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USE OF THE ION PAIRING MODEL TO ESTIMATE ACTIVITY COEFFICIENTS OF THE IONIC COMPONENTS OF NATURAL WATERS

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ABSTRACT. *The basic assumptions of using the ion pairing model to estimate ionic activity coefficients has been examined. The activity coefficients (γ) of free ions (i) have been determined by using the mean salt method. The ionic strength dependence of γ_i can be estimated by using Pitzer's (1973) equation for ions*

$$In\ \gamma_i = Z_i^2 f + IB_i^0 + B_i^1 f^1 + I^2 C_i$$

where f and f^1 are functions of ionic strength; B_i^0, B_i^1, and C_i are parameters determined from the coefficients of Pitzer and Mayorga (1973) for K^+ and Cl^- salts. Values of the thermodynamic (K_A) and stoichiometric (K_A^* at $I = 0.7$ m) association constants for the formation of ion pairs have been selected from literature data. The presently available values of K_A, K_A^*, and γ_i (at $I = 0.7$ m) indicate that the activity coefficients of neutral ion pairs are 1.1 ± 0.1 for $(M^+, X^-)^0$ and 1.0 ± 0.04 for $(M^{2+}, X^{2-})^0$ pairs. The activity coefficients of monovalent anion pairs $(M^+, X^{2-})^-$ are 0.64 ± 0.08, while monovalent cations pairs $(M^{2+}, X^-)^+$ are 0.8 ± 0.2. These findings support the earlier work of Garrels and Thompson (1962).

The ionic strength dependence of K_A^* can be determined from equations of the form (to $I = 1.0$ m)

$$In\ K_A^* = In\ K_A + Z_A^2 f + IB_A^0 + f^1 B_A^1 + I^2 C_A$$

where the parameters Z_A, B_A^0, B_A^1, and C_A are obtained from the Pitzer parameters for ions and ion pairs. These values of K_A^* have been used to determine the total or stoichiometric activity coefficients (γ_T) for seawater from 0.1 to 40 per mil salinity. The calculated values of γ_T are in good agreement with experimentally determined values. The agreement is especially good for anions formed from the ionization of weak acids (OH^-, $B(OH)_4^-$, HCO_3^-, CO_3^{2-}, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}).

INTRODUCTION

One of the most popular methods of estimating activity coefficients in natural waters is the use of the ion pairing model (Sillen, 1961; Garrels and Thompson, 1962; Lafon, ms; Pytkowicz and Kester, 1969; Atkinson, Dayhoff, and Ebdon, 1973; van Breemen, 1973; Millero, 1974, 1975, 1977; Dyrssen and Wedborg, 1974; Stumm and Brauner, 1975; Johnson and Pytkowicz, 1978). In the present paper we will examine some of the basic assumptions of using the ion pairing model to estimate activity coefficients. Simple equations will be given for the ionic strength dependence of association constants and activity coefficients. These equations will be used to determine the total or stoichiometric activity coefficients of ions in average seawater diluted with pure water. The calculated values of the

total activity coefficients are found to be in good agreement with the measured values.

The activity of a free ion i using the ion pairing model is given by

$$a_i = [i]_F \gamma_F(i) \tag{1}$$

where $[i]_F$ is the concentration, and $\gamma_F(i)$ is the activity coefficient of the free or uncomplexed i. The value of $\gamma_F(i)$ is assumed to be only a function of the ionic strength and is independent of the relative composition. Since the activity of ion i is also related to the total concentration and activity coefficient by

$$a_i = [i]_T \gamma_T(i) \tag{2}$$

The desired total or stoichiometric activity coefficient is given by

$$\gamma_T(i) = \{[i]_F/[i]_T\} \gamma_F(i) \tag{3}$$

The term $[i]_F/[i]_T$ is the fraction of free ions in the solution of fixed composition and constant ionic strength. It is important to point out that the form of the complexed species does not affect its thermodynamic activity. If one to one complexes are formed between metal cations, M_i^+, and various anions, X_i^-,

$$M_i^+ + X_i^- \rightarrow M_iX_i^0 \tag{4}$$

the fraction of free metal ion can be determined from

$$[M]_F/[M]_T = (1 + \Sigma K^*_{MX_i}[X_i]_F)^{-1} \tag{5}$$

The fraction of the free anions are determined from a similar equation

$$[X]_F/[X]_T = (1 + \Sigma K^*_{M_iX}[M_i]_F)^{-1} \tag{6}$$

The values of K^*_{MX} are the stoichiometric association constant at the effective ionic strength of the solution. The K^*_{MX} is related to the thermodynamic association constant, K_{MX}, by

$$K^*_{MX} = K_{MX}[\gamma_F(M)\gamma_F(X)/\gamma_F(MX)] \tag{7}$$

The fraction of free cations and anions is related to the magnitude of K^*_{MX} (the strength of the interactions between M^+ and X^-) and the concentration of the free counterion.

Eqs (5) and (6) can be solved using known values of K^*_{MX} and the concentration of the solution by a series of iterations. Several computer programs are available (Perrin and Sayce, 1967; Ingri and others, 1967, 1968; Morel and Morgan, 1972; Crerar, 1975; Knowles and Wakeford, 1978) to determine $[M]_F/[M]_T$ and $[X]_F/[X]_T$ as well as the fraction of M_i or X_i complexed to a given anion or cation

$$[MX_i]/[M]_T = K^*_{MX_i}[X_i]_F/(1 + \Sigma K^*_{MX_i}[X_i]_F) \tag{8}$$

$$[M_iX]/[X]_T = K^*_{M_iX}[M_i]_F/(1 + \Sigma K^*_{M_iX}[M_i]_F) \tag{9}$$

As mentioned before, the form of the complex does not affect the thermodynamic activity or chemical potential of M or X.

The computer programs are useful tools to aid in the mathematical solution; however, the results are only as good as the input data (K^*_{MX}, $[M_i]_T$ and $[X_i]_T$). The use of unreliable values of K^*_{MX} can completely change the predominant form of a complexed species (Millero, 1975, 1977); however, the fraction of free cations or anions, needed to calculate γ_T, is not greatly affected in some cases.

Most of the recent papers on ion pairing in natural waters have been concerned with determination of the forms or speciation of ions, not in determining activity coefficients (Truesdell and Jones, 1969; Kester and Pytkowicz, 1969; Elgquist, 1970; Wigley, 1971; Zirino and Yamamoto, 1972; van Breemen, 1973; Gardner, 1974; Dyrssen and Wedborg, 1974; Byrne and Kester, 1974; Pytkowicz and Hawley, 1974; Stumm and Brauner, 1975; Kester, Byrne, and Liang, 1975; Miller and Kester, 1976; Atlas, Culberson, and Pytkowicz, 1976; Long and Angino, 1977; Paulson, ms; Mantoura, Dickson, and Riley, 1978; Wilson, 1978; Johnson and Pytkowicz, 1978; Elgquist and Wedborg, 1975, 1978; Johansson and Wedborg, 1979; Elgquist and Wedborg, 1979; Sipos and others, 1980). The activity coefficients of M and X are determined from

$$\gamma_T(M) = ([M]_F/[M]_T)\,\gamma_F(M) \tag{10}$$

$$\gamma_T(X) = ([X]_F/[X]_T)\,\gamma_F(X) \tag{11}$$

The mean activity coefficient ($\gamma_\pm$) is determined from the ionic values using

$$\gamma_\pm = \gamma_\pm(MX)_F \left[\left(\frac{[M]_F}{[M]_T}\right)^{\nu_M} \left(\frac{[X]_F}{[X]_T}\right)^{\nu_X}\right]^{1/\nu} \tag{12}$$

To use the ion pairing model to estimate γ_T in natural waters of known composition, it is necessary to have reliable values of K^*_{MX} (or K_{MX}) and γ_F for ions (and ion pairs if K^*_{MX} is estimated from K_{MX}). The assumptions used to determine these quantities are discussed in the following sections.

Thermodynamic and stoichiometric association constants.—The form of an ion in natural waters can be determined by two methods: (1) using thermodynamic association constants and estimating the activity coefficients of free ions and ion pairs; (2) using stoichiometric association constants experimentally determined in the medium of interest or another medium at the same ionic strength. The first method is used by many geochemists and works very well in dilute solutions where the values of K_A are normally determined, and reasonable estimates can be made for the activity coefficients of ions and ion pairs. The second method is used by marine chemists and does not require the estimation of activity coefficients. Unfortunately, marine chemists normally do not measure the values of K^*_A below a salinity of 20 per mil ($I \sim 0.4$). Thus, it is difficult to link the seawater studies to the more dilute solution studies. Different experimental methods are normally used to determine K_A and K^*_A causing an uncertainty, due to the technique used to sense free ions (for

TABLE 1

Thermodynamic association constants, K_A, for the major sea salts at 25°C

Ion pair	log K_A	Ref.	Ion pair	log K_A	Ref.
$NaSO_4^-$	1.11	1	CaF^+	1.04	23
	1.10	2	$CaB(OH)_4^+$	1.80	12
	0.98	3	$CaH_2PO_4^+$	1.40	32
	1.03	4		1.0	33
	0.82	5		1.07	34
$NaHCO_3^\circ$	0.16	6		0.57	35
	−0.19	7	$CaHPO_4^\circ$	2.73_3	32
	−0.25	8		2.58	33
$NaCO_3^-$	0.55	6		2.70	34
	0.77	7		2.42	35
	1.27	9	$CaPO_4^-$	6.46_2	32
$NaOH^\circ$	−0.18	10	KSO_4^-	0.96	1
NaF°	−0.26	11		1.0	26
$NaB(OH)_4^\circ$	0.22	12		0.75	14
$MgSO_4^\circ$	2.21	13		0.85	36
	2.33	14		0.85	37
	2.25	15		1.02	4
	2.36	16		0.85	5
$MgHCO_3^+$	1.21	17	$SrSO_4^\circ$	2.31	17
	1.16	8		2.10	38
	1.23	18	$SrHCO_3^+$	1.25	17
	0.95	19	$SrCO_3^\circ$	3.92	17
$MgCO_3^\circ$	3.28	17	$SrOH^+$	0.82	39
	3.26	18		0.71	10
	3.4	9	SrF^+	1.04	17
	2.88	20	$SrB(OH)_4^+$	1.55	12
$MgOH^+$	2.58	21	HSO_4^-	1.98	14
	2.20	22		1.97_9	40
	2.56	10		1.89	5
MgF^+	1.82	23	HF°	3.17_3	41
$MgB(OH)_4^+$	1.62	12	$NH_4SO_4^-$	0.94	5
$CaSO_4^\circ$	2.31	24	$LiSO_4^-$	0.77	5
	2.31	25	$RbSO_4^-$	0.60	5
	2.28	26	$CsSO_4^-$	0.33	5
	2.43	14	$NaNO_3^\circ$	−0.60	26
$CaHCO_3^+$	1.25	17	KNO_3°	0.08	26
	1.26	8	$CaNO_3^+$	0.28	26
	1.0	27	$SrNO_3^+$	0.82	26
	1.23	28	$BaSO_4^\circ$	2.30	38
	1.225	29	$BaOH^+$	0.64	42
$CaCO_3^\circ$	3.92	17	$BaB(OH)_4^+$	1.49	12
	3.2	8			
	3.15	20			
	3.1	30			
$CaOH^+$	1.27	31			
	1.38	24			
	1.15	10			

REFERENCES

(1) Jenkins and Monk (1950) as corrected by Fisher and Fox (1975); (2) Fisher and Fox (1975); (3) Truesdell and Jones (1969); (4) Fisher and Fox (1977); (5) Reardon (1975); (6) Nakayama (1970); (7) Butler and Huston (1970a); (8) Garrels and Thompson (1962); (9) Garrels, Thompson, and Siever (1961); (10) Baes and Mesmer (1976); (11) Duer, Robinson, and Bates (1972); Robinson, Duer, and Bates (1971); (12) Reardon (1976); (13) Atkinson and Petrucci (1966); (14) Izatt, Eatough, Christensen, and Bartholomew (1969); (15) Nair and Nancollas (1958); (16) Jones and Monk (1952); (17) Atkinson, Dayhoff, and Ebdon (1973); (18) Nakayama (1971); (19) Hostetler (1963); (20) Reardon and Langmuir (1974); (21) Stock and Davies (1948); (22) McGee and Hostetler (1973); (23) Connick and Tsao (1954); (24) Bell and George (1953); (25) Nakayama and Rasnick (1967); (26) Davies (1962); (27) Jacobson and Langmuir (1974); (28) Bauman, Hostetler, and Almon (1973); (29) Christ, Hostetler, and Siebert (1974); (30) Lafon (1970); (31) Gimblett and Monk (1954); (32) Chughtai, Marshall, and Nancollas (1968); (33) McDowell, Brown, and Sutter (1971); (34) Davies and Hoyle (1953); (35) Gregory, Moreno, and Brown (1960); (36) Truesdell and Hostetler (1968); (37) Chlebek and Lister (1967); (38) Lieser (1965); (39) Harned and Paxton (1953); (40) Pitzer, Roy, and Silvester (1977); (41) Broene and DeVries (1947); (42) Harned and Geary (1937).

example, conductance and specific ion electrodes). Many workers (Millero, 1974) have pointed out the advantages (Dyrssen and Wedborg, 1974; Pytkowicz and Kester, 1969; Pytkowicz, 1969; Sillen, 1961) and disadvantages (Atkinson, Dayhoff, and Ebdon, 1973; Bond, 1970; Ginstrup, 1970) of using the ionic medium method. As pointed out earlier (Millero, 1974) both methods should yield the same results providing the experimental data are reliable. More will be said about this later in the paper.

