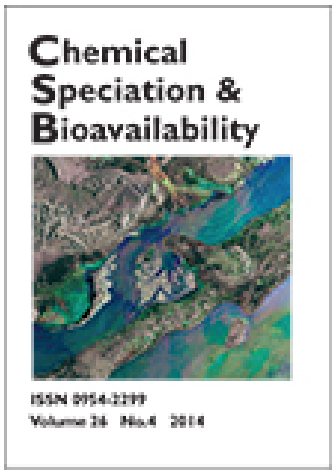
This article was downloaded by: [New York University]
On: 22 April 2015, At: 08:48
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Chemical Speciation & Bioavailability
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/tcsb20

A new approach in the use of SIT in determining the dependence on ionic strength of activity coefficients. Application to some chloride salts of interest in the speciation of natural fluids

Clemente Bretti[a], Claudia Foti[a] & Silvio Sammartano[a]
[a] Dipartimento di Chimica Inorgánica, Chimica Analitica e Chimica Fisica, Università di Messina, Salita Sperone 31, 98166 Messina (Vill. S. Agata), Italy
Published online: 12 Jan 2015.

To cite this article: Clemente Bretti, Claudia Foti & Silvio Sammartano (2004) A new approach in the use of SIT in determining the dependence on ionic strength of activity coefficients. Application to some chloride salts of interest in the speciation of natural fluids, Chemical Speciation & Bioavailability, 16:3, 105-110

To link to this article: http://dx.doi.org/10.3184/095422904782775036

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

A new approach in the use of SIT in determining the dependence on ionic strength of activity coefficients. Application to some chloride salts of interest in the speciation of natural fluids†

Clemente Bretti, Claudia Foti and Silvio Sammartano*

Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica, Università di Messina, Salita Sperone 31, 98166 Messina (Vill. S. Agata), Italy

Downloaded by [New York University] at 08:48 22 April 2015

ABSTRACT

This paper describes a modified version of the SIT (Specific ion Interaction Theory) method and its use in determining the dependence on ionic strength of activity coefficients. In the new approach the interaction coefficients (ε) are not constant but depend on ionic strength (I /mol kg^{-1}) according to the simple relationship:

$$\varepsilon = \varepsilon_\infty + (\varepsilon_0 - \varepsilon_\infty) / (I + 1)$$

where ε_0 and ε_∞ are true constants for $I \rightarrow 0$ and $I \rightarrow \infty$, respectively. To check the two parameter SIT equation, we calculated ε_0 and ε_∞ for the activity coefficients of HCl, LiCl, NaCl, KCl, $MgCl_2$, $CaCl_2$ and $SrCl_2$, in a wide ionic strength range ($0.1 \leq I$ /mol kg$^{-1} \leq 4.5$, for KCl; $0.1 \leq I$ /mol kg$^{-1} \leq 6$, for HCl, LiCl, NaCl; $0.3 \leq I$ /mol kg$^{-1} \leq 12$, for $SrCl_2$; $0.3 \leq I$ /mol kg$^{-1} \leq 15$, for $MgCl_2$; $0.3 \leq I$ /mol kg$^{-1} \leq 18$, for $CaCl_2$). Results show that the γ values calculated using this approach fit quite well over the whole I-range for all the electrolytes considered. Comparison is made with the analogous one parameter SIT equation. The temperature coefficients of interaction coefficients were also calculated using γ_∞ (HCl) in the range $0 \leq t$ /°C ≤ 60.

Keywords: activity coefficients, strong electrolytes, specific ion interaction theory, speciation, concentrated aqueous electrolyte solutions

INTRODUCTION

As is well known, besides a knowledge of the chemical species formed by the various components, the speciation of different biological fluids and natural waters implies estimation of the activity coefficients of both components and species at the ionic strength of the solution. To this end, several different approaches have been proposed (Bromley, 1973; Brönsted, 1922; Guggenheim, 1935, 1966; Guggenheim and Turgeon, 1955; Millero, 2001; Pitzer, 1973, 1991; Pitzer and Mayorga, 1973; Scatchard, 1976; Whitfield, 1973, 1975). The most popular models are the Pitzer (Pitzer, 1973, 1991; Pitzer and Mayorga, 1973) and SIT (Specific ion Interaction Theory) equations (Biederman, 1975, 1986; Brönsted, 1922; Guggenheim and Turgeon, 1955). Both models have their advantages and these can be summarized as follows: Pitzer equations are quite complete and allow activity coefficients to be modeled in a wide range of ionic strengths. They also allow for interactions between ions with same sign charges and triple interaction. Nevertheless, Pitzer equations are quite complicated and in some cases difficult to handle. The SIT approach, while quite

†Calculation of SIT parameters: Part I

*To whom correspondence should be addressed:
E-mail: Sammartano@chem.unime.it

simple and (in its original version) requiring only one parameter to perform calculations, is not very accurate in fitting γ values at $I < 0.5$ mol kg^{-1} and at $I > 3$ mol kg^{-1}.

