

The physical chemistry of natural waters

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Abstract - Ionic interactions have been shown to affect the thermodynamic and transport properties of natural waters as well as bio- and geo-chemical processes taking place in these waters. The ionic interaction models used to account for these interactions have been examined. Simple additivity models are used to estimate the density and sound speed of the mixtures of sea salts and seawater. The estimated values are shown to be in good agreement with the measured values. The ion pairing and specific interaction models are used to estimate the activity coefficients of ions in seawater and brines. The results are shown to be in good agreement with measured values. The estimated activity coefficients are shown to yield reliable values of the pK for the ionization of acids.

INTRODUCTION

A knowledge of ionic interactions is necessary to understand the chemical processes that occur in natural waters such as rivers, lakes, estuaries, seas and ocean waters. Short range ion-water and ion-ion interactions have been shown to affect equilibria processes (acid-base, solubility, oxidation-reduction) as well as the physical-chemical properties of natural waters (ref. 1-13). Since ionic interactions affect the state of metal ions, many have suggested that biological activity is affected by ionic interactions (ref. 7,10,14, 15). Recent work (ref. 16) has also shown that ionic interactions can affect the rates of chemical processes in natural waters.

As a physical chemist there are two basic questions that one would like to answer concerning natural waters: 1. How are the physical chemical properties affected by ionic interactions? and 2. How do these ionic interactions affect bio-, geo-chemical processes that occur in natural waters? To answer these questions it is necessary to have ionic interaction models that can be used to estimate the effect of ion-water and ion-ion interactions in multi-component electrolyte solutions of known composition. In recent years a number of major advances have been made on developing ionic interaction models for multi-component electrolyte solutions (ref. 17-26). Over the past few years we and others have attempted to use these models to examine how ionic interactions affect the chemical processes that occur in natural waters. In this paper I will briefly review some of this recent work.

CONDITIONS IN NATURAL WATERS

Before we examine the physical chemistry of natural waters it is appropriate to examine the conditions of the natural electrolyte solutions we are considering. In Table 1, the ranges

TABLE 1. Conditions of Natural Waters

Water	Temp. Ranges/ $^{\circ}C$	Pressure Ranges/b	Concentration Ranges/m
Ocean Waters	-2 to 40	0 to 1000	0.1 to 0.8
Lakes	0 to 40	0 to 50	0.002 to 6
Lagoons	0 to 40	0 to 1	0.1 to 17
Seas	0 to 40	0 to 10	0.1 to 7
Hydrothermal Brines	0 to 400	0 to 500	0.7 to 6

of temperature, pressure and ionic strength are given for some typical natural waters. The maximum ranges are -2 to 400°C in temperature, 0 to 1100b in pressure and 0 to saturation in ionic strength. The relative composition of the major components of natural waters can be quite variable depending upon the local drainage basins. Some comparisons of the major components of some rivers, lakes, seas and ocean waters are compared in Fig. 1.

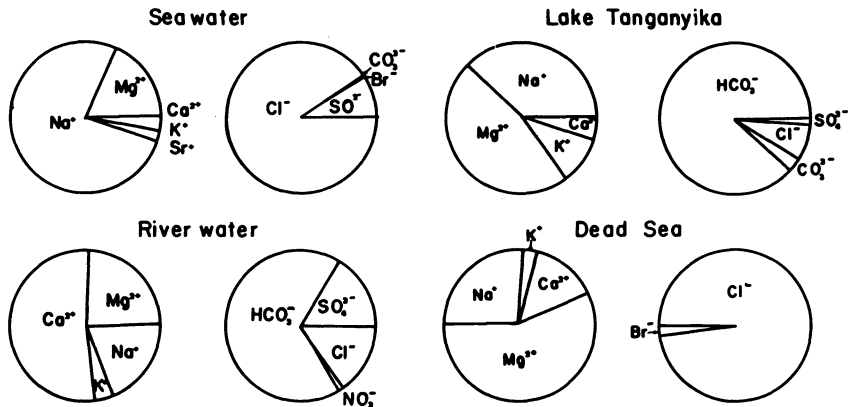


Fig. 1. The equivalent fraction of cations and anions in natural waters.

As is quite apparent from this comparison not only does the ionic strength vary over a wide range, but the composition of cations and anions can differ considerably for natural waters.

If the composition of a natural water is known, it is possible to use ionic interaction models to estimate the physical properties of these waters and the effect these ionic interactions have on thermodynamic and rate processes. In the next two sections we will examine these estimations for some natural waters.

