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# Short communication

# The single salt approximation for the major components of seawater: association and acid–base properties

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## ABSTRACT

In this note we propose the use of the single salt approximation for the composition of seawater. This approximation has been applied to a synthetic seawater. Association and acid–base properties have been determined.

*Keywords:* Artificial seawater; seawater major components; complexing ability of seawater; single salt approximation.

Minor and trace components of seawater interact to different extents with inorganic major constituents ($Na^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$, $Cl^-$ and $SO_4^{2-}$). Metal ions are complexed by $Cl^-$ and $SO_4^{2-}$ both as free ions (Smith and Martell, 1976), *i.e.* $M^{z+}$, and as hydroxo species $M(OH)_n^{(z-n)}$ (unpublished results). *O*-ligands (carboxylates, phenols, hydroxycarboxylates) form weak species with $Na^+$ and $K^+$, and fairly stable complexes with $Mg^{2+}$ and $Ca^{2+}$. Amines form quite weak complexes with $Cl^-$ and $SO_4^{2-}$ in their protonated form (Daniele *et al.*, 1995; De Robertis *et al.*, 1993) and with $Mg^{2+}$ and $Ca^{2+}$ (these laboratories, unpublished results). Amino acids show an intermediate behaviour (De Stefano *et al.*, 1995).

In order to quantify these interactions, two approaches have been followed (1) by studying the effect of seawater major components on the activity coefficients of metal ions and ligands (Pitzer, 1991; Whitfield, 1975); and (2) by building up appropriate complex formation models based on all significative binary interactions (Garrels and Thompson, 1962; Millero, 1982, 1990). Hybrid models have been also proposed (Millero and Schreiber, 1982). For these studies, artificial seawaters have been used (Demianov *et al.*, 1995; De Robertis *et al.*, 1997; De Stefano *et al.*, 1994; Fiol *et al.*, 1995; Garrels and Thompson, 1962; Khoo *et al.*, 1977; Johnson and Pytkowicz, 1979, 1981; Millero and Schreiber, 1982; Millero *et al.*, 1987). However, results are often not easy to read, and the comparisons between the strength of interactions of the inorganic components of seawater with different ligands (or classes of ligands) cannot be made in a simple way.

For this reason we considered the inorganic major components of seawater as a single salt (BA), in order to study the anion and cation interactions in a more simple way, and to study self association and acid–base properties of this salt by considering an artificial seawater (SSWE, Synthetic Sea Water for Equilibrium Studies, De Stefano *et al.*, 1994) whose composition[1] is reported in Table 1. The concentration of the single salt BA was calculated as mean ionic concentration, and the result-

**Table 1** *Composition of SSWE , at 25°C and S = 35‰ (De Stefano et al., 1994).*

|  | C (mol dm$^{-3}$) | m (mol kg$^{-1}$) |
|---|---|---|
| NaCl | 0.4221 | 0.42740 [a] |
| Na$_2$SO$_4$ | 0.0288 | 0.02919 |
| KCl | 0.0110 | 0.01112 |
| CaCl$_2$ | 0.0111 | 0.01121 |
| MgCl$_2$ | 0.0548 | 0.05552 |
| BA | 0.5751 | 0.58240 |
| *I* | 0.717 | 0.726 |

[a] molalities at other salinities can be calculated by the equation

$$m_s = m_{35}\ 27.56572\ S\ /(1000 - 1.005714\ S)$$

[1]*Many other recipes for artificial seawater have been proposed (De Stefano et al., 1994) with very similar composition. As regards studies on the complexing ability of the inorganic contents of seawater towards different ligand classes, different seawaters should give quite close results.*

**Table 2** *Protonation constants of $A^{z-}$.*

| S% | log $K_{HA} \pm 3s$[a] |
|----|------------------------|
| 5  | $0.07 \pm 0.03$        |
| 15 | $0.00 \pm 0.03$        |
| 25 | $-0.04 \pm 0.03$       |
| 35 | $-0.05 \pm 0.03$       |
| 45 | $-0.075 \pm 0.04$      |

[a] s = standard dev.