The link between K_A and K^*_A (eq 6) is the activity coefficients of the various species in solution. Before we examine the methods of estimating activity coefficients, we will review briefly the recent values of K_A and K^*_A determined by various workers. In tables 1 and 2 we have tabulated

TABLE 2

Stoichiometric association constants, K_A^* for the major sea salts at I = 0.7 and 25°C

Ion pair	log K_A^*	Ref.	Ion pair	log K_A^*	Ref.
$NaSO_4^-$	0.31	1		1.36	3
	0.09	2	$MgH_2PO_4^+$	0.37	11
	0.26	3	$MgHPO_4^\circ$	1.47	11
	0.41	4,5		1.60 (1.54)	15
$NaHCO_3^\circ$	−0.55	6	$MgPO_4^-$	3.56 (3.76)	11
	−0.51	7		4.2 (3.9)	15
$NaCO_3^-$	0.63	6	$CaSO_4^\circ$	1.03	16
	0.20	7		1.49	2
NaF°	−1.30	8		1.24	17
	−0.80	9	$CaHCO_3^+$	0.29 (0.30)	6
$NaB(OH)_4^\circ$	−0.24	10		0.02 (0.35)	4
$NaH_2PO_4^\circ$	−0.54	11	$CaCO_3^\circ$	2.21 (2.15)	6
$NaHPO_4^-$	0.05	11		1.51 (1.95)	4
$NaPO_4^{2-}$	0.52	11	CaF^+	0.63	13
$MgSO_4^\circ$	1.01	12		0.65	8
	1.09	2		0.51	14
	0.80	3	$CaB(OH)_4^+$	1.11	10
$MgHCO_3^+$	0.21 (0.23)	6		0.41	18
	0.02 (0.32)	4		0.73 (0.95)	4
$MgCO_3^\circ$	2.05 (1.93)	6	$CaH_2PO_4^+$	0.24	11
	1.51 (1.95)	4	$CaHPO_4^\circ$	1.25	11
$Mg_2(CO_3)^{2+}$	2.59	6		1.39 (1.31)	15
$MgCaCO_3^{2+}$	3.02	6	$CaPO_4^-$	4.98 (4.9)	11
$MgOH^+$	1.58 (1.70)	4		4.80 (4.5)	15
$MgB(OH)_4^+$	0.90	10	KSO_4^-	0.26	2
	0.73 (0.95)	4	HSO_4^-	1.49	19
MgF^+	1.27	13		1.51	4
	1.30	14		1.49	20
	1.29	8	HF°	2.94	17

REFERENCES

(1) Pytkowicz and Kester (1969); (2) Elgquist and Wedborg (1974, 1975): The values in parentheses have been corrected for Na^+ pairing; (3) Elgquist and Wedborg (1978); (4) Dyrssen and Hansson (1973); (5) Santos, Guedes de Carvalho, and Guedes de Carvalho (1975); (6) Pytkowicz and Hawley (1974); (7) Butler and Huston (1970a); (8) Miller and Kester (1976); (9) Butler and Huston (1970b); (10) Byrne and Kester (1974); (11) Atlas, Culberson, and Pytkowicz (1976); (12) Kester and Pytkowicz (1968); (13) Elgquist (1970); (14) Connick and Tsao (1954); (15) Johansson and Wedborg (1979): The values in parentheses have been corrected for Na^+ pairing; (16) Kester and Pytkowicz (1969); (17) Elgquist and Wedborg (1979); (18) Dyrssen and Wedborg (1974); (19) Culberson, Pytkowicz, and Hawley (1970); (20) Khoo, Ramette, Culberson, and Bates (1977).

these values of K_A and K^*_A (I = 0.7) at 25°C. When a number of workers have studied the same system, it is possible to select a consensus value with an estimated uncertainty. To evaluate critically the K_A results, it is necessary to go back to the experimental data (if it is available) and determine if the assumptions made are valid. This is a mammoth undertaking, and one we have not attempted. Fisher and Fox (1975) have, for example, shown that if the early conductivity data for Na_2SO_4 solutions (Jenkins and Monk, 1950) are re-evaluated using modern conductance theories, a thermodynamic value is obtained that is more consistent with the K^*_A for $NaSO_4^-$ obtained by Pytkowicz and Kester (1969). It should also be pointed out that many of the quoted values of K_A have been determined at high concentrations and are linked to the method used to extrapolate the data to infinite dilution. The values of K_A we have selected are summarized in table 3 along with our estimates of the uncertainties.

Many of the stoichiometric constants, K^*_A, determined at I = 0.7 have been obtained by making different assumptions for the ideal behavior (that is, when no ion pairing occurs). Dyrssen and coworkers frequently assume that no ion pairing occurs between various anions with Na^+; while Pytkowicz, Kester, and coworkers assume that no ion pairing occurs between anions and K^+. The constants determined by using these

TABLE 3

Selected values for K_A and K_A^* (I = 0.7) for some major ion pairs at 25°C†

Ion pair	log K_A	log K_A*	Ion pair	log K_A	log K_A*
HSO_4^-	1.979 ± 0.005	1.49 ± 0.01	$MgPO_4^-$	(5.8 ± 0.1)	3.84 ± 0.1
HF°	3.17 ± 0.03	2.92 ± 0.03			
			$CaSO_4^\circ$	2.28 ± 0.02	1.03 ± 0.02
KSO_4^-	0.88 ± 0.02	0.26 ± 0.02	$CaHCO_3^+$	1.0 ± 0.1	0.33 ± 0.05
KNO_3°	0.08 ± 0.03	−0.43 ± 0.02	$CaCO_3^\circ$	3.2 ± 0.05	2.1 ± 0.1
			$CaOH^+$	1.3 ± 0.1	(0.74 ± 0.08)
$NaSO_4^-$	0.95 ± 0.05	0.30 ± 0.06	CaF^+	(1.31 ± 0.06)	0.65 ± 0.06
$NaHCO_3^\circ$	−0.19 ± 0.1	−0.53 ± 0.03	$CaNO_3^+$	0.28 ± 0.03	(−0.51 ± 0.02)
$NaCO_3^-$	1.02 ± 0.2	0.42 ± 0.2	$CaB(OH)_4^+$	1.80 ± 0.03	1.11 ± 0.02
$NaOH^\circ$	−0.18 ± 0.16	(−0.43 ± 0.03)	$CaH_2PO_4^+$	1.0 ± 0.2	0.24 ± 0.02
NaF°	(−0.64 ± 0.2)	−1.0 ± 0.2	$CaHPO_4^\circ$	2.66 ± 0.1	1.28 ± 0.03
$NaNO_3^\circ$	−0.60 ± 0.03	(−1.09 ± 0.05)	$CaPO_4^-$	6.46 ± 0.02	4.5 ± 0.1
$NaB(OH)_4^\circ$	0.22 ± 0.12	−0.24 ± 0.08			
$NaH_2PO_4^\circ$	(−0.04 ± 0.02)	−0.54 ± 0.02	$SrSO_4^\circ$	2.10 ± 0.1	(0.85 ± 0.1)
$NaHPO_4^-$	(0.80 ± 0.02)	0.05 ± 0.02	$SrOH^+$	0.82 ± 0.1	(0.25 ± 0.09)
$NaPO_4^{2-}$	(1.60 ± 0.02)	0.52 ± 0.02	$SrNO_3^+$	0.82 ± 0.04	(0.02 ± 0.04)
			$SrB(OH)_4^+$	1.55 ± 0.03	(0.85 ± 0.03)
$MgSO_4^\circ$	2.21 ± 0.02	1.01 ± 0.02			
$MgHCO_3^+$	0.95 ± 0.19	0.28 ± 0.08	$NH_4SO_4^-$	0.94 ± 0.05	(0.27 ± 0.1)
$MgCO_3^\circ$	2.9 ± 0.1	1.94 ± 0.05	$LiSO_4^-$	0.77 ± 0.05	(0.26 ± 0.05)
$MgOH^+$	2.2 ± 0.2	1.70 ± 0.05	$RbSO_4^-$	0.60 ± 0.05	(−0.09 ± 0.05)
MgF^+	(1.90 ± 0.05)	1.29 ± 0.02	$CsSO_4^-$	0.33 ± 0.05	(−0.41 ± 0.05)
$MgB(OH)_4^+$	(1.57 ± 0.02)	0.93 ± 0.03			
$MgH_2PO_4^+$	(1.13 ± 0.02)	0.37 ± 0.02	$BaSO_4^\circ$	2.30 ± 0.05	(0.98 ± 0.05)
$MgHPO_4^\circ$	(2.84 ± 0.06)	1.51 ± 0.07	$BaOH^+$	0.64 ± 0.1	(0.01 ± 0.05)
			$BaB(OH)_4^+$	1.49 ± 0.03	(0.73 ± 0.03)

† The values in parentheses have been estimated (see text). Our estimates of the uncertainties are based on the agreement between various workers. The actual uncertainties could be significantly larger than our estimates.

TABLE 4

Comparison of the activity coefficients of free ions in river and sea water obtained by various methods

Ion	River water†			Sea water††		
	Davies	Kielland	MacInnes	Davies	Kielland	MacInnes
Na^+	0.951	0.951	0.951	0.75	0.62	0.71
K^+	0.951	0.950	0.950	0.75	0.58	0.62
Mg^{2+}	0.816	0.825	0.820	0.32	0.29	0.29
Ca^{2+}	0.816	0.821	0.819	0.52	0.22	0.26
La^{3+}	0.634	0.653	0.640	0.18	0.08	0.05
Cl^-	0.951	0.950	0.950	0.75	0.58	0.62
Br^-	0.951	0.950	0.951	0.75	0.58	0.64
HCO_3^-	0.951	0.951	0.951	0.75	0.62	0.67
SO_4^{2-}	0.816	0.816	0.814	0.32	0.15	0.21
CO_3^{2-}	0.816	0.818	0.814	0.32	0.17	0.21
PO_4^{3-}	0.634	0.634	0.636	0.08	0.01	0.02

†I = 2.09×10^{-3}
††I = 0.723

different assumptions will differ considerably, although the fraction of free anions are quite similar. When possible we have attempted to rectify these differences by examining the experimental measurements. The results for carbonate, phosphate, hydroxide, and borate ion pairs determined in this manner are given in parentheses in table 2. The values of K^*_A at I = 0.7 we have selected are tabulated in table 3 along with our estimates of the uncertainty. Our selections are based on the agreement of independent studies and the internal consistency of K^*_A and K_A.