PHYSICAL PROPERTIES

The effect of ionic interactions on the physical properties of natural waters has been studied by a number of workers (ref. 1,3,6,9,11). To estimate the physical properties of natural waters of known composition it is necessary to know the properties of the major ionic components of the mixtures (ref. 3). One can then use additivity methods to estimate the property of the solution (P). This is done using apparent molal properties (ϕ)

$$P = P^0 + \phi e_T \quad (1)$$

where P^0 is the property for water and e_T is the total equivalents (or moles) of ionic components in the mixture. One of the most important generalizations concerning the behavior of ϕ for mixed electrolyte solutions is that first developed by Young (ref. 27). In this classic study it was shown that the apparent molal property of a mixed electrolyte solution is given by

$$\phi = \sum N_i \phi_i \quad (2)$$

where $N_i = m_i/m_T$ is the mole fraction of electrolyte i and ϕ_i is the molal property of i at the ionic strength of the mixture. This simple additivity rule assumes that as a first approximation the excess mixing properties can be neglected ($\Delta P_{\text{ex}} = 0$). Improvements in eq. (2) have been made by Wood and co-workers (ref. 18,28,29). The new equation is

$$\phi = \sum_M \sum_X E_M E_X \phi(\text{MX}) \quad (3)$$

where E_M and E_X are the equivalent fractions of cations (M) and anions (X). This method of adding the components of the mixture accounts for all the plus-minus interactions and yields more reliable estimates for ϕ of the mixture.

As has been demonstrated in numerous studies eq. (3) can be used to estimate reliable

thermodynamic (ref. 2,6,30-37) and transport (ref. 3,38) properties of rivers, lakes and seawater.

Comparisons of the measured and calculated densities of seawater (ref. 6) diluted with water shown in Table 2 demonstrate the reliability of using eq. 3.

The calculated densities agree with the measured values to $+ 25 \times 10^{-6} \text{ g cm}^{-3}$. Although eq. (3) gives reliable estimates for dilute natural waters, for brines the estimates are not as reliable due to the larger excess mixing properties at higher ionic strengths. This is demonstrated in Table 3 for Red Sea brines (ref. 37).

TABLE 2. Comparisons of the Measured and Calculated Densities (g cm^{-3}) of Seawater at 25°C ^a (S = salinity)

I	S	$\delta d, 10^6$
0.11	5	-4
0.21	10	-7
0.31	15	-7
0.41	20	-5
0.51	25	1
0.61	30	11
0.72	35	24

a) Millero (ref. 6)

TABLE 3. Comparison of the Measured and Calculated Relative Densities (g cm^{-3}) of Red Sea Brines Diluted with Water at 25°C ^a

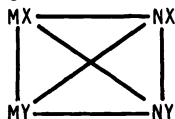
I	Measured	
	$(d-d_0)10^3$	$\delta d, 10^6$
0.470	18.360	-18
1.218	46.136	81
1.752	64.986	134
2.614	93.984	199
3.561	123.974	211
4.234	144.207	235
5.333	175.610	297
6.124	197.281	444

a) Millero, et al. (ref. 37).

To add the excess mixing parameters to the additivity relationship one takes advantage of the findings of Young and co-workers (ref. 39,40). In these studies they demonstrated that as a first approximation the excess mixing properties of two electrolytes with a common ion (MX + NX) are independent of the uncommon ion (X). This gives

$$\Delta P_{\text{ex}} (\text{MX} + \text{NX}) \cong \Delta P_{\text{ex}} (\text{MY} + \text{NY}) \quad (4)$$

They also demonstrated that the excess properties for reciprocal salt pairs (MX + NY) given by the diagram



can be approximated by the so called cross square rule given by

$$\Sigma \square = \Sigma X \quad (5)$$

This cross square rule states that the sum of the excess mixing properties around the sides of the diagram is equal to the sum of the excess properties of the cross mixtures. This gives the following

$$\begin{aligned} \Delta P_{\text{ex}} (\text{MX} + \text{NX}) + \Delta P_{\text{ex}} (\text{NX} + \text{NY}) + \Delta P_{\text{ex}} (\text{MY} + \text{NY}) + \Delta P_{\text{ex}} (\text{MY} + \text{MX}) = \\ \Delta P_{\text{ex}} (\text{MX} + \text{NY}) + \Delta P_{\text{ex}} (\text{NX} + \text{MY}) \end{aligned} \quad (6)$$

This cross square rule has been shown to hold for a number of electrolyte systems (ref. 41,42). More recent work has demonstrated the reliability of this rule for the volume and compressibility properties of the major sea salts, $\text{NaCl} + \text{MgSO}_4$. This is demonstrated in Table 4 for the changes in volume (ΔV_m) and compressibility (ΔK_m) of mixing the major sea salts at 25°C (ref. 18).

