X_i$  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  $X_2 = \Delta\beta^{(1)} = 0$ ) and IV give unreliable estimations of the parameters and should be avoided. Only model II which includes  $X_1$  ( $\approx \Delta\beta^{(0)}$ ) and  $X_2$  ( $\Delta\beta^{(1)}$ ) can be recommended. Model V gives an estimate of the uncertainty of the Pitzer parameters, and shows that it is not possible to determine precise values, even from these precise  $\log K$  data, and with a known value of  $\log K^\circ$ .

The examples can be multiplied, and our experience shows that the conclusions remain essentially the same as for the reaction discussed above: as a rule, it is impossible to get a statistically significant value of the ternary interaction parameter  $X_3$ , for a reaction from the set of experimental  $\log K$  data; the value of  $\log K^\circ$  will have a larger uncertainty than the corresponding SIT estimate; the estimation of  $X_2$  ( $\Delta\beta^{(1)}$ ) is very uncertain. These conclusions are similar to those of Marshall *et al.*<sup>5</sup> 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.

The example does not indicate that the Pitzer model should be replaced by the simpler SIT model, only that some simplifications are required when applied to equilibrium constant data. The previous example indicates that an estimate of the parameter  $\Delta\beta^{(1)}$  is particularly useful, a method analogous to the one described by eqn. (16) is described in the following:

For chemical equilibria studied in the presence of an ionic medium ( $I < 4$  mol kg<sup>-1</sup>) one may neglect all para-

Table 2. Regression results for data of  $\log K$  for the reaction  $\text{H}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{HSO}_4^-$  in  $\text{NaClO}_4$  medium at 298.15 K; see text for details.<sup>a</sup>

Pitzer model, the values of parameters in variants I–V							
SIT model	Parameter	I	II	III	IV	V	'Tabulated' values
$\log K^\circ = 1.989 \pm 0.084$	$\log K^\circ$	$2.10 \pm 0.27$	$2.04 \pm 0.20$	$2.13 \pm 0.13$	$2.23 \pm 0.11$	1.987	$1.987 \pm 0.009$
$\Delta\varepsilon = 0.003 \pm 0.051$	$X_1$	$-0.45 \pm 0.88$	$-0.19 \pm 0.16$	$-0.56 \pm 0.21$	$-0.34 \pm 0.21$	$-0.18 \pm 0.60$ $(-0.16 \pm 0.11)$	$-0.15 \pm 0.05$
	$X_2$	$-0.46 \pm 3.40$	$-1.39 \pm 1.34$	(0)	(0)	$-1.67 \pm 1.67$ $(-1.73 \pm 0.57)$	-0.995
	$X_3$	$0.05 \pm 1.02$	(0)	$0.07 \pm 0.07$	(0)	$0.005 \pm 0.128$ (0)	$-0.006 \pm 0.010$

<sup>a</sup>The symbol (0) means that this parameter was set equal to zero in the data fitting. Note, that  $\Delta\varepsilon = \Delta\varepsilon_\gamma/\ln(10)$ . All uncertainties are given as  $3\sigma$ . The values within parenthesis in column V denote a refinement of only  $X_1$  and  $X_2$ . The 'Tabulated' values have been taken from the literature, cf. previous page.

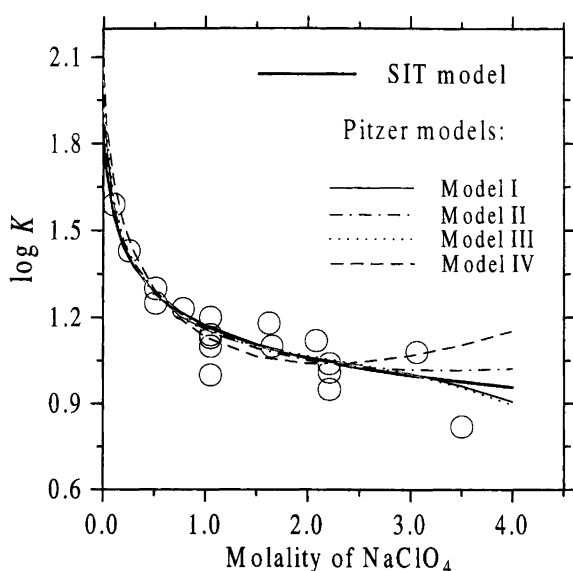


Fig. 4. Experimental and calculated concentration equilibrium constants for the reaction  $\text{H}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{HSO}_4^-$  in  $\text{NaClO}_4$  medium at 298.15 K and 1 atm. The various curves have been calculated using the models and parameters given in Table 2 (see text for details).

