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FORMULAS FOR ACTIVITY COEFFICIENTS OF INDIVIDUAL IONS

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C O N T E N T S

1. INTRODUCTION

For chemical calculations with gaseous equilibria and for non-ionic reactions in solution one can calculate in terms of concentrations to a fairly good approximation. However, in dealing with ionic reactions, with certain aspects of kinetics in solution, and with electromotive force studies, substitution of concentrations for activities is frequently not possible. For this reason it is essential to consider how ionic concentrations can be converted to activities.

The activity of an ion can be calculated by multiplying the concentration with the activity coefficient. For solutions with an ionic strength lower than 0.1 mole.1^{-1} theoretical formulas for the activity coefficients are available. Five known equations are those of DEBEYE and HÜCKEL (1923), frequently refered to as the limiting law of Debeye and Hückel, GÜNTELBERG (1926), DAVIES (1938), SCATCHARD (1936) and BJERRUM (1926).

For more concentrated solutions these formulas cannot be used because the activity coefficients will increase at higher ionic strenghts. Several authors proposed formulas that do count for this phenomena (HÜCKEL, 1925; MAYER, 1950; SCATCHARD, 1961; FRIEDMAN, 1972; PITZER, 1975; etc.). However, values for the (several) ion dependent parameters in these formulas are not given by these authors.

In this note experimental data will be given as curvefitted formulas of the extended Debeye-Hückel equation as proposed by HÜCKEL (1925):

$$\log(f_i) = \frac{-A.z_i^2.(I)^{0.5}}{1+B.\overset{o}{a}.(I)^{0.5}} + C.I \tag{1}$$

where: f_i = the activity coefficient of ion i

$\mathring{a}$ = curvefitted ion dependent parameter ($\mathring{A}$)

C = curvefitted ion dependent parameter ($mole^{-1}.l$)

z_i = valencie of ion i

I = ionic strength ($mole.l^{-1}$)

A = temperature dependent coefficient ($mole^{-0.5}.l^{0.5}$)

B = temperature dependent coefficient ($\mathring{A}^{-1}.mole^{-0.5}.l^{0.5}$)

Aim of this study is to obtain values for the ion dependent parameters $\mathring{a}$ and C for 29 frequently mentioned soil ions.

2. THEORY

2.1. Definitions

The following definitions are necessary when dealing with activities of strong electrolytes. Consider an electrolyte A_xB_y that dissociates in solution according to:

$$A_xB_y = x.A^{z_+} + y.B^{z_-} \tag{2}$$

where: x and y = the stochiometric coefficients

z_+ and z_- = the valencies of the ions

The total activity of the electrolyte as a whole, a_t, is defined in terms of the single ion activities of the two ions a_+ and a_- as:

$$a_t = a_+^x.a_-^y \tag{3}$$

where: $a_+ = A^{z_+}$ $mole.l^{-1}$

$a_- = B^{z_-}$ $mole.l^{-1}$

Equation 3 is in fact the chemical equilibrium equation with K=1 because a strong electrolyte dissociates completely.

The total number of ions resulting from one molecule of electrolyte can be written as $v=x+y$. The geometric mean activity of the electrolyte or the mean activity, $a_{\pm}$, is then defined as:

$$a_{\pm} = (a_t)^{1/v} = (a_+^x . a_-^y)^{1/v} \tag{4}$$

The relation between concentrations and activities is given according to Henry's law by:

$$a_+ = c_+ . f_+ \tag{5a}$$

$$a_- = c_- . f_- \tag{5b}$$

where: c_+ and c_- = concentrations $(mole.l^{-1})$

f_+ and f_- = single ion activity coefficients

The single ion activities of the cation and anion are defined in such a way that their activity will equal their concentration in an infinite diluted solution. In other words f_- and f_- approach unity in an infinitely diluted solution. Combining equations 5a and 5b with equation 3 yields

$$a_t = (c_+ f_+)^x . (c_- . f_-)^y$$

$$= (c_+^x . c_-^y) . (f_+^x . f_-^y) \tag{6}$$

and for the mean activity from equation 4

$$a_{\pm} = (a_t)^{1/v} = (c_+^x . c_-^y)^{1/v} . (f_+^x . f_-^y)^{1/v} \tag{7}$$

The factor $(f_+^x . f_-^y)^{1/v}$ is called the mean activity coefficient of the electrolyte, $f_{\pm}$, i.e.

$$f_{\pm} = (f_+^x . f_-^y)^{1/v} \tag{8}$$

Similarly, the factor $(c_+^x . c_-^y)^{1/v}$ is defined as the mean molarity of the electrolyte, $c_{\pm}$.

$$c_{\pm} = (c_+^x . c_-^y)^{1/v} \tag{9}$$

In terms of the mean molarity and mean activity coefficients, equations 6 and 7 may be written as

$$a_t = a_{\pm}^v = (c_{\pm} . f_{\pm})^v \tag{10}$$

$$a_{\pm} = (a_t)^{1/v} = c_{\pm} . f_{\pm} \tag{11}$$

Finally, since for any electrolyte of molarity c, $c_+ = x.c$ and $c_- = y.c$ equations 10 and 11 become also

$$a_t = (c_{\pm} . f_{\pm})^v$$

$$= (((x.c)^x . (y.c)^y)^{1/v} . f_{\pm})^v$$

$$= ((x^x . y^y)^{1/v} . (c^{x+y})^{1/v} . f_{\pm})^v$$

$$= ((x^x . y^y)^{1/v} . (c^v)^{1/v} . f_{\pm})^v$$

$$= (x^x . y^y) . c^v . f_{\pm}^v \tag{12}$$

and

$$a_{\pm} = c_{\pm} \cdot f_{\pm}$$

$$= (x.c)^x \cdot (y.c)^y)^{1/v} \cdot f_{\pm}$$

$$= (x^x.y^y)^{1/v} \cdot (c^{x+y})^{1/v} \cdot f_{\pm}$$

$$= (x^x.y^y)^{1/v} \cdot (c^v)^{1/v} \cdot f_{\pm}$$

$$= (x^x.y^y)^{1/v} \cdot c \cdot f_{\pm} \tag{13}$$

With equations 12 and 13 activities can be converted into concentrations and visa versa. Although these expressions may appear complicated, they are actually rather simple when applied to specific cases. For a 1-1 electrolyte, such as sodium chloride, of molarity c, x=1, y=1 and v=2, and, therefore

$$a_t = (1.1) \cdot c^2 \cdot f_{\pm}^2 = c^2 \cdot f_{\pm}^2$$

$$a_t = (1.1)^{\frac{1}{2}} \cdot c \cdot f_{\pm} = c \cdot f_{\pm}$$

For an electrolyte of the 2-1 type, such as barium chloride, we obtain x=1, y=2 and v=3, and hence

$$a_t = (1.2^2) \cdot c^3 \cdot f_{\pm}^3 = 4 \cdot c^3 \cdot f_{\pm}^3$$

$$a_{\pm} = (1.2^2)^{1/3} \cdot c \cdot f_{\pm} = (4)^{1/3} \cdot c \cdot f_{\pm}$$

In table 1 the relations of $c_{\pm}$, $a_{\pm}$ and a_t to c and $f_{\pm}$ are summarized for a number of different types of electrolytes.

The definitions for the ionic and mean activity coefficients have been expressed in terms of concentration in moles per liter of solu-

tion. In electrochemical work quite frequently concentrations are expressed on a molality basis, m, in moles per kilogram solution. When this is the case, equations 12 and 13 become

$$a_t = a_\pm^v = (x^x . y^y) . m^v . \gamma_\pm^v \qquad (14)$$

and

$$a_\pm = (x^x . y^y)^{1/v} . m . \gamma_\pm \qquad (15)$$

where: m = total concentration of the electrolyte on molal basis

$\gamma_\pm$ = molal mean activity coefficient

Table 1. Relation of $a_\pm$ and a_t to c and $f_\pm$ for various electrolytes (after MARON and PRUTTON, 1965)