Our research group has for several years been involved in the study of the dependence on ionic strength of formation constants and, therefore, in the use of different equations for taking into account the function $\gamma = f(I)$. Several models have been considered, including Pitzer, Bromley and different Debye–Hückel (or SIT) type equations (Daniele *et al.*, 1997; De Robertis *et al.*, 1999; Foti *et al.*, 1997, 1998; and references therein). Considering both the simplicity and the popularity of the SIT model, we thought it would be interesting to investigate the possibility of refining it in order to make it applicable over a broader ionic strength range. This paper describes a new approach applied to the activity coefficients of some chloride salts.

Downloaded by [New York University] at 08:48 22 April 2015

THE MODEL

For a single ion having a charge z, a simple Debye–Hückel type equation for calculating the dependence of activity coefficients on ionic strength containing a linear term can be written thus:

$$\log \gamma = -z^2 D + L(I) \quad (1)$$

where D is the Debye–Hückel term

$$D = A I^{1/2} / (1 + b I^{1/2}) \quad (2)$$

and $L(I)$ is a linear term containing one or more empirical parameters. In Equation (2), the b value is arbitrarily chosen, generally $1 \le b \le 1.5$. The SIT model[a] is based on the assumption that in Equation (1) the linear term $L(I)$ depends on the interaction between ions of opposite charge, and this can be expressed as:

$$L(I) = \Sigma \varepsilon m_i \quad (3)$$

where the sum is extended to the interactions between the ion under examination and all the ions i of opposite charge.[b] Considering the mean molal activity coefficient $\gamma_{\pm}$, for a single binary electrolyte $M_{\nu+}X_{\nu-}$ (M^{z+},X^{z-})

$$\gamma_{\pm} = (\gamma_{\pm}^{\nu+} \gamma_{\pm}^{\nu-})$$

and for eqs (1) and (3) we have:

$$\log \gamma_{\pm} = -|z_+ z_-| D + \varepsilon(M^{z+},X^{z-}) m \left(\frac{2\nu + \nu -}{\nu}\right) = -|z_+ z_-| D + \varepsilon(M^{z+},X^{z-}) 2 m\nu \quad (4)$$

or

$$\log \gamma_{\pm} = -z_+ z_- D + \varepsilon(M^{z+},X^{z-}) 4 I / (z_+ + z_-)^2 \quad (4a)$$

To derive this equation it is assumed that ε (M^{z+},X^{z-}) $\equiv$ ε (X^{z-},M^{z+}) as a consequence of the cross differential equation (Guggenheim, 1949). Equations (4) or (4a) can be extended to mixtures of electrolytes under the assumption that (a) $\varepsilon_{i,k} = 0$ if ions i and k have the same sign and (b) triple interactions are negligible. In the primary application of equation (4), the interaction coefficients ε were considered to be true constants, *i.e.* independent of ionic strength. Unfortunately this is true only for some electrolytes and/or in some ionic strength ranges. Ciavatta (1980), for example, found several simple electrolytes to have good constancy of ε in the range $0.5 \le I$ /mol kg^{-1} ≤ 3.5. In general ε is a function of I and some corrections have been proposed. A simple concentration dependence may be described by a Ciavatta type equation (1980):

$$\varepsilon = a + b (1 + \log I) \quad (5)$$

where a and b are true constants. Pitzer (1973) proposed the equation:

$$\varepsilon = \varepsilon_{\infty} + (\varepsilon_0 - \varepsilon_{\infty}) F(I) \quad (6)$$

where

$$F(I) = [1 - (1 + 2 I^{1/2} - 2 I) \exp(-2 I^{1/2})] / (4 I) \quad (7)$$

with

$$\lim_{I \to 0} F(I) = 1$$

$$\lim_{I \to \infty} F(I) = 0$$

and therefore

$$\lim_{I \to 0} \varepsilon = \varepsilon_0$$

$$\lim_{I \to \infty} \varepsilon = \varepsilon_{\infty}$$

[a]The background of the SIT was introduced by Brönsted (1922) and developed by Guggenheim (1966) and Scatchard (1976). Its use in equilibrium analysis was proposed by Biedermann (1975) and Ciavatta (1980, 1990).