meters accounting for triple ionic interactions ( $C_{\text{NX}}$ ) and binary higher-order mixing terms [ ${}^E\theta_{ij}(I)$ ]. These approximations will be discussed later. For 1–1 ionic media we then obtain the following Pitzer-type statement for the ionic medium dependence of  $\ln K$ :

$$\begin{aligned} \ln K^\circ &= \ln K + r \ln a_{\text{H}_2\text{O}} - \Delta Z^2 A_\Phi \\ &\times \left( \frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) \right) \\ &+ \Delta Z^2 m^2 B'_{\text{NX}} + 2mX_1 + 2mg(\alpha I^{1/2})X_2 \end{aligned} \quad (23)$$

[see eqn. (19) for notation]. The corresponding relation for the SIT model is given by eqn. (22). After elementary transformations we obtain:

$$\begin{aligned} Y &= \left[ A_\Phi \left( \frac{I^{1/2}}{1 + bI^{1/2}} + \frac{2}{b} \ln(1 + bI^{1/2}) - \frac{3I^{1/2}}{1 + 1.5I^{1/2}} \right) \right. \\ &\quad \left. - m^2 B'_{\text{NX}} \right] / 2m \\ &= \frac{1}{\Delta Z^2} \left( X_1 - \frac{\Delta\varepsilon_\gamma}{2} \right) + \frac{X_2}{\Delta Z^2} g(\alpha I^{1/2}) \end{aligned} \quad (24)$$

i.e.  $Y$  is a linear function of  $g(\alpha I^{1/2})$ , with the slope  $X_2/\Delta Z^2$  and the intercept  $(X_1 - \Delta\varepsilon_\gamma/2)/\Delta Z^2$ .  $\alpha$  is a fixed empirical Pitzer parameter equal to  $2.0 \text{ kg}^{1/2} \text{ mol}^{-1/2}$  for all electrolytes.  $Y$  can be calculated from the known ionic strength, the Debye–Hückel parameter  $A_\Phi$  and  $B'_{\text{NX}}$ , i.e. the known value of  $\beta^{(1)}$  for the 1–1 ionic medium electrolyte. The values of  $g(\alpha I^{1/2})$  are obtained from the ionic strength of the solution. In Fig. 5 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 parameters  $(X_1 - \Delta\varepsilon_\gamma/2)/\Delta Z^2$  and  $X_2/\Delta Z^2$  determined for each electrolyte are given in Table 3. As these parameters, especially the slope, do not vary much with the nature of the 1–1 electrolyte, one can use all the data to determine one common set of parameters (see the last line of Table 3, where 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 show that for isocoulombic reactions, where  $\Delta Z^2 = 0$ , the proposed result is consistent with  $\Delta\beta^{(1)} = 0$ . Using the data in Table 3 we can now estimate the values of  $X_1$  and  $X_2$  for the protonation of sulfate. We obtain  $X_1 = -0.11 \pm 0.07$  and  $X_2 = -1.35 \pm 0.05$ , in good agreement with the results in Table 2.

The relationship (19) was obtained by neglecting the contribution of the terms for higher-order electrostatic unsymmetrical mixing. By including these terms the slope of the function  $Y$  is changed somewhat, particularly for ions of charge 3, or higher.

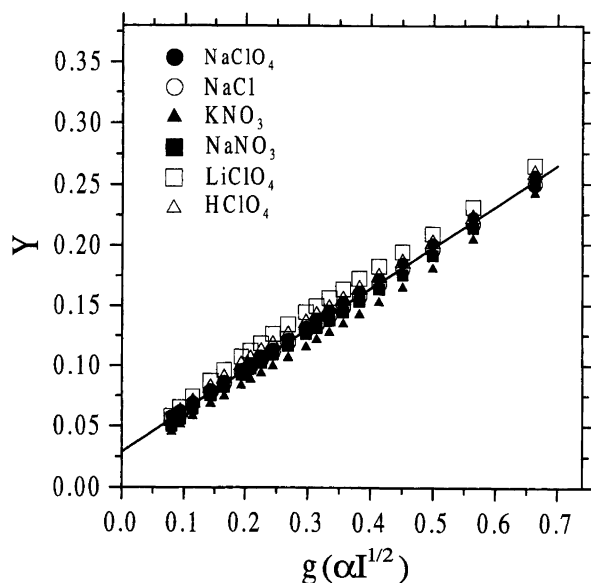


Fig. 5. The relationship between the SIT parameter  $\Delta\epsilon_\gamma$  and the Pitzer parameters  $\Delta\beta^{(0)}$  and  $\Delta\beta^{(1)}$  for reactions studied in solutions of different 1–1 ionic medium electrolytes at 298.15 K and 1 atm. The solid lines corresponds to the common slope accepted for all 1–1 electrolytes, see text and Table 3 for details. The various symbols are calculated values from eqn. (23), using known Pitzer parameters for the different ionic media. The full-drawn curves are least-squares fits, which show an excellent linearity over the ionic strength range from 0.1 to 6 mol kg<sup>-1</sup>.

