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A simplified MSA model for the description of activity coefficients in electrolyte mixtures

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Abstract

A simple model is proposed within the framework of the mean spherical approximation (MSA) for a description of activity coefficients in aqueous electrolyte solutions. For simple salts, the model involves only one parameter per salt, which is the diameter of the hydrated cation. The optimum value of the latter is determined from a fit of the mean salt activity coefficient as a function of concentration in binary solutions of strong salts, up to an ionic strength of 3 mol kg^{-1} . This model is the simplest that can be devised within the MSA. It is thermodynamically consistent for the ion activity coefficients. Its capability to predict activity coefficients in mixtures, without introducing any additional parameter, is examined by testing the results against experimental data for ternary solutions. The results are also compared with those from the (empirical) Davies equation, which is used in speciation programs. Finally, some predictions for the speciation of the self-complexing salt ZnCl_2 , in binary solutions and in mixtures with NaCl , are presented. They are compared with experimental data in the case of binary solutions. Such evaluations may provide relevant information for the speciation of toxic metal cations in brines.

1 Introduction

The modeling of the thermodynamic properties of electrolyte solutions has long been the subject of intense work since the seminal work of Debye and Hückel (DH).¹ Since then, various noteworthy formulas have been derived from this theory, such as the Davies equation,² the specific interaction theory (SIT) by Guggenheim,³ the Pitzer model (inspired by the former).⁴ In these models with implicit solvent, the solvent is regarded as a dielectric continuum that manifests itself only through its dielectric constant.

Another well-known equation at the same level was obtained using the mean spherical approximation (MSA).⁵⁻⁸ This theory has been employed in many descriptions with implicit solvent in many various situations,⁹⁻¹⁴ and with explicit solvent as, e.g., in conjunction with a NRTL term¹⁵ or within the SAFT framework.¹⁶⁻¹⁸

The MSA theory may be seen as an extension of the DH theory in which excluded volume effects between ions are taken into account in a correct and consistent way, in the case of solutions of pure salts and electrolyte mixtures.⁸ In particular, volume exclusion between ions in the screening cloud is taken into account properly. In contrast, the DH theory overlooks this effect, which becomes more and more important as concentration is increased. An interesting property of the MSA is that, similarly, e.g., to SIT, the thermodynamic properties of mixed electrolytes may be deduced from those of single electrolytes,³ which is not the case of the original DH theory as highlighted by Guggenheim^{3,19} (in SIT, this drawback is overcome by ascribing the same minimum distance of approach to all ions).

The assessment of ion activity coefficients is useful for the determination of speciation in aqueous electrolyte solutions. Speciation programs are used worldwide to determine the distribution of complexes and the amount of free metal ions, in complex multicomponent aqueous solutions met in environmental situations. These programs include, e.g., MINEQL+,²⁰ CHESS,²¹ SPECIES,²² MINTEQ,²³ PHREEQC,²⁴ ChemEQL,²⁵ and CHEAQS Next,²⁶ the last five being free of charge. Deviations from ideality caused by electrostatic interactions are generally computed using the Davies equation² or, more rarely, the specific interaction theory¹⁹ (SIT), like in MINTEQ, for more concentrated solutions. CHEAQS Next (implemented by one of us,

W.V.) is a frequently used speciation program.²⁷ It offers the possibility of using either the MSA or the Davies equation to compute speciation.

In two recent works,^{28,29} we used a simplified version of the MSA for a description of mean salt activity coefficients at 25°C in moderately concentrated aqueous solutions of 2-1 salts (up to ionic strengths of 3 mol kg⁻¹). The MSA was employed in its most simple form in which ions have a constant diameter, and the solution permittivity is constant, equal to that of pure water (here constant means independent of salt concentration).

A similar procedure was employed by Triolo et al. in 1976 for a representation of the osmotic coefficient of binary aqueous electrolytes within the MSA.³⁰ Since the activity and osmotic coefficients do not fulfill the Gibbs-Duhem relation in this simple model (because no McMillan-Mayer to Lewis-Randall conversion^{14,31,32} is performed on them), the two treatments do not yield exactly the same values for the fitted cation diameters. Therefore, the latter must be evaluated in the present MSA model. In another study by Corti in 1987,³³ the activity coefficient of CaCl₂ in mixtures with NaCl was represented up to an ionic strength of 1.15 mol kg⁻¹ by employing a procedure similar to the one of the present work. To our best knowledge, this simple procedure has not been utilized ever since.

In the present MSA framework, ion sizes are assumed to be the main factor responsible for specific ion effects. The diameter of the cation is deemed to represent the effective size of the *hydrated* cation (of the bare ion plus a hydration shell). As in former work,^{13,14} the Pauling diameter was taken for the simple monovalent halide anions because they are expected to be more weakly hydrated than the alkali and alkaline earth cations considered here. In this most simple description within the MSA, the sole value of the cation diameter is adjusted in a fit of the mean salt activity coefficient in pure binary solution.

Then, it is naturally appealing to employ these same ion size values to describe electrolyte mixtures, for which the MSA can be used in a straightforward and consistent way. This method involves no new free parameter once the diameters of the cations present in the mixture have been determined from the consideration of pure binary solutions.

The purpose of the present work is to more systematically examine the reliability and

accuracy of this procedure to model activity coefficients in various binary and ternary aqueous solutions. In a first step, this assessment is made in the case of moderately concentrated solutions of strong salts. Then, if the test is conclusive, it may be expected that the model can be used in speciation programs when associating electrolytes are present, e.g. for environmental purposes involving ionic solutions such as natural brines.

Note that we are not looking for a very accurate description here (a more accurate and elaborate MSA model, with ion diameters and solution permittivity that vary with concentration, is already available^{14,34,35}). Instead, we want to develop a model that has some physical meaning, with only one free parameter per salt (the cation size), and which can give an estimation of ion activity coefficients with a reasonable accuracy up to higher ionic strengths than with most available speciation programs, typically to 3 mol kg⁻¹. It will be seen below that the Davies equation (employed in speciation programs up to ionic strengths of 0.1 or oftentimes 1 mol kg⁻¹) generally cannot give satisfactory results up to this value. In the same way it may be noted that Guggenheim recommended not to use his SIT theory above 0.1 mol kg⁻¹.³⁶

This work is organized as follows. In the next section, the MSA equations for arbitrary mixtures of strong salts are presented. Then, they are used to assess suitable cation diameter values in the case of binary solutions. After this step, these values are utilized to compute activity coefficients in ternary mixtures of strong salts, and these predictions are compared with experimental data, and results from the Davies equation. The case of solutions of the self-associating salt ZnCl₂ is finally considered. Some predictions for the speciation in binary, and ternary ZnCl₂+NaCl, solutions are reported. They are compared with some available experimental data in the case of binary solutions. Finally, a conclusion closes this work.