[b]According to Brönsted (1922) only interaction between oppositely charged ions are significant. Often, also the dependence on ionic strength of neutral molecules is taken into account, according to Setchenow (Harned and Owen, 1958) equation: $\log \gamma = k_m I$, where k_m is the molal salting coefficient.

Downloaded by [New York University] at 08:48 22 April 2015

Another class of functions F(I) in equation (6) may be of the type:

$$F(I) = \exp(-2\, I^{1/2}) \quad (8)$$

Some of us have recently applied a simple relationship for F(I) to the dependence on ionic strength of diamine (Crea *et al.*, 2004) and dicarboxylate (Crea and Sammartano, work in progress) protonation constants as follows:

$$F(I) = (1 + I)^{-1} \quad (9)$$

with the same limits as F(I) in equation (7). The results were good in the whole range $0.1 \leq I$ /mol kg$^{-1} \leq 5$.

In equation (2) we must define parameters A and b. For the latter parameter we chose the value b = 1.5 according to Scatchard (1976). Values of A were tabulated at different temperatures (Rombinson and Stokes, 1955; Helgeson *et al.*, 1981). In the range $273 \leq T$ /K ≤ 348, we obtained the functions:[c]

$$A_T = 0.510 + 76.286\, f_1(T) + 1.4189\, f_2(T) \quad (10)$$

where

$$f_1(T) = \left(\frac{1}{\theta} - \frac{1}{T}\right) \quad (11)$$

$$f_2(T) = \left(\frac{\theta}{T} - 1 + \ln\frac{T}{\theta}\right) \quad (11a)$$

($\theta = 298.15$), with a mean deviation $|A - A_{calcd}| < 0.0006$.[d]

RESULTS AND DISCUSSION

Equation (4), with ε split up according to equation (6) and F(I) calculated using equation (9), was applied to the mean molal activity coefficients taken from the tabulations of Robinson and Stokes (1955). The interaction coefficients ε_0 and ε_∞ were calculated by least squares refinement and are reported in Tables 1 and 2. For purposes of comparison, the same tables show the results obtained when the interaction coefficient ε was considered to be a true constant, calculated (i) in the whole ionic strength range; (ii) in the restricted ionic strength ranges $0.5 \leq I$ /mol kg$^{-1} \leq 3$ and $0.1 \leq I$ /mol kg$^{-1} \leq 1$, for HCl and alkali metal chlorides; and $0.3 \leq I$ /mol kg$^{-1} \leq 6$ for alkaline earth metal chlorides. We also report the ε values calculated by Ciavatta (1980).[e]

Analysis of the results in Tables 1–2 reveals that:

(i) The two parameter SIT approach gives excellent results for the electrolytes examined in this study. The standard deviation in the fit is always ≤ 0.02, which is quite satisfactory for most equilibrium analysis problems in speciation studies.[f]
(ii) For HCl and alkali metal chlorides there is a good fit of log $\gamma_\pm$ in the range $0.1 \leq I$ /mol kg$^{-1} \leq 1$ (and fairly good fits are also observed in the range $0.5 \leq I$ /mol kg$^{-1} \leq 3$) even using the traditional one parameter SIT approach.
(iii) The application of the one parameter approach is still acceptable for HCl and alkali metal chlorides, but the two parameter model ($\sigma_1 >> \sigma_2$) always gives very different results.
(iv) For alkali earth metal chlorides, deviations are quite large with both the two parameter and the traditional one parameter SIT approach. The use of the two parameter approach gives good results in a very wide ionic strength range ($0.3 \leq I$ /mol kg$^{-1} \leq 15$).

Figure 1 shows the error plot $\log\gamma_{\pm(exp)} - \log\gamma_{\pm(calcd)}$ *vs.* I for HCl. The different fitting abilities of the one and two parameter SIT approaches can be seen clearly over the whole ionic strength range considered.