Table 3. Relation between the Pitzer and the SIT parameters for the complex formation reactions studied in different 1–1 electrolyte ionic media at 298.15 K and 1 atm.

1–1 electrolyte	$(X_1 - \Delta\epsilon_\gamma/2)/\Delta Z^2$	$X_2/\Delta Z^2$
NaClO <sub>4</sub>	0.031	0.340
LiClO <sub>4</sub>	0.038	0.348
HClO <sub>4</sub>	0.032	0.342
NaNO <sub>3</sub>	0.026	0.334
KNO <sub>3</sub>	0.019	0.327
NaCl	0.030	0.332
All data	0.029 ± 0.005	0.337 ± 0.014

Because the determination of the Pitzer parameters for a reaction (or for complexes) from  $\log K$  data is an ill-conditioned problem it is rarely possible to determine more than one interaction parameter. We therefore suggest the following strategy when using  $\log K$  data determined in 1–1 electrolyte ionic media, to determine the Pitzer parameters for complexes: (1) Use the SIT equation to obtain  $\log K^\circ$ . (2) Estimate  $X_2$  from the  $\Delta Z^2$  value for the reaction if the charge of the reactants/products do not exceed 2 and calculate  $X_1$  using  $X_2$  as a fixed parameter. Terms, including  $m^2\Delta|Z|C_{NX}$  [see eqn. (21)] and higher-order electrostatic unsymmetrical mixing terms for all ions, including the complexes, could be taken into account in the regression procedure. (3) Calculate the Pitzer parameters for the

complexes from the values of  $\Delta\beta^{(0)}$  and with  $\Delta\beta^{(1)}$  and the corresponding quantities  $\beta^{(0)}$  and  $\beta^{(1)}$  for the reactants. (4) In order to describe equilibrium data at higher ionic strengths or mixed electrolyte systems, it is necessary to determine additional interaction parameters. This can only be achieved by additional equilibrium constant measurements under these conditions.

#### Determination of the Pitzer parameters for aqueous species of uranium at 298.15 K and 1 atm

We have used the procedure outlined above for the determination of the Pitzer parameters for aqueous species of uranium at 298.15 K and 1 atm. These data may be used with existing computer codes for the modeling of equilibrium systems in different environmental and geochemical applications.

There is the extensive and well documented review on the thermodynamics of chemical compounds of uranium, including aqueous complex species,<sup>12</sup> which is used as a source of  $\log K$  values, both in concentrated ionic media and at infinite dilution. Note that only very few  $\log K$  data were judged to have an uncertainty  $\pm 0.15$  log units, or less, by the reviewers.

Based on the previous discussion, we determined the Pitzer parameters for aqueous complexes of uranium as follows:

(1) All values of  $\log K$  for a reaction, accepted as reliable in Ref. 12, have been considered. If the  $\log K$  values were reported in molar units, they were recalculated to the molality scale as described in Ref. 12, p. 23, using the values of solution density from Söhnel and Novotny.<sup>25</sup>

(2) The values of  $\beta^{(0)}$ ,  $\beta^{(1)}$ ,  $C^\phi$ , and of the mixing parameters for the ionic species were taken from Pitzer,<sup>3</sup> and the values of  $\theta$  for the  $\text{UO}_2^{2+}\text{-Na}^+$ , and  $\psi$  for the  $\text{UO}_2^{2+}\text{-Na}^+\text{-ClO}_4^-$  interactions from Kim and Frederic.<sup>26</sup> The values used in our analysis are given in Table 4. The values of the higher-order electrostatic terms for unsymmetrical mixing of ions of the same sign were calculated for all species including the uranium ones, following the numerical procedure recommended by Pitzer.<sup>3</sup>

(3) A weighted general linear regression method, as outlined in Ref. 23, was used to derive the interaction parameters. The weight  $w$  of an experimental value was defined as  $w=1/\delta^2$ , where  $\delta=\ln(10)[\delta^2(\log K)+\delta^2(\log K^\circ)]^{1/2}$ . The uncertainties in the experimental  $\log K$  data,  $\delta(\log K)$ , and in  $\log K^\circ$ ,  $\delta(\log K^\circ)$ , were taken from Grenthe *et al.*<sup>12</sup> The values of  $\log K^\circ$  from the same source were used as a fixed parameter in the regression.