Activity coefficients of free ions.—In dilute solutions below I = 0.1 the activity coefficients of ions can be determined from an extended form of the Debye-Hückel limiting law. Two equations used by geochemists are the Davies (1962) equation

$$\log \gamma_i = -0.509 Z_i^2 [I^{1/2}/(1 + I^{1/2}) - 0.3I] \quad (13)$$

and the Kielland (1937) equation

$$\log \gamma_i = -0.509 Z_i^2 I^{1/2}/(1 + \text{å } 0.33 I^{1/2}) \quad (14)$$

where Z_i is the charge on the ion, I is the molal ionic strength, and å is an adjustable ion size parameter (Kielland, 1937). The first equation has the advantage that it needs no adjustable parameters; however, it is normally valid only for dilute solutions (below I = 0.1). The second equation accounts for the size of ions; however, it yields equal values of γ_i for cations and anions of the same size which is not very realistic in concentrated solutions. A comparison of the values of γ_i for cations and anions in average river water (Millero, 1975) and average seawater obtained from eqs (13) and (14) is given in table 4. For river waters the two equations yield similar values of γ_i; however, there are large differences in seawater.

More reliable estimates of the activity coefficients of ions in concentrated solutions can be made by dividing the measured mean activity coefficients, $\gamma_\pm$, into ionic components

$$\gamma_\pm(MX) = (\gamma_M^{\nu_M} \gamma_X^{\nu_X})^{1/\nu} \quad (15)$$

where ν_i are the numbers of cations (M) and anions (X) formed when the electrolyte completely dissociates ($\nu = \nu_M + \nu_X$). To divide the measured mean activity coefficients into ionic components, it is necessary to make some assumptions about the value of γ_M or γ_X for a given electrolyte.

Since the absolute value of γ_M or γ_X cannot be experimentally determined, the assumption made to separate mean activity coefficients is not unique. It is, thus, important to use a common scale when comparing activity coefficients obtained by different techniques (for example, the specific interaction model and the ion pairing model). Since the activity coefficients of electrolytes in a mixed electrolyte media of fixed composition are additive (similar to partial molal properties, Millero, 1977), any convention can be used provided that it is applied consistently. Since many of the measure values of K^*_{MX} are based on the MacInnes (1919) convention, we have adopted its use in determining ionic activity coefficients.

The MacInnes (1919) convention assumes $\gamma_K = \gamma_{Cl}$ at every ionic strength. This gives

$$\gamma_K = \gamma_{Cl} = \gamma_\pm(KCl) \tag{16}$$

The value of γ_M for cations can be estimated from chloride salts

$$\gamma_M = \gamma_\pm{}^\nu/[\gamma_\pm(KCl)]^{\nu_{Cl}} \tag{17}$$

while γ_X for anions can be estimated from potassium salts

$$\gamma_X = \gamma_\pm{}^\nu/[\gamma_\pm(KCl)]^{\nu_K} \tag{18}$$

Since K^+ and Cl^- salts do not normally form strong ion pairs, this method gives reasonable estimates for the activity coefficient of free ions. Calculations of ionic values of some ions at $I = 2.09 \times 10^{-3}$ (the ionic strength of average river water) and $I = 0.723$ (the ionic strength of average seawater) using values of $\gamma_\pm$ from the equations of Pitzer and Mayorga (1973) are given in table 4. These comparisons at $I = 0.723$ indicate that the Kielland equation yields values of γ_i that are in slightly better (± 0.05) agreement with the MacInnes estimates than the results from the Davies equation (± 0.08). It is interesting to note that, if the constant factor (0.3) in the Davies equation is reduced to 0.2 (Atkinson, Dayhoff, and Ebdon, 1973), the calculated results are in good agreement (± 0.03) with the values determined by the MacInnes method. By adjusting the values of å the differences between the Kielland equation and the MacInnes method can also be lowered.

It should be pointed out that the values of γ_M obtained from chloride salts are not unique. The values of γ_M obtained from other halide salts have been calculated and are shown adjusted to the same value of γ_K in table 5. Although F^-, NO_3^- and ClO_4^- salts may form ion pairs, the differences for γ_M obtained from Cl^-, Br^- and I^- salts clearly demonstrate the limitations of the mean salt method in obtaining absolute values of ionic activity coefficients. It should also be pointed out the differences are much greater at higher ionic strengths.

TABLE 5

Comparison of the activity coefficients of cations obtained by the mean salt method using different salts (I = 0.7226)†

Cation	F^-	Cl^-	Br^-	I^-	NO_3^-	ClO_4^-
H^+	—	0.964	1.051	1.117	1.331	1.321
Li^+	—	0.903	0.910	1.020	1.391	1.176
Na^+	0.528	0.708	0.737	0.769	0.878	0.707
K^+	0.623	0.623	0.623	0.623	0.623	0.623
Rb^+	0.718	0.586	0.563	0.517	0.595	—
Cs^+	0.745	0.525	0.490	0.453	0.573	—
NH_4^+	—	0.617	0.619	—	0.614	0.467
Mg^{2+}	—	0.285	0.326	0.324	0.734	0.501
Ca^{2+}	—	0.256	0.274	0.293	0.496	0.401
Sr^{2+}	—	0.248	0.168	0.281	0.422	0.345
Ba^{2+}	—	0.215	0.234	0.264	0.230	0.303
Co^{2+}	—	0.261	0.307	0.320	0.701	—
Zn^{2+}	—	0.224	0.310	0.340	0.749	0.458

† Calculated from mean activity coefficients obtained from the equations of Pitzer and Mayorga (1973). The values have been adjusted to a common scale using $\gamma(K^+) = 0.623$.

Since most natural waters contain Cl^- as the major anion, one would expect the chloride salts to yield relative values of γ_M that are reasonable. For anions the picture is not as clear due to the formation of K^+ ion pairs and the predominance of Na^+ in most natural waters. This can be demonstrated by examining the values of γ_X obtained from K^+ and Na^+ salts at the same ionic strength (see table 6, adjusted to the same γ value for Cl). The large differences for some of the anions is due to ion pairing (for example, F^- and OH^-).

For anions that form ion pairs with K^+, it is necessary to make a correction to the $\gamma_\pm$ before a reliable value for γ_X can be determined by the mean salt method. For K_2SO_4 solutions the value of γ_{SO_4} can be determined from

$$\gamma_{SO_4} = \frac{\gamma_\pm^3(K_2SO_4)}{\gamma_\pm^2(KCl)} \left[\left(\frac{[K]_T}{[K]_F}\right)^2 \frac{[SO_4]_T}{[SO_4]_F}\right] \tag{19}$$

The values of the fractions of free K^+ and SO_4^{2-} at the ionic strength of the solution can be estimated from infinite dilution values of K_A by making estimates of the activity coefficients of the free ions and ion pairs (Reardon, 1975) or by using experimentally determined values of K_A^* (Van Breeman, 1973). If one takes αm_T as the concentration of sulfate paired, the value of K_A^* is given by

$$K_A^* = \frac{[KSO_4]}{[K]\,[SO_4]} = \frac{\alpha}{(2-\alpha)\,(1-\alpha)m_T} \tag{20}$$

where K_A^* is taken at the ionic strength of the solution $I = (3 - 2\alpha)m_T$. The substitution of $[K]_T/[K]_F = 2/(2 - \alpha)$ and $[SO_4]_T/[SO_4]_F = 1/(1 - \alpha)$ into eq (19) gives

$$\gamma_{SO_4} = \frac{\gamma_\pm^3(K_2SO_4)}{\gamma_\pm^2(KCl)} \left[\left(\frac{2}{2-\alpha}\right)^2 \left(\frac{1}{1-\alpha}\right)\right] \tag{21}$$

where $\gamma_{\pm}^{3}(K_2SO_4)$ is the experimental value at m_T, and the value of $\gamma_{\pm}^{2}(KCl)$ is at $I = (3 - 2\alpha)m_T$. The values of γ_{SO_4} determined from the values of K_A^* of Reardon (1975) are given in table 7. We have made similar calculations for Na_2SO_4 solutions using values of K_A^* from Pytkowicz and Kester (1969)

$$K_A^*(NaSO_4) = 2.73 - 2.58I + 2.28I^2 \qquad (22)$$

A sample calculation of γ_{SO_4} from $\gamma_{\pm}(Na_2SO_4)$ is given in table 8. The values of γ_{SO_4} determined from $\gamma_{\pm}$ for Na_2SO_4 (Pitzer and Mayorga, 1973) are also given in table 8. The values of γ_{SO_4} determined from K_2SO_4 and

TABLE 6

Comparison of the activity coefficients of anions obtained by using the mean salt method for Na^+ and K^+ salts†

Anion	K^+ Salt	Na^+ Salt	Δ(K − Na)
F^-	0.681	0.508	0.173
Cl^-	0.623	0.623	0
Br^-	0.642	0.668	−0.026
I^-	0.689	0.749	−0.060
OH^-	0.863	0.638	0.225
ClO_3^-	0.422	0.527	−0.105
BrO_3^-	0.387	0.447	−0.060
CNS^-	0.618	0.712	−0.094
NO_2^-	0.487	0.524	−0.037
NO_3^-	0.382	0.474	−0.092
$H_2PO_4^-$	0.349	0.363	−0.014
Ac^-	0.926	0.779	0.147
$H_2AsO_4^-$	0.408	0.446	−0.038
SO_4^{2-}	0.100	0.087	0.013
HPO_4^{2-}	0.124	0.091	0.033
$HAsO_4^{2-}$	0.181	0.116	0.065
PO_4^{3-}	0.018	0.009	0.009
AsO_4^{3-}	0.025	0.010	0.015
			ave. ± 0.067

† Based on $\gamma_{Cl} = 0.623$ which gives $\gamma_K = 0.623$ and $\gamma_{Na} = 0.707$ (I = 0.72262).

TABLE 7

Comparisons of the values of $\gamma_F(SO_4^{2-})$ estimated from K_2SO_4 and Na_2SO_4 solutions after corrections for ion pairing

I	K_2SO_4†	Na_2SO_4††	Δ†††
0.1	0.421	0.415	0.006
0.2	0.352	0.340	0.012
0.3	0.312	0.298	0.014
0.4	0.283	0.269	0.014
0.5	0.260	0.248	0.012
0.6	0.240	0.233	0.007
0.7	0.222	0.222	0.000
0.7226	0.219	0.220	−0.001
0.8	0.207	0.215	−0.008
0.9	0.193	0.211	−0.018
1.0	0.181	0.211	−0.030

† $K_A^*(KSO_4^-) = 2.81 - 2.06\ I + 0.62\ I^2$ (Reardon, 1975).
†† $K_A^*(NaSO_4^-) = 2.73 - 2.58\ I + 2.28\ I^2$ (Pytkowicz and Kester, 1969).
††† An error of ± 2 in K_A^* is equivalent to an error of ± 0.02 in $\gamma_{SO_4^{2-}}$.

TABLE 8

Correction of γ_{SO_4} from Na_2SO_4 solutions for ion pairing

I_T	$\gamma_\pm(Na_2SO_4)$†	α††	I_F†††	γ_{Na}	γ_{SO_4}
0.1	0.583	0.1804	0.0880	0.789	0.423
0.2	0.502	0.2732	0.1636	0.759	0.354
0.3	0.454	0.3312	0.2338	0.740	0.319
0.4	0.420	0.3712	0.3010	0.728	0.294
0.5	0.394	0.4008	0.3664	0.720	0.276
0.6	0.373	0.4244	0.4303	0.715	0.261
0.7	0.355	0.4444	0.4926	0.712	0.247
0.8	0.340	0.4628	0.5532	0.710	0.238
0.9	0.327	0.4806	0.6117	0.708	0.231
1.0	0.315	0.4986	0.6676	0.707	0.224
1.1	0.305	0.5171	0.7208	0.707	0.220
1.2	0.295	0.5360	0.7712	0.707	0.216
1.3	0.287	0.5553	0.8188	0.707	0.215
1.4	0.279	0.5746	0.9636	0.708	0.212
1.5	0.272	0.5939	0.9061	0.709	0.212
1.6	0.265	0.6129	0.9463	0.710	0.211
1.7	0.259	0.6314	0.9845	0.711	0.211
1.8	0.253	0.6493	1.0209	0.712	0.211

† Equation of Pitzer and Mayorga (1973).

†† $K_A^* = \alpha/(2-\alpha)\ (1-\alpha)m_T = 2.73 - 2.58I_F + 2.28I_F^2$ (Kester and Pytkowicz, 1969).

††† $I_F = (3-2\alpha)m_T = (1-2\alpha/3)I_T$.