Temperature dependence of interaction coefficients

The dependence on temperature of interaction coefficients can be expressed as

$$\varepsilon = \varepsilon_\theta + a\, f_1(T) + b\, f_2(T) \quad (12)$$

where a and b are empirical parameters and f_1 and f_2 are the temperature functions defined in (11)–(11a). Using the re-evaluated $\gamma_\pm$ (HCl) of Partanen and Covington (2002), in the ranges $0.01 \leq I$ /mol kg$^{-1} \leq 2$ and $0 \leq t$ /°C ≤ 60 we obtained:

[c]Values of A in both molar and molal scales were fitted to the same equation. In the considered temperature range this does not imply a relevant error, being the maximum deviation, at 75 °C, less than 0.6% (at 25 °C the difference is < 0.15 %).

[d]An alternative equation, with a fairly better fit, is $A = -8.945 + 356.0/T + 1.4505 \ln(T)$, with mean deviation 0.00051.

[e]Ciavatta (1980) calculated the interaction coefficients from osmotic coefficients, in the range $0.5 \leq I$ /mol kg$^{-1} \leq 3.5$, and applied to each point the weight $w = I$.

[f]Standard deviation in the fit of equation (4) (Tables 1–2) are always < 0.02, and for HCl and alkali metal chlorides < 0.01. Equilibrium data (protonation constants, hydrolysis constants, metal complex formation constants) are generally affected by higher errors, and therefore the ionic strength correction using the two parameter SIT approach should be satisfactory.

Downloaded by [New York University] at 08:48 22 April 2015

Table 1. The interaction coefficients of equation (4), with F(*I*) calculated using equation (9), for the activity coefficients of HCl, LiCl, NaCl and KCl

Electrolyte	ε_∞	ε_0	σ [a]	μ[b]	*I*-range[c]
HCl	0.136	0.0848	0.0027	0.0025	0.1-6
LiCl	0.125	0.0513	0.0065	0.0036	0.1-6
NaCl	0.0514	-0.0136	0.0041	0.00080	0.1-6
KCl	0.0168	-0.0480	0.0090	0.00056	0.1-4.5
	ε				
HCl	0.125		0.012	0.011	0.1-6
LiCl	0.110		0.019	0.017	0.1-6
NaCl	0.0380		0.016	0.014	0.1-6
KCl	-0.00002		0.013	0.012	0.1-4.5
HCl	0.117		0.0056	0.0050	0.5-3
LiCl	0.0977		0.0060	0.0054	0.5-3
NaCl	0.0277		0.0069	0.0062	0.5-3
KCl	-0.00608		0.0092	0.0083	0.5-3
HCl	0.110		0.0009	0.00085	0.1-1
LiCl	0.0906		0.0016	0.0014	0.1-1
NaCl	0.0194		0.0013	0.0011	0.1-1
KCl	-0.0190		0.0028	0.0026	0.1-1
HCl	0.12[d]				0.5-3.5
LiCl	0.10				0.5-3.5
NaCl	0.03				0.5-3.5
KCl	0.00				0.5-3.5

[a]Standard deviation in the fit of equation (4); [b]mean deviation in the fit of equation (4); [c]in mol kg^{-1}; [d]Ciavatta (1980)

Table 2. The interaction coefficients of equation (4), with F(*I*) calculated using equation (9), for the activity coefficients of $MgCl_2$, $CaCl_2$ and $SrCl_2$

Electrolyte	ε_∞	ε_0	σ [a]	μ[b]	*I*-range[c]
$MgCl_2$	0.315	-0.0823	0.015	0.0096	0.3-15
$CaCl_2$	0.251	-0.0966	0.019	0.012	0.3-18
$SrCl_2$	0.224	-0.125	0.020	0.013	0.3-12
$MgCl_2$	0.320	-0.0858	0.017	0.012	0.3-6
$CaCl_2$	0.276	-0.132	0.019	0.013	0.3-6
$SrCl_2$	0.249	-0.158	0.020	0.014	0.3-6
	ε				
$MgCl_2$	0.221		0.11	0.11	0.3-15
$CaCl_2$	0.181		0.11	0.11	0.3-18
$SrCl_2$	0.123		0.088	0.083	0.3-12
$MgCl_2$	0.150		0.059	0.055	0.3-6
$CaCl_2$	0.105		0.059	0.054	0.3-6
$SrCl_2$	0.0781		0.060	0.055	0.3-6
$MgCl_2$	0.19[d]				0.5-3.5
$CaCl_2$	0.14				0.5-3.5

[a]Standard deviation in the fit of eq. (4); [b]mean deviation in the fit of eq. (4); [c]in mol kg^{-1}; [d]Ciavatta (1980).