Electrolyte type	Example	x	y	v	$c_\pm$	$a_\pm = c_\pm . f_\pm$	$a_t = a_\pm^v$
1-1	$NaCl$	1	1	2	c	$c.f_\pm$	$c^2.f_\pm^2$
2-2	$CaSO_4$	1	1	2	c	$c.f_\pm$	$c^2.f_\pm^2$
3-3	$AlPO_4$	1	1	2	c	$c.f_\pm$	$c^2.f_\pm^2$
1-2	Na_2SO_4	2	1	3	$(4)^{1/3}.c$	$(4)^{1/3}.c.f_\pm$	$4.c^3.f_\pm^3$
2-1	$BaCl_2$	1	2	3	$(4)^{1/3}.c$	$(4)^{1/3}.c.f_\pm$	$4.c^3.f_\pm^3$
1-3	Na_3PO_4	3	1	4	$(27)^{1/4}.c$	$(27)^{1/4}.c.f_\pm$	$27.c^4.f_\pm^4$
3-1	$La(NO_3)_3$	1	3	4	$(27)^{1/4}.c$	$(27)^{1/4}.c.f_\pm$	$27.c^4.f_\pm^4$
2-3	$Ca_3(PO_4)_2$	3	2	5	$(108)^{1/5}.c$	$(108)^{1/5}.c.f_\pm$	$108.c^5.f_\pm^5$
3-2	$LA_2(SO4)_3$	2	3	5	$(108)^{1/5}.c$	$(108)^{1/5}.c.f_\pm$	$108.c^5.f_\pm^5$

$f_{\pm}$ and $\gamma_{\pm}$ are related by the expression

$$f_{\pm} = \frac{\rho_0 \cdot m}{c} \cdot \gamma_{\pm} \qquad (16)$$

where: ρ_0 = the density of the pure solvent

and

$$\frac{m}{c} = \frac{1 + 0.001 \cdot m \cdot M}{\rho} \qquad (17)$$

where: M = the molecular weight of the electrolyte

ρ = density of the solution

From equations 16 and 17 it can be shown that for dilute aqueous solutions $f_{\pm}$ will be essentially equal to $\gamma_{\pm}$; however, in more concentrated solutions the two will have different values.

The conversion from molalities to molarities with equation 16 will give problems because ρ is not commonly known. For some solutions the Handbook of Chemistry gives data for ρ in relation with m and c. These data are used to calculate the deviation between $f_{\pm}$ and $\gamma_{\pm}$ for a range of molal concentrations and electrolytes (see table 2). The deviation is calculated according to the equation

$$\text{deviation} = \frac{|\gamma_{\pm} - f_{\pm}|}{\gamma_{\pm}} \times 100\% \qquad (18)$$

where: $\gamma_{\pm}$ = molal mean activity coefficient (data from ROBINSON and STOKES, 1959)

$f_{\pm}$ = calculated molar mean activity coefficient

It can be concluded from table 2 that the differences between $f_{\pm}$ and $\gamma_{\pm}$ are small and usually can be neglected. The calculations carried out in the following chapters are based on the assumption that electrolyte concentrations on molarity basis equals those based on molality basis, i.e. m=c.

Table 2. Deviation between measured molal mean activity coefficient and calculated molar mean activity coefficient for several electrolytes (%)

m	KCl	NaCl	NH_4Cl	$MgCl_2$	$CaCl_2$	$BaCl_2$
0.1	0.4	0.2	0.2	1.2	1.1	0.6
0.2	0.1	0.0	1.0	0.9	0.7	0.2
0.3	0.6	0.2	1.7	0.7	0.5	0.0
0.4	1.0	0.3	2.2	1.2	0.9	0.4
0.5	1.3	0.3	2.6	2.4	2.1	1.5
0.6	1.5	0.4	3.0	3.3	3.0	2.4
0.7	1.7	0.4	3.2	4.1	3.8	3.2
0.8	1.9	0.5	3.4	4.8	4.4	3.9
0.9	2.0	0.5	3.6	5.4	5.0	4.5
1.0	2.1	0.5	3.8	6.0	5.5	5.0
1.2	2.3	0.6	3.4	5.2	4.9	3.1

2.2. Ion-pair formation

Although complete ionic dissociation applies to many salts dissolved in water, it is not a rule of universal validity. For example, a large fraction of the cations and anions of certain strong electrolytes are so attracted to one another in solution that they behave as if un-ionized. Ions associated in this manner are called 'ion-pairs'. If the ions are of equal but opposite charge, the ion-pair will be uncharged, e.g. Ca^{2+} and SO_4^{2-} ions form the $CaSO_4^0$ ion-pair; if the ions are of unequal charge, the ion-pair will have a charge, e.g. K^+ and SO_4^{2-} form KSO_4^-.

The extent to which free ions associate in solution is expressed by the traditional method for presenting the dissociation of weak electrolytes. Thus for the ion-pair $CaSO_4^0$, the dissociation reaction is written as

$$CaSO_4^o \rightleftharpoons Ca^{2+} + SO_4^{2-} \tag{19}$$

and

$$K = \frac{(Ca^{2+}).(SO_4^{2-})}{(CaSO_4^o)} \tag{20}$$

where parenthese denote activity. The activity coefficient of the ion-pair is generally assumed to be unity. Equilibrium constants for several ion-pairs in aqueous solution are given by TRUESDELL and JONES (1974), BOLT and BRUGGENWERT (1978), LINDSAY (1979) and STUMM and MORGAN (1981).

As a result of ion-pairing, a soil-solution ion may actually be present as several different species. For example, soil solution Ca may be present as Ca^{2+}, $CaSO_4^o$, $CaHPO_4^o$, $CaH_2PO_4^+$ and $CaHCO_3^+$. However, the analytical procedure for determining solution Ca makes no distinction among these species so that 'measured Ca' is actually the sum of Ca^{2+} + $CaSO_4^o$ + $CaHPO_4^o$ + $CaH_2PO_4^+$ + $CaHCO_3^+$. Since the measured Ca concentration of a soil solution, then, is actually the combined total of all Ca species in solution, the actual concentration of the 'free' Ca^{2+} ion must be calculated.

The following general principes apply to ion-pairing of common soil solution cations and anions (after ADAMS, 1971):

- there is no ion-pairing of cations with Cl^-
- ion-pairing of cations with NO_3^- is small enough to be neglected
- ion-paring with SO_4^{2-} is general: it is slight with univalent cations but extensive with multivalent cations
- ion-paring with $H_2PO_4^-$ or HPO_4^{2-} is only slight for univalent cations and can be ignored: ion-pairing between $H_2PO_4^-$ and multivalent cations is significant but not extensive; ion-pairing between HPO_4^{2-} and multivalent cations is extensive

- ion-pairing between HCO_3^- and univalent cations is insignificant;

  ion-pairing of multivalent cations with HCO_3^- is significant at high pH or at abovenormal CO_2 pressure.

2.3. Debeye-Hückel theory

Due to electrostatic attractions between charged ions, each positive ion in solution must be surrounded on an average with more negative ions than ions of like charge; and conversely for each negative ion. This means that each ion in solution is surrounded by an ionic atmosphere whose net charge is opposite to that of the central ion. Further, Debeye and Hückel postulated that the properties of the electrolyte can be determined by the interaction of the central ion and its atmosphere.

The effect of the concentration of the ions is described with the ionic strength, which is a measure of the electrical environment of the solution. It is defined as

$$I = \frac{1}{2} \sum_i z_i^2 . c_i \tag{21}$$

where: I = ionic strength $(mole.l^{-1})$

z_i = charge of ion i

c_i = concentration of ion i $(mole.l^{-1})$

The summation in equation 21 must include all ionic species present in the solution. It is generally assumed that the activity coefficients and association coefficients are independent of the medium composition at a given ionic strength. Using this principle, activity coefficients can be calculated.

The interactions can be divided into longrange Coulomb forces and shortrange interactive forces between the central ion and its atmosphere of ions with opposite charge. The quotient of these two forces is infact the Debeye-Hückel equation:

$$\log f_i = -\frac{A.z_i^2.(I)^{0.5}}{1+B.\overset{o}{a}.(I)^{0.5}} \tag{22}$$

where: f_i = activity coefficient of ion i

z_i = charge of ion i

I = ionic strength (mole.l^{-1})

$\overset{o}{a}$ = diameter of the hydrated ion i (Å)

A = temperature dependent coefficient (at 25°C A = 0.5085 mole$^{-0.5}$.$l^{0.5}$)

B = temperature dependent coefficient (at 25°C B = 0.3281 Å^{-1}.mole$^{-0.5}$.$l^{0.5}$)

This equation is only valid for dilute solutions with ionic strengths up ot 0.1 mole.l^{-1}.