2 Theoretical

2.1 The MSA model

The MSA equations for the activity coefficients of ions in mixtures of strong (fully dissociated) salts dissolved in water are given in this section.

In the present model, the ions are modeled as charged hard spheres (HS) of constant diameter σ_i , and valence z_i . At the McMillan-Mayer level, the size of a significantly hydrated cation is expected to be larger than its crystallographic diameter, because the former includes the thickness of a hydration shell. The electrolyte is dissolved in a dielectric continuum with relative permittivity ε_W (generally water), that is assumed not to vary with salt concentration.

The total activity coefficient of an ion i within the model, y_i , is composed of two terms,^{7,13,14} one arising from volume exclusion and another from electrostatic interactions between ions. It is given on *molar scale* by,

$$\ln y_i = \ln y_i^{HS} + \ln y_i^{el} \quad (1)$$

where the superscripts ‘HS’ and ‘el’ indicate hard sphere and electrostatic contributions, respectively.

For an ion i the electrostatic contribution is expressed within the MSA by,¹³

$$\ln y_i^{el} = -\lambda \left[\frac{\Gamma z_i^2}{1 + \Gamma \sigma_i} + \eta \sigma_i \left(\frac{2z_i - \eta \sigma_i^2}{1 + \Gamma \sigma_i} + \frac{\eta \sigma_i^2}{3} \right) \right] \quad (2)$$

in which,

$$\lambda = \frac{\beta e^2}{4\pi \varepsilon_0 \varepsilon_W}, \quad \eta = \frac{1}{\Omega} \frac{\pi}{2\Delta} \sum_k \frac{\rho_k \sigma_k z_k}{1 + \Gamma \sigma_k} \quad (3)$$

$\beta = 1/k_B T$ (with T the temperature and k_B the Boltzmann constant), e is elementary charge, ε_0 is the permittivity of a vacuum,

$$\Omega = 1 + \frac{\pi}{2\Delta} \sum_k \frac{\rho_k \sigma_k^3}{1 + \Gamma \sigma_k}, \quad \Delta = 1 - \frac{\pi}{6} \sum_k \rho_k \sigma_k^3 \quad (4)$$

where Δ is the volume fraction of free space (not occupied by solute particles), and ρ_i is the number density of ion i (number of ions per cubic meter).

Moreover, Γ is the inverse of the MSA screening length which satisfies the equation,

$$\Gamma^2 = \pi \lambda \sum_k \rho_k \left[(z_k - \eta \sigma_k^2) / (1 + \Gamma \sigma_k) \right]^2 \quad (5)$$

Its value can be easily determined numerically by using a simple iterative procedure. By rewriting eq. 5 as $\Gamma = f(\Gamma)$, then it suffices to compute the sequence, $\Gamma_{n+1} = f(\Gamma_n)$, starting, e.g., with the initial value $\Gamma_0 = \kappa/2$ where κ is the classic DH screening parameter defined by $\kappa^2 = 4\pi\lambda \sum_i \rho_i z_i^2$. Generally, iterations converge in a few steps.

Moreover we have for the HS part,

$$\ln y_i^{HS} = -\ln \Delta + \sigma_i F_1 + \sigma_i^2 F_2 + \sigma_i^3 F_3 \quad (6)$$

in which F_1 , F_2 and F_3 are given by,¹³

$$F_1 = \frac{3X_2}{\Delta}, \quad F_2 = \frac{3X_1}{\Delta} + 3\frac{X_2^2}{X_3} \frac{1}{\Delta^2} + 3\frac{X_2^2}{X_3^2} \ln \Delta$$

$$F_3 = \left(X_0 - \frac{X_2^3}{X_3^2} \right) \frac{1}{\Delta} + \frac{3X_1X_2 - X_2^3/X_3^2}{\Delta^2} + 2\frac{X_2^3}{X_3} \frac{1}{\Delta^3} - 2\frac{X_2^3}{X_3^2} \ln \Delta$$

where

$$X_n = \frac{\pi}{6} \sum_k \rho_k \sigma_k^n$$

The mean activity coefficient of a salt S is given by,

$$\ln y_S = \frac{\nu_+ \ln y_+ + \nu_- \ln y_-}{\nu_+ + \nu_-} \quad (7)$$

in which + and - denote the cation and the anion of the salt, and ν_+ and ν_- are their stoichiometric numbers, respectively. For a comparison with experimental data, the activity coefficient on molar scale, y_S , are converted to *molal scale*, γ_S , by using the classic formula,³⁷

$$\gamma_S = y_S / (V d_W) \quad (8)$$

where V is the specific volume of solution (volume of solution per kg of solvent), and d_W is the

density of pure solvent. V may be computed from the relation,

$$V = (1 + \sum_s m_s M_s) / d \quad (9)$$

where m_s and M_s are the molality and molar mass of salt s , respectively, and d is the density of solution.

In the present work (as in the previous ones^{28,29}) no McMillan-Mayer-to-Lewis-Randall (MM-LR) conversion^{14,31,32} is performed on y_S . As any theory with implicit solvent, the MSA is a theory at the McMillan-Mayer level, and experimental data are obtained at the Lewis-Randall level. It has been shown³² that when the ionic strength is sufficiently low, the MM-LR conversion on activity coefficients does not modify appreciably their value. In the present case, for ionic strengths below 3 mol kg⁻¹, the modification would generally be of a few percent only. This approximation moreover provides some simplification in the treatment because the MM-LR conversion would require a knowledge of densities for binary solutions and salt mixtures.¹⁴ In the present simplified treatment, the MSA results for activity coefficients on molal scale, γ_S (eq. 8), will be compared with experimental data on the same scale.

In passing, it should be noticed that, because no MM-LR conversion is applied, it will not be possible to compare MSA results for the osmotic coefficient with experimental data. The reason is that the MM osmotic coefficient (not given here) would not be thermodynamically consistent with γ_S , that is the two would not fulfill the Gibbs-Duhem relation.