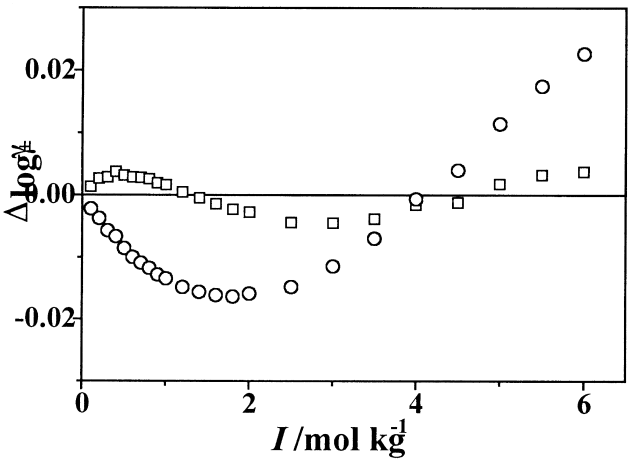


Figure 1 *Error plot ($\log\gamma_{\pm(exp)} - \log\gamma_{\pm(calcd)}$ vs I) for HCl activity coefficients using the two parameter model (□) and the one parameter model (○).*

$$\varepsilon_\infty = 0.136 + 0.07165\ f_1(T) + 0.1159\ f_2(T)$$

$$\varepsilon_0 = 0.0848 - 0.1024\ f_1(T) + 0.1970\ f_2(T)$$

Comparisons and correlations

Figures 2 and 3 show different plots in order to evidence: (i) the error behavior observed using different F(*I*) in equations (6) [F(*I*) of equations (7)–(9)]; and (ii) the scatter in log $\gamma_\pm$ calculated using the two parameter SIT and Pitzer approaches. Figure 2 shows that the performance of the different F(*I*) functions are (for HCl) very similar [σ = 0.002, 0.006 and 0.003 for equations (7), (8) and (9), respectively]. Similar behavior is observed for the other electrolytes, but with higher deviations. We did not consider equation (5) since it is indefinite at $I = 0$. Figure 3 shows the differences in $\gamma_\pm$ calculated using Pitzer and two parameter SIT equations at three different temperatures and in the range $0.01 \leq I$ /mol

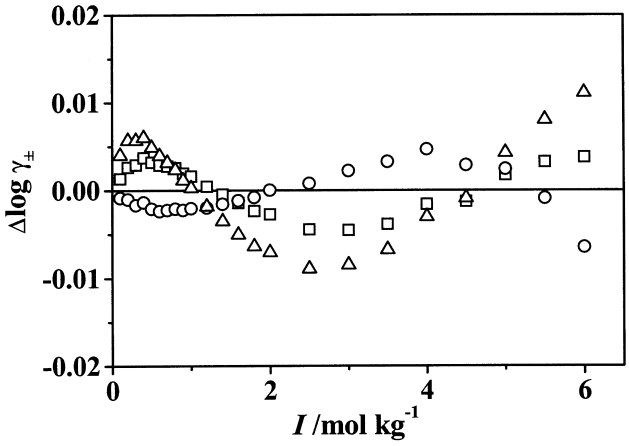


Figure 2 *Error plots ($\log\gamma_{\pm(exp)} - \log\gamma_{\pm(calcd)}$ vs. I) for HCl activity coefficients using the two parameter model with F(I) calculated by equation 7 (○), equation 8 (△) and equation 9 (□).*

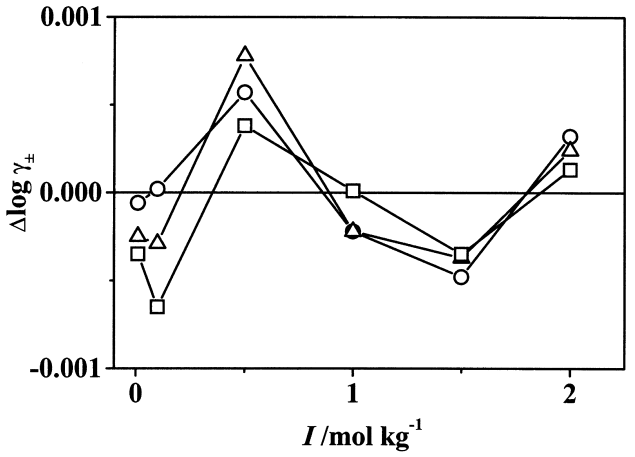


Figure 3 *Differences in $\gamma_{\pm}$ of HCl calculated by Pitzer and two parameter SIT equations, at t = 0 (○), 30 (△) and 60°C (□).*