Measurements of the activity coefficients at various ionic strengths show that at low ionic strengths the activity coefficients decrease to a certain point, and increase again beyond that point to values that might be greater than unity. This is illustrated in figure 1.
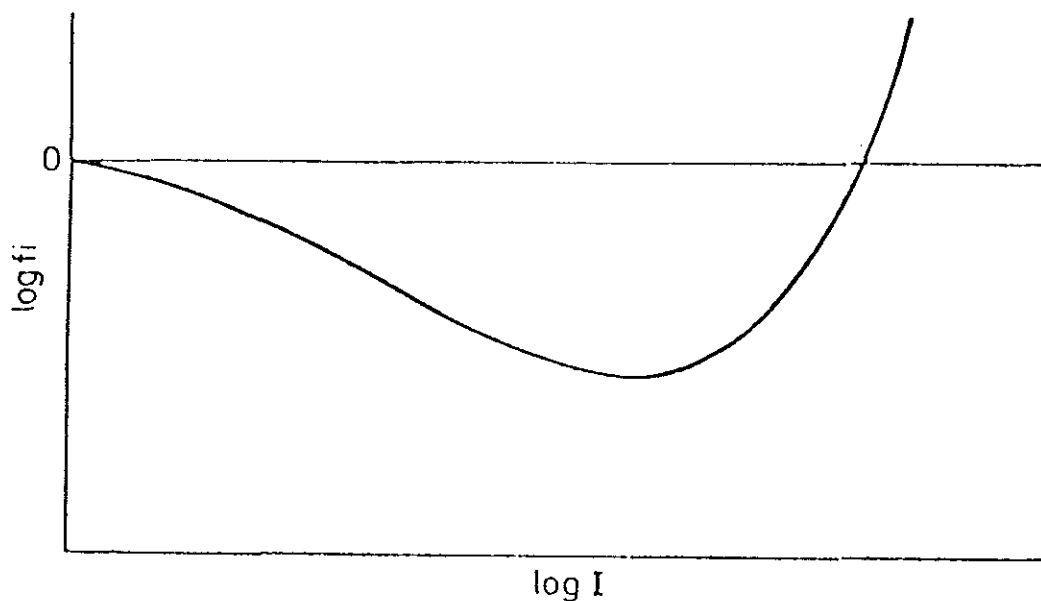

Fig. 1. Log fi versus log I for ion i

This phenomena of increasing coefficients can be explained with the interaction of hydrated ions with their solvent. Due to an increase of ionic strength more ions have to use the same quantity of solvent (water) to hydrate. This causes a larger deviation from ideal behaviour where ions are not assumed to interact due to a large amount of solvent relative to the solute. In order to account for this phenomena HÜCKEL (1925) has pointed out that equation 20 can be extended by the introduction of another term lineair in I:

$$- \log f_i = \frac{A.z_i^2.(I)^{0.5}}{1+B.\mathring{a}.(I)^{0.5}} - C.I \qquad (23)$$

where: C = an ion dependent constant (mole^{-1}.l)

Several other authors postulated second, third or even higher degree extensions of the Debeye-Hückel equation (MAYER, 1950; SCATCHARD, 1961; SCATCHARD et al, 1970; FRIEDMAN, 1972; REILLY et al, 1971; HAMER and WU, 1972; PITZER, 1975; PITZER and MAYORGA, 1973, 1974; PITZER and KIM, 1974; JUSTICE et al, 1976, 1977; JUSTICE, 1978). According to HELGESON et al (1981) practical application of these complicated theoretical equations is hardly justified because they improve accuracy over equation 23 only to the extent of a percent at ionic strengths ranging up to 6 mole.l^{-1}.

2.4. Determination of mean activity coefficients

A number of experimental methods have been developed or perfected for the determination of mean activity coefficients of solutes (electrolytes) in a selected solvent.
These are based on:

- freezing-point depression
- boiling-point devation
- vapor-pressure lowering
- isopiestic or vapor-pressure equilibrium
- electromotive forces of galvanic cells without liquid junction
- electromotive forces of galvanic cells with transference
- solubility
- diffusion

The first four involve measurements of the escaping tendency of the solvent and the subsequent evaluation of the solute activity through the Gibbs-Duhem equation (see HAMER and WU, 1972). The last four give direct measures of the solute activity. The solubility method is generally applicable only to sparingly soluble salts and therefore not frequently used.

A ninth method involving the measurement of the osmotic pressure of a solution across a semi-permeable membrane is subject to many experimental difficulties.

A tenth method involving bithermal equilibration in the vapor phase has not been tested sufficiently to be classed as a precision method.

Data of measured mean activity coefficients are available abundantly in literature. e.g. ROBINSON and STOKES (1959), HARNED and OWEN (1967), HAMER and WU (1972) and PYTKOWICZ (1979).

2.5. The mean-salt method

With the mean-salt method, which has been described extensively by GARRELS and CHRIST (1965), the measured mean activity coefficients can be converted into single ion activity coefficients. This conversion is based on the MacInnes convention stating that the single ion activity coefficients of K^+ and Cl^- are equal. By this convention the behaviour of KCl in solution can be used as the standard for calculating single ion activity coefficients. Writing the convention in terms of activity coefficients according to equation 8 gives:

$$f_{\pm}(KCl) = [f(K^+).f(Cl^-)]^{0.5} = f(K^+) = f(Cl^-) \tag{24}$$

Using this relationship other single ion activity coefficients can be calculated, e.g. a n-valent chloride MCl

$$f_{\pm}(MCl_n) = [f(M^{n+}).f(Cl^-)^n]^{\frac{1}{n+1}}$$

$$= [f(M^{n+}).f_{\pm}(KCl)^n)^{\frac{1}{n+1}} \tag{25}$$

gives

$$f(M^{n+}) = \frac{[f_{\pm}(MCl_n)]^{n+1}}{[f_{\pm}(KCl)]^n} \tag{26}$$

For obtaining single ion activity coefficients of anions $f_{\pm}(KCl)$ should be substituted for $f(K^+)$, e.g. K_2SO_4 gives for the $f(SO_4^{2-})$:

$$f_{\pm}(K_2SO_4) = [f(K^+)^2 \cdot f(SO_4^{2-})]^{1/3}$$

$$= [f_{\pm}(KCl)^2 \cdot f(SO_4^{2-})]^{1/3} \tag{27}$$

and

$$f(SO_4^{2-}) = \frac{[f_{\pm}(K_2SO_4)]^3}{[f_{\pm}(KCl)]^2} \tag{28}$$

3. WORKING PROCEDURES

In order to obtain formulas for activity coefficients of individual ions the mean salt method has been applied to data given by ROBINSON and STOKES (1959). These data consist of tables describing mean activity coefficients as function of molality. Following the conclusions described in chapter 2.1 it has been assumed that molality equals molarity. Furthermore, following the conclusions of ADAMS (1971) and HELGESON et al (1981, p. 1328 and 1335), it has been assumed that ion-pair formation in the electrolyte solutions used for calculating the single activity coefficients can be neglected.

These electrolyte solutions are all single salt solutions. Ion-pair formation can only play a minor role in these solutions because of the restricted number of ion species involved. Furthermore, most of these electrolyte solutions are chlorides and according to ADAMS (1971) not sensitive to ion-pair formation. The electrolyte solutions that are used to calculate the single activity coefficients are summarized in table 3.

Table 3. The various electrolyte solutions used to calculate
single activity coefficients

1-1	2-1	3-1	1-1	1-2	1-3
KCl	$FeCl_2$	$AlCl_3$	KCl	K_2SO_4	K_3PO_4
HCl	$CaCl_2$		KOH	K_2HPO_4	
NaCl	$MgCl_2$		KH_2PO_4	K_2CO_3	
NH_4Cl	$BaCl_2$		$KHCO_3$		
	$MnCl_2$		KI		
	$CrCl_2$		KNO_3		
	$CoCl_2$		KBr		
	$NiCl_2$		KF		
	$CuCl_2$				
	$ZnCl_2$				
	$CdCl_2$				
	$Pb(NO_3)_2$				

The calculations are carried out as follows:
First, the molar data are multiplied by a factor given in table 4 in
order to obtain ionic strengths (see for instance HAMER, 1968).

Table 4. Conversion factors for obtaining ionic strenghth
from molar data

Electrolyte type		molarity	ionic strength
1-1	NaCl	1.0	1.0
1-2	Na_2SO_4	1.0	3.0
2-1	$MgCl_2$	1.0	3.0
2-2	$MgSO_4$	1.0	4.0
3-1	$AlCl_3$	1.0	6.0

Secondly, the mean-salt method has been applied to data points of the same ionic strength. Where necessary the data at a specific ionic strength has been derived with quadratic interpolation from the given data.

Thirdly, the results of the mean-salt method have been curvefitted with the extended Debeye-Hückel equation (23) with å and C as parameters.