The addition of the excess mixing term to eq. (3) gives

$$\phi = \sum_M \sum_X E_M E_X \phi(\text{MX}) + \Delta P_m / e_T \quad (7)$$

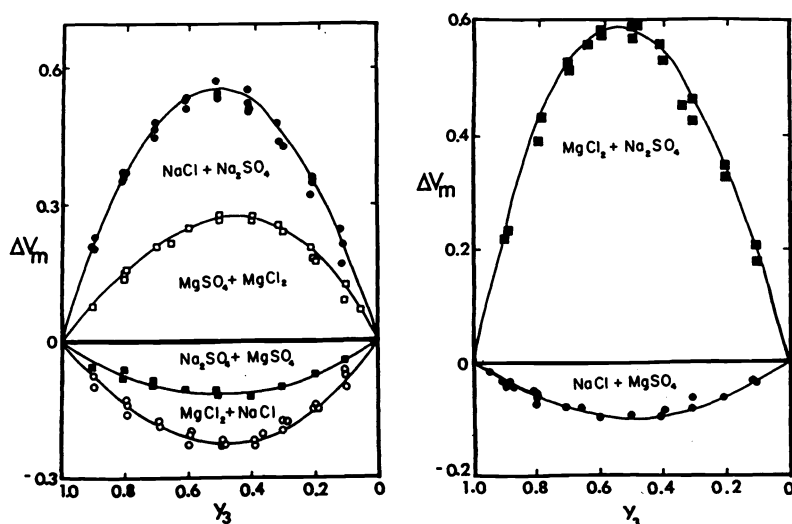
TABLE 4. Verification of the Cross Square Rule For the Major Sea Salts at $I = 3.0$ and $t = 25^\circ\text{C}$

Common Ion	$\Delta V_m(\text{max})/$ $\text{cm}^{-3} \text{ mol kg}^{-1}$	$10^4 \Delta K_m(\text{max})/$ $\text{cm}^3 \text{ mol kg}^{-1} \text{ b}^{-1}$
NaCl - Na ₂ SO ₄	0.56	1.65
Na ₂ SO ₄ - MgSO ₄	-0.11	-0.67
MgSO ₄ - MgCl ₂	0.27	0.65
MgCl ₂ - NaCl	-0.22	-1.03
Uncommon Ion		
NaCl - MgSO ₄	-0.06	-1.34
MgCl ₂ - Na ₂ SO ₄	0.59	1.98
Comparison of $\Sigma \square$ and ΣX		
$\Sigma \square$	0.50	0.60
ΣX	0.53	0.64
	-0.03	-0.04

The excess mixing term in eq. (7) has been formulated by Reilly and Wood (ref. 29) using the cross-mixing rule (ref. 33)

$$\Delta P_m/e_T = (e_T/4) [\Sigma E_M E_N E_X (Z_M + Z_X) (Z_N + Z_X) P_0(M,N)^X + \Sigma E_X E_N E_M (Z_M + Z_X) (Z_M + Z_Y) P_0(X,Y)^M] \quad (8)$$

where Z_i is the absolute charge on the ion i , $P_0(M,N)^X$ and $P_0(X,Y)^M$ are the mixing interaction parameters for mixing cations $M + N$ or anions $X + Y$ of the same charge type in the presence of ion X or M of opposite sign. This equation attempts to account for cation-cation and anion-anion interactions and neglects higher-order triplicate interactions (ref. 18).


 Fig. 2. The changes in the volume of mixing the major sea salts at $I = 3.0$.

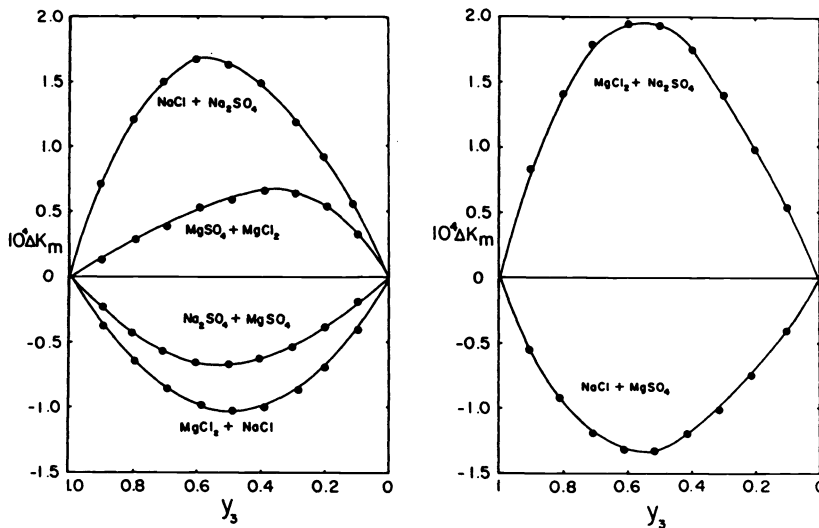


Fig. 3. The changes in the adiabatic compressibility of mixing the major sea salts at $I = 3.0$.

The values of P_0 are determined from the excess mixing properties fit to an equation of the form (ref. 17)

$$\Delta P_m = y_2 y_3 I^2 [P_0 + P_1 (1 - 2y_3)] \quad (9)$$

where I is the ionic strength of the mixture, y_i is the ionic strength fraction of electrolyte i and P_0 and P_1 are parameters related to ionic interactions. Since the values of ΔP_m are symmetrical around y_3 (See Fig. 2 and 3), the P_1 parameter is normally very small. The parameter P_0 is thus equal to $\Delta P_m(\max)/0.25I^2$, where $\Delta P_m(\max)$ is the maximum ΔP_m at $y_2 = y_3 = 0.5$.