Na_2SO_4 are in good agreement. Since the values determined from Na_2SO_4 are determined using directly measured values of K_A^*, we feel they are more reliable.

For many anions [for example, $B(OH)_4^-$] mean activity coefficients for K^+ salts are not available. It is, thus, necessary to estimate the free ion values using Na^+ salts using known values for the association constants. We have used the methods described above to estimate the free ion activity coefficients of a number of ions at the total ionic strength equivalent to various salinities.

Recently, Pitzer and Mayorga (1973, 1974) have fit the mean activity coefficients of a number of electrolytes to equations of the form

$$\ln \gamma_{MX} = Z_M Z_X f^\gamma + m\left(\frac{2\nu_M\nu_X}{\nu_M+\nu_X}\right) B_{MX}^\gamma + m^2 \frac{2(\nu_M\nu_X)^{3/2}}{\nu_M+\nu_X} C_{MX}^\gamma \tag{23}$$

where f^γ is the Debye-Hückel limiting law given by

$$f^\gamma = -0.392\left[\frac{I^{1/2}}{1+1.2I^{1/2}} + \frac{2}{1.2}\ln(1+1.2I^{1/2})\right] \tag{24}$$

For 1-1, 2-1, 1-2, 3-1, 4-1, and 5-1 electrolytes, the values of B_{MX}^γ and C_{MX}^γ are given by

$$B_{MX}^\gamma = 2\beta_{MX}^0 + \frac{\beta_{MX}^1}{2I}\left[1-e^{-2I^{1/2}}(1+2I^{1/2}-2I)\right] \tag{25}$$

$$C_{MX}^\gamma = 1.5\, C_{MX}^\phi \tag{26}$$

Values of β_{MX}^{0}, β_{MX}^{1}, and C_{MX}^{ϕ} have been tabulated by Pitzer and Mayorga (1973). For Cl^- salts and K^+ salts that do not form ion pairs, it is possible to use the mean salt method to convert Pitzer's equations to an ionic form

$$\ln \gamma_i = Z_i^2 f^{\gamma} + I(B_i^0) + f^1 B_i^1 + I^2 C_i \tag{27}$$

where

$$f^1 = [1 - e^{-2I^{1/2}}(1 + 2I^{1/2} - 2I)]$$

and

$$\begin{aligned}
B^0{}_i &= 4\beta_{MCl}{}^0 - 2\beta_{KCl}{}^0 \\
&= 8/3\beta_{MCl_2}{}^0 - 4\beta_{KCl}{}^0 \\
&= 2\beta_{MCl_3}{}^0 - 6\beta_{CKl}{}^0 \\
&= 8/5\beta_{MCl_4}{}^0 - 8\beta_{KCl}{}^0 \\
B_i^1 &= \beta_{MCl}{}^1 - 1/2\beta_{KCl}{}^1 \\
&= 2/3\beta_{MCl_2}{}^1 - \beta_{KCl}{}^1 \\
&= 1/2\beta_{MCl_3}{}^1 - 3/2\beta_{KCl}{}^1 \\
&= 2/5\beta_{MCl_4}{}^1 - 2\beta_{KCl}{}^1 \\
C_i &= 3C_{MCl}{}^{\phi} - 1.5C_{KCl}{}^{\phi} \\
&= (2^{3/2}/3)C_{MCl_2}{}^{\phi} - 3C_{KCl}{}^{\phi} \\
&= (3^{1/2}/4)C_{MCl_3}{}^{\phi} - 4.5C_{KCl}{}^{\phi} \\
&= (6/25)C_{MCl_4}{}^{\phi} - 6C_{KCl}{}^{\phi}
\end{aligned}$$

respectively for 1-1, 2-1, 3-1, and 4-1 electrolytes. Values of B^0, B^1, and C for various ions determined from the coefficients given by Pitzer and Mayorga (1973) are given in table 9. The values for some of the anions have been obtained by fitting the ion pairing corrected values to eq (27). By assuming that the $\ln \gamma_i$ are additive at a given ionic strength, it is possible to estimate ionic values of B^0, B^1, and C from salts other than K^+ and Cl^- (for example, ClO_4^- and Na^+ salts). For example, the values for Formate ion (For^-) can be determined from

$$B^0 = 4\beta_{NaFo}{}^0 - B^0{}_{Na} \tag{28}$$

$$B^1 = \beta_{NaFo}{}^1 - B^1{}_{Na} \tag{29}$$

$$C = 3.0C_{NaFo}{}^{\phi} - C_{Na} \tag{30}$$

using values for Na^+ taken from table 9. Values of the coefficients for anions determined in this manner are given in table 10 (also in table 9 for some ions). The activity coefficients of a number of major seawater ions are given at various salinities in table 11.

Bates (1978) has suggested that the activity coefficients of free cations and anions can be estimated from mean activity coefficients using a hydra-

TABLE 9
Coefficients for eq (27) for the activity coefficients of ions

Ion	B_i^0	B_i^1	C_i
H^+	0.6133	0.1884	0.00366
Li^+	0.5009	0.2013	0.01203
Na^+	0.2093	0.1603	0.00507
K^+	0.0967	0.1061	−0.00126
Rb^+	0.0797	0.0422	−0.00177
Cs^+	0.0233	−0.0503	0.00240
Ag^+	0.0807*	0.0592	−0.00333
Tl^+	−0.3603**	−0.1382	0.00861
NH_4^+	0.1121	0.0857	−0.00777
Me_4N^+	−0.0371	−0.1891	0.01836
Et_4N^+	0.0377	−0.2591	0.02646
Pr_4N^+	0.3293	−0.4601	0.03066
Bu_4N^+	0.7265	−0.5701	−0.17514
Mg^{2+}	0.7462	0.9088	0.00742
Ca^{2+}	0.6490	0.8638	0.00220
Sr^{2+}	0.5686	0.8993	0.00129
Ba^{2+}	0.5074	0.7853	−0.01575
Mn^{2+}	0.6792	0.8213	−0.01681
Fe^{2+}	0.7024	0.8093	−0.00560
Co^{2+}	0.7780	0.7713	−0.01183
Ni^{2+}	0.7344	0.8418	−0.00099
Cu^{2+}	0.6280	0.7053	−0.03560
Zn^{2+}	0.5004	0.8828	−0.08043
Cd^{2+}	1.6102***	1.2254	−0.06630
Pb^{2+}	0.8640†	0.9176	0.00889
UO_2^{2+}	0.9462	0.8838	−0.03224
Al^{3+}	1.1086	2.6040	0.00496
Sc^{3+}	1.1099	2.3410	−0.01022
Y^{3+}	0.9898	2.4037	−0.00600
La^{3+}	0.9310	2.4254	−0.01007
Ce^{3+}	0.9348	2.4240	−0.00970
Pr^{3+}	0.9139	2.4087	−0.00834
Nd^{3+}	0.9332	2.3830	−0.00850
Sm^{3+}	0.9539	2.4394	−0.00835
Eu^{3+}	0.9592	2.4767	−0.00767
Cr^{3+}	1.1827	2.3094	−0.01575
Ga^{3+}	1.4081	2.9090	0.00004
Th^{3+}	1.2352	4.9081	−0.01978

* From $AgNO_3$ and NKO_3.
** From $TlClO_4$ and $NaClO_4$.
*** From $Cd(NO_3)_2$ and KNO_3.

tion model. The values of γ for cations (M) and anions (X) are estimated from

$$\log \gamma_M = \log \gamma_{\pm}(MX) + 0.00782(h_M - h_X)m\phi_{MX} \quad (31)$$

$$\log \gamma_X = \log \gamma_{\pm}(MX) + 0.00782(h_X - h_M)m\phi_{MX} \quad (32)$$

where h_M and h_X are the hydration numbers of M and X, m is the molality, and ϕ_{MX} is the osmotic coefficient of MX. He has tabulated values of the hydration numbers for some ions assuming $h_{Cl} = 0$. A comparison of the values of γ_i at the ionic strength of seawater determined using the hydration model and the mean salt method are shown in table 12 (using

determined by the mean salt method at 25°C

Ion	B_i^0	B_i^1	C_i
F^-	0.2269	0.0960	0.00405
Cl^-	0.0967	0.1061	−0.00126
Br^-	0.1309	0.1151	−0.00414
I^-	0.2017	0.1456	−0.01116
OH^-	0.4225	0.2139	0.01356
ClO_3^-	−0.4807	0.1420	0.00126
BrO_3^-	−0.6127	0.1504	0.00126
CNS^-	0.0697	0.1241	−0.00630
NO_2^-	−0.0363	−0.0911	0.00336
NO_3^-	−0.4231	−0.0567	0.02106
	(−0.0227)††	(0.2095)††	(−0.44897)††
HCO_3^-	0.0707 †††	0.2273 †††	0.00312 †††
$H_2PO_4^-$	−0.3679	−0.2103	0.00126
	(0.0285)††	(0.0949)††	(−0.37620)††
$H_2AsO_4^-$	−0.3303	−0.0435	0.00126
PtF_5^-	−0.7487	−0.3881	0.00126
ClO_4^-	0.0123 §	0.1152 §	0.00861 §
BO_2^-	0.4197 §	−0.0499 §	0.04113 §
	(0.0718)††	(0.3657)††	(−0.31841)††
BF_4^-	−0.3101 §	0.0221 §	0.00123 §
For^-	0.1187 §	0.1269 §	−0.02076 §
Ac^-	0.5381	0.2190	−0.01854
$Prop^-$	0.5407 §	0.1186 §	−0.04338 §
Mal^-	−0.1347 §	0.0362 §	0.00627 §
Suc^-	0.0523 §	0.0503 §	0.00948 §
Adi^-	0.0697 §	0.1462 §	0.00126 §
CO_3^{2-}	0.2922 †††	0.9011 †††	0.00990 †††
SO_4^{2-}	−0.0602	0.3073	0.00252
	(−1.0410)††	(1.7422)††	(0.75121)††
$S_2O_3^{2-}$	−0.2422 §	0.5299 §	−0.00662 §
CrO_4^{2-}	0.0088	0.6138	0.00179
$Pt(CN)_4^{2-}$	−0.0172	1.3698	0.01487
HPO_4^{2-}	−0.1274	0.6373	0.01797
	(−3.6639)††	(3.1610)††	(1.65380)††
$HAsO_4^{2-}$	0.1522	0.8868	−0.01428
PO_4^{3-}	0.4558	1.6677	−0.03380
	(−6.3750)††	(6.9085)††	(2.29342)††
AsO_4^{3-}	0.7087	1.8520	−0.05249
$Fe(CN)_6^{3-}$	0.3812	2.0554	−0.01582
$Co(CN)_6^{3-}$	0.4570	1.6200	−0.02294

† From $Pb(ClO_4)_2$ and $NaClO_4$.

†† Corrected for ion pair formation.

††† The values for HCO_3^- and CO_3^{2-} are from K salts determined by Walker et al. (1927).

§ From Na^+ salts.

K^+ and Cl^- salts). The hydration model predicts values that agree to within ± 0.05 with those obtained using the mean salt method — the exceptions being H^+, Li^+, Cs^+, Mg^{2+}, and F^-. By making adjustments in the values of h one can decrease the differences between the two methods.

The values of γ_i determined from the hydration model are reasonable; however, the estimates are quite dependent upon the values selected for the hydration numbers. The values of $\gamma_\pm$ for MX calculated from the ionic values frequently are not in agreement with the experimental

values. For example, the $\gamma_{\pm}$ for NaCl is calculated to be 0.657 which is slightly lower than the experimental value (0.664). We prefer the estimates of free single ion activity coefficients made using the mean salt method, since they are determined directly from the experimental values on salts that are not considered to ion pair and are the major components of most marine waters.