4. RESULTS

4.1. Individual ions

The data used and the results of the mean-salt method, i.e. the calculated single activity coefficients, are given in the appendix. For each chemical compound values for the (measured) mean activity coefficient and the calculated single activity coefficients are given against ionic strength.

The results of the curvefitting between the single activity coefficients and ionic strengths (equation 23) are given in table 5.

In the limiting law of Debeye-Hückel (equation 22) parameter å stands for the diameter of the hydrated ion i, and thus is a real physical property. In the extended Debeye-Hückel equation (equation 23) å has lost its physical meaning and is only an ion-dependent constant just as the C-parameter (HELGESON et al, 1981). However, the å values calculated by the curvefitting procedure for the extended Debey-Hückel equation differ not very much from the å values given by BOLT et al (1978) for the limiting Debeye-Hückel equation (see table 6). Besides values of å and C, the deviation between the observed and calculated single activity coefficients is given in table 5 according to:

$$S^2 = \sum (f-f_i)^2 \tag{29}$$

where: S^2 = the sum of the squares of the differences between observed and calculated data

f = single activity coefficients derived from the data given by ROBINSON and STOKES (1959)

f_i = calculated single activity coefficients according to the equations obtained by the curvefitting procedures

Table 5. Results of the curve fitting procedure

Ion	Electro-lyte used	No. of datapairs	$\overset{o}{a}$	C	s^2	I-range
Na$^+$	NaCl	22	4.152	0.07000	0.4020E-3	0.002-3.0
H$^+$	HCl	23	4.272	0.24629	0.6727E-3	0.001-3.0
NH$_4^+$	NH$_4$	20	4.124	0.00000	0.9616E-3	0.1 -4.5
Fe^{2+}	FeCl$_2$	12	4.816	0.18586	0.6699E-3	0.3 -4.2
Ca^{2+}	CaCl$_2$	17	4.853	0.17807	0.1038E-2	0.006-4.2
Mg^{2+}	MgCl$_2$	12	4.720	0.24143	0.2432E-2	0.3 -4.2
Mn^{2+}	MnCl$_2$	12	5.119	0.14650	0.1445E-3	0.3 -4.2
Ba^{2+}	BaCl$_2$	12	5.040	0.07143	0.4333E-4	0.3 -4.2
Cr^{2+}	CrCl$_2$	11	0.002	1.01100	0.9847E-2	0.3 -3.6
Co^{2+}	CoCL$_2$	12	4.804	0.20500	0.6998E-3	0.3 -4.2
Ni^{2+}	NiCl$_2$	12	4.730	0.21371	0.9510E-3	0.3 -4.2
Cu^{2+}	CuCl$_2$	12	5.308	0.07500	0.1108E-3	0.3 -4.2
Zn^{2+}	ZnCl$_2$	12	7.082	-0.06857	0.4061E-3	0.3 -4.2
Cd^{2+}	CdCl$_2$	12	0.020	-1.51500	0.1295E-3	0.3 -4.2
Pb^{2+}	Pb(NO$_3$)$_2$	9	3.048	0.19643	0.2225E-3	0.3 -2.7
Al^{3+}	AlCl$_3$	7	5.188	0.21771	0.5169E-5	0.6 -4.2
Cl$^-$	KCl	26	3.550	0.01614	0.2231E-3	0.001-4.5
OH$^-$	KOH	17	3.181	0.20090	0.5393E-3	0.1 -3.0
I$^-$	KI	20	4.960	0.03357	0.2753E-3	0.1 -4.5
F$^-$	KF	19	3.176	0.08643	0.7061E-3	0.1 -4.0
Br$^-$	KBr	20	3.878	0.02321	0.3576E-4	0.1 -4.5
NO$_3^-$	KNO$_3$	18	1.410	-0.13843	0.1414E-3	0.1 -3.5
HCO$_3^-$	KHCO$_3$	14	5.340	0.00169	0.2706E-4	0.01 -2.5
H$_2$PO$_4^-$	KH$_2$PO$_4$	14	0.989	-0.14493	0.1388E-3	0.1 -1.8
CO$_3^{2-}$	K$_2$CO$_3$	14	5.381	0.00386	0.6825E-4	0.01 -2.5
HPO$_4^{2-}$	K$_2$HPO$_4$	10	4.418	-0.16429	0.4781E-4	0.3 -3.0
SO$_4^{2-}$	K$_2$SO$_4$	7	2.989	-0.10129	0.1848E-5	0.3 -2.1
PO$_4^{3-}$	K$_3$PO$_4$	7	5.414	0.16071	0.2594E-2	0.6 -4.2

Table 6. Comparison between some calculated $\overset{o}{a}$ values
according to equation 23 and $\overset{o}{a}$ values given by
BOLT et al (1978) for equation 22

ion	$\overset{o}{a}$ fitted for the extended D-H eq.	$\overset{o}{a}$ given by Bolt et al for the limiting D-H eq.
HPO_4^{2-}	4.42	4
K^-	3.55	3
HCO_3^-	5.34	4
Na^-	4.15	4
CO_3^{2-}	5.38	5
H^-	4.27	9
SO_4^{2-}	2.99	4
Cl^-	3.55	3
Ca^{2-}	4.85	6
Fe^{2-}	4.82	6
Mg^{2-}	4.72	8
Al^{3-}	5.19	9

In all cases the value of S^2 is very small which implicates that the various equations fit the measured data well. In the last column of table 5 the ionic strength range is given in which the equations are fitted. Extrapolation of these formulas to lower ranges of I is assumed to be possible which extends the usefulness of the equations (see Maron and Prutton, p. 442).

The curvefitted equations are represented graphically showing the relations between the activity coefficient of individual ions against ionic strength (see figures 2 until 8). The figures are divided in graphical representations showing the relations for univalent, divalent and trivalent cations and anions. It can be concluded that high charged ions in general have activity coefficients that are minor in value to activity of less charged ions for any given ionic strength. Further, there is not much difference in values of activity coefficients between equally charged cations and anions in the lower ionic strength range.
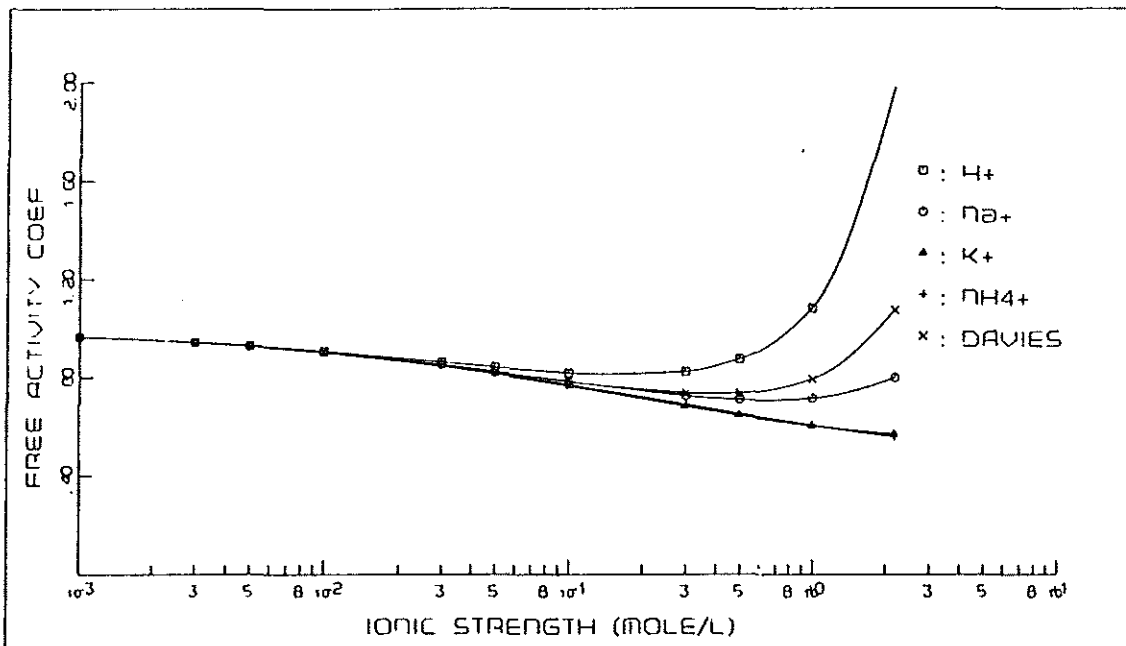
Fig. 2. Free activity coefficient versus ionic strength for the ions
H^+, Na^+, K^+, H^+
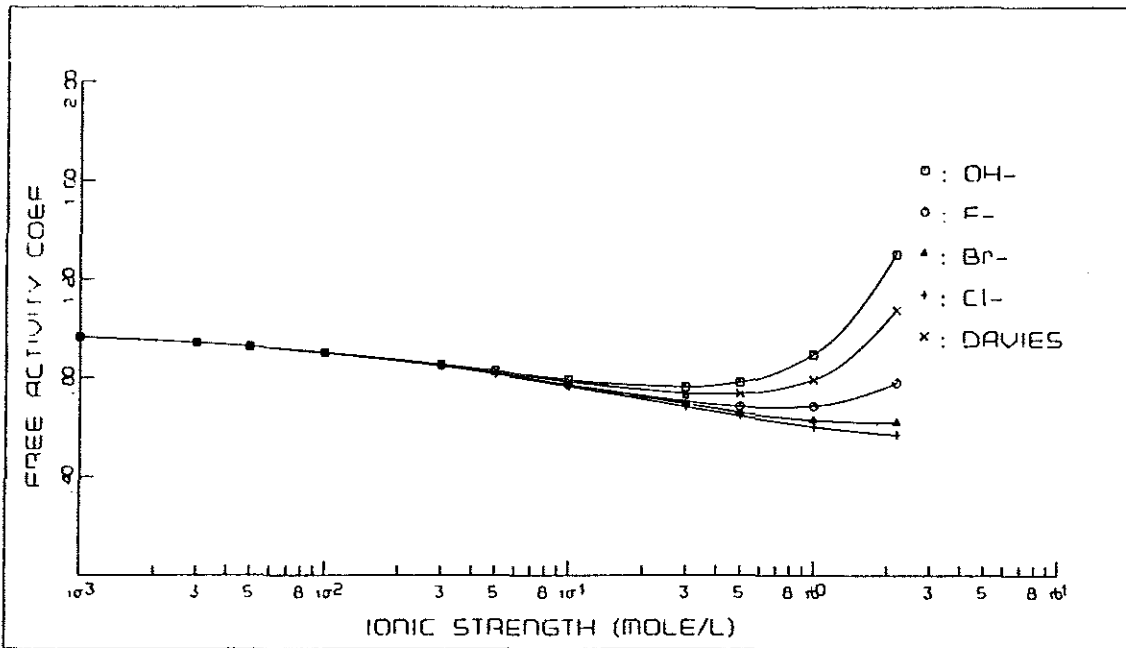
Fig. 3. Free activity coefficient versus ionic strength for the ions
OH^-, F^-, Br^-, Cl^-