Downloaded by [New York University] at 08:48 22 April 2015

$kg^{-1} \leq 2$. As can be seen, these differences are quite negligible and therefore, at least in the above ionic strength range, the two models can be considered to be equivalent. Several correlations have been proposed between interaction coefficients and other physical parameters, such as crystal radius. Moreover, it is likely that different interaction coefficients from different models can be correlated. These correlations will constitute the basis of the future development of this work, and here we report only the plot (Figure 4) $\varepsilon_0 = f(\beta^{(0)})$, where $\beta^{(0)}$ is the first interaction coefficient of Pitzer equations for HCl, LiCl, NaCl and KCl (Pitzer, 1991). The linear fit is quite satisfactory ($\sigma = 0.0047$; linear correlation coefficient $R = 0.9982$) and this indicates that general rules might be found for conversion from one model to another.

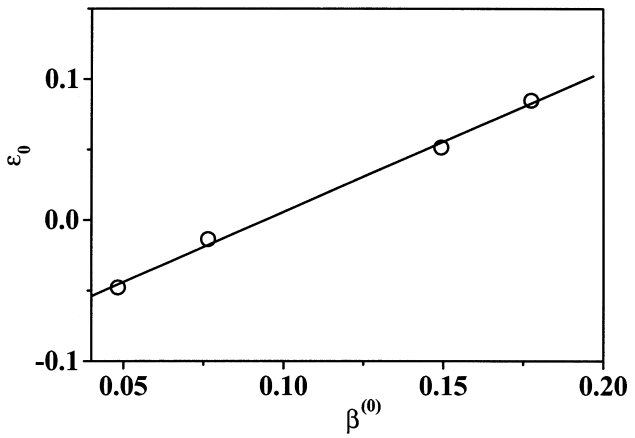


Figure 4 *Correlation between ε_0 (this work) and the first Pitzer interaction coefficient $\beta^{(0)}$ (–) for HCl, LiCl, NaCl and KCl, at t = 25°C.*

CONCLUSIONS

This paper describes a simple modification of the SIT model, *i.e.* a two parameter SIT equation that makes it possible, in the calculation of activity coefficients, to extend the ionic strength range to (at least) 6 mol kg^{-1}. The use of this model is compatible with the large volumes of traditional SIT data (ε = constant) present in literature; for small *I*-ranges one can set $\varepsilon = \varepsilon_0 = \varepsilon_\infty$. Future developments of this work will include: (a) the analysis of $\gamma_{\pm}$ for several other electrolytes; (b) the analysis of equilibrium data (protonation, metal complex formation and hydrolysis constants) at different ionic strengths; (c) the correlation between the interaction coefficients of different models and the correlation between interaction coefficients and other physical parameters.

ACKNOWLEDGEMENTS

We thank the University of Messina for financial support (PRA).

NOTATION

M, X	cations and anions
z_+, z_-	number of positive and negative charges in the cation and in the anion, respectively
ν_+, ν_-	number of cations and anions per molecule of electrolyte, respectively
ν	$\nu = \nu_+ + \nu_-$
$\underline{\nu}$	harmonic mean of ν_+ and ν_- ($\underline{\nu}^{-1} = \nu_+^{-1} + \nu_-^{-1}$)
m_M, m_X	concentrations (molal scale)
I	ionic strength (molal scale)
γ	activity coefficient (molal scale)
A	coefficient of Debye–Hückel equation
ε	interaction coefficient
T	temperature /K
t	temperature °C
θ	reference temperature /K

REFERENCES

Biedermann, G. 1975. Ionic media, in *Dahlem workshop on the nature of seawater*, pp. 339–362. Dahlem Konferenzen, Berlin.

Biederman, G. 1986. Introduction to the specific interaction theory with emphasis on chemical equilibria. In: Jenne, E.A., Rizzarelli, E., Romano, V. and Sammartano, S. (eds), *Metal complexes in solution*. pp. 303–314. Piccin, Padua, Italy.