The activity coefficients of ion pairs.—One of the major difficulties of using the ion pairing model is the assignment of values to the activity coefficients of ion pairs. Garrels and Thompson (1962) assigned a value of 1.13 to neutral ion pairs, 0.68 to plus and minus ion pairs, and 0.22 to plus two and minus two ion pairs. Atkinson, Dayhoff, and Ebdon (1973) have assumed that the activity coefficient of neutral ion pairs is 1.0. The values of γ for neutral ion pairs are based on the behavior of nonelectrolytes in salt solutions. The salting coefficient (k) for a nonelectrolyte in an electrolyte solution like seawater is given by

$$\log (\beta^{o}/\beta) = \log \gamma = kI \qquad (33)$$

where β^{o} and β are the solubilities in water and seawater, and γ is the activity coefficient of the nonelectrolyte. From the equations of Weiss

TABLE 10

Coefficients for eq (27) for the activity coefficients of anions determined from Na salts

Ion	B^0	B^1	C
F^-	−0.1233	0.1008	−0.00507
Cl^-	0.0967	0.2122	−0.00126
Br^-	0.1799	0.2376	−0.00159
I^-	0.2687	0.3672	0.00033
OH^-	0.1363	0.1854	0.00813
ClO_3^-	−0.1097	0.1704	−0.00387
ClO_4^-	0.0123	0.2334	−0.00861
BrO_3^-	−0.2913	0.0614	0.01263
CNS^-	0.1927	0.3958	−0.01416
NO_2^-	0.0471	−0.1176	−0.01977
NO_3^-	−0.1821	0.0360	−0.00723
$H_2PO_4^-$	−0.4225	−0.2414	0.01878
$H_2AsO_4^-$	−0.3861	0.2584	−0.00507
BO_2^-	0.4197	−0.0998	0.04113
BF_4^-	−0.3101	0.0442	0.00123
For$^-$	0.1187	0.2538	−0.02076
Ac$^-$	0.3611	0.3268	−0.02394
Prop$^-$	0.5407	0.2372	−0.04338
Mal$^-$	−0.1177	−0.0006	−0.00825
Suc$^-$	−0.0677	0.0006	−0.00387
Adi	−0.0205	0.3130	−0.00507
SO_4^{2-}	−0.3664	0.8428	−0.00545
$S_2O_3^{2-}$	−0.2422	1.0598	-0.00661_5
CrO_4^{2-}	−0.1686	1.1848	-0.01217_5
CO_3^{2-}	0.0874	0.4868	-0.05542_5
HPO_4^{2-}	−0.5749	1.3128	0.01756
$HAsO_4^{2-}$	−0.3372	1.5318	−0.00844
PO_4^{3-}	−0.27163	2.88953	-0.03752_5
AsO_4^{3-}	−0.1503	2.9682	-0.03587_5

(1974), we have determined the values of k for various gases in seawater of S = 35 per mil and t = 25°C. The resulting activity coefficients and salting coefficients are given in table 13. The values of γ are between 1.03 to 1.25 for gases. The salting coefficients of most nonelectrolytes in NaCl at an ionic strength of seawater are of the same order of magnitude as gases. The value of k is related (Masterton, 1975) to two effects — the free energy of making a cavity in the solution to accommodate the nonelectrolyte (a positive term) and the free energy change of transferring the nonelectrolyte into the cavity (a negative term).

Garrels and Thompson (1962) assumed that neutral ion pairs had a structure similar to H_2CO_3 and used $\gamma_{MX^\circ} = \gamma_{CO_2} = 1.13$ (the value in NaCl). One can question (Reardon and Langmuir, 1976) this assumption since most of the CO_2 is in the nonhydrated form. The activity coefficients of acids in salt solutions at the same ionic strength of seawater also have values near 1.1 (see table 14). The question thus becomes can hydrated acids serve as a reasonable model for estimating the value of γ for neutral ion pairs? Since many ion pairs exist as outer sphere pairs, one might expect the activity coefficients of some neutral ion pairs to be less than

TABLE 11

The activity coefficients of free ions determined by the mean salt method*

Ion	Salinity 5	10	15	20	25	30	35	40
H^+	0.824	0.820	0.835	0.859	0.890	0.926	0.967	1.011
Li^+	0.817	0.806	0.813	0.829	0.850	0.875	0.904	0.936
Na^+	0.786	0.748	0.728	0.717	0.711	0.708	0.707	0.708
K^+	0.767	0.715	0.685	0.663	0.647	0.634	0.623	0.614
Rb^+	0.754	0.695	0.660	0.634	0.614	0.599	0.586	0.575
Cs^+	0.734	0.663	0.619	0.587	0.562	0.542	0.525	0.511
Ag^+	0.757	0.700	0.665	0.640	0.621	0.606	0.593	0.582
Tl^+	0.691	0.593	0.528	0.477	0.437	0.402	0.373	0.347
NH_4^+	0.765	0.712	0.680	0.658	0.642	0.629	0.618	0.609
Mg^{2+}	0.403	0.341	0.313	0.293	0.290	0.287	0.285	0.286
Ca^{2+}	0.395	0.328	0.297	0.279	0.268	0.261	0.256	0.254
Sr^{2+}	0.395	0.327	0.295	0.276	0.263	0.255	0.248	0.244
Ba^{2+}	0.382	0.382	0.309	0.273	0.251	0.236	0.224	0.209
F^-	0.775	0.732	0.709	0.695	0.687	0.683	0.681	0.681
Cl^-	0.767	0.715	0.685	0.663	0.647	0.634	0.623	0.614
Br^-	0.771	0.723	0.695	0.676	0.661	0.651	0.642	0.635
I^-	0.782	0.742	0.720	0.707	0.699	0.693	0.689	0.687
OH^-	0.813	0.797	0.799	0.809	0.823	0.842	0.863	0.887
NO_3^-	0.773	0.715	0.668	0.624	0.579	0.535	0.490	0.445
HCO_3^-	0.799	0.743	0.724	0.697	0.692	0.681	0.673	0.663
$B(OH)_4^-$	0.809	0.778	0.754	0.727	0.699	0.666	0.633	0.596
$H_2PO_4^-$	0.757	0.693	0.645	0.603	0.562	0.522	0.483	0.446
CO_3^{2-}	0.389	0.305	0.276	0.236	0.229	0.215	0.205	0.196
SO_4^{2-}	0.393	0.333	0.303	0.280	0.258	0.237	0.219	0.197
HPO_4^{2-}	0.441	0.361	0.301	0.252	0.211	0.179	0.157	0.141
PO_4^{3-}	0.192	0.128	0.090$_4$	0.064$_3$	0.046$_1$	0.033$_3$	0.025$_2$	0.018$_8$

* Calculated from eq 27 using the coefficients in table 9. The values for NO_3^-, SO_4^{2-}, CO_3^{2-}, $B(OH)_4^-$ = BO_2^-, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} have been corrected for ion pair formation. The ionic strength was determined from I = 19.9201S/(1000 − 1.00488S) (Millero, 1981a).

1.1. Kester (ms), for example, has estimated that the activity coefficient of $MgSO_4^o$ is 0.8 in seawater (S = 35). The $MgSO_4^o$ ion pair is well known from ultrasonic studies (Eigen and Tamm, 1962) to be mostly in an outer sphere form.

Reardon and Langmuir (1976) have recently estimated the activity coefficients of $MgCO_3^o$ and $CaSO_4^o$ ion pairs. They found the values could be represented by

$$\log \gamma_{MX^o} = -BI \tag{34}$$

where B = 0.63 ± 0.1 for $MgCO_3^o$ and B = 0.45 ± 0.15 for $CaSO_4^o$ ion pairs. At I = 0.7 this equation gives $\gamma_{MgCO_3^o} = 0.36 \pm 0.05$ and $\gamma_{CaSO_4^o} = 0.48 \pm 0.07$. These values are quite a lot lower than the estimates made by other workers.

One can clarify these apparent discrepancies by considering the existing data for the formation of ion pairs of the major ionic components of seawater. The thermodynamic and stoichiometric constants given in table 3 can be combined with our activity coefficient estimates of free ions to estimate the activity coefficients of various types of ion pairs. For the formation of a neutral ion pair, we have

$$\gamma_{MX^o} = (K_A/K_A^*)\,\gamma_M\,\gamma_X \tag{35}$$

Our estimates of the activity coefficients of neutral ion pairs are summarized in table 15. For neutral ion pairs formed between monovalent cations and anions the activity coefficients are equal to 1.1 within the experimental error of the calculations. The value of γ_{NaF^o} is not shown due to the inconsistencies of the K_A and K_A^*. If one uses $K_A(NaF^o) = 0.55$

TABLE 12

Comparisons of the values of γ_i for some ions at I = 0.723 using the mean salt method and the hydration method

Ion	Mean salt	Hydration*	Δ
H^+	0.967	0.860	0.107
Li^+	0.902	0.822	0.080
Na^+	0.707	0.693	0.014
K^+	0.623	0.637	−0.014
Rb^+	0.583	0.612	−0.029
Cs^+	0.525	0.572	−0.047
NH_4^+	0.618	0.632	0.014
Mg^{2+}	0.285	0.232	0.053
Ca^{2+}	0.256	0.216	0.040
Sr^{2+}	0.248	0.211	0.037
Ba^{2+}	0.215	0.192	0.023
F^-	0.681	0.636	0.045
Cl^-	0.623	0.623	0
Br^-	0.631	0.632	−0.001
I^-	0.689	0.655	0.034

* Calculated using the hydration numbers of $h_H = 8.0$, $h_{Li} = 7.1$, $h_{Na} = 3.5$, $h_K = 1.9$, $h_{Rb} = 1.2$, $h_{Cs} = 0$, $h_{NH_4} = 1.6$, $h_{Mg} = 13.7$, $h_{Ca} = 12.0$, $h_{Sr} = 10.7$, $h_{Ba} = 7.7$ (Bates, Staples, and Robinson, 1970), $h_F = 1.9$, $h_{Cl} = h_{Br} = h_I = 0.0$ (Bates, 1978). The values of ϕ_{MX} were taken from the tabulations of Robinson and Stokes (1959). The anions were obtained from K^+ salts.

(Robinson, Duer, and Bates, 1971; Duer, Robinson, and Bates, 1972), $\gamma_{NaF^0} = 1.7$ is obtained from the $K_A^* = 0.16$ (Butler and Huston, 1970b) and $\gamma_{NaF^0} = 5.3$ is obtained using $K_A^* = 0.05$ (Miller and Kester, 1976). Both values are higher than 1.1 and indicate that the K_A may be too high. A value of $K_A = 0.2 \pm 0.1$ is obtained if γ_{NaF} is taken as 1.1. These calculations point out the difficulties of estimating the values of γ for weakly complexed ions (K_A below 1.0). We do feel, however, that the calculations for HF^0, $NaHCO_3^0$, and $NaB(OH)_4^0$ are consistent and indicate that the assignment of $\gamma_{(M^+,X^-)^0} = 1.1$ is reasonable ($\ln \gamma = 0.14I$).

The activity coefficients of neutral ion pairs formed between divalent cations and anions are also given in table 15. For $MgSO_4^0$ and $CaSO_4^0$, we obtain 1.0 ± 0.05. The γ value for $CaHPO_4^0$ is slightly lower ($0.9_7 \pm 0.2$), while the values for $CaCO_3$ and $MgCO_3^0$ (0.6 ± 0.1) are lower than expected. Our value for $CaSO_4^0$ (1.0) is higher than found by Reardon and Langmuir (1976) using solubility data. This difference could be related to the incorporation of ions in the solid phase in the $CaSO_4$ solubility studies or the formation of triplet ion pairs, $Ca(SO_4)_2^{2-}$ or $Ca_2SO_4^{2+}$. The lower values of γ for $MgCO_3^0$ and $CaCO_3^0$ are in agreement with the findings of Reardon and Langmuir (1976). It should be pointed out, however, that both the measurements and calculations are based on activity coefficients of $KHCO_3$ and K_2CO_3 of Walker, Bray, and Johnson (1927)

TABLE 13

The salting out and activity coefficients of gases in seawater at 25°C

Gas	k	γ_g*
N_2	0.131_3	1.24
O_2	0.121_1	1.22
Ar	0.121_2	1.22
Ne	0.101_3	1.18
He	0.091_0	1.16
Kr	0.127_8	1.23
CO_2	0.094_0	1.17
CO	0.134_1	1.25
CH_4	0.129_3	1.24
H_2S	0.019_7	1.03

* For S = 35‰, or I = 0.7226. The value for H_2S is taken from Douabul and Riley (1979).