It would also need to be mentioned that eqs. 2-5 could have been replaced by simpler, explicit, but approximate, MSA expressions.^{38,39} These involve the introduction of a mean ion diameter which provides an explicit formula for the screening MSA parameter Γ , from which the thermodynamic functions are derived. However, these approximations would lead to a loss of thermodynamic consistency for the ion activity coefficients because they would contravene the fundamental relation,

$$\partial \ln y_i / \partial \rho_j = \partial \ln y_j / \partial \rho_i \quad (10)$$

In contrast, the above formulas 2-5 for the full MSA satisfy this relation. Therefore their use

should be recommended in applications employing the MSA. They do not add much complexity, and eq. 5 can always be solved very easily by simple iterations.

2.2 The Davies equation

The MSA results will be compared with those from the Davies equation. This equation was proposed by Davies in 1938 as an empirical extension of the DH limiting equation.² Speciation programs utilize it for the calculation of the activity coefficients of a species i at 25°C in the form,

$$\log_{10} y_i^{Davies} \simeq -0.51 z_i^2 \left(\frac{\sqrt{I_c}}{1 + \sqrt{I_c}} - a I_c \right) \quad (11)$$

(after correction of a misprint in eq. 11 of Ref. 28), with I_c the ionic strength on concentration (molar) scale,

$$I_c \equiv \frac{1}{2} \sum_k z_k^2 C_k \quad (12)$$

calculated with the concentrations of all solutes k , and a is a parameter that was taken to be $a = 0.2$ originally by Davies² for a representation of activity coefficients of 2-1 salts up to $I_c \simeq 0.1 \text{ mol L}^{-1}$. In most speciation programs, the value $a = 0.3$ seems to be preferentially used up to $I_c \simeq 1 \text{ mol L}^{-1}$.

It is noted that the Davies equation is a function of the sole ionic strength. It does not make difference between ions of the same charge. Clearly, this equation was originally proposed for not too concentrated solutions in which specific ion effects are weak.

If one sets, $L = -\log_{10} y_i^{Davies} / z_i^2$, which is independent of i according to eq. 11, then it is easy to show that, for a salt $S = MX_n = (M^{n+}, nX^-)$ where $n = 1$ or 2 , one gets from eq. 7,

$$I_c = \frac{1}{2} n(n+1) C_S \quad (13)$$

for a binary solution of salt S, in which C_S is the molar concentration, and one gets from eqs. 7 and 11,

$$y_S^{Davies} = 10^{-nL} \quad (14)$$

Hereafter, the ionic strength on molal scale, $I_m \equiv 1/2 \times \sum_k z_k^2 m_k$, will also be used, with m_k the molality of ion k .

3 Results

3.1 Binary solutions of strong salts

In this section, results for solutions of strong 1-1 (uni-univalent) and 2-1 (di-univalent) salts are reported in Table 1. For the salts considered in this table, the chlorides were regarded as being fully dissociated up to 3 mol kg^{-1} when no evidence for complexation was found in conductivity experiments as reported by Sillen and Martell.⁴⁰ The bromides and iodides were also assumed to be strong electrolytes. These salts are considered accordingly in the CHEAQS database. Sodium hydroxide, to which a low association constant may be ascribed,^{34,40} was viewed as a strong electrolyte below 3 mol kg^{-1} .

Eqs. 1-9 were used to compute the MSA mean salt activity coefficients in solutions at 25°C . The molar concentrations of the solutions were determined by utilizing their densities which were obtained using the correlation of Ref. 41. Values for the cation diameters were determined from a fit of experimental activity coefficients obtained from a program developed at NBS at that time (now NIST), Gamphi,⁴² which provides recommended values for γ_S . The data above 0.1 mol kg^{-1} were fitted up to an ionic strength of 3 mol kg^{-1} , that is up to $m_S = 3 \text{ mol kg}^{-1}$ for 1-1 salts and $m_S = 1 \text{ mol kg}^{-1}$ for 2-1 salts. Data below 0.1 mol kg^{-1} were not included in the fits because they are not very effective in the determination of the cation diameter; including them would artificially lower the deviation of fit because they are much easier to describe than data at higher concentrations.

The results of these fits are presented in Table 1, and, to illustrate, in Figures 1-4 for the chloride salts LiCl, NaCl, SrCl₂, and BaCl₂. Salts of rubidium and cesium were not considered because they exhibit some significant ion-pairing association.⁴⁰ Pauling diameters were used for halide ions. Values obtained previously within the MSA model¹⁴ were adopted for the following anions: nitrate, NO₃⁻ (3.4 Å), and perchlorate, ClO₄⁻ (4.53 Å).

The mean values of the cation diameters for the halide salts given in Table 1 are listed in Table 2. The optimum diameter of the hydroxide ion OH^- in NaOH solution is found to be $\sim 3.57 \text{ \AA}$ (AARD= 2%) when taking the mean diameter of Na^+ from Table 1, which is very close to the value of 3.55 \AA previously found with the full MSA model.³⁴

Table 1: Adjusted values of ion diameters^a.

Ion	Salt	$\sigma_+ / (\text{\AA})$	AARD ^b
H ⁺	HClO ₄	3.735	2.2 %
	HCl	4.284	2.8 %
	HBr	4.432	3.2 %
	HI	4.467	5.9 %
Li ⁺	LiClO ₄	3.968	4.4 %
	LiCl	4.050	2.4 %
	LiBr	4.108	1.7 %
	LiI	4.227	5.1 %
	LiNO ₃	4.011	3.1 %
Na ⁺	NaClO ₄	1.572	3.6 %
	NaCl	2.887	2.6 %
	NaBr	3.010	2.4 %
	NaI	3.075	2.6 %
K ⁺	KCl	2.256	2.5 %
	KBr	2.167	2.7 %
	KI	2.093	3.3 %
Mg ²⁺	Mg(ClO ₄) ₂	6.120	2.5 %
	MgCl ₂	5.796	2.5 %
	MgBr ₂	6.096	2.0 %
	MgI ₂	6.126	2.4 %
Ca ²⁺	Ca(ClO ₄) ₂	5.593	1.7 %
	CaCl ₂	5.320	1.9 %
	CaBr ₂	5.679	2.8 %
	CaI ₂	5.757	3.0 %
Sr ²⁺	Sr(ClO ₄) ₂	5.209	1.3 %
	SrCl ₂	5.064	1.8 %
	SrBr ₂	5.404	3.0 %
	SrI ₂	5.632	3.7 %
Ba ²⁺	Ba(ClO ₄) ₂	4.630	2.5 %
	BaCl ₂	4.619	1.6 %
	BaBr ₂	4.969	2.2 %
	BaI ₂	5.593	3.6 %