The reliability of using eqs. (7) and (8) to estimate the properties of brines can be demonstrated by estimating the densities and sound speeds of mixtures of the major sea salt cross mixtures ($\text{NaCl} + \text{MgSO}_4$ and $\text{Na}_2\text{SO}_4 + \text{MgCl}_2$). Comparisons of measured and calculated densities and sound speeds for these systems are given in Tables 5 and 6.

As is quite apparent from these comparisons, the addition of the ΔV_m and ΔK_m terms greatly improves the estimates.

TABLE 5. Comparison of the Measured and Calculated Densities (10^6 g cm^{-3}) for $\text{NaCl} - \text{MgSO}_4$ and $\text{Na}_2\text{SO}_4 - \text{MgCl}_2$ Mixtures at $I = 3.0$

y_3	$\text{NaCl}(2) - \text{MgSO}_4(3)$		$\text{Na}_2\text{SO}_4(2) - \text{MgCl}_2(3)$	
	a	b	a	b
0	0	0	0	0
0.1	-113	-12	-58	32
0.2	-214	-34	-106	41
0.3	-286	-50	-149	47
0.4	-340	-79	-197	31
0.5	-367	-99	-222	15
0.6	-366	-115	-230	-2
0.7	-344	-123	-221	-21
0.8	-273	-107	-191	-32
0.9	-161	-71	-97	-3
1.0	0	0	0	0

a) Without ΔV_m
b) With ΔV_m

TABLE 6. Comparison of the Measured and Calculated Speed of Sound (m sec^{-1}) for $\text{NaCl} - \text{MgSO}_4$ and $\text{Na}_2\text{SO}_4 - \text{MgCl}_2$ Mixtures at $I = 3.0$

y_3	$\text{NaCl}(2) - \text{MgSO}_4(3)$		$\text{Na}_2\text{SO}_4(2) - \text{MgCl}_2(3)$	
	a	b	a	b
0	0	0	0	0
0.1	-0.54	-0.51	-0.35	0.47
0.2	-0.89	-0.73	-0.42	0.64
0.3	-0.98	-0.66	-0.23	0.26
0.4	-1.00	0.50	-0.10	0.01
0.5	0.91	0.28	-0.39	-0.21
0.6	-0.88	-0.17	-0.61	-0.35
0.7	-0.17	-0.01	-0.72	-0.34
0.8	-0.43	0.18	-0.63	-0.30
0.9	-0.20	0.17	-0.47	-0.30
1.0	0	0	0	0

a) Without ΔK_m
b) With ΔK_m

At present reliable PVT data is available for the ϕ_i properties of most of the components of natural waters from 0 to 50°C and $I = 0$ to saturation (ref. 8,12). For the major sea salts this data base has been expanded to 100°C (ref. 43,44). For the major sea salts excess volume data are available from 25 to 100°C (ref. 43). At 25°C excess volume and compressibility data are available (ref. 8,12) for the major sea salts as well as other components of brines such as NaCl + MCl and NaCl + NaX, where $M = \text{Li}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+, \text{NH}_4^+, \text{Mg}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}$ and $X = \text{F}^-, \text{Br}^-, \text{I}^-, \text{NO}_3^-, \text{HCO}_3^-, \text{CO}_3^{2-}, \text{OH}^-$ at $I = 0.7$ and 25°C. Further measurements for these systems are needed at higher ionic strengths and higher temperatures.

ACTIVITY COEFFICIENTS

To understand the chemical behavior of ionic solutes in natural waters, it is necessary to know the thermodynamic activity a_i rather than the total concentration $[i]_T$. The activity and total concentration are related by

$$a_i = [i]_T \gamma_T(i) \quad (10)$$

where $\gamma_T(i)$ is the total or stoichiometric activity coefficient of i . The value of γ_T is related to the non-ideal behavior of i due to ionic interactions. These ionic interactions are controlled by the composition of the natural waters. The effect of composition on the activity of electrolytes can be estimated by using various ionic interaction models (ref. 20-26,45-50). A number of workers (ref. 6-8,10,13,20-26,50-68) have applied these models to seawater, rivers, lakes and brines. These models can be divided into two major types 1. Specific interaction and 2. Ion-pairing models. The specific interaction models yield reliable estimates for the major ionic components; while the ion pairing models yield reliable estimates for the minor ionic components (ref. 21,24,62). The combination of the two models (ref. 21,24-26,62) yields a consistent model that can be used for all the components of natural waters.

In this section we will briefly review the recent progress made in using these models. A more detailed description of using the specific interaction model developed by Pitzer (ref. 20) and the ion pairing model is given elsewhere (ref. 23,24).