In all the figures the, frequently used, Davies equation has been included:

$$- \log f_i = 1/2 \ . \ |z_i^2| \ . \ (\frac{(I)^{0.5}}{1 + (I)^{0.5}} - 0.3 \ . \ I) \tag{30}$$

where: f_i = single activity coefficient of ion i

z_i = charge of ion i

I = ionic strength (mole.1^{-1})

it can be seen that the Davies equation fits the single activity coefficients of most ions quite well in the lower ionic strength range, but deviates from the data above ionic strengths of 0.01 mole.1^{-1}. In the range between 0.01 and 0.3 mole.1^{-1}, especially the activity coefficients for the H^-, K^-, NH_4^-, Cd^{2-}, Cr^{2+}, Pb^{2+}, NO_3^-, $H_2PO_4^-$, HPO_4^{2-} and SO_4^{2-} ions can not be calculated accurately by the Davies equation. Above an ionic strength of 0.3 mole.1^{-1} the Davies equation is not suitable at all for the calculation of free activity coefficients of the ions involved.
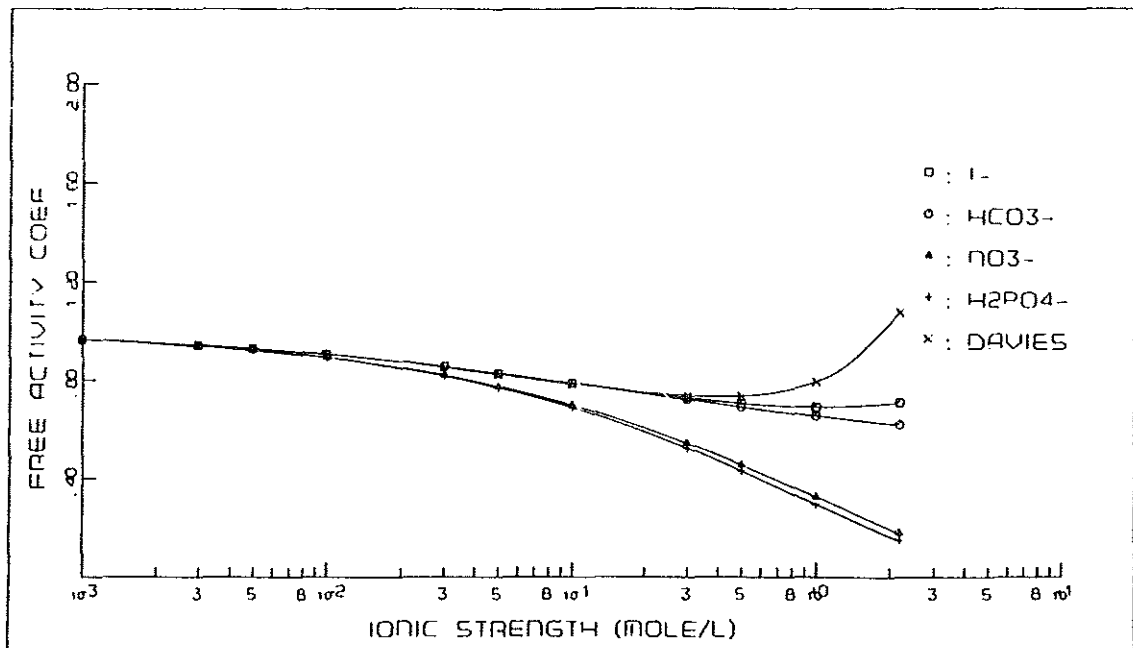
Fig. 4. Free activity coefficient versus ionic strength for the ions I^-, HCO_3^-, NO_3^-, $H_2PO_4^-$
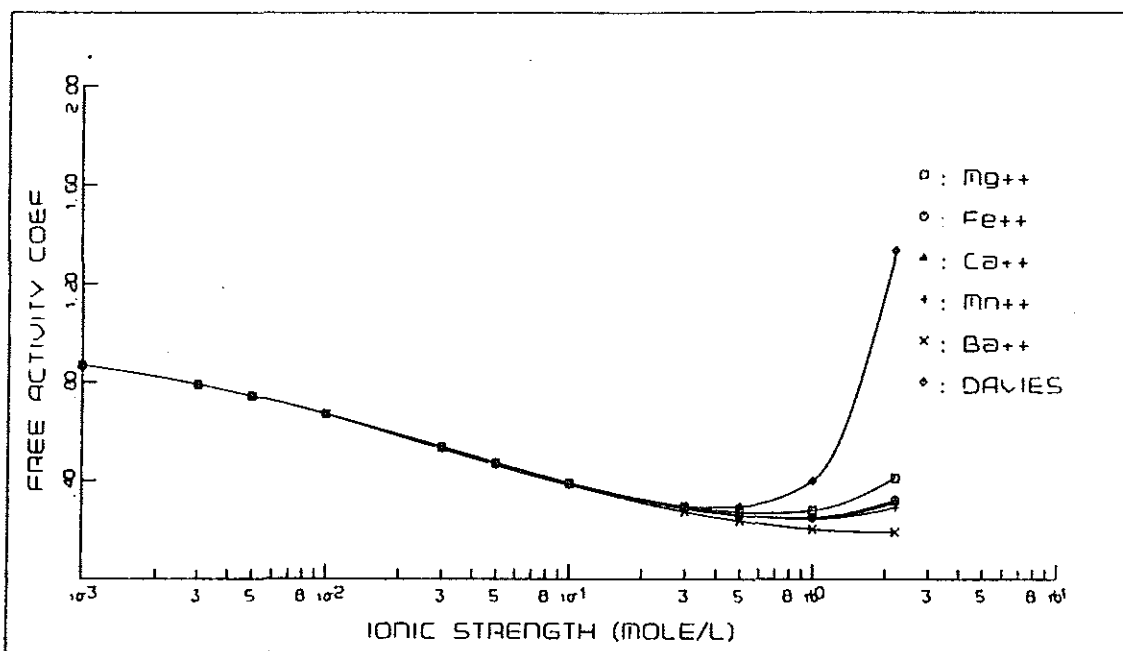
Fig. 5. Free activity coefficients versus ionic strength for the ions
Mg^{2+}, Fe^{2+}, Ca^{2+}, Mn^{2+}, Ba^{2+}
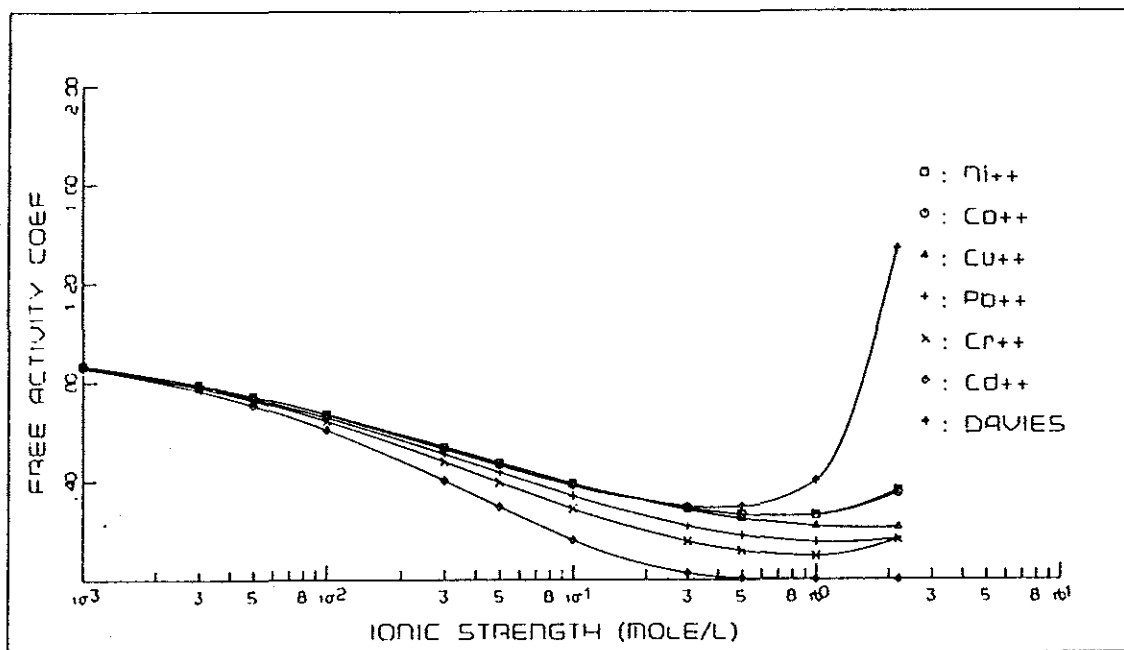