(4) All terms accounting for triple ion interaction of the uranium complexes were neglected, and only the parameters  $\beta^{(0)}$  and  $\beta^{(1)}$  are used to describe the ion interactions of the charged complexes. The interaction parameter  $\beta^{(0)}$  determined from the  $\log K$  data in this



**Table 4.** The values of the Pitzer parameters (in  $\text{kg mol}^{-1}$ ) used (source: Pitzer,<sup>3</sup> except for  $\theta$  for  $\text{Na}^+$ ,  $\text{UO}_2^{2+}$  and  $\psi$  for  $\text{Na}^+$ ,  $\text{UO}_2^{2+}$ ,  $\text{ClO}_4^-$  interactions).<sup>26</sup>

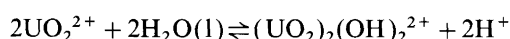
Ion combination	$\beta^{(0)}$	$\beta^{(1)}$	$C^\oplus$
$\text{H}^+$ , $\text{Cl}^-$	0.1775	0.2945	0.00080
$\text{H}^+$ , $\text{Br}^-$	0.2085	0.3477	0.00152
$\text{H}^+$ , $\text{I}^-$	0.2211	0.4907	0.00482
$\text{H}^+$ , $\text{ClO}_4^-$	0.1747	0.2931	0.00819
$\text{H}^+$ , $\text{NO}_3^-$	0.1168	0.3546	-0.00539
$\text{H}^+$ , $\text{HSO}_4^-$	0.2065	0.5556	
$\text{Na}^+$ , $\text{F}^-$	0.0215	0.2107	
$\text{Na}^+$ , $\text{Cl}^-$	0.0765	0.2664	0.00127
$\text{Na}^+$ , $\text{ClO}_4^-$	0.0554	0.2755	-0.00118
$\text{Na}^+$ , $\text{NO}_3^-$	0.0068	0.1783	-0.00072
$\text{Na}^+$ , $\text{CNS}^-$	0.1005	0.3582	-0.00303
$\text{Na}^+$ , $\text{HSO}_4^-$	0.0454	0.398	
$\text{K}^+$ , $\text{NO}_3^-$	-0.0816	0.0494	0.00660
$\text{K}^+$ , $\text{CNS}^-$	0.0416	0.2302	-0.00252
$\text{Na}^+$ , $\text{CO}_3^{2-}$	0.0363	1.510	0.0052
$\text{UO}_2^{2+}$ , $\text{ClO}_4^-$	0.6113	2.144	0.02168
$\text{UO}_2^{2+}$ , $\text{Cl}^-$	0.4274	1.644	-0.0368
$\text{UO}_2^{2+}$ , $\text{NO}_3^-$	0.4607	1.613	-0.0316

Ion combination	$\Theta$	Ion combination	$\Psi$
$\text{H}^+$ , $\text{K}^+$	0.005	$\text{H}^+$ , $\text{Na}^+$ , $\text{Cl}^-$	-0.004
$\text{H}^+$ , $\text{Na}^+$	0.036	$\text{H}^+$ , $\text{Na}^+$ , $\text{ClO}_4^-$	-0.016
$\text{Na}^+$ , $\text{UO}_2^{2+}$	0.0231	$\text{Na}^+$ , $\text{UO}_2^{2+}$ , $\text{ClO}_4^-$	-0.0437

way is equal to the sum  $\beta^{(0)} + \theta$ , where  $\theta$  is the mixing parameter accounting for the interaction of a charged uranium complex with the ion of the ionic medium with the same charge sign. However, there is usually no information available to separate these two terms.

(5) For equilibria involving ions with charges one or two, we used the correlation between  $\Delta Z^2$  and  $\Delta\beta^{(1)}$  to estimate  $\Delta\beta^{(1)}$  for a reaction. Using the values of  $\beta^{(1)}$  of the other reaction participants the unknown  $\beta^{(1)}$  parameter for the complexes was calculated. As an example we consider the equilibrium:



in a  $\text{NaClO}_4$  medium.  $\Delta Z^2$  is equal to  $-2$ , and from the correlation derived above it follows that  $\Delta\beta^{(1)} = 0.67$ , where

$$\Delta\beta^{(1)} = \beta_{(\text{UO}_2)_2(\text{OH})_2^{2+}, \text{ClO}_4^-}^{(1)} + 2\beta_{\text{H}^+, \text{ClO}_4^-}^{(1)} - 2\beta_{\text{UO}_2^{2+}, \text{ClO}_4^-}^{(1)}$$

With  $\beta_{\text{H}^+, \text{ClO}_4^-}^{(1)} = 0.2931$  and  $\beta_{\text{UO}_2^{2+}, \text{ClO}_4^-}^{(1)} = 2.1443$  (Pitzer)<sup>3</sup> we obtain  $\beta_{(\text{UO}_2)_2(\text{OH})_2^{2+}, \text{ClO}_4^-}^{(1)} = 3.03$ . The values of  $\beta^{(1)}$  estimated in this way are given without uncertainty limits in Table 5. For two of these reactions the number of data was sufficiently large to permit a determination of both  $\beta^{(0)}$  and  $\beta^{(1)}$ , and their uncertainty, which is very large for  $\beta^{(1)}$ .