The ion pairing model estimates the activity coefficient of ionic solutes from the equation (ref. 24)

$$\gamma_T(i) = ([i]_F/[i]_T) \gamma_F(i) \quad (11)$$

where $\gamma_F(i)$ is the activity coefficient of the free ion and $[i]_F/[i]_T$ is the fraction of free ion. For a metal ion (M) this fraction is given by

$$[M]_F/[M]_T = (1 + \sum K_{MX}^* [X_i]_F)^{-1} \quad (12)$$

where X_i is a ligand interacting with M. The association constant K_{MX}^* for the formation of an ion pair MX is given by

$$K_{MX}^* = K_{MX} \gamma_F(M) \gamma_F(X) / \gamma_F(MX) \quad (13)$$

where K_{MX} is the thermodynamic association constant.

The total activity coefficients for some ions in average seawater (salinity $S = 35$ and $I = 0.7$) are given in Table 7 along with values determined experimentally (ref. 24).

The agreement is good and demonstrates the reliability of the ion pairing method for estimating activity coefficients. The estimation of values of γ_T for weak acid anions can be useful in determining the dissociation of acids in natural waters (ref. 24,66). A comparison of the measured and calculated pK_{HA}^* for acids in seawater is shown in Table 8 (ref. 24,66). Again the agreement is quite good.

TABLE 7. Values of γ_T for ions determined from the ion pairing model compared to measured values ^a

Ion	Meas.	Calc.	Ion	Meas.	Calc.
H ⁺	0.70	0.69	OH ⁻	0.22	0.24
Na ⁺	0.71	0.69	HCO ₃ ⁻	0.53	0.54
K ⁺	0.66	0.62	B(OH) ₄ ⁻	0.36	0.35
Mg ²⁺	0.26	0.26	H ₂ PO ₄ ⁻	0.42	0.40
Ca ²⁺	0.22	0.23	CO ₃ ²⁻	0.03	0.03
Sr ²⁺	0.19	0.23	SO ₄ ²⁻	0.10	0.09
F ⁻	0.30	0.33	HPO ₄ ²⁻	0.07	0.05
			PO ₄ ³⁻	3.7X10 ⁻⁵	4.2X10 ⁻⁵

^a From ref. 24, based on $\gamma_T(\text{Cl}^-) = 0.63$.

TABLE 8. Comparison of the measured and calculated pK_{HA}^* for the ionization of acids in seawater ^a

Acid	Meas.	Calc.	Acid	Meas.	Calc.
H ₂ O	13.18	13.21	HF	2.44	2.47
B(OH) ₃	8.60	8.59	H ₂ S	6.59	6.62
H ₂ CO ₃	5.84	5.86	HSO ₄ ⁻	0.94	0.96
HCO ₃ ⁻	8.93	8.96	H ₂ PO ₄ ⁻	5.94	6.14
NH ₄ ⁺	9.35	9.34	H ₃ PO ₄	1.57	1.55
HPO ₄ ²⁻	9.11	8.93			

^a From ref. 24 and 66

Although the ion pairing model gives reasonable estimates of activity coefficients for dilute solutions (below $I = 1.0$), at higher concentrations it is not as reliable due to the problems of estimating the activity coefficients of ion pairs and free ions (ref. 24). This difficulty can be overcome by using the specific interaction models described below.

Most of the early models used to estimate the activity coefficients of ions were based on extensions of the Debye-Hückel equation

$$-\ln \gamma_i = A I^{1/2} / (1 + C a_i I^{1/2}) \quad (14)$$

where A and C are Debye-Hückel parameters and, a_i , the ion size parameter is an adjustable term. By adjusting a_i or adding a $B_i I$ term this equation can be used to make reasonable estimates of activity coefficients to 1 m (ref. 69). Extensions to higher ionic strengths require an ionic strength dependence for the B_i term (ref. 20,49). Ionic solution theory (ref. 20) suggests that the value of γ_i in a mixture should be of the form

$$\ln \gamma_i = D.H. + \sum_j B_{ij} m_j + \sum_{jk} C_{ijk} m_j m_k \quad (15)$$

where D.H. is the Debye-Hückel limiting law, B_{ij} and C_{ijk} are, respectively, second and third virial coefficients which are functions of ionic strength. To $I = 4.0$, the second

virial coefficient is sufficient (ref. 20). Pitzer and coworkers (ref. 20,70-78) have developed a simple functional form for the ionic strength dependence of the B_{ij} term and pointed out the importance of the C_{ijk} term at high ionic strengths. The semi-empirical approaches of Pitzer (ref.20) and Scatchard (ref.49) include the basic features of the Brønsted-Guggenheim specific interaction model (ref. 46,47) and account for the interactions of like charged ions and triplet interactions.