^aPauling diameter for simple monoatomic ions: Cl⁻=3.62 Å, Br⁻=3.9 Å, I⁻=4.32 Å; other anions: NO₃⁻= 3.4 Å, ClO₄⁻= 4.53 Å;¹⁴ ^bAverage absolute relative deviation of fit with the present MSA model, AARD(%) = 100/N × ∑_{k=1}^N | [γ_S^{cal}(k) - γ_S^{exp}(k)] | / γ_S^{exp}(k), with N the number of data points.

It is observed in Table 1 that the cation diameter values of the 3 halides and the perchlorate (in the case of divalent cations) of a given cation are in fair agreement. The values of Table 2 are seen to decrease in the series of 1-1 and 2-1 salts when going from H⁺ to K⁺, and from Mg²⁺ to Ba²⁺, respectively. This outcome is consistent with the expected drop of ion hydration when

Table 2: Average values of adjusted cation diameters for halide salts, $\bar{\sigma}_+$.

Ion	$\bar{\sigma}_+ /(\text{\AA})$	AARD
H ⁺	4.39	4.2 %
Li ⁺	4.13	3.1 %
Na ⁺	2.99	2.7 %
K ⁺	2.17	2.9 %
Mg ²⁺	6.01	3.6 %
Ca ²⁺	5.58	4.3 %
Sr ²⁺	5.37	5.0 %
Ba ²⁺	5.06	7.0 %

^aAARD defined in note *b* of Table 1.

the diameter of the bare ion rises. The diameters are also observed to be larger for divalent cations than for monovalent, which is in accord with the expected higher hydration of the divalent cations. It is also seen in Table 2 that the size of the K⁺ ion is smaller than the Pauling value (2.66 Å). This outcome is due to the fact that the solution relative permittivity in the model is taken constant, equal to that for pure water (ε_W), while it should decrease and be always smaller than ε_W . Actually, all cation diameter values of Table 2 are smaller than those fitted in Ref. 14 where the solution permittivity was allowed to vary with concentration. In the present model, a smaller ion diameter introduces an enhanced attraction between unlike ions, which compensates for the permittivity being kept constant. The K⁺ cation is the first one in the series of alkali cations for which the fitted diameter falls below the Pauling diameter.

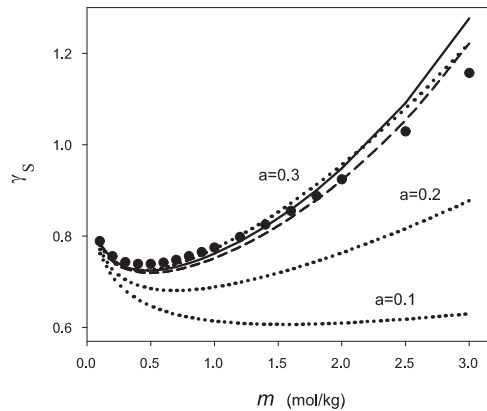


Figure 1: Activity coefficient of LiCl in water. Symbols = experimental data; Solid line = MSA result with mean Li⁺ diameter value (4.13 Å, see Table 2); Dashed line = MSA result with adjusted Li⁺ diameter value for LiCl solution (4.05 Å, see Table 1); Dotted lines = result from Davies equation with $a = 0.1, 0.2,$ and 0.3 in eq. 11.

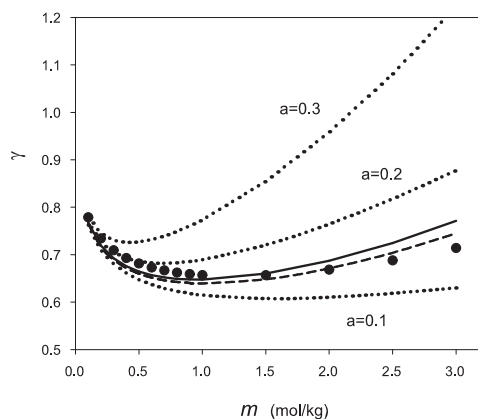


Figure 2: Same as Fig. 1 in the case of NaCl solution.

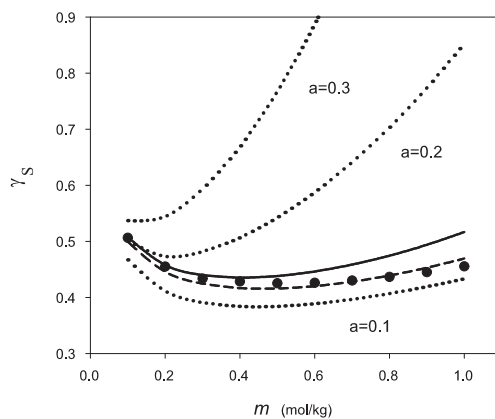


Figure 3: Same as Fig. 1 in the case of SrCl₂ solution.

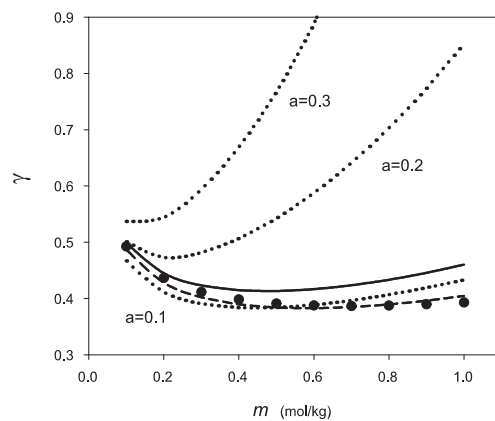


Figure 4: Same as Fig. 1 in the case of BaCl₂ solution.