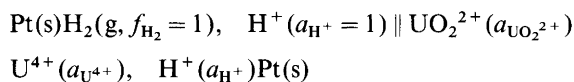
For equilibria involving ions of charge three, or higher, the contribution of  $\beta^{(1)}g(\alpha I^{1/2})$  to the virial coefficient  $B$  is sufficiently large to allow a determination of both  $\beta^{(0)}$  and  $\beta^{(1)}$ , as indicated in Table 5. We have also calculated the value of  $\beta^{(0)}$  using a fixed average value of  $\beta^{(1)}$  for

these charge types. These values are given within parenthesis in Table 5. Both models give very nearly the same accuracy in the calculated activity coefficients, indicating that estimates of both  $\beta^{(0)}$  and  $\beta^{(1)}$  are possible even if few experimental  $\log K$  data are available.

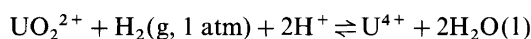
(6) For some reactions only 1 to 3 values of  $\log K$  have been experimentally determined, sometimes only at one ionic strength. Nevertheless, Grenthe *et al.*<sup>12</sup> estimated the values of  $\epsilon_\gamma(i, j)$  for these complexes or  $\Delta\epsilon_\gamma$  for reactions and  $\log K^\circ$ . The values of  $\beta^{(0)}$  and  $\beta^{(1)}$  for these species are crude estimates only, therefore they are denoted by  $\sim$  in Table 5.

The dependence of  $\log K$  on the concentration of the ionic medium for some reactions calculated using the interaction coefficients in Table 5 are shown in Fig. 6; the two curves refer to the Pitzer (full-drawn line) and SIT (dashed line) models. Both models in general describe the experimental data with the same accuracy in the ionic strength range studied. The scattering of the experimental data around the calculated curves is within the estimated uncertainties of the experimental  $\log K$  values.

Table 5 also includes interaction parameters for  $\text{UO}_2^{2+}$  and  $\text{U}^{4+}$ . These have been obtained from redox data, as described below for the case of  $\text{U}^{4+}$ . The published redox potentials,  $E^\circ$ , on the NHE (normal hydrogen electrode) scale for the couple  $\text{UO}_2^{2+}/\text{U}^{4+}$  refer to the following cell:



with the cell reaction



and the equilibrium constant

$$\frac{nF}{RT} E^\circ = \ln K^\circ = \ln K + \ln \gamma_{\text{U}^{4+}} - \ln \gamma_{\text{UO}_2^{2+}} - 2 \ln \gamma_{\text{H}^+} - \ln f_{\text{H}_2} + 2 \ln a_{\text{H}_2\text{O}}$$

where  $f_{\text{H}_2}$  is the fugacity of hydrogen, which is equal to one in the NHE. The activity coefficients refer to the right-hand half-cell (in the left they are by definition equal to unity).

## Conclusions

We have discussed methods to estimate the Pitzer parameters for complexes from a small number of equilibrium constants obtained in 'constant ionic media'. Since it is often impossible to determine both  $\log K^\circ$  and all Pitzer parameters for the ion interactions between the complex and other species present, some estimates of the parameters, or other simplifications are necessary. We suggest that the value of  $\log K^\circ$  estimated from the SIT equation is used as a fixed parameter, and that the Pitzer parameters are estimated as follows: For reactions involving species of charges one and two in an ionic medium of an 1-1 electrolyte, we suggest the use of the correlation

Table 5. The evaluated values of the Pitzer parameters  $\beta^{(0)}$  and  $\beta^{(1)}$  in  $\text{kg mol}^{-1}$ , for uranium aqueous species, the errors are given as  $3\sigma$ .<sup>a</sup>