Bromley, L.A. 1973. Thermodynamic properties of strong electrolytes in aqueous solutions. *AIChE J.*, **19**, 313–320.

Brönsted, J.N. 1922. Studies on solubility IV. Principle of the specific interaction of ions. *J. Am. Chem. Soc.*, **44**, 877–898.

Ciavatta, L. 1980. The specific interaction theory in the evaluating ionic equilibria. *Ann. Chim. (Rome)*, **70**, 551–562.

Ciavatta L. 1990. The specific interaction theory in equilibrium analysia. Some empirical rules for estimatine interaction coefficients of metal ion complexes. *Ann. Chim. (Rome),* **80**, 255–263.

Crea, F., De Stefano, C., Giuffrè, O. and Sammartano, S. 2004. Ionic strength dependence of protonation constants of N-Alkylsubstituted open chain diamines in NaCl. *J. Chem. Eng. Data*, **49**, 109–115.

Daniele, P.G., De Stefano, C., Foti, C. and Sammartano, S. 1997. The effect of ionic strength and ionic medium on the thermodynamic parameters of protonation and complex formation. *Curr. Top. Sol. Chem.*, **2**, 253–274.

De Robertis, A., De Stefano, C. and Foti, C. 1999. Medium effects on the protonation of carboxylic acids at different temperatures. *J. Chem. Eng. Data*, **44**, 262–270.

Foti, C, Gianguzza, A. and Sammartano, S. 1997. A comparison of equations for fitting protonation constants of carboxylic acids in aqueous tetramethylammonium chloride at various ionic strengths. *J. Sol. Chem.*, **26**(6), 631–648.

Foti, C., Sammartano, S. and Signorino, G. 1998. The dependence on ionic strength of protonation constants of carboxylic acids in aqueous tetraethylammonium iodide solution, at different temperatures. *Fluide Phase Equilibria*, **149**, 91–101.

Guggenheim, E.A. 1935. The specific thermodynamic properties of aqueous solutions of uni-univalent electrolytes. *Philos. Mag.*, **19**, 588–643.

Guggenheim, E.A. 1949. Thermodynacis, an advanced treatment for chemist and physicist. North Holland Publishing Co., Amsterdam.

Guggenheim, E.A. and Turgeon, J.C. 1955. Specific interaction of ions. *Trans. Faraday Soc.*, **51**, 747–761.

Guggenheim, E.A. 1966. *Application of statistical mechanics*. Clarendon Press, Oxford.

Harned, H.S., Owen, B.B. 1958. *The physical chemistry of electrolytic solutions*. Reinhold Publishing Corporation, New York.

Helgenson, H.C., Kirkhan, D,H., Flowers, G.C. 1981. Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600°C and 5kb. *Am. J. Sci.*, **281**, 1249–1516.

Millero, F.J. 2001. *Physical chemistry of natural waters*. Wiley Interscience, New York.

Partanen, J.I. and Covington, A.K. 2002. Re-evaluation of the activity coefficients of aqueous hydrochloric acid solutions up to a molality of 2.0 using two-parameter Hückel and Pitzer equations. Part II. Results from 0 to 95°C. *J. Sol. Chem.*, **31**(3), 197–210.

Pitzer, K.S. 1973. Thermodynamics of electrolytes. I. Theoretical basis and general equations *J. Phys. Chem.,* **77**(2), 268–277.

Pitzer, K.S. and Mayorga, G. 1973. Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent. *J. Phys. Chem.,* **77**(19), 2300–2308.

Pitzer, K.S. 1991. *Activity Coefficients in Electrolyte Solutions*, 2nd Edition, CRC Press, Boca Raton, Florida.

Robinson, R.A., Stokes, R.H. 1955. Electrolyte solutions. Butterworths scientific publications, London.

Scatchard, G. 1976. *Equilibrium in solution: surface and colloid chemistry*. Harvard University Press, Cambridge, Massachussetts.

Whitfield, M. 1973. A chemical model for the major electrolyte component of seawater based on the Brønsted-Guggenheim hypothesis. *Mar. Chem.,* **1**, 251–266.

Whitfield, M. 1975. An improved specific interaction model for seawater at 25 °C and 1 atmosphere total pressure. *Mar. Chem.,* **3**, 197–213.

Downloaded by [New York University] at 08:48 22 April 2015