Figures 1-4 show the results for the activity coefficient γ_S up to 3 mol kg⁻¹ for the 1-1 salts LiCl and NaCl, and to 1 mol kg⁻¹ for the 2-1 salts SrCl₂ and BaCl₂. These fits are of

reasonable accuracy. The latter is of course better when the individual diameter values of Table 1 is employed. The values for the chlorides given in Table 1 might be used for applications in which NaCl is the major salt in the mixture. Otherwise, the accuracy will be sufficient for use in speciation programs when those of Table 2 are used.

On the other hand, a look at these results for chloride salts shows that no common value for a is capable of describing the data for rather concentrated solutions. The same outcome is observed in the case of bromides and iodides (not shown). Clearly, this result does not come as a surprise since the Davies equation gives a result for the activity coefficient y_S that is a function of the sole ionic strength while y_S varies with the nature of the salt for a given I_c in sufficiently concentrated solutions.

Somewhat surprisingly, it is seen that the experimental data of the 2-1 chloride salts are extremely poorly described by the Davies equation with $a = 0.3$, and better described with $a = 0.1$. The same trend was observed for the other 2-1 salts. It may be recalled that, originally, the value taken by Davies for a was 0.2, up to an ionic strength of 0.1 mol kg^{-1} ,² and it is generally taken to be $a = 0.3$ in speciation programs up to 1 mol kg^{-1} . The suitable value of a for 2-1 salts therefore decreases when their concentration is raised.

3.2 Ternary solutions of strong salts

The cation diameter values of Table 2 were employed to compute the activity coefficients of salts in aqueous ternary mixtures at 25°C . Hence, no new free parameter was introduced to compute the activity coefficients from the MSA model. The Pauling diameters were used for simple monoatomic ions (see note a of Table 1, and for the size of the nitrate ion NO_3^- and that of the perchlorate ion ClO_4^-).

Experimental data for γ_S were retrieved from the literature. Such data are not plentiful because the measurement of activity coefficients in mixtures is not easy. Most experiments have been conducted for the measurement of osmotic coefficients. Note that the activity coefficient data for CaCl_2 in mixtures with NaCl,⁴³ described by Corti³³ using a MSA model, are not considered here because these data were not obtained by direct measurements, but resulted from

osmotic and NaCl activity data from various sources combined with the use of thermodynamic assumptions.

Densities of mixtures were determined using a relation proposed in eq. 33 of Ref. 44.

The systems examined in this work are collected in Table 3. Experimental data for which the ionic strength was lower than 3 mol kg⁻¹ were considered in the calculations.

Table 3: Results for MSA activity coefficients in mixtures with average cation diameters taken from Table 2. Pauling diameters for simple anions (see note *a* of Table 1), and anions: NO₃⁻ = 3.4 Å, OH⁻ = 3.57 Å.

Mixture A + B	Measured γ_S	AARD ^a	Ref.
HCl + LiCl	γ_A	2.1 %	45
HCl + KCl	γ_A	3.2 %	46
LiCl + LiNO ₃	γ_A, γ_B	2.6 %, 2 %	47
NaCl + NaOH	γ_A, γ_B	1.5 %, 1.2 %	48
HBr + NaBr	γ_A	3.4 %	49
HBr + KBr	γ_A	1.1 %	49
HCl + BaCl ₂	γ_A	3.1 %	50
HCl + SrCl ₂	γ_A	2.6 %	51
LiCl + BaCl ₂	γ_A, γ_B	3.5 %, 4.3 %	52

^aAverage absolute relative deviation on γ_A , and γ_B when available, respectively.

The results for the mixture NaCl+NaOH, for which experimental data for the activity coefficients of *either salt* are available, are presented in Figures 5 and 6 at ionic strengths of 0.5 and 1 mol kg⁻¹, respectively, together with those from the Davies equation with $a = 0.3$. The latter value of 0.3 was used because it is commonly employed in speciation programs. It is observed that the MSA result is much more accurate than that from the Davies equation. At the same time, the discrepancy is not huge because the ionic strength is not high (0.5 and 1 mol kg⁻¹).

The result for the mixture HBr+KBr is displayed in Figure 7 up to 3 mol kg⁻¹ of KBr, for a constant HBr concentration of 0.01 mol kg⁻¹. It is found that the activity coefficient of HBr is very well described by the MSA model in which the mean diameter values of H⁺ and K⁺ of Table 2 were used. This is a very satisfactory outcome because the concentration of HBr in these mixtures is much lower than that of KBr (up to 300 times), so one could have expected a less good result in this very asymmetric solution. On the other hand, it is observed that the result from the Davies equation increasingly deviates from the experimental data when the

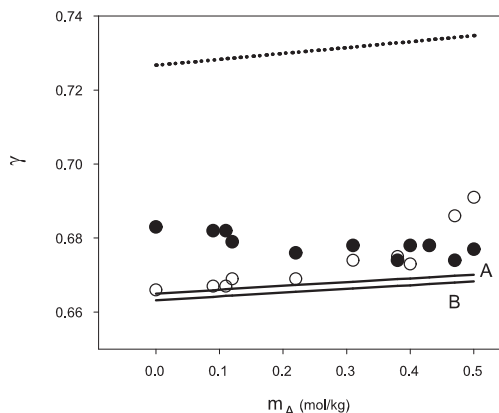


Figure 5: Activity coefficients of NaCl (salt A) and NaOH (salt B) in the ternary aqueous mixture NaCl+NaOH as a function of the molality of NaCl, for a constant ionic strength of 0.5 mol kg^{-1} . Filled symbols = experimental data for γ_{NaCl} ; empty symbols = same for γ_{NaOH} ; solid lines = MSA result; dotted line = result from Davies equation ($a=0.3$).

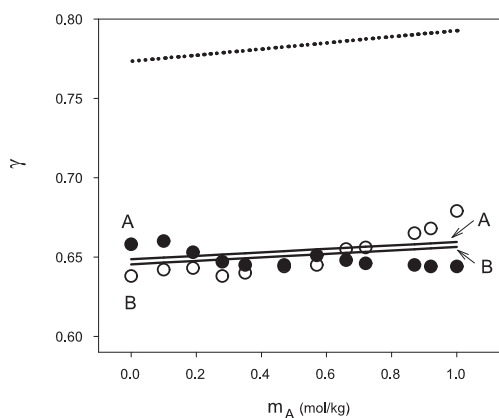


Figure 6: Same as Figure 5 for a constant ionic strength of 1 mol kg^{-1} .

concentration is raised.