Fig. 6. Free activity coefficient versus ionic strength for the ions
Ni^{2+}, Co^{2+}, Cu^{2+}, Pb^{2+}, Cr^{2+}, Cd^{2+}
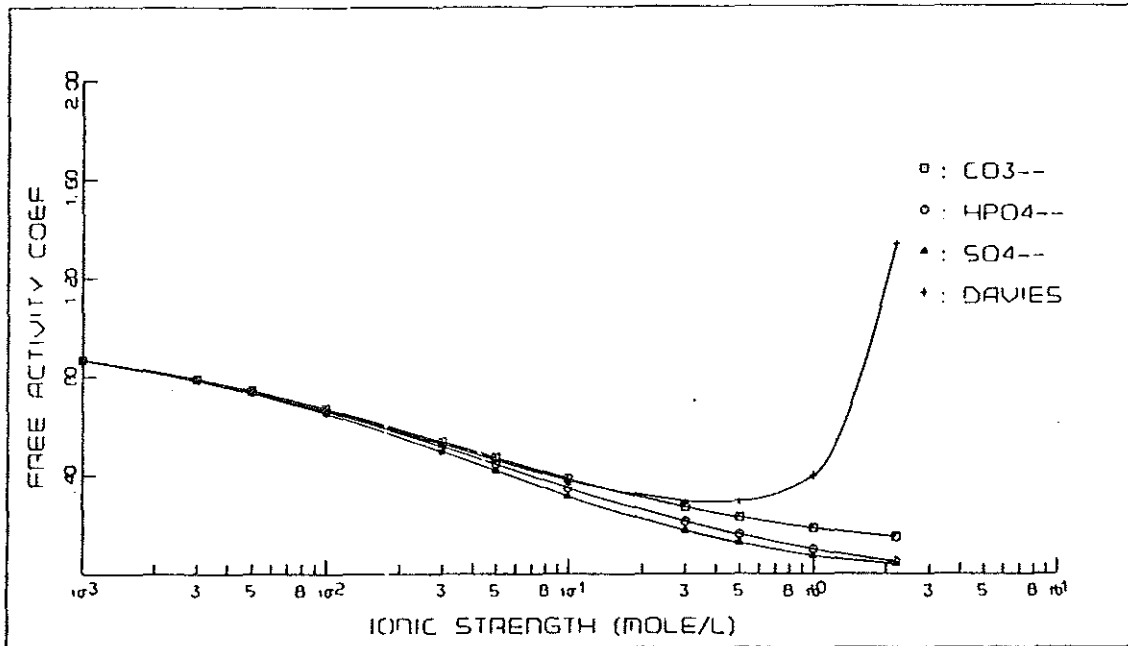
Fig. 7. Free activity coefficient versus ionic strength for the ions CO_3^{2-}, HPO_4^{2-}, SO_4^{2-}
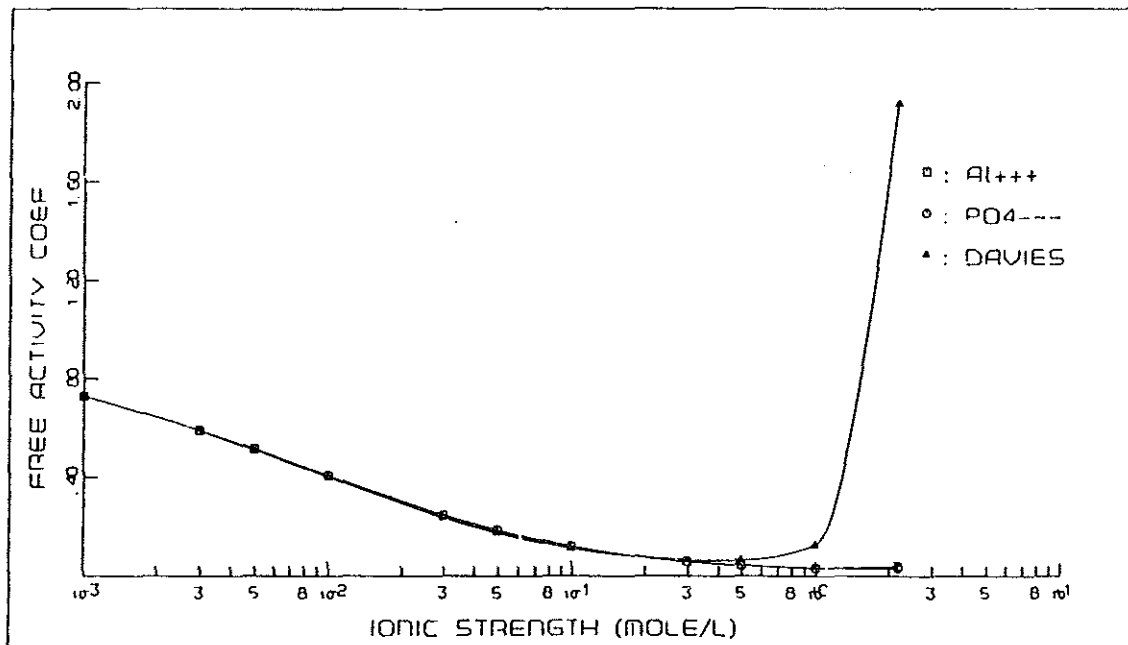
Fig. 8. Free activity coefficient versus ionic strength for the ions Al^{3+}, PO_4^{3-}

4.2. Ion-pairs

In order to develop a complete set of formulas which can be used
in hydrochemical calculations it is necessary to assign values to the
activity coefficients of ion-pairs.

GARRELS and THOMPSON (1962) have assigned a value of 1.13 to
neutral ion-pairs, 0.68 to single charged plus and minus ion-pairs,
and 0.22 to doubly charged plus and minus ion-pairs. ATKINSON, DAYHOFF
and EBDON (1973), SIEBERT and HOSTETLER (1977) and ABDEL KHALIK and
BLÖMER (1984) have assumed that the activity coefficient of neutral
ion-pairs is 1.0. ABDEL KHALIK and BLÖMER (1984) have assumed that the
activity coefficients for the uni-charged ion-pairs can be described
by the extended Debeye-Hückel equation for HCO_3^- because the size of
the ion-pairs is approximately the same as the HCO_3^- ion. REARDON
(1983) has assumed that the activity coefficient of $SrHCO_3^+$ is equal to
that of HCO_3^-.