TABLE 14

The salting out and activity coefficients of acids in 0.723 m NaCl solutions at 25°C

Acid*	k	γ_a
Phosphoric	0.052	1.09
Acetic	0.066	1.12
Chloro-acetic	0.088	1.16
Benzoic	0.191	1.37

* Taken from Harned and Owen (1958). The value for phosphoric acid is from Pitzer and Silvester (1976).

which may be unreliable (see Pitzer and Peiper, 1980). The importance of triplet ion pairs found by Pytkowicz and Hawley (1974) also needs further studies. In summary, we feel that the γ for neutral ion pairs formed between divalent cations and most anions can be assigned a value of 1.0. For neutral pairs formed with CO_3^{2-}, we have selected $\gamma = 0.6$ ($\ln \gamma = -0.731$).

The activity coefficients of negatively charged ion pairs can be estimated from

$$\gamma_{MX^-} = (K_A/K_A^*)\,(\gamma_{M^+}\,\gamma_{X^{2-}}) \tag{36}$$

The values of γ_{MX^-} given in table 15 for HSO_4^-, $NaSO_4^-$, KSO_4^-, and $NaCO_3^-$ vary from 0.57 to 0.74. The average value of 0.64 ± 0.08 is in good agreement with the value of 0.68 used by Garrels and Thompson (1962). Since the activity coefficient of Br^- is equal to 0.64 at I = 0.7, it can serve as a model for the ionic strength dependence of negatively charged ion pairs formed between monovalent cations and divalent anions.

Since values of K_A and K_A^* are available for the formation of $CaPO_4^-$, it is possible to estimate the activity coefficient formed between a divalent cation and trivalent anion.

$$\gamma_{M^{2+},\,X^{3-}} = (K_A/K_A^*)\gamma_{M^{2+}}\,\gamma_{X^{3-}} \tag{37}$$

We obtain a value of 0.61 ± 0.05 which is slightly lower than 0.64 found for M^+, X^{2-} ion pairs. Since the differences are within the experimental error of the estimates, we do not consider the difference to be significant.

TABLE 15

Estimates of the activity coefficients of ion pairs at I = 0.7 and t = 25°C

Type	Ion pair	γ ion pair*	Selected value
(M^+X^-)	HF^0	1.1 ± 0.1	1.1
	$NaHCO_3^0$	1.0 ± 0.2	
	$NaB(OH)_4^0$	1.3 ± 0.3	
$(M^{2+}X^{2-})^0$	$MgSO_4^0$	1.0 ± 0.1	1.0
	$CaSO_4^0$	1.0 ± 0.1	
	$CaHPO_4^0$	1.0 ± 0.2	
	$MgCO_3^0$	0.5 ± 0.3	0.6
	$CaCO_3^0$	0.7 ± 0.2	
$(M^+X^{2-})^-$	HSO_4^-	0.65 ± 0.02	0.64
	$NaSO_4^-$	0.74 ± 0.08	
	KSO_4^-	0.57 ± 0.09	
	$NaCO_3^-$	0.59 ± 0.10	
$(M^{2+}X^{3-})^-$	$CaPO_4^-$	0.61 ± 0.05	0.64
$(M^{2+}X^-)^+$	MgF^+	0.6 ± 0.1	0.80
	CaF^+	0.5 ± 0.1	
	$MgB(OH)_4^+$	0.9 ± 0.2	
	$CaB(OH)_4^+$	0.8 ± 0.2	
	$MgHCO_3^+$	0.9 ± 0.2	
	$CaHCO_3^+$	0.8 ± 0.2	
	$MgOH^+$	0.8 ± 0.2	
	$CaH_2PO_4^+$	0.7 ± 0.3	

* The errors are related to the estimated uncertainties in K_A^* and K_A.

The activity coefficient of positively charged ion pairs formed between Mg^{2+} and Ca^{2+} ions and monovalent ligands can be estimated from

$$\gamma_{MX^+} = (K_A/K_A^*)\,(\gamma_{M^{2+}}\,\gamma_{X^-}) \qquad (38)$$

The values of γ_{MX^+} for Mg^{2+} and Ca^{2+} complexes with HCO_3^-, OH^-, F^-, $B(OH)_4^-$, and $H_2PO_4^-$ estimated from eq (38) are given in table 15. The values vary from 0.5 to 0.9 for the various MX^+ ion pairs. The average value of $0.7_5 \pm 0.1_4$ obtained for all the ion pairs is in reasonable agreement with the value (0.68) assigned by Garrels and Thompson (1962). The lower values for MgF^+ and CaF^+ are probably related to the errors in the values of K_A. Using $\gamma_{M^{2+}X^-} = 0.8$ we obtain $K_A = 80.0 \pm 5.0$ and 20.2 ± 3.0, respectively, for MgF^+ and CaF^+. Since no simple cation has an activity coefficient of 0.8 at I = 0.7, it is difficult to use a given ion as a model. We have, thus, taken a hypothetical ion with Pitzer coefficients obtained by averaging the values for Li^+($\gamma = 0.9$ at I = 0.7) and Na^+($\gamma = 0.7$ at I = 0.7) as a model for the ionic strength dependence of the activity coefficients of ion pairs formed between divalent cations and monovalent anions ($B_i^0 = 0.3551$, $B_i^1 = 0.1808$, and $C_i = 0.0086$).

To summarize, we feel that the presently available K_A and K_A^* data are consistent (with the exception of $MgCO_3^\circ$ and $CaCO_3^\circ$) with the original assignments made by Garrels and Thompson (1962) for the activity coefficients of ion pairs in seawater. Due to the importance of carbonate ion pairing with heavy metals (Zirino and Yammamoto, 1972), further experimental measurements of Ca^{2+} and Mg^{2+} carbonate interactions at

TABLE 16

Comparisons of the measured and calculated values of K_A^* for ion pairs at I = 0.7 and t = 25°C

Ion pair	Measured	Calculated	Δ
HF°	871 ± 80	887	−16
NaF°	0.1 ± 0.05	0.2_4	−0.1
$NaHCO_3^\circ$	0.30 ± 0.02	0.28	0.02
$NaB(OH)_4^\circ$	0.6 ± 0.1	0.7	−0.1
$MgSO_4^\circ$	10.2 ± 0.5	10.3	−0.1
$CaSO_4^\circ$	10.8 ± 0.5	10.9	−0.1
$MgCO_3^\circ$	87 ± 11	47(78)†	40(9)†
$CaCO_3^\circ$	126 ± 26	84(141)†	42(−15)†
$CaHPO_4^\circ$	19.0 ± 1.4	19.0	0
HSO_4^-	30.9 ± 0.7	31.5	−0.6
$NaSO_4^-$	2.0 ± 0.3	2.2	−0.2
KSO_4^-	1.8 ± 0.2	1.6	0.2
$NaCO_3^-$	2.6 ± 0.5	2.4	0.2
$MgHCO_3^+$	1.9 ± 0.3	2.1	−0.2
$CaHCO_3^+$	2.1 ± 0.3	2.2	−0.1
$MgOH^+$	50 ± 6	49	1
MgF^+	20 ± 0.9	16	4
CaF^+	4.5 ± 0.6	2.4	−2.1
$MgB(OH)_4^+$	7.9 ± 0.6	9.6	−1.7
$CaB(OH)_4^+$	12.9 ± 0.6	13.0	−0.1
$CaHPO_4^+$	1.7 ± 0.1	1.6	0.1
$CaPO_4^-$	$(3.1 \pm 0.7)10^4$	3.0×10^4	0.1×10^4

† Values calculated using $\gamma_{MX^\circ} = 0.6$.

high ionic strengths are desirable. Since little data are available for the ionic strength dependence of K_A*, it is necessary at present to use model ions to determine the ionic strength dependence of charged ion pairs. Hopefully marine chemists in the future will make reliable measurements of K_A* over a wide range of ionic strengths found in natural waters.

Ionic strength dependence of K_A.*—The internal consistency of the values of K_A and the activity coefficients of ions and ion pairs can be demonstrated by comparing the calculated values of K_A* (using eq 7) and the experimentally measured values. The comparisons shown in table 16 demonstrate that reasonable estimates of K_A* can be made from K_A using values of γ for ions from K^+ and Cl^- salts and values of $\gamma_{M^+, X^-} = 1.1$, $\gamma_{M^{2+}, X^{2-}} = 1.0$, $\gamma_{M^+, X^{2-}} = 0.64$ and $\gamma_{M^{2+}, X^-} = 0.80$ (at I = 0.7). For systems where no experimental measurements are available at I = 0.7, one is forced to use estimated values of K_A* (values given in table 3). For some of the systems [NaF^o, MgF^+, CaF^+, and $MgB(OH)_4^+$], the differences between the measured and calculated K_A*'s are larger than expected. These differences can be attributed to errors in K_A or errors in the assigned value of γ for the ion pair. At present it is not possible to be certain which cause is affecting the calculated K_A*'s. Since we wish to make the form of γ_{MX} for various ion pairs as simple as possible, we have made a small adjustment of the values of K_A for NaF^o, MgF^+, CaF^+, and $MgB(OH)_4^+$.

Since experimental data are not normally available for the ionic strength dependence of K_A*, it is necessary to use estimated values. Recently, this has been done from $I = 2 \times 10^{-3}$ to 0.8 (equivalent to S = 0.105 to 40 per mil) by using estimated activity coefficients and experimental values of K_A and K_A* (Millero, 1981a). As shown in figure 1 the values of K_A* for most ion pairs are not strongly dependent upon ionic strength from I = 0.1 to 0.8. By using Pitzer's equations in ionic form

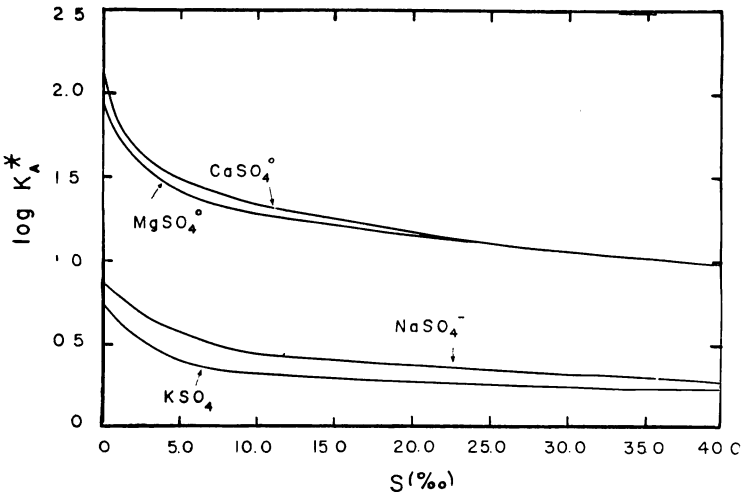

Fig. 1. The effect of salinity on K_A*.