Finally, the mixture LiCl+BaCl₂ is another ternary system for which the experimental activity coefficients of *both salts* are available at 25°C. This system is interesting also because one of the 2 salts possesses a divalent cation, which generally produces larger deviations from ideality than monovalent cations do. The results are shown in Figures 8-10 at ionic strengths of 0.5, 1, and 3 mol kg⁻¹.

It is seen in these figures that the MSA results with the fitted individual diameter values of Table 1 at the higher ionic strength of 3 mol kg⁻¹ are better than with those of Table 2, and they are unexpectedly worse at the two lower of 0.5 and 1 mol kg⁻¹. Both are significantly

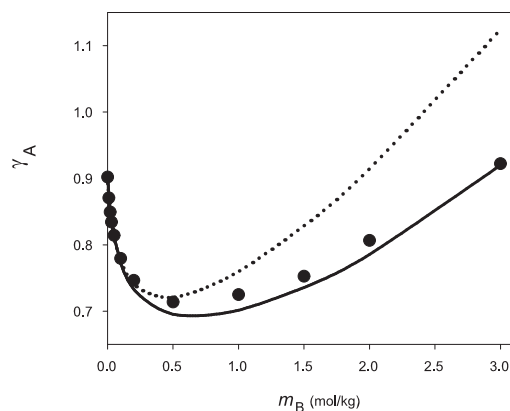


Figure 7: Activity coefficient of HBr at a constant molality of 0.01 mol kg^{-1} in the ternary aqueous mixture HBr (salt A) + KBr (salt B) as a function of m_B at 25°C . Filled symbols = experimental data for γ_{HBr} ; solid line = MSA result with cation diameters of Table 2; dotted line = result from the Davies equation with $a=0.3$.

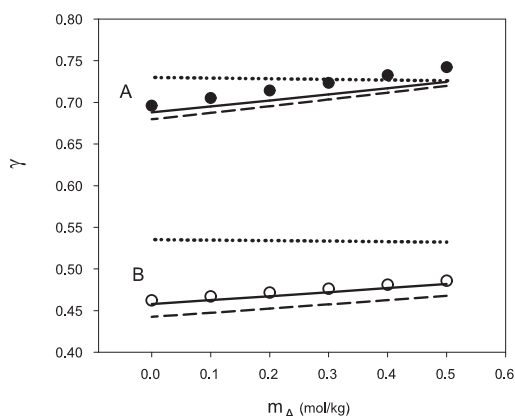


Figure 8: Activity coefficients of LiCl (salt A) and BaCl_2 (salt B) in the ternary aqueous mixture $\text{LiCl}+\text{BaCl}_2$ for a constant ionic strength of 0.5 mol kg^{-1} . Filled symbols = experimental data for γ_{LiCl} ; empty symbols = same for γ_{BaCl_2} ; solid lines = MSA result with average diameters of Table 2; dashed lines = MSA result with diameters of Table 1 for the 2 salts; dotted lines = result from the Davies equation ($a=0.3$).

better than those from the Davies equation, especially at 3 mol kg^{-1} , where the MSA activity coefficient of BaCl_2 is about more than 3 times lower. The activity coefficient from the Davies equation deviates most from experimental data for low LiCl concentrations.

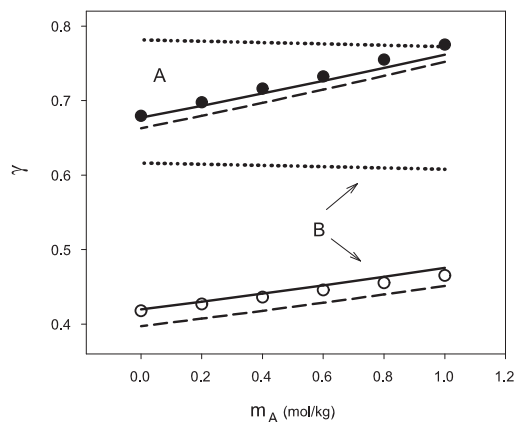


Figure 9: Same as Figure 8 for a constant ionic strength of 1 mol kg^{-1} .

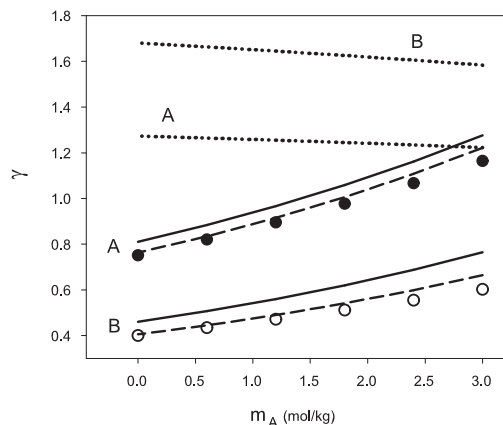


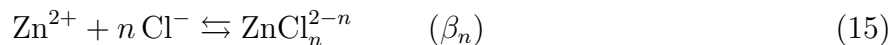
Figure 10: Same as Figure 8 for a constant ionic strength of 3 mol kg^{-1} .

3.3 Speciation in mixtures of a self-associating salt with a strong salt: case of $\text{ZnCl}_2 + \text{NaCl}$

The preceding sections have shown that the present MSA model gives acceptable results for mixtures when it is parameterized by considering one-salt solutions. This satisfactory outcome suggests that the model may now be used to make *predictions* in the case of mixtures forming complexes, for which realistic diameter values for the complexes can be assessed in an independent procedure as, e.g., in the case of divalent metal cations that associate with anions.²⁸

To illustrate, such predictions are made here for mixtures of ZnCl_2 with the strong salt NaCl , which is the major constituent of seawater and natural brines. The estimation of activity coef-

coefficients is used to calculate the speciation in this system. The results are compared with those from the Davies equation. For this purpose, the program ‘CHEAQS NEXT’,^{26,29} and FORTRAN programs implemented in Refs. 28 and 53, were employed. The two were cross-checked against each other. In these programs, the equations for the various complexation equilibria, and the conservation of total zinc and chloride ions, are solved numerically by iterations (e.g., by using a multidimensional Newton-Raphson algorithm in the FORTRAN program). The HS and electrostatic (MSA or Davies) contributions to the activity coefficients y_i of all ions i are computed by using their diameters and concentrations. The stepwise complexation equilibria are,



where β_n is the equilibrium complexity constant,

$$\beta_n = \frac{y_n}{y_0 (y_{\text{Cl}^-})^n} \frac{C_n}{C_0 (C_{\text{Cl}^-})^n} \quad (16)$$

in which subscript n indicates the number of chloride anions in the complex, $n = 0$ designates the free zinc ion Zn^{2+} , and C_n is the concentration of complex of order n .