In their simplest form the activity coefficients of cations M and anions X for the Pitzer equations are given by

$$\ln \gamma_M = Z_M f + 2 \sum_a m_a (B_{Ma} + EC_{Ma}) + Z_M^2 \sum_c \sum_a m_c m_a B'_{ca} + Z_M \sum_c \sum_a m_c m_a C_{ca} \quad (16)$$

$$\ln \gamma_X = Z_X f + 2 \sum_c m_c (B_{cX} + C_{cX}) + Z_X^2 \sum_c \sum_a m_c m_a B'_{ca} + Z_X \sum_c \sum_a m_c m_a C_{ca} \quad (17)$$

where Z_i is the charge, m_i is the molality of cations (c) and anions (a) in the mixed solution, and $E = \sum_c Z_c m_c = \sum_a Z_a m_a = 1/2 \sum_i m_i Z_i$ (the equivalent molality). The f term is a Debye-Hückel term

$$f = -0.392 [I^{1/2}/(1 + 1.2 I^{1/2}) + (2/1.2) \ln (1 + 1.2 I^{1/2})] \quad (18)$$

$$B_{MX} = \beta_{MX}^0 + (\beta_{MX}^1/2I) [1 - (1 + 2I^{1/2}) \exp(-2I^{1/2})] \quad (19)$$

$$B'_{MX} = (\beta_{MX}^1/2I^2) [-1 + (1 + 2I^{1/2} + 2I) \exp(-2I^{1/2})] \quad (20)$$

$$C_{MX} = C_{MX}^\phi / (2/ Z_M Z_X I^{1/2}) \quad (21)$$

Tabulations of β_{MX}^0 , β_{MX}^1 and C_{MX}^ϕ for binary solutions are given elsewhere (ref. 21,62,64,70-73,75). Terms are added to eqs. 16 and 17 for the interaction of like charge ions (θ_{ij}) and triplet interactions (ψ_{ijk}) and for higher order electrical interactions for unsymmetrical mixing effects (θ_{ij} and $E \theta'_{ij}$). Tabulations of θ_{ij} and ψ_{ijk} terms are given elsewhere (ref. 25,26,72-75).

The equations of Pitzer have been applied to seawater (ref. 13,21,25,26,53,54, 57,62-64) and to brines (ref. 13,25,26,61,68,79-81). Weare and coworkers (ref. 25,26) have used the equations of Pitzer to generate interaction coefficients for the major components of natural waters (Na, Mg, K, Ca, H, Cl, SO_4 , OH, HCO_3 , CO_3 and CO_2). With these interaction coefficients they have successfully determined the solubility of a number of minerals in evaporated seawater (ref. 25,26,82,83).

The reliability of the Pitzer equations can be demonstrated by comparing the calculated activity coefficients of ions with the measured values. A comparison for seawater solutions is shown in Table 9 (ref. 62,63). The agreement is quite good and better for the major components than obtained with the ion pairing model (Table 7). The estimated values of pK_{HA}^* for the ionization of acids in seawater are also in good agreement with the measured values (ref. 63).

In summary, at present the equations of Pitzer combined with the ion pairing model, for systems with strong plus-minus interactions, can be used to make reliable activity coefficients to saturation at 25°C. Further measurements are needed to extend this model to high temperatures and pressures. Studies are also needed on the use of ionic interaction models to examine the effect of ionic interactions on rate processes in natural waters (ref. 16).

TABLE 9. Values of γ_T for ions determined from Pitzer's equations compared to measured values ^a

Ion	Meas.	Calc.	Ion	Meas.	Calc.
H ⁺	0.590	0.586	HS ⁻	0.673	0.663
Na ⁺	0.668	0.666	B(OH) ₄ ⁻	0.419	0.427
K ⁺	0.625	0.619	HCO ₃ ⁻	0.576	0.569
NH ₄ ⁺	0.619	0.624	H ₂ PO ₄ ⁻	0.492	0.511
Ca ²⁺	0.203	0.213	SO ₄ ²⁻	0.104	0.109
Sr ²⁺	0.190	0.212	CO ₃ ²⁻	0.040	0.038
F ⁻	0.348	0.238	HPO ₄ ²⁻	0.046	0.045
OH ⁻	0.242	0.244	PO ₄ ³⁻	1.4X10 ⁻⁵	0.9X10 ⁻⁵

^a From ref. 62,63, based on $\gamma_T(\text{Cl}^-) = 0.666$.