TABLE 17

Coefficients for eq 39

$$\ln K_A^* = \ln K_A + Z_A^2 f + IB_A^0 + f^1 B_A + I^2 C_A$$

Ion pair	$\ln K_A$	Z_A^2	B_A^0	B_A^1	C_A
HSO_4^-	4.55$_7$	4.0	−0.5586	1.8155	0.75901
HF^0	7.31	2.0	0.7040	0.2844	0.00771
KSO_4^-	2.03	4.0	−1.0752	1.7332	0.75409
KNO_3^0	0.18	2.0	−0.0622	0.3156	−0.45023
$NaSO_4^-$	2.17	4.0	−0.9626	1.7874	0.76042
$NaHCO_3^0$	−0.43	2.0	0.1438	0.3876	0.00819
$NaCO_3^-$	2.35	4.0	0.3706	0.9463	0.01911
$NaOH^0$	−0.41	2.0	0.4956	0.3742	0.01863
NaF^0	−1.47‡	2.0	0.3000	0.2563	0.00912
$NaNO_3^0$	−1.38	2.0	0.0504	0.3698	−0.44390
$NaB(OH)_4^0$	0.51	2.0	0.1449	0.5260	−0.31334
$NaH_2PO_4^0$	−0.10	2.0	0.1016	0.2552	−0.37113
$NaHPO_4^-$	1.84	4.0	−3.5855	3.2062	1.66301
$NaPO_4^{2-}$	3.68	6.0	−5.1247	5.3267	1.54728
$MgSO_4^0$	5.09	8.0	−0.2948	2.6510	0.75863
$MgHCO_3^+$	2.19	4.0	0.4618	0.9553	0.00199
$MgCO_3^0$	6.68	8.0	1.0384(1.7682)$^\phi$	1.8099	0.01732
$MgOH^+$	5.07	4.0	0.8136	0.9419	0.01243
MgF^+	4.38‡	4.0	0.6180	0.8240	0.00292
$MgB(OH)_3^+$	3.54‡	4.0	0.4629	1.0937	−0.31955
$MgH\ PO_4^+$	2.59	4.0	0.4196	0.8229	−0.37734
$MgHPO_4^0$	6.55	8.0	−2.9177	4.0698	1.66122
$MgPO_4^-$	13.30	12.0	−5.7597	7.7022	2.30498
$CaSO_4^0$	5.25	8.0	−0.3920	2.6060	0.75341
$CaHCO_3^+$	2.30	4.0	0.3646	0.9103	−0.00323
$CaCO_3^0$	7.37	8.0	0.9412(1.6710)$^\phi$	1.7649	0.01210
$CaOH^+$	2.99	4.0	0.7164	0.8969	0.00721
CaF^+	3.02‡	4.0	0.5208	0.7790	0.00230
$CaNO_3^+$	0.64	4.0	0.2712	0.8925	−0.45532
$CaB(OH)_4^+$	4.14	4.0	0.3657	1.0487	−0.32476
$CaH\ PO_4^+$	2.30	4.0	0.3224	0.7779	−0.38255
$CaHPO_4^0$	6.12	8.0	−3.0149	4.0248	1.65600
$CaPO_4^-$	14.87	12.0	−5.8565	7.6572	2.29976
$SrSO_4^0$	4.84	8.0	−0.4724	2.6415	0.75250
$SrHCO_3^+$	2.30†	4.0	0.2842	0.9458	−0.00414
$SrCO_3^0$	7.37†	8.0	0.8638(1.5906)$^\phi$	1.8004	0.01119
$SrOH^+$	1.89	4.0	0.6360	0.9324	0.00630
SrF^+	2.39†	4.0	0.4404	0.8145	−0.00321
$SrNO_3^+$	1.89	4.0	0.1908	0.9280	−0.45623
$SrB(OH)_4^+$	3.57	4.0	0.2853	1.0842	−0.32567
$BaSO_4^0$	5.30	8.0	−0.5336	2.5275	0.73546
$BaHCO_3^+$	2.30†	4.0	0.2230	0.8318	−0.02118
$BaCO_3^0$	7.37†	8.0	0.7996(1.5294)$^\phi$	1.6864	−0.00585
$BaOH^+$	1.47	4.0	0.5748	0.8184	−0.01074
BaF^+	2.39†	4.0	0.3792	0.7005	−0.02025
$BaB(OH)_4^+$	3.43	4.0	0.2241	0.9702	−0.34271
$NH_4SO_4^+$	2.16	4.0	−1.10598	1.7128	0.74758
$LiSO_4^+$	1.77	4.0	−0.6710	1.8284	0.76738
$RbSO_4^+$	1.38	4.0	−1.0922	1.6693	0.75358
$CsSO_4^+$	0.76	4.0	−1.1486	1.5768	0.75775

$^\phi$ The values in parenthesis use $\gamma_{MX^\circ} = 0.6$.

† Equated to values for CaX.

‡ Adjusted to give values of K* that agree with literature data.

(eq 27), it is possible to determine the values of K_A^* from equations of the form

$$\ln K_A^* = \ln K_A + Z_A^2 f^\gamma + I B_A^\circ + f^1 B_A^1 + I^2 C_A \qquad (39)$$

where $Z_A^2 = Z_M^2 + Z_X^2 - Z_{MX}^2$, $B_A^\circ = B_M^\circ + B_X^\circ - B_{MX}^\circ$, and $C_A = C_M + C_X - C_{MX}$ (M and X are the free ions and MX is the ion pair). Values of $\ln K_A$, Z_A^2, B_A°, and C_A for various ion pairs are given in table 17. The values of B_i°, B_i^1, and C_i for ions were taken from table 9. The values of B_A° for neutral ion pairs were taken as 0.1362 and 0, respectively, for $(M^+X^-)^\circ$ and $(M^{2+}X^{2-})^\circ$ ion pairs (for $MgCO_3^\circ$ and $CaCO_3^\circ$ pairs, $B_A^\circ = -0.7298$ can also be used). For charged ion pairs we have used the values of B_i°, B_i^1, and C_i for model ions (Br^- for M^+X^{2-}, $(Li^+ + Na^+)/2$ for $M^{2+}X^-$ and SO_4^{2-} for M^+X^{3-}). The coefficients of eq (39) can be easily modified when more reliable values of K_A become available or more reliable estimates can be made for the activity coefficients of ion pairs. It is also possible to use eq (39) to make reasonable estimates of K_A^* for minor constituents of natural waters using the best available values of K_A.

We wish to issue a word of caution in using eq (39) to estimate values of K_A^* at high ionic strengths. The equation is strictly valid only to $I = 1.0$; thus, its use at higher ionic strengths may lead to large errors. This is largely due to our inability at present to predict with certainty the ionic strength dependence of ion pairs. Direct measurements of K_A^* at high ionic strengths are needed to prove the reliability of eq (39) for brines.

Speciation calculations.—From the ionic strength dependence of K_A^* (eq 39) of the major ion pairs of seawater it is quite easy to determine the fraction of free cations and anions in natural waters. The errors in these calculations are dependent upon the reliability of the stoichiometric constants. At the ionic strength of seawater ($I_F = 0.67$), it is possible to examine the effects of using experimentally measured values of K_A^* with

TABLE 18

Effects of using various K_A^*'s on the fraction of free metals and anions in seawater (S = 35 and t = 25°C)

Ion	% Free			
	Calculated	Measured	Δ%	Δγ
H^+	72.63	72.37	0.26	0.004
Na^+	97.63	97.72	−0.09	−0.001
K^+	98.01	97.81	0.20	0.001
Mg^{2+}	89.13	89.05	0.08	0.000_1
Ca^{2+}	88.44	88.42	0.02	0.000_3
Sr^{2+}	92.01	91.83	0.18	0.001
F^-	48.84	48.42	0.42	0.003
OH^-	27.69	27.30	0.39	0.003
$B(OH)_4^-$	53.21	54.90	−1.69	−0.011
HCO_3^-	79.24	79.68	−0.60	−0.007
CO_3^{2-}	16.04	15.19	0.85	0.002
SO_4^{2-}	37.47	38.94	−1.47	−0.003
$H_2PO_4^-$	78.59	78.56	0.03	0.000_1
HPO_4^{2-}	29.68	29.75	−0.07	-0.000_1
PO_4^{3-}	0.15	0.15	0	0

those obtained from thermodynamic constants, K_A, and estimates of the activity coefficients of ions and ion pairs. The differences obtained in using the various K_A*'s are shown in table 18. The differences for cations are quite small (less than 0.6 percent); however, the differences for anions can be as much as 1.7 percent. The equivalent errors in the calculated activity coefficients are also given in table 18. For cations the differences are less than ± 0.004; while for some anions the differences are as large as 0.01. At higher ionic strengths one would expect the errors in γ_T due to errors in K_A* to be significantly greater.

The errors in γ_T due to errors in the assigned values of γ_F are difficult to assess. The errors in the experimental mean activity coefficients are generally within ± 0.005 for K^+ and Cl^- salts. The errors in γ_F due to corrections for ion pairing are less than 0.02 (table 7) for SO_4^{2-} below I = 0.8 (~5 percent). Thus, one would expect that the errors in γ_T due to errors in γ_F to be within 5 percent below I = 0.8. If the values of K_A* are determined using the MacInnes convention, the errors in γ_T due to the assigned value of γ_F and K_A* tend to cancel (that is, at I = 0.7 where experimental data is available).

The speciation of a number of ions in seawater diluted with water has been determined using the values of K_A* determined from eq 39. The values of γ_T calculated by using mean salt estimates of γ_F are given in table 19 at various salinities.

Comparisons with experimental measurements.—The reliability of the estimated values of γ_T can be examined by making comparisons with experimental measurements. Direct measurements of mean activity coefficients of electrolytes are normally available only at S = 35 per mil; thus, little can be said about the concentration dependence of γ_T. Comparisons of the measured and estimated mean activity coefficients of a number of electrolytes are given in table 20. The calculated values agree with the measured values to ± 0.04 (10 percent). Also given in table 20 are the calculated values of $\gamma_\pm$ obtained by Whitfield (1975a, b) using the equations of Pitzer and Kim (1974). The specific interaction model predictions for the major sea salts (NaCl, Na_2SO_4, KCl, and K_2SO_4) are better than those obtained using the ion pairing model. For the electrolytes that interact strongly (HCl, $CaSO_4$, $SrSO_4$, and $CaCO_3$) the ion pairing model predicts values that are in better agreement with the experimental measurements. This is clearly demonstrated by comparing the calculated and measured values of γ_T for ions (see table 21). The measured values of γ_X for weak acid anions (F^-, OH^-, HCO_3^-, $B(OH)_4^-$, $H_2PO_4^-$, CO_3^{2-}, SO_4^{2-}, HPO_4^{2-}, and PO_4^{3-}) have been determined from the thermodynamic and stoichiometric dissociation constants of the acids (Pytkowicz, 1969).

For some of the major ionic components of seawater (Na^+, K^+, and SO_4^{2-}) the specific interaction model predicts values that are in better agreement with the measurements. For the minor ionic components, however, the ion pairing estimates of γ_T are more reliable. This is not surprising since the specific interaction coefficients for Mg^{2+} and Ca^{2+} with

TABLE 19

Values of γ_T for ions in seawater + water at 25°C

Ion	S = 0.105	0.25	0.5	1	2	3	4	5	10	15	20	25	30	35	40
H^+	0.946	0.918	0.886	0.847	0.801	0.771	0.750	0.734	0.691	0.675	0.671	0.673	0.679	0.688	0.698
Li^+	0.952	0.929	0.907	0.879	0.850	0.832	0.821	0.813	0.798	0.801	0.812	0.829	0.849	0.872	0.898
Na^+	0.951	0.927	0.902	0.871	0.835	0.811	0.794	0.780	0.739	0.718	0.706	0.698	0.693	0.690	0.690
K^+	0.950	0.926	0.900	0.867	0.826	0.800	0.780	0.763	0.710	0.679	0.657	0.640	0.626	0.615	0.606
Rb^+	0.950	0.925	0.899	0.864	0.822	0.794	0.772	0.754	0.696	0.660	0.634	0.615	0.599	0.586	0.575
Cs^+	0.949	0.924	0.896	0.859	0.813	0.781	0.756	0.736	0.667	0.623	0.592	0.567	0.547	0.530	0.516
NH_4^+	0.950	0.925	0.899	0.866	0.825	0.797	0.777	0.760	0.706	0.674	0.652	0.635	0.621	0.610	0.601
Mg^{2+}	0.812	0.732	0.655	0.570	0.483	0.434	0.401	0.378	0.315	0.287	0.272	0.263	0.258	0.255	0.254
Ca^{2+}	0.810	0.729	0.650	0.563	0.474	0.424	0.391	0.366	0.300	0.270	0.252	0.241	0.234	0.228	0.225
Sr^{2+}	0.813	0.734	0.657	0.572	0.484	0.434	0.401	0.376	0.309	0.278	0.259	0.246	0.237	0.231	0.226
Ba^{2+}	0.809	0.727	0.647	0.558	0.466	0.415	0.380	0.354	0.284	0.250	0.229	0.215	0.205	0.197	0.191
F^-	0.940	0.906	0.866	0.811	0.741	0.694	0.657	0.627	0.526	0.464	0.420	0.385	0.357	0.333	0.312
Cl^-	0.950	0.927	0.901	0.870	0.831	0.805	0.786	0.770	0.719	0.689	0.668	0.651	0.638	0.628	0.619
Br^-	0.951	0.927	0.902	0.871	0.833	0.808	0.789	0.774	0.726	0.699	0.680	0.665	0.655	0.646	0.639
I^-	0.951	0.928	0.904	0.873	0.838	0.815	0.798	0.785	0.745	0.723	0.710	0.701	0.695	0.691	0.688
OH^-	0.932	0.888	0.837	0.768	0.680	0.622	0.578	0.543	0.430	0.365	0.319	0.285	0.258	0.236	0.218
NO_3^-	0.951	0.927	0.902	0.870	0.831	0.805	0.784	0.767	0.704	0.656	0.613	0.571	0.530	0.489	0.448
$B(OH)_4^-$	0.945	0.915	0.881	0.835	0.776	0.735	0.702	0.675	0.578	0.512	0.461	0.419	0.383	0.351	0.323
$H_2PO_4^-$	0.947	0.920	0.889	0.849	0.796	0.760	0.730	0.706	0.619	0.558	0.509	0.467	0.429	0.395	0.363
HCO_3^{2-}	0.949	0.924	0.897	0.862	0.818	0.789	0.766	0.747	0.683	0.640	0.607	0.580	0.557	0.536	0.518
SO_4^{2-}	0.797	0.705	0.614	0.513	0.409	0.351	0.311	0.281	0.197	0.154	0.128	0.109	0.095	0.085	0.076
HPO_4^{2-}	0.758	0.642	0.535	0.424	0.320	0.266	0.231	0.205	0.136	0.103	0.082	0.068	0.057	0.050	0.044
CO_3^{2-}	0.726	0.594	0.474	0.358	0.255	0.205	0.173	0.151	0.094	0.068	0.053	0.042	0.034	0.029	0.024
PO_4^{3-}	6.31*	2.88	1.57	0.874	0.494	0.356	0.282	0.236	0.133	0.094	0.072	0.058	0.049	0.042	0.036

* $PO_4^{3-} \times 10^3$ for all the values.

acid anions are not available. It is possible to determine these terms from the experimental measurements used to determine K_A*; however, until this is done one is forced to use the ion pairing method to determine reliable estimates of γ_T for the minor components of natural waters.