The diameters of the free Zn^{2+} and the 4 zinc complexes with the chloride anion, $\sigma_n = \sigma(\text{ZnCl}_n^{2-n})$, and the values of the complexity constants, β_n , were taken from previous work:²⁸ $\sigma_0 = 6.03 \text{ \AA}$, $\sigma_1 = 6.35 \text{ \AA}$, $\sigma_2 = 6.06 \text{ \AA}$, $\sigma_3 = 5.55 \text{ \AA}$, and $\sigma_4 = 5.44 \text{ \AA}$ (with $\sigma_{\text{Cl}^-} = 3.62 \text{ \AA}$); $\log_{10} \beta_n = 0.15, 0.27, 0.30, \text{ and } -2.3$ for $n = 1, \dots, 4$. The diameter of the free Zn^{2+} ion was obtained from a fit of the mean activity coefficient of $\text{Zn}(\text{ClO}_4)_2$, which is a strong salt.^{54,55} In the case of complexes, their volume was assessed by adding the volumes of their constituents, and their diameter was taken to be that of a sphere having the same volume.²⁸

3.3.1 Binary solutions of ZnCl_2

The mean activity coefficient of ZnCl_2 was computed from the activity coefficients and the fractions of free Zn^{2+} and Cl^- (eqs. 5-7 of Ref. 28). In the Davies equation, the ionic strength was determined from the values of the concentrations of the complexes and the free ions (determined

using the Davies equation).

With these ingredients, the mean activity coefficient of ZnCl_2 in a binary aqueous solution is very well described up to a molality of 2 mol kg^{-1} with the present MSA model, as shown in Figure 11 (AARD = 0.15%). This is not the case with the Davies equation. It was found that no value of a can satisfactorily describe the mean activity coefficient of ZnCl_2 in the range of 0.1 to 2 mol kg^{-1} (with the same complexity constants). At this upper molality value the ionic strength is $I_m \sim 2.7 \text{ mol kg}^{-1}$ ($I_c \sim 2.55 \text{ mol L}^{-1}$) when using the MSA (association lowers the value of I_c as compared to a fully dissociated electrolyte). They are of $\sim 2.9 \text{ mol kg}^{-1}$, 2.3 mol kg^{-1} , and 1.9 mol kg^{-1} , when employing the Davies equation with $a = 0.1$, 0.2 and 0.3 , respectively.

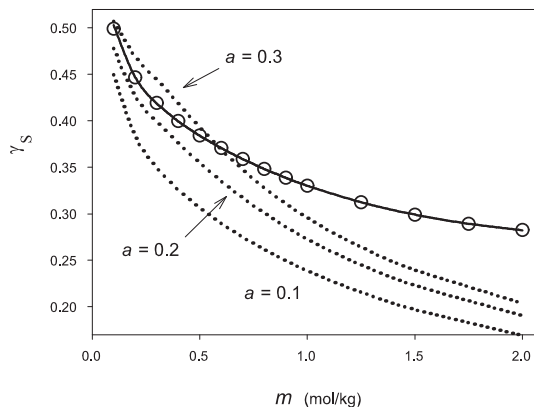


Figure 11: Mean activity coefficient of ZnCl_2 in binary aqueous solution. Symbols = experimental data; Solid line = MSA result (see text); Dotted lines = results from Davies equation with $a = 0.1$, 0.2 , and 0.3 in eq. 11.

The mean activity coefficient of ZnCl_2 at 0.1 mol kg^{-1} computed from the Davies equation with $a = 0.3$ is nearly equal to the MSA value and, as expected, both coincide with the experimental value. For $0.1 \text{ mol kg}^{-1} < m < 0.7 \text{ mol kg}^{-1}$ and $a = 0.3$, γ_S^{Davies} is a bit larger than the experimental data, and it deviates more and more from them above 0.7 mol kg^{-1} . With $a = 0.1$ and 0.2 , γ_S^{Davies} is always below the experimental results, and it deviates progressively more as the concentration is increased.

Some experimental measurements are available in the literature about the amount of free Zn^{2+} and of the first complex ZnCl^+ , and about the mean coordination number of zinc with

chlorides (average number of chlorides in the complexes), defined by $N_{Cl} = \sum_{n=1}^4 n f_n$ where f_n is the fraction of complex n at a given concentration ($f_n = C_n/C_S$). It is possible to compute these quantities in our speciation programs.

A comparison was made between the computed values for f_0 , f_1 , and N_{Cl} and their experimental measurements. The results are collected in Table 4.

Table 4: Experimental and calculated results for the speciation and N_{Cl} in pure $ZnCl_2$ solutions.

Ref.	Concentration	Experimental data	Calculated
56	1.62 M	$f_0 = 0.51 \pm 0.12$	0.45
56	2.08 M	$f_0 = 0.46 \pm 0.09$	0.39
56	1.47 M	$f_1 = 0.14 \pm 0.03$	0.12
56	1.89 M	$f_1 = 0.12 \pm 0.02$	0.11
57	1 mol kg ⁻¹	$N_{Cl} = 0.9 \pm 0.1$	0.9
57	2 mol kg ⁻¹	$N_{Cl} = 1.6 \pm 0.1$	1.4

These results show that the model predicts very well the results from these experimental measurements about speciation in $ZnCl_2$ solutions. This agreement is a very satisfactory, and admittedly somewhat startling, outcome from this simple model.

3.3.2 $ZnCl_2$ in NaCl solutions

Next, the case of ternary mixtures of $ZnCl_2$ at tracer concentrations in concentrated NaCl was investigated. It is generally believed that the *free* metal ion is the most toxic species⁵⁸ in the environment. Hence, the amount of free metal cation is a key parameter in toxicological studies.^{59,60} A zinc tracer concentration of 2×10^{-5} mol L⁻¹ has been observed in natural brines.⁶¹ For these reasons, the amount of free Zn(II) ion in ternary aqueous solutions $ZnCl_2 + NaCl$ was studied for a constant $ZnCl_2$ concentration of 2×10^{-5} mol L⁻¹ and a concentration of NaCl varying in the range of 0.1 mol L⁻¹ to 3 mol L⁻¹. Since this zinc content is very low compared with that of NaCl, any $ZnCl_2$ concentration below this value would nearly yield the same result for the relative amount of free Zn^{2+} .