Combination of ions	$\beta^{(0)}$	$\beta^{(1)}$
1-1 interactions		
$(\text{UO}_2)_3(\text{OH})_5^+$ , $\text{ClO}_4^-$	$0.07 \pm 0.09$	3.0
$(\text{UO}_2)_3(\text{OH})_5^+$ , $\text{Cl}^-$	$-0.02 \pm 0.20$	1.4
$(\text{UO}_2)_3(\text{OH})_5^+$ , $\text{NO}_3^-$	$-0.15 \pm 0.53$	1.1
$\text{UO}_2\text{F}^+$ , $\text{ClO}_4^-$	$0.20 \pm 0.08$	1.0
$\text{Na}^+$ , $\text{UO}_2\text{F}_3^-$	$-0.31 \pm 0.14$	0.5
$\text{UO}_2^+$ , $\text{ClO}_4^-$	$0.24 \pm 0.02$	0.7
$\text{UO}_2\text{CNS}$ , $\text{ClO}_4^-$	$0.19 \pm 0.08$	1.1
$\text{UO}_2\text{CNS}$ , $\text{NO}_3^-$	$0.27 \pm 0.11$	0.6
2-1 interactions		
$(\text{UO}_2)_2(\text{OH})_2^{2+}$ , $\text{ClO}_4^-$	$0.56 \pm 0.03$	3.0
$(\text{UO}_2)_2(\text{OH})_2^{2+}$ , $\text{Cl}^-$	$0.40 \pm 0.03$	2.0
$(\text{UO}_2)_2(\text{OH})_2^{2+}$ , $\text{NO}_3^-$	$0.42 \pm 0.14$	1.9
$(\text{UO}_2)_3(\text{OH})_4^{2+}$ , $\text{ClO}_4^-$	$0.76 \pm 0.48$	3.9
$(\text{UO}_2)_3(\text{OH})_4^{2+}$ , $\text{Cl}^-$	$-0.15 \pm 0.31$	2.4
$(\text{UO}_2)_3(\text{OH})_4^{2+}$ , $\text{NO}_3^-$	$0.50 \pm 0.63$	2.1
$\text{Na}^+$ , $\text{UO}_2\text{F}_4^{2-}$	$-0.17 \pm 0.50$	1.4
$\text{UF}_2^{2+}$ , $\text{ClO}_4^-$	$0.61 \pm 0.38$	$1.1 \pm 3.1$
$\text{U}(\text{NO}_3)_2^{2+}$ , $\text{ClO}_4^-$	$0.99 \pm 0.20$	$1.5 \pm 1.5$
$\text{Na}^+$ , $\text{UO}_2(\text{SO}_4)_2^{2+}$	$0.30 \pm 0.16$	1.9
$\text{USO}_4^{2+}$ , $\text{ClO}_4^-$	$\sim 0.42$	$\sim 3.7$
$\text{Na}^+$ , $\text{UO}_2(\text{CO}_3)_3^{2-}$	$-0.12 \pm 0.12$	2.5
$\text{U}(\text{CNS})_2^{2+}$ , $\text{ClO}_4^-$	$\sim 0.67$	$\sim 2.2$
3-1 interactions		
$\text{UOH}^{3+}$ , $\text{ClO}_4^-$	$1.29 \pm 0.13$ ( $1.26 \pm 0.07$ )	$5.0 \pm 0.6$ (5.2)
$\text{UOH}^{3+}$ , $\text{Cl}^-$	$0.81 \pm 0.21$ ( $0.64 \pm 0.08$ )	$4.6 \pm 0.7$ (5.2)
$\text{UF}^{3+}$ , $\text{ClO}_4^-$	$0.95 \pm 0.20$ ( $1.14 \pm 0.13$ )	$7.2 \pm 1.9$ (5.2)
$\text{UNO}_3^{3+}$ , $\text{ClO}_4^-$	$1.42 \pm 0.17$ ( $1.44 \pm 0.04$ )	$5.3 \pm 1.2$ (5.2)
$\text{UCI}^{3+}$ , $\text{ClO}_4^-$	$1.38 \pm 0.41$ ( $1.49 \pm 0.11$ )	$5.9 \pm 2.0$ (5.2)
$\text{UCI}^{3+}$ , $\text{Cl}^-$	$\sim 1.2$ ( $\sim 0.9$ )	$\sim 4.1$ (5.2)
$\text{UBr}^{3+}$ , $\text{ClO}_4^-$	$\sim 1.4$ ( $\sim 1.5$ )	$\sim 5.5$ (5.2)
$\text{UI}^{3+}$ , $\text{ClO}_4^-$	$\sim 1.3$ ( $\sim 1.5$ )	$\sim 6.1$ (5.2)
$\text{UCNS}^{3+}$ , $\text{ClO}_4^-$	$\sim 1.3$ ( $\sim 1.6$ )	$\sim 6.6$ (5.2)
4-1 interactions		
$\text{U}^{4+}$ , $\text{ClO}_4^-$	$2.00 \pm 0.21$ ( $2.24 \pm 0.12$ )	$13.3 \pm 1.5$ (11.4)
$\text{U}^{4+}$ , $\text{Cl}^-$	$\sim 1.5$ ( $\sim 1.8$ )	$\sim 12.9$ (11.4)
$\text{Na}^+$ , $\text{UO}_2(\text{CO}_3)_3^{4-}$	$0.88 \pm 0.64$ ( $0.94 \pm 0.22$ )	$11.8 \pm 3.8$ (11.4)
$\text{Na}^+$ , $\text{U}(\text{CO}_3)_4^{4-}$	$\sim 1.1$ ( $\sim 1.0$ )	$\sim 10.7$ (11.4)
5-1 interaction		
$\text{Na}^+$ , $\text{UO}_2(\text{CO}_3)_3^{5-}$	$1.41 \pm 0.69$	$22.2 \pm 5.0$
Interactions involving neutral complexes		
$\text{UO}_2\text{F}_2(\text{aq})$ , $\text{Na}^+ + \text{ClO}_4^-$	$-0.10 \pm 0.11$	
$\text{U}(\text{SO}_4)_2(\text{aq})$ , $\text{H}^+ + \text{ClO}_4^-$	$0.45 \pm 0.12$	
$\text{UCO}_3(\text{aq})$ , $\text{Na}^+ + \text{ClO}_4^-$	$-0.07 \pm 0.08$	
$\text{UO}_2(\text{CNS})_2(\text{aq})$ , $\text{Na}^+ + \text{ClO}_4^-$	$\sim -0.08$	
$\text{UO}_2(\text{CNS})_2(\text{aq})$ , $\text{Na}^+ + \text{NO}_3^-$	$0.17 \pm 0.16$	