The predicted values of γ_T for H^+, Ca^{2+}, and Sr^{2+} using the ion pairing and specific interaction model are higher than the measured values determined, respectively, from HCl, $CaSO_4$, and $SrSO_4$. For H^+ this effect could be related to liquid junction potentials included in the association constant of HSO_4^- and HF^o (for the ion pairing estimate) or neglecting $H^+ - SO_4^{2-}$ interactions (for the specific interaction estimate). The measured values of γ_T of Ca^{2+} and Sr^{2+} could be too low due to the formation of mixed surface interactions with Mg^{2+}.

The ability to use the ion pairing model to give reliable estimates for the activity coefficients of weak acid anions can be quite useful in determining the dissociation constants of acids in natural waters (Millero, 1981b). Comparisons of the measured and calculated pKs of weak acids in seawater (S = 35 percent) are shown in table 22. The agreement is quite good (within 7 percent) for all the acids. In summary, we expect the total activity predicted from the ion pairing model to be reliable to within 10 percent for ionic strengths below 0.8.

Improvements in the model.—To improve the ion pairing model one can go in two directions: (1) consider that all cations and anions form ion pairs (Johnson and Pytkowicz, 1979) or (2) use a hybrid model that uses

TABLE 20

Comparison of the measured and calculated mean activity ($\gamma_\pm$) coefficients of electrolytes in seawater

Salt	Measured	Calculated: Ion pairing	Δ	Calculated: Specific interaction††	Δ
NaCl	0.667*	0.658	0.009	0.667	0
	0.668**		0.010		0.001
	0.672***		0.014		0.005
Na_2SO_4	0.378****	0.343	0.035	0.373	0.005
	0.385†		0.042		0.012
KCl	0.645††	0.621	0.024	0.648	−0.003
K_2SO_4	0.352††	0.318	0.034	0.358	−0.006
HCl	0.627†††	0.657	−0.030	0.701	−0.074
$CaSO_4$	0.136††††	0.139	−0.003	0.159	−0.023
$SrSO_4$	0.140††††	0.140	0	0.157	−0.017
$CaCO_3$	0.090§	0.081	0.009	0.151	−0.061
	0.086§§		0.005		−0.065

* Johnson and Pytkowicz (1980).
** Gieskes (1966).
*** Platford (1965).
**** Platford and Dafoe (1965).
† Value of Platford and Dafoe (1965) corrected by Culberson, Pytkowicz, and Hawley (1978).
†† Whitfield (1975a, b), using Pitzer's equation.
††† Khoo and others (1977).
†††† Culberson, Pytkowicz, and Hawley (1978).
§ Pytkowicz (1975).
§§ Morse, Mucci, and Millero (1980).

TABLE 21

Comparison of the measured and calculated total activity coefficients of ions in seawater

Ion	Measured	Ion pairing	Δ	Specific interaction	Δ
H^+	0.699*	0.688	0.011	0.782	−0.083
	0.696**		0.008		−0.086
	0.726***		0.038		−0.056
	0.626****		−0.062		−0.156
Na^+	0.708†	0.690	0.018	0.708	0
K^+	0.662†	0.615	0.047	0.668	−0.006
Mg^{2+}	0.257††	0.255	0.002	0.269	−0.012
Ca^{2+}	0.217†††	0.228	−0.011	0.241	−0.024
	0.178††††		−0.050		−0.063
	0.261§		0.033		0.020
Sr^{2+}	0.188††††	0.231	−0.043	0.239	−0.051
Cl^-	0.628§§	0.628	—	0.628§	—
F^-	0.296§§§	0.333	−0.037	0.519	−0.223
OH^-	0.218§§§§	0.236	−0.018	0.562	−0.344
HCO_3^-	0.532■	0.536	−0.004	—	—
$B(OH)_4^-$	0.360■■	0.351	0.009	—	—
$H_2PO_4^-$	0.416■■■	0.395	0.021	0.456	−0.040
CO_3^{2-}	0.029■■■■	0.029	0.000	0.095	−0.066
SO_4^{2-}	0.104◊	0.085	0.019	0.103	0.001
HPO_4^{2-}	0.072◊◊	0.050	0.022	0.095	−0.023
PO_4^{3-}	(3.7×10^{-5})◊◊	4.2×10^{-5}	-0.5×10^{-5}	901×10^{-5}	-897×10^{-5}

* Mehrbach and others (1973).

** Culberson and Pytkowicz (1973).

*** Culberson, Pytkowicz, and Hawley (1970).

**** From $\gamma_\pm$ (HCl) of Khoo and others (1977) using $\gamma_{Cl} = 0.628$.

† From $\gamma_\pm$ for NaCl (Johnson and Pytkowicz, 1980) and γ_{Cl} (Whitfield, 1975a) using $\gamma_{Cl} = 0.628$.

†† From Thompson (1966) using $\gamma_F(Mg) = 0.286$.

††† From Thompson and Ross (1966) using $\gamma_F(Ca) = 0.258$.

†††† From $\gamma_\pm$ for $CaSO_4$ and $SrSO_4$ (Culberson, Latham, and Bates, 1978) using $\gamma_{SO_4} = 0.104$.

§ From $\gamma_\pm$ for $CaCO_3$ using $\gamma_{CO_3} = 0.031$ (Pytkowicz, 1975).

§§ Assigned value.

§§§ Calculated from the ionization of HF (Culberson, Pytkowicz, and Hawley, 1970) using $\gamma_H = 0.70$ and $\gamma_{HF} = 1.1$.

§§§§ Calculated from the ionization of H_2O (Culberson and Pytkowicz, 1973; Hansson, 1972 and Dickson and Riley, 1979a) using $\gamma_H = 0.70$ and $a_{H_2O} = 0.981$ (Millero and Leung, 1976).

■ Calculated from the ionization of H_2CO_3 (Mehrbach and others, 1973; Lyman, 1957; and Hansson, 1972) using fitted results of Millero (1979), $\gamma_{CO_2} = 1.17$ (Weiss, 1974), $a_{H_2O} = 0.981$ (Millero and Leung, 1976) and $\gamma_H = 0.70$.

■■ From the ionization of $B(OH)_3$ (Lyman, 1957; Hansson, 1972) using $\gamma_H = 0.70$.

■■■ From the ionization of H_3PO_4 (Kester and Pytkowicz, 1967; Dickson and Riley, 1979b) using $\gamma_{H_3PO_3} = 1.09$ (Pitzer and Silvester, 1976) and $\gamma_H = 0.20$.

■■■■ From the ionization of HCO_3^- (Mehrbach and others, 1973; and Hansson, 1972) using the fitted results of Millero (1979) and $\gamma_H = 0.70$.

◊ From the $\gamma_\pm$ for Na_2SO_4 (Platford and Dafoe, 1965) and K_2SO_4 (Whitfield, 1975a) using $\gamma_{Na} = 0.708$ and $\gamma_K = 0.662$.

◊◊ From the ionization of $H_2PO_4^-$ and HPO_4^{2-} (Kester and Pytkowicz, 1967; Dickson and Riley, 1979b; Johansson and Wedborg, 1979) and $\gamma_H = 0.70$.

the specific interaction model to estimate the major ionic components (Whitfield, 1975). The first method requires an enormous amount of additional work and requires corrections for most of the presently available association constants (that did not consider chloride ion pairs). The inclusion of ion pairs between all the ions of natural waters complicates the calculations considerably and at present does not yield simple functions for the activity coefficients of free ions. The small improvement (see table 23) in the estimated activity coefficients using Cl^- pairing does not make the extra work worthwhile. We, thus, favor the approach suggested by Whitfield (1975b) and are presently preparing a paper on the details of using a hybrid model using the equations of Pitzer and Kim (1974).

TABLE 22

Comparison of measured and calculated pK_{HA} for the ionization of acids in seawater at S = 35‰

Acid	pK_{HA} Calculated*	pK_{HA} Measured	Δ	Author
H_2O	13.21	13.18 ± 0.05	−0.03	Culberson and Pytkowicz (1973)
	13.21	13.16 ± 0.04	−0.05	Hansson (1972)
	13.21	13.18 ± 0.05	−0.03	Dickson and Riley (1979a)
$B(OH)_3$	8.75	8.68 ± 0.11	0.07	Lyman (1957)
	8.59	8.60 ± 0.02	0.01	Hansson (1972)
H_2CO_3	6.02	5.99 ± 0.02	−0.03	Mehrbach and others (1973)
	5.86	5.84 ± 0.05	−0.02	Hansson (1972)
HCO_3^-	9.12	9.09 ± 0.08	−0.03	Mehrbach and others (1973)
	8.96	8.93 ± 0.10	−0.03	Hansson (1972)
NH_4^+	9.345	9.351 ± 0.007	0.006	Khoo, Culberson, and Bates (1977)
H_3PO_4	1.71	1.58 ± 0.05	−0.13	Kester and Pytkowicz (1967)
	1.55	1.57 ± 0.03	0.02	Dickson and Riley (1979b)
$H_2PO_4^-$	6.30	6.02 ± 0.10	−0.28	Kester and Pytkowicz (1967)
	6.14	5.93 ± 0.10	−0.21	Dickson and Riley (1979b)
	6.14	5.94 ± 0.10	−0.20	Johansson and Wedborg (1979)
HPO_4^{2-}	9.27	8.65 ± 0.20	−0.62	Kester and Pytkowicz (1967)
	9.11	8.61 ± 0.20	−0.50	Dickson and Riley (1979b)
	9.11	8.93 ± 0.20	−0.18	Johansson and Wedborg (1979)

* Estimations made using $\gamma_{CO_2} = 1.17$, $\gamma_{HA} = 1.09$ and $a_{H_2O} = 0.981$.

TABLE 23

Comparisons of the measured and calculated values of the total activity coefficients of ions using Cl^- pairs and the specific interaction model

Ion	Measured*	Ion pairing**	Δ	Specific interaction***	Δ
Na^+	0.708	0.696	0.012	0.708	0
K^+	0.662	0.656	0.006	0.668	−0.006
Mg^{2+}	0.257	0.258	−0.001	0.269	−0.012
Ca^{2+}	0.217	0.244	−0.027	0.241	−0.024
	0.185		−0.059		−0.056
	0.261		0.017		−0.020
Cl^-	0.628	0.628	—	0.628	—
SO_4^{2-}	0.104	0.093	0.011	0.103	0.001

* From table 22.
** Johnson and Pytkowicz (1979).
*** Whitfield (1975a, b).

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