Predictions for the ratio of free Zn^{2+} ion to total zinc, $r_0 = [Zn^{2+}]/[Zn_{tot}]$, in these solutions is plotted in Figure 12. This ratio was computed by using the present MSA model and the Davies equation with $a = 0.1, 0.2, \text{ and } 0.3$. The predictions for r_0 from the Davies equation

are below the MSA for $a = 0.2$ and 0.3 , and above it for $a = 0.1$.

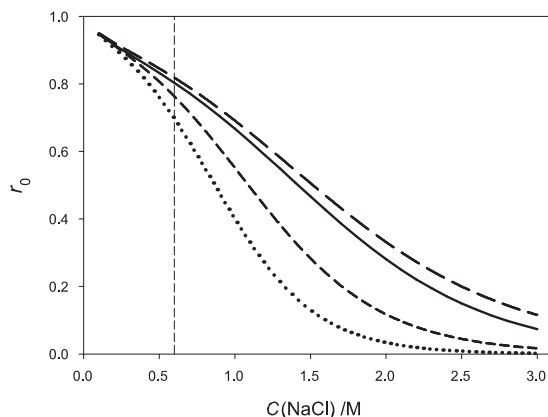


Figure 12: Fraction of free Zn^{2+} in ternary aqueous solutions $\text{ZnCl}_2+\text{NaCl}$ (log scale). Solid line = MSA result; Long-dashed, short-dashed, and dotted lines = results from Davies equation with $a = 0.1, 0.2,$ and 0.3 , respectively. The vertical line indicates the concentration of NaCl in seawater (~ 0.6 M).

The ratio of the two, $r_0(\text{MSA})/r_0(\text{Davies}) = [\text{Zn}^{2+}(\text{MSA})]/[\text{Zn}^{2+}(\text{Davies})]$, is plotted in Figure 13. This figure shows that the deviation between the results from the MSA and the Davies equation rises with the NaCl concentration. The free Zn^{2+} concentration at 3M NaCl, obtained from the MSA, is predicted to be more than 35 times that from the Davies equation with $a = 0.3$, and ~ 4 times that with $a = 0.2$. For seawater ($C(\text{NaCl}) \sim 0.6\text{M}$), the ratio $[\text{Zn}^{2+}(\text{MSA})]/[\text{Zn}^{2+}(\text{Davies})]$ is predicted to be of the order of 1.15 for $a = 0.3$, 1.05 for $a = 0.2$, and 0.98 for $a = 0.1$. So, in the case of seawater, and at lower concentrations, the Davies equation and the MSA yield nearly the same value for the free zinc concentration. Notable differences occur at higher NaCl contents. However, it was found that taking $a \sim 0.124$ gives results for r_0 that are in keeping with those from the MSA. It would be interesting to see whether this outcome is also true for other divalent metal cations in tracer amounts in NaCl brines.

4 Conclusion

Satisfactory descriptions for the activity coefficient of a number of salts in binary and ternary aqueous solutions has been obtained within the MSA up to ionic strengths of 3 mol kg^{-1} . In this

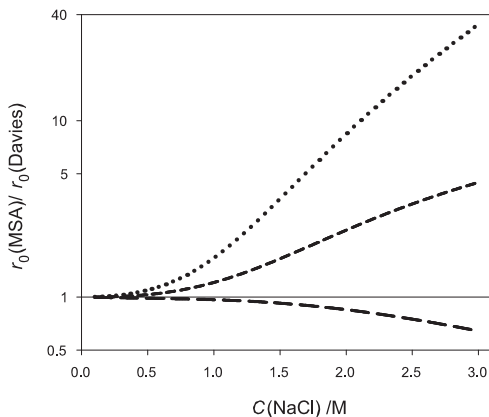


Figure 13: Ratio, $r_0(\text{MSA})/r_0(\text{Davies}) = [\text{Zn}^{2+}(\text{MSA})]/[\text{Zn}^{2+}(\text{Davies})]$, as a function of NaCl concentration (log scale). Long-dashed, short-dashed, and dotted lines = results from Davies equation with $a = 0.1, 0.2,$ and $0.3,$ respectively.

model, a salt is characterized by the diameters of the cation and anion. They can be adjusted by considering the deviations from ideality in binary solutions. No additional free parameter is required to predict the activity coefficient of ions in mixtures. This model generally performs much better than the Davies equation, which was originally proposed for much lower ionic strengths (below 0.1 mol kg^{-1}), but often used up to 0.5 or 1 mol kg^{-1} in speciation programs.

In solutions in which ionic strength can reach 3 mol kg^{-1} , there is no common value of a that can describe the activity coefficients of 1-1 and 2-1 salts. However, in the case of brines, in which a salt like NaCl is at a high concentration, the speciation, for an ion like Zn^{2+} that forms complexes with the anion of the dominant salt, might be described with a value of a of the order of 0.1.

The present study strongly suggests that use of this simplified MSA model in speciation programs will allow for an improved determination of speciation up to ionic strengths significantly higher than with the Davies equation, and with a higher accuracy. Application to binary solutions of the self-complexing ZnCl_2 salt shows that this MSA model is able to reliably predict experimental speciation results for this salt.

An interesting feature of the model in the case of associating electrolytes is that the value for the size of a given complex (which is the only parameter characterizing the complex) may be estimated on the basis of geometric considerations. The size of the free cation can in general

be adjusted by considering a binary solution comprised of a strong salt of this cation (such as the perchlorate). If so, no new parameter is required within the model to predict the activity coefficients of the species, and the speciation. This feature provides some predictive capability to this MSA model.

This property is in contrast with other models, like SIT or Pitzer, in which the parameters for the complexes have little or no clear physical meaning, and would consequently need to be adjusted.

The present MSA model is currently being developed within the CHEAQS NEXT speciation program,²⁶ which is devised for multicomponent mixtures.

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Note

The authors declare no competing financial interest.

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