ing charge is $\pm 1.117$. The anion $A^{z-}$ can be protonated and the protonation constants have been obtained experimentally by potentiometric measurements[2]. Results at different salinities are reported in Table 2. The self association of BA and the hydrolysis of $B^{z+}$ [to give $B(OH)^{(z-1)}$] can be calculated by considering the complex formation model already proposed for SSWE (De Robertis *et al.*, 1994). In this model all the interactions with $K > 0.1$ mol$^{-1}$ dm$^3$ were taken into account and the free concentrations of all the components can be estimated. From the difference between total and free mean ionic concentration, the association constant for $BA^0$ can be evaluated. The hydrolysis constant for $B(OH)^{(z-1)}$ is obtained from the differences between effective and apparent $K_w$. All the equilibrium constants, at 25°C and $I = 0$ mol dm$^{-3}$, are reported in Table 3. The dependence on temperature and ionic strength of log $K$ for the species $HA^{(1-z)}$, $BA^0$ and $B(OH)^{(z-1)}$ is given by the equations (De Stefano *et al.*, 1997)

$$\log K = \log {}^T K_{25} + G(I) + F(T)$$

$$G(I) = -z^* \, DH + C \, I + C'I \, (T\text{-}\theta)$$
$$= a_1 \, S^{1/2} + a_2 \, S + a_2{}' \, S \, (T\text{-}\theta)$$

$$F(T) = \frac{\Delta H'}{R'}\left(\frac{1}{\theta} - \frac{1}{T}\right) + \frac{\Delta C_p{}'}{R'}\left(\frac{\theta}{T} - 1 + \ln\frac{T}{\theta}\right)$$

where $\log {}^T K$ is the equilibrium constant at $I = 0$ mol dm$^{-3}$, $DH = I^{1/2}/(2+3I^{1/2})$, $z^* = \Sigma(\text{charge})^2_{\text{reactants}} - \Sigma(\text{charge})^2_{\text{products}}$, and $\theta$ is the reference Temperature (25°C). Values of the refined parameters are reported in Table 3.

The thermodynamic parameters[3] in Table 3 allow the complete definition of the salt BA, and therefore, the formation parameters of complexes formed by the minor and trace components of seawater (ligand and /or metal ions) can be calculated with $B^{z+}$ and /or $A^{z-}$.

The single salt approximation has been applied to the study of interactions of BA with some classes of ligands [carboxylic and hydroxocarboxylic acids, amine and amino acids (these laboratories, work in progress); $PO_4^{3-}$, $P_2O_7^{4-}$ and $P_3O_{10}^{5-}$ (De Stefano *et al.*, 1998)]. As an example , we report in Figure 1, the stability of BL (L = carboxylic ligand) and $L'AH_i$ ($L'H_i^{i+}$ = protonated poliamine) complexes as a function of ligand charge. The use of the single salt approximation gives a simple picture of the strength of inorganic major

component–ligand class interactions, to compare different classes, and to draw interesting stability–charge relationships[4].

## AKNOWLEDGEMENTS

**Table 3** *Thermodynamic parameters for the self association of BA, for the protonation of $A^{z-}$ and the hydrolysis of $B^{z+}$, at 25°C and I = 0 mol dm$^{-3}$.*

| Reaction | log ${}^T K_{25}$ | $\Delta H'_{25}$ | $\Delta C'_{p25}$ |
|----------|-------------------|------------------|-------------------|
| (1) $B^{z+} + A^{z-} = BA^0$ | $-0.03$ | 0 | 0 |
| (2) $H^+ + A^{z-} = HA^{(1-z)}$ | $0.24 \pm 0.05$[a] | $14.6 \pm 1.5$[a] | $100 \pm 35$[a] |
| (3) $B^{z+} = B(OH)^{(z-1)} + H^+$ | $-12.75$ | 65.5 | $-102$ |

| | $z^*$ | C | C' | $a_1$ | $a_2$ | $a_2'$ |
|----|-------|------|----------|---------|---------|----------|
| (1) | $-2.494$ | 0.105 | $-4.2 \cdot 10^{-3}$ | $-0.1224$ | 0.01122 | $-6.6 \cdot 10^{-5}$ |
| (2) | $-2.233$ | 0.095 | – | $-0.04826$ | 0.00145 | – |
| (3) | 0.234 | $-0.205$ | – | $-0.0163$ | $-0.00169$ | – |