Several authors have estimated activity coefficients for ion-
pairs. For example KESTER (1969) has estimated that the activity coef-
ficient of $MgSO_4^0$ in seawater is 0.8 and RIDDEL et al (1972) computed
an activity coefficient of 0.311 fore $NaNO_3^0$ at an ionic strength of
1.23 mole.1^{-1}.

There is growing evidence to suggest that activity coefficients
for (neutral) ion-pairs decrease with ionic strength (YEATTS and
MARSHALL, 1969; KESTER, 1969; RIDDEL et al, 1972; REARDON and
LANGMUIR, 1976; WHITFIELD, 1979; PLUMMER and SUNDQUIST, 1982; MILLERO
and SCHREIBER, 1982; REARDON, 1983 and BUSENBERG and PLUMMER, 1984).
In fact there are several approximations for estimating individual ion
activity coefficients of ion-pairs. Well known relations or procedures
are those of KIRKWOOD (1939), REARDON and LANGMUIR (1976), WHITFIELD
(1979) and MILLERO and SCHREIBER (1982). The theoretical Debeye-Hückel
equation, however, is not suitable for describing the relations
between f_i and I of ion-pairs because it was originally formulated for
completely dissociated electrolytes (DEBEYE and HÜCKEL, 1923; HÜCKEL,
1925; HAMER, 1968).

A theoretical explanation for the variation of the activity coef-
ficients of neutral ion-pairs with ionic strength is given by KIRKWOOD
(1939). This theory is based on the assumption that ion-pairs can be
considered as dipoles. Recently, YEATTS and MARSHALL (1969) and KESTER
and PYTKOWICZ (1970) postulated that it is appropriate to consider
$MgCO_3^0$ and $CaSO_4^0$ as dipoles which interact with a solution to varying
degrees, depending on the interatomic distance and charge of the
constituent ions and structure of the dipole.

Nevertheless, REARDON and LANGMUIR (1976) concluded that Kirk-
wood's equation is inadequate to explain their empirical data for di-
divalent ion-pairs. They observed a lineair decrease in log f_i with
ionic strength and suggest the empirical equation

$$\log f_i = - C \cdot I \tag{31}$$

to describe the relation between the activity coefficient of neutral
ion-pairs and ionic strength. C coefficients of 0.63 $\pm$ 0.10 for $MgCO_3^0$
and 0.45 $\pm$ 0.15 for $CaSO_4^0$ were obtained from lineair regression of log
f_i values versus i between 0.04 and 0.6 mole.l^{-1}. They propose that
the activity coefficients of other di-divalent ion-pairs (at 25°C) can
propably be estimated with a C value of 0.5. For mono-monovalent
neutral ion-pairs they suggest a C value of 0.125.

WHITFIELD (1979) has reviewed the procedures for estimating acti-
vity coefficients of ion-pairs and mentioned a C value of 0.25 for
singly charged ion-pairs (p. 215). This results in:

$$\log f_i = -0.25 \ I \tag{32}$$

MILLERO and SCHREIBER (1982) selected values of the thermodynamic
and stochiometric association constants for the formation of ion-pairs
from literature, and indicated that the activity coefficient at an
ionic strength of 0.7 mole.l^{-1} is 1.1 for uni-univalent ion-pairs: 1.0
for di-divalent ion-pairs; 0.64 for monovalent anion-pairs and 0.8 for
monovalent cation ion-pairs. They concluded that these findings sup-
port the earlier work of GARRELS and THOMPSON (1962). However, these

findings are not in accordance with the observed data and the sugges-
ted formulas given by REARDON and LANGMUIR (1976) and WHITFIELD (1979).

In order to calculate the activity coefficient of ion-pairs it is
necessary to make use of one of the relations or procedures mentioned
in the literature.

For neutral ion-pairs the formulas suggested by REARDON and
LANGMUIR (1976) can be used. The formula for single charged ions as
mentioned by WHITFIELD (1979) is propably a good choice. However it is
not entirely clear how he achieved the value of 0.25 for coefficient C.

In literature no relation or procedure was found to calculate acti-
vity coefficients of divalent ion-pairs such as $AlH_2PO_4^{2+}$ or $AlNO_3^{2+}$

Table 7 gives a summary of the equations which can used for calcu-
lating activity coefficients of ion-pairs.

Table 7. f_i-I relations for ion-pairs

Type of ion-pair	f_i-I relation
zero charged	
* uni-univalent	$\log f_i = -0.125 \ I$
* di-divalent	$\log f_i = -0.500 \ I$
single charged	
* uni-divalent	$\log f_i = -0.250 \ I$
* di-univalent	

A graphical representation of these formulas is given in fig. 9.
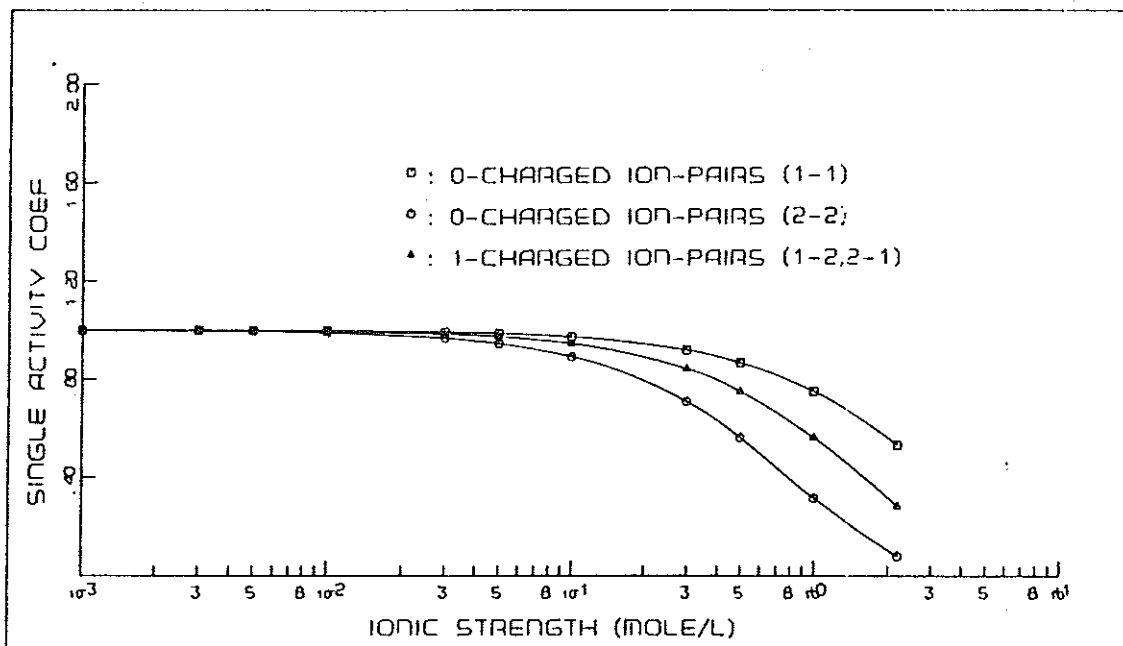
Fig. 9. Single activity coefficient versus ionic strength for zero and
single charged ion-pairs

5. SUMMARY AND CONCLUSIONS

- The best estimate of the activity of an ion in soil solution is
  obtained by use of the Debeye-Hückel theory (ADAMS, 1971; HELGESON
  et al, 1981). The limited Debeye-Hückel equation is valid for dilute
  solutions with ionic strengths up to 0.1 mole.l^{-1}. The relation
  between activity coefficients and ionic strength in strong electro-
  lytes (for instance soil solutions in semi-arid areas or coastal
  lowlands) can be described by the extended Debeye-Hückel equation
  (HÜCKEL, 1925; HELGESON et al, 1981).

$$- \log f_i = \frac{A.z_j^2.(I)^{0.5}}{1+B.\overset{0}{a}.(I)^{0.5}} - C.I$$

where: $\overset{0}{a}$ and C = ion dependent parameters

- Electrochemical data (WALKER et al. 1927; ROBINSON and STOKES, 1959;
  HARNED and OWEN, 1967) have been used to calculate the activity coef-
  ficients of individual ions with the mean-salt method described by
  GARRELS and CHRIST (1965). In order to do this it has been assumed
  that the molality of the various electrolyte solutions equals mola-
  rity, i.e. m=c.