<sup>a</sup>The values of  $\beta^{(1)}$  given without uncertainty were estimated using the proposed correlation between  $\Delta Z^2$  and  $\Delta\beta$  for reaction, the ' $\sim$ ' stands for a preliminary estimation, based on very few data, see text. The values given within parenthesis for the 3-1 and 4-1 interactions have been obtained using the fixed average value of  $\beta^{(1)}$  given within parenthesis in the last column.

between  $\Delta Z^2$  and  $\Delta\beta^{(1)}$ . For ions of higher charge it is possible to obtain estimates of both  $\Delta\beta^{(0)}$  and  $\Delta\beta^{(1)}$  from a least squares treatment of the equilibrium constant data. In this way, we have estimated the Pitzer parameters

for more than 30 combination of ions involving different uranium species. We have also pointed out that it is not advisable to 'simplify' the Pitzer model by setting  $\beta^{(1)}$  for individual complexes equal to zero. The procedure out-

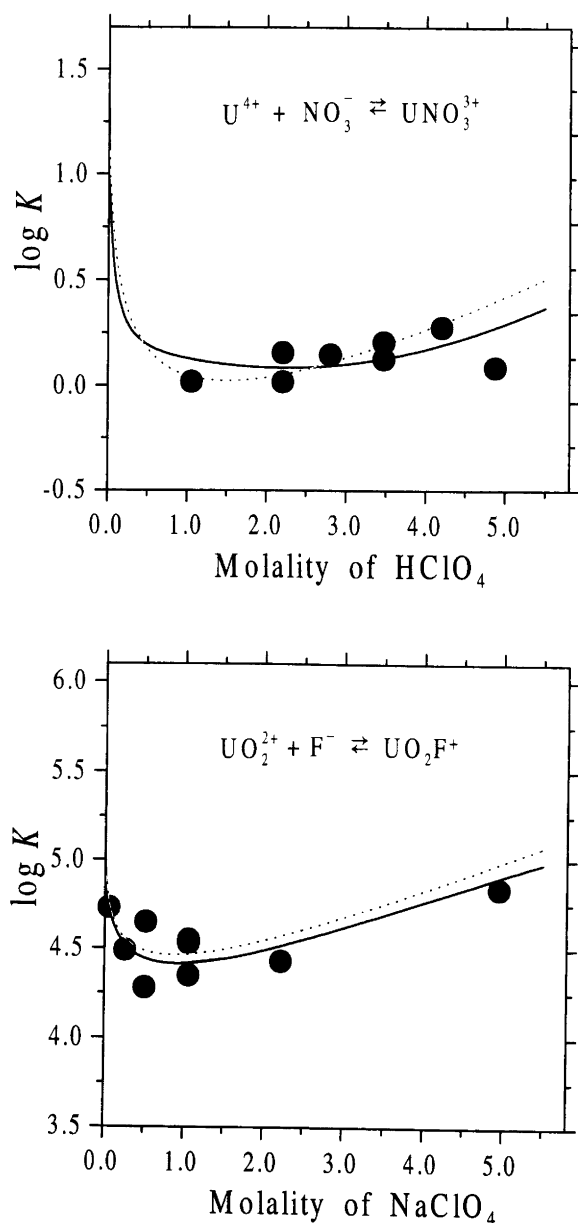


Fig. 6. Two examples of experimental and calculated  $\log K$  for complex formation equilibria using the estimated Pitzer parameters from Table 5 (solid line) and the SIT model (dashed line).