[a] $\pm 3$ (standard deviation)
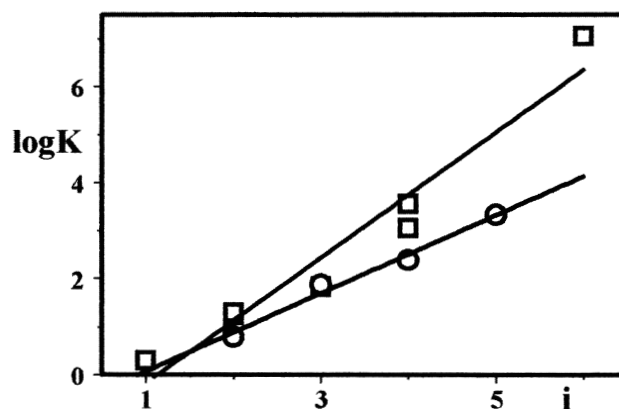


**Figure 1** *Log K values vs charge of ligands.*

□ *logK for the reaction: $H_i(am)^{i+} + A^{z-} = H_i(am)A^{(z-i)+}$ (i = 2, ethylenediamine; i = 3, diethylenetriamine; i = 4, triethylentetzamine; i = 5, tetraethylenpentamine);*

○ *logK for the reaction: $B^{z+} + L^{i-} = BL^{(z-i)+}$ (i = 1, acetate; i = 2, malate and tartrate; i = 3, propan-1,2,3-tricarboxylate; i = 4, butane-1,2,3,4-tetracarboxylate and pyromellitate; i = 6, benzenehexacarboxylate);*

[2] *Potentiometric measurements were performed using [H$^+$]-glass electrode at T = 5, 15, 25, 35, 45°C. Solutions containing SSWE at different salinities (with NaCl in part substituted by HCl) were titrated with NaOH. The electrode couple was calibrated by titrating SSWE (without SO$_4^{2-}$, and NaCl in part substituted by HCl). Apparatus, procedure and calculations were as previously reported (De Robertis et al., 1993; Daniele et al., 1995; De Stefano et al., 1995).*
[3] *$\Delta H'$ and $\Delta Cp'$ values (molal scale) can be converted to $\Delta H^0$ and $\Delta C_p^0$ values (molal scale) by using appropriate conversion factors (De Stefano et al., 1994).*
[4] *Other major components of seawater are HCO$_3^-$ and F$^-$ which play a negligible role as regards the interactions with ligands. In contrast, they are quite important in the speciation of metal ions and must be considered, at least as 'external' components, when studying hydrolysis and complexation reactions in SSWE.*

# REFERENCES

Daniele, P.G., Prenesti, E., De Stefano, C. and Sammartano, S. 1995. Formation and Stability of Proton-Amine-Inorganic Anion Complexes in Aqueous Solution. *J. Solut. Chem.*, **24**, 325.

Demianov, P., De Stefano, C., Gianguzza, A. and Sammartano, S. 1995. Equilibrium Studies in Natural Waters: Speciation of Phenolic Compounds in Synthetic Seawater at Different Salinities. *Environ. Toxicol. Chem.*, **14**, (5), 767.

De Robertis, A., De Stefano, C., Patanè, G. and Sammartano, S. 1993. Effects of Salt on the Protonation in Aqueous Solution of Triethylenetetramine and Tetraethylenepentamine. *J. Solut. Chem.*, **22**, 927.

De Robertis, A., De Stefano, C., Gianguzza, A. and Sammartano, S. 1994. Equilibrium Studies in Natural Fluids: a Chemical Speciation Model for the Major Constituents of Seawater. *Chem Speciat Bioavail*, **6**, 65–84.

De Robertis, A., Foti, C., Gianguzza, A. and Sammartano, S. 1997. Chemical Speciation of Some Classes of Low Molecular Weight Ligands in Seawater. In: Gianguzza, A., Pelizzetti, E. and Sammartano, S. (eds), *Marine Chemistry: An Environmental Analytical Chemistry Approach*, Water Science and Technology Library, Vol. 25, pp. 59–69. Kluwer Academic, Dordrecht.

De Stefano, C., Foti, C., Gianguzza, A., Rigano, C. and Sammartano S. 1994. The Equilibrium Studies in Natural Fluids. The Use of Synthetic Sea Waters and Other Media as Background Salts. *Ann. Chim. (Rome)*, **84**, 159–175.