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REFERENCES

1. F.J. Millero, Biophysical Properties of Skin, (H.R. Elden, ed.), Wiley, New York, Chpt. 9, 329-371 (1971).
2. F.J. Millero, Water and Aqueous Solutions, (R.A. Horne, ed.), Wiley, New York, Chpt. 13, 519-595 (1972).
3. F.J. Millero, The Sea, Vol. 5 (E.D. Goldberg, ed.), Wiley, New York, Chpt. 1, 3-80 (1974).
4. F.J. Millero, Structure of Water and Aqueous Solutions, (W. Luck, ed.), Verlag Chemie, Weinheim, Bergstr., Chpt. 1 X 2, 513-522 (1974).
5. F.J. Millero, Ann. Rev. Earth Planet. Sci., 2, 101-150 (1974).
6. F.J. Millero, Marine Chemistry in the Coastal Environment, (T.M. Church, ed.), ACS Pub. Ser. 18, Washington, Chpt. 2, 25-55 (1975).
7. F.J. Millero, The Sea, Vol. 6, (E.D. Goldberg, ed.), Wiley and Sons, New York, Chpt. 6, 653-693 (1977).
8. F.J. Millero, Activity Coefficients in Electrolyte Solutions, (R.M. Pytkowicz, ed.), CRC Press, Boca Raton, 63-151 (1979).
9. F.J. Millero, Thermodynamics of Aqueous Systems with Industrial Applications, (S.A. Newman, ed.), ACS Symp. Ser. 133, Washington, Chpt. 31, 581-622 (1981).
10. F.J. Millero, River Inputs to Ocean Systems, (J.M. Martin, J.D. Burton and D. Ersma, eds.), UNEP, UNESCO Switzerland, 116-131 (1981).
11. F.J. Millero, Proceedings of the First International Symposium on Hydrothermal Reactions, Gakiyutsu Bunken Fukyu-Kai, Japan, 111-122 (1983).
12. F.J. Millero, Chemical Oceanography, Vol. 8, (J.P. Riley and R. Chester, eds.), Academic Press, London, Chpt. 43, 1-88 (1983).
13. F.J. Millero, Complexation of Trace Metals in Natural Waters, (C.J.M. Kramer and J.C. Duinker, eds.), W. Junk Publ., The Hague, 187-200, (1984).
14. A. Gordon and F.J. Millero. Thalassia Jug., 16, 405-424 (1980).
15. D.R. Schreiber, A.S. Gordon and F.J. Millero, Canad. J. Microbiol., 31, 000-000 (1985).
16. F.J. Millero, Geochim. Cosmochim. Acta, 49, 547-553 (1985).
17. H.L. Friedman, Ionic Solution Theory, Inter. Publ., New York (1962).
18. R.H. Wood and P.J. Reilly, Ann Rev. Phys. Chem., 21, 287-406 (1970).
19. H.L. Anderson and R.H. Wood, Water, (F. Franks, ed.), Plenum Press, New York, (1973).
20. K.S. Pitzer, J. Phys. Chem., 77, 268-277 (1973).
21. M. Whitfield, Geochim. Cosmochim. Acta, 39, 1545-1557 (1975).
22. R.M. Pytkowicz (ed.), Activity Coefficients in Natural Waters, Vol. I and II, CRC Press, Boca Raton, Fla. (1979).
23. A.G. Dickson and M. Whitfield, Mar. Chem., 10, 315-333 (1981).