lined makes it possible to use the information on complex formation, acid/base and redox equilibria obtained in ionic media, and the Pitzer parameters for strong electrolytes for the modeling of complex equilibrium systems over a large range of ionic strengths/ionic compositions. The most important use of such models is often to determine the predominant chemical processes and the chemical form of the components in complicated equilibrium systems. Data of this type are essential in performance and safety assessments of waste repositories of

various types and for the discussion of trace metal transport in ground and surface water systems.

*Acknowledgements.* This work has been supported by grants from the Swedish Natural Science Research Council through the CAMPADA Consortium, and The Royal Swedish Academy of Sciences.

## References

- Laffitte, M. *J. Chem. Thermodyn.* 14 (1982) 805.
- Pitzer, K. S. *J. Phys. Chem.* 77 (1973) 268.
- Pitzer, K.S. In Pitzer, K. S., Eds., *Activity Coefficients in Electrolyte Solutions*, 2nd Edn., CRC Press, Boca Raton, FL 1991.
- Harvie, Ch. E., Møller, N. and Weare, J. H. *Geochim. Cosmochim. Acta* 48 (1984) 723.
- Marshall, S. L., May, P. M. and Hefter, G. T. *J. Chem. Eng. Data* 40 (1995) 1041.
- Sillén, L. G. and Martell, A. E. *Stability Constants of Metal-Ion Complexes*, Special Publication No. 17, The Chemical Society, London 1964.
- Sillén, L. G. and Martell, A. E. *Stability Constants of Metal-Ion Complexes*, Special Publication No. 25, Supplement No.1 to Special Publication No. 17. The Chemical Society, London 1971.
- Högfeldt, E. *Stability Constants of Metal-Ion Complexes. Part A: Inorganic Ligands*, IUPAC Chemical Data Series, No. 21, Pergamon Press, Oxford 1982.
- Beck, M. T. and Nagypál, I. *Chemistry of Complex Equilibria*, Ellis Horwood, New York 1990.
- Biedermann, G. In *Dahlem Workshop on the Nature of Seawater*, Dahlem Konferenzen, Berlin 1975, p. 339.
- Ciavatta, L. *Ann. Chim. Roma* (1980) 551.
- Grenthe, I., Fuger, J., Konings, R. J. M., Lemire, R. J., Mueller, A. B., Nguyen-Trung, C. and Wanner, H. *Chemical Thermodynamics of Uranium*, Elsevier, Amsterdam 1992.
- Ciavatta, L. *Ann. Chim. Roma* (1990) 255.
- Guggenheim, E. A. *Philos. Mag.* 19 (1935) 588.
- Brønsted, J. N. *J. Am. Chem. Soc.* 44 (1922) 877.
- Pitzer, K. S. and Brewer, L. *Revision of Lewis and Randall's Thermodynamics*, McGraw-Hill, New York 1961.
- Scatchard, G. (1959) In Hamer, W. J., Ed., *The Structure of Electrolytic Solutions*, Wiley, New York 1959.
- Scatchard, G. *Equilibrium in Solution: Surface and Colloid Chemistry*, Harvard University Press, Cambridge, MA 1976.
- Pitzer, K. S. *Acc. Chem. Res.* 10 (1977) 371.
- Millero, F. J. *Geochim. Cosmochim. Acta* 47 (1983) 2121.
- Rossotti, F. J. C. and Rossotti, H. *The Determination of Stability Constants and Other Equilibrium Constants in Solution*, McGraw-Hill, New York 1961.
- Sapieszko, R. S., Patel, R. C. and Matijević, E. *J. Phys. Chem.* 81 (1977) 1061.
- Shchigolev, B. M. *Mathematical Analysis of Observations*, American Elsevier, New York 1965.
- Cox, J. D., Wagman, D. D. and Medvedev, V. A. *CODATA Key Values for Thermodynamics*, HPC, New York 1989.
- Söhnel, O. and Novotny, P. *Densities of Aqueous Solutions of Inorganic Substances*, Physical Science Data 22, Elsevier, Amsterdam 1985.
- Kim, H.-T. and Frederic, W. J., Jr. *J. Chem. Eng. Data* 33 (1988) 177.

Received April 1, 1997.