De Stefano, C., Foti, C., Gianguzza, A., Rigano, C. and Sammartano S. 1995. Chemical Speciation of Amino acids in Electrolyte Solutions Containing Major Components of Natural Fluids. *Chem Speciat Bioavail,* **7**, 1–7

De Stefano, C., Sammartano, S., Mineo, P. and Rigano, C. 1997. Computer Tools for the Speciation of Natural Fluids. In: Gianguzza, A., Pelizzetti, E. and Sammartano, S. (eds), *Marine Chemistry: An Environmental Analytical Chemistry Approach*. Water Science and Technology Library, Vol. 25, pp. 71–85. Kluwer Academic, Dordrecht.

De Stefano, C., Foti, C., Gianguzza, A. and Sammartano S. 1998. Equilibrium Studies in Natural Fluids: Interactions of $PO_4^{3-}$, $-P_2O_7^{4-}$ and $-P_3O_{10}^{5-}$ with the Major Constituents of Sea Water. *Chem Speciat Bioavail,* **10**(1), 19–26.

Dyrssen, D. and Wedborg, M. 1974. Equilibrium Calculations of the Speciation of Elements in Seawater. In: Goldberg, E.D. (ed.), *The Sea* Vol. 5, pp. 181–195, Wiley Interscientia.

Fiol, S., Brandariz, I. and Sastre de Vincente, M. 1995. The Protonation Constants of Glycine in Artificial Seawater at 25°C. *Marine Chem.*, **49**, 215–219.

Hepler, L.G. 1981. Correct Calculation of $\Delta H°$, $\Delta C_p°$ and $\Delta V°$ from Temperature and Pressure Dependences of Equilibrium Constants: the Importance of Thermal Expansion and Compressibility of the Solvent, *Thermochim. Acta*, **50**, 69–72.

Garrels, R.M. and Thompson, M.E. 1962. A Chemical Model for Sea Water at 25°C and One Atmosphere Pressure. *Am. J. Sci.*, **260**, 57–66.

Johnson, K.S. and Pytkowicz, R.M. 1979. Ion association and activity coefficients in multicomponents solution, in *Activity Coefficients in Electrolyte Solutions*, Pytkowicz, R.M. Editor, Vol. II, 1–61, CRC Press Inc.

Johnson, K.S. and Pytkowicz, R.M. 1981. The activity of NaCl in seawater of 10–40% salinity and 5–25 °C at 1 atmosphere. *Marine Chem.*, **10**, 85–91.

Khoo, K.H., Ramette, R.W., Culberson, C.H. and Bates, R.G. 1977. Determination of hydrogen ion concentration in sea water from 5 to 45 °C: standard potentials at salinities from 20 to 45‰. *Analytical Chem.*, **49**, 29–34.

Millero, F.J. 1982. Use of the models to determine ionic interactions in natural waters. *Thalassia Jugosl.*, **18**, 253–291.

Millero, F.J. 1990. Marine solution chemistry and ionic interactions. *Marine Chem.*, **30**, 205–229.

Millero, F.J., Hershey, J.P. and Fernandez, M. 1987. The pK* of TRISH in Na-K-Mg-Ca-Cl-SO₄ brines – pH scales. *Geochim. Cosmochim. Acta*, **51**, 707–711.

Millero F.J. and Schreiber, D.R. 1982. Use of the ion pairing model to estimate activity coefficients of the ionic components of natural waters. *Am. J. Sci.*, **282**, 1508–1540.

Pitzer, K.S. 1991. Ion interaction approach: theory and data correlation, in *Activity coefficients in electrolyte solution*, 2^ ed., CRC Press, Boca Raton.

Smith, R.M. and Martell, A.E. 1976, Critical Stability Constants, Volume 4: Inorganic Complexes, Plenum Press, New York.

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

# Erratum

In the article 'Chemical Speciation of cadmium in controlling Indian soil types' by V. Ramachandran and T.J. D'Souza Volume 9(4), 1997, on page 126 the legend to the Figure should read 'Figure 6. Extraction of cadmium from sewage sludge', and on page 129 the legend to the Figure should read 'Figure 3. Extraction of cadmium from alfisol'.