24. F.J. Millero and D. Schreiber, Am. J. Sci., **282**, 1508-1540 (1982).
25. C.E. Harvie and J.H. Weare, Geochim. Cosmochim. Acta, **44**, 981-997 (1980).
26. C.E. Harvie and N. Moeller and J.H. Weare, Geochim. Cosmochim. Acta, **48**, 723-751 (1984).
27. T.F. Young, Rec. Chem. Progr., **12**, 81-87 (1951).
28. R.H. Wood and H.L. Anderson, J. Phys. Chem., **70**, 1877-1879 (1966).
29. R.J. Reilly and R.H. Wood, J. Phys. Chem., **73**, 4292-4297 (1968).
30. F.J. Millero and F.K. Lepple, Mar. Chem., **1**, 89-104 (1973).
31. F.J. Millero, D. Lawson and A. Gonzalez, J. Geophys. Res., **81**, 1177-1179 (1975).
32. F.J. Millero, Thalassia Jugosl., **14**, 1-46 (1978).
33. W.C. Duer, W.H. Leung, G.B. Oglesby and F.J. Millero, J. Solution Chem., **5**, 509-528 (1976).
34. F.J. Millero, A. Lo Surdo, P.V. Chetirkin and N.L. Guinasso, Limnol. Oceanogr., **24**, 218-225 (1979).
35. H. Fernandez, F. Vazquez and F.J. Millero, Limnol. Oceanogr., **27**, 315-321 1982.
36. F.J. Millero and P.V. Chetirkin, Deep Sea Res., **27**, 265-271 (1980).
37. F.J. Millero, A. Mucci, J. Zullig and P. Chetirkin, Mar. Chem., **11**, 463-475 (1982).
38. F.J. Millero, Limnol. Oceanogr., **29**, 1317-1321 (1984).
39. T.F. Young, Y.C. Wu and A.A. Krawetz, Disc. Faraday Soc., **24**, 37-41 (1957).
40. Y.C. Wu, M.B. Smith and T.F. Young, J. Phys. Chem., **69**, 1868-1872, 1873-1877 (1965).
41. F.J. Millero, L.M. Connaughton, F. Vinokurova and P.V. Chetirkin, J. Solution Chem., in press (1985).
42. F.J. Millero and M. Lampreia, J. Solution Chem., submitted (1985).
43. L.M. Connaughton and F.J. Millero, in preparation.
44. F.J. Millero, J.P. Hershey, F. Vinokurova and M. Fernandez, J. Solution Chem., submitted (1985).
45. N. Bjerrum, Kgl. Danske Vidensk. Selsk. Fys. Medd., **7**, 1-48, (1962).
46. J.N. Brønsted, J. Am. Chem. Soc., **44**, 877-898 (1922).
47. E.A. Guggenheim, Phil. Mag., **19**, 588-643 (1935).
48. P.J. Reilly, R.H. Wood and R.A. Robinson, J. Phys. Chem., **75**, 1305-1315 (1971).
49. G. Scatchard, R.M. Rush and J.S. Johnson, J. Phys. Chem., **74**, 3786-3796 (1970).
50. R.M. Garrels and M.E. Thompson, Am. J. Sci., **260**, 57-66 (1962).
51. J.V. Leyendekkers, Mar. Chem., **1**, 75-88 (1972).
52. G. Atkinson, M.O. Dayhoff and D.W. Ebdon, Marine Electrochemistry, (J. Berkowitz et al., eds.), Electro. Soc., London 124-138 (1973).
53. M. Whitfield, Mar. Chem., **1**, 251-266 (1973).
54. M. Whitfield, Mar. Chem., **3**, 197-213 (1975).
55. A.H. Truesdell and B.J. Jones, Chem. Geol., **4**, 51-62, (1969).
56. N. van Breeman, Geochim. Cosmochim. Acta, **37**, 101-107 (1973).
57. R.A. Robinson and R.H. Wood, J. Solution Chem., **1**, 481-488 (1972).
58. R.M. Rush and J.S. Johnson, J. Chem. Eng. Data, **11**, 590-592 (1966).
59. K.S. Johnson and R.M. Pytkowicz, Am. J. Sci., **278**, 1428-1447 (1978).
60. M.W. Watson, R.H. Wood and F.J. Millero, Marine Chemistry in the Coastal Environment, (T.M. Church, ed.), ACS Symp. Ser. 18, Washington, 112-118 (1975).
61. B. Krungalz and F.J. Millero, Mar. Chem., **11**, 209-222 (1982).
62. F.J. Millero, Thalass. Jugo., **18**, 253-291 (1982).
63. F.J. Millero, Geochim. Cosmochim. Acta, **47**, 2121-2129 (1983).
64. F.J. Millero and R.H. Byrne, Geochim. Cosmochim. Acta, **48**, 1145-1150, (1984).
65. F.J. Millero, G. Macchi and M. Pettine, Est. and Coastal Mar. Sci., **13**, 517-534 (1981).
66. F.J. Millero, Geochim. Cosmochim. Acta, **45**, 2085-2089, (1981).
67. F.J. Millero, Geochim. Cosmochim. Acta, **46**, 11-22 (1982).
68. B.S. Krungalz and F.J. Millero, Mar. Chem., **13**, 129-139 (1983).
69. R.A. Robinson and R.H. Stokes, Electrolyte Solutions, Butterworths, London (1959).
70. K.S. Pitzer and G. Mayorga, J. Phys. Chem., **77**, 2300-2308 (1973).
71. K.S. Pitzer and G. Mayorga, J. Solution Chem., **3**, 539-546 (1973).
72. K.S. Pitzer and J.J. Kim, J. Am. Chem. Soc., **96**, 5701-5707 (1974).
73. K.S. Pitzer and L.F. Silvester, J. Solution Chem., **5**, 269-278 (1968).
74. K.S. Pitzer, J. Solution Chem., **4**, 249-265 (1975).
75. K.S. Pitzer, Activity Coefficients (R.M. Pytkowicz, ed.), Vol. I, CRC Press, Boca Raton, 157-208 (1979).
76. J.C. Peiper and K.S. Pitzer, J. Chem. Thermodyn., **14**, 631-638 (1982).
77. R.N. Roy, J.J. Gibbons, M.D. Wood, R.W. Williams, J.C. Peiper and K.S. Pitzer, J. Chem. Thermodyn., **15**, 37-47 (1983).
78. K.S. Pitzer, R.N. Roy and L.F. Silvester, J. Am. Chem. Soc., **99**, 4930-4936 (1977).
79. V. Thurmond and F.J. Millero, J. Solution Chem., **11**, 447-456 (1982).
80. F.J. Millero and V. Thurmond, J. Solution Chem., **12**, 401-412 (1983).
81. F.J. Millero, P.J. Milne and V.L. Thurmond, Geochim. Cosmochim. Acta, **48**, 1141-1153 (1984).
82. C.E. Harvie, J.H. Weare, H.P. Eugster and L.A. Hardie, Science, **208**, 498-499 (1980).
83. H.P. Eugster, C.E. Harvie and J.H. Weare, Geochim. Cosmochim. Acta, **44**, 1335-1347 (1980).