- For various (29) ions these activity coefficients have been used in
  a curvefitting procedure to obtain values for the ion dependent con-
  stants $\overset{o}{a}$ and C of the extended Debeye-Hückel equation.

- These curvefitted equations have been derived from single salt solu-
  tions in which ion-pairing can be neglected (ADAMS, 1971; HELGESON
  et al. 1981).

- In a real soil solution however, which is in fact a complex mixed
  electrolyte solution, ion-pair formation will be important and can
  not be neglected.

- There are several approximations for estimating individual ion acti-
  vity coefficients of ion-pairs (KIRKWOOD, 1939; REARDON and
  LANGMUIR, 1976; WHITFIELD, 1979). The theoretical Debeye-Hückel
  equation, however, is not suitable for describing the relation
  between activity coefficients of ion-pairs and ionic strength
  because it was originally formulated for completely dissociated
  electrolytes (DEBEYE and HÜCKEL, 1923; HÜCKEL, 1925; HAMER, 1968
  etc.). For neutral ion-pairs the formulas suggested by REARDON and
  LANGMUIR (1976) can be used. The formula for single charged ion-
  pairs as mentioned by WHITFIELD (1979) is probably a good choice. No
  relation or procedure was found to calculate activity coefficients
  of divalent ion-pairs.

- With these equations for ion-pairs a complete set of formulas descri-
  bing the relations between the activity coefficients of ions in the
  soil solution and the ionic strength is available.

- Using these formulas in hydrochemical studies will result in calcu-
  lations that can be carried out more easily and at the same time
  will give higher accuracies.

- Use of the Davies equation will give deviations in the calculations
  of activity coefficients above an ionic strength of 0.01 mole.l^{-1}.
  Above an ionic strength of 0.3 mole.l^{-1} the Davies equation is not
  suitable anymore to calculate activity coefficients of any of the
  ions involved in this study.

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I (mole.l^{-1})	f$_\pm$(KCl)	f$_\pm$(ZnCl$_2$)	f$_+$(Zn^{2+})	f$_-$(CO$_3^{2-}$)	f$_\pm$(K$_2$HPO$_4$)	f$_-$(HPO$_4^{2-}$)	f$_\pm$(K$_2$SO$_4$)	f$_-$(SO$_4^{2-}$)	f$_\pm$(K$_3$PO$_4$)	f$_-$(PO$_4^{3-}$)	f$_\pm$(AlCl$_3$)	f$_+$(Al^{3+})
0.001	0.965											
0.002	0.954											
0.005	0.930											
0.006	0.925											
0.010	0.904			0.667								
0.015	0.888											
0.020	0.872			0.589								
0.030	0.854											
0.040	0.836			0.503								
0.050	0.818											
0.060	0.808			0.453								
0.080	0.789			0.415								
0.100	0.770			0.389								
0.150	0.744											
0.200	0.718			0.309								
0.300	0.688	0.518	0.294		0.469	0.218	0.436	0.175				
0.400	0.666			0.246								
0.500	0.649											
0.600	0.637	0.465	0.248	0.216	0.387	0.143	0.356	0.111	0.312	0.037	0.320	0.041
0.700	0.626											
0.800	0.618			0.198								
0.900	0.610	0.435	0.221		0.342	0.108	0.313	0.082				
1.000	0.604			0.183								
1.200	0.593	0.413	0.200		0.310	0.085	0.283	0.064	0.244	0.017	0.288	0.033
1.400	0.586											
1.500	0.583	0.396	0.183	0.164	0.288	0.070	0.261	0.052				
1.600	0.580											
1.800	0.576	0.382	0.168		0.270	0.059	0.243	0.043	0.211	0.010	0.282	0.033
2.000	0.573			0.154								
2.100	0.572	0.371	0.156		0.256	0.051	0.229	0.037				
2.400	0.570	0.359	0.143		0.243	0.044			0.190	0.007	0.287	0.037
2.500	0.569			0.147								
2.700	0.569	0.350	0.133		0.234	0.039						
3.000	0.569	0.341	0.122		0.225	0.035			0.175	0.005	0.298	0.043
3.500	0.572											
3.600	0.573	0.325	0.105						0.164	0.004	0.316	0.053
4.000	0.577											
4.200	0.579	0.311	0.090						0.156	0.003	0.339	0.068
4.500	0.583											

I (mole.l^{-1})	$f_\pm$(KCl)	$f_\pm$(BaCl$_2$)	f_+(Ba^{2+})	$f_\pm$(NiCl$_2$)	f_+(Ni^{2+})	$f_\pm$(CoCl$_2$)	f_+(Co^{2+})	$f_\pm$(CuCl$_2$)	f_+(Cu^{2+})	$f_\pm$(Pb(NO$_3$)$_2$)	f_+(Pb^{2+})	$f_\pm$(CrCl$_2$)	f_+(Cr^{2+})	$f_\pm$(CdCl$_2$)	f_+(Cd^{2+})
0.001	0.965														
0.002	0.954														
0.005	0.930														
0.006	0.925														
0.010	0.904														
0.015	0.888														
0.020	0.872														
0.030	0.854														
0.040	0.836														
0.050	0.818														
0.060	0.808														
0.080	0.789														
0.100	0.770														
0.150	0.744														
0.200	0.718														
0.300	0.688	0.508	0.277	0.523	0.302	0.523	0.302	0.510	0.280	0.405	0.221	0.331	0.077	0.228	0.025
0.400	0.666														
0.500	0.649														
0.600	0.637	0.450	0.225	0.479	0.271	0.479	0.271	0.457	0.235	0.316	0.176	0.298	0.065	0.164	0.011
0.700	0.626														
0.800	0.618														
0.900	0.610	0.425	0.206	0.463	0.267	0.463	0.267	0.431	0.215	0.267	0.160	0.294	0.068	0.133	0.006
1.000	0.604														
1.200	0.593	0.411	0.197	0.460	0.277	0.459	0.275	0.419	0.209	0.234	0.153	0.300	0.077	0.114	0.004
1.400	0.586														
1.500	0.583	0.403	0.193	0.464	0.294	0.462	0.290	0.413	0.207	0.210	0.151	0.314	0.091	0.101	0.003
1.600	0.580														
1.800	0.576	0.397	0.189	0.471	0.315	0.470	0.313	0.411	0.209	0.192	0.156	0.335	0.113	0.091	0.002
2.000	0.573														
2.100	0.572	0.397	0.191	0.482	0.342	0.479	0.336	0.411	0.212	0.176	0.157	0.362	0.145	0.083	0.002
2.400	0.570	0.397	0.193	0.496	0.376	0.492	0.367	0.412	0.215	0.164	0.166	0.397	0.193	0.077	0.002
2.500	0.569														
2.700	0.569	0.397	0.193	0.515	0.422	0.511	0.412	0.415	0.221	0.154	0.177	0.436	0.256	0.071	0.001
3.000	0.569	0.401	0.199	0.536	0.476	0.531	0.462	0.419	0.227			0.481	0.344	0.067	0.001
3.500	0.572														
3.600	0.573	0.411	0.211	0.586	0.613	0.578	0.588	0.427	0.237			0.584	0.607	0.060	0.001
4.000	0.577														
4.200	0.579	0.424	0.227	0.647	0.807	0.634	0.759	0.436	0.247					0.055	0.001
4.500	0.583														

I (mole.l⁻¹)	f±(KCl)	f±(HCl)	f₊(H⁺)	f±(NaCl)	f₊(Na⁺)	f±(NH₄Cl)	f₊(NH₄⁺)	f±(KOH)	f₋(OH⁻)	f±(KF)	f₋(F⁻)	f±(KBr)	f₋(Br⁻)	f±(KI)	f₋(I⁻)
0.001	0.965	0.966	0.967												
0.002	0.954	0.952	0.950	0.954	0.954										
0.005	0.930	0.929	0.928	0.931	0.931										
0.006	0.925														
0.010	0.904	0.905	0.906	0.905	0.905										
0.015	0.888														
0.020	0.872	0.876	0.880	0.874	0.876										
0.030	0.854														
0.040	0.836														
0.050	0.818	0.830	0.842	0.823	0.828										
0.060	0.808														
0.080	0.789														
0.100	0.770	0.796	0.823	0.778	0.786	0.770	0.770	0.776	0.782	0.775	0.780	0.772	0.774	0.778	0.786
0.150	0.744														
0.200	0.718	0.767	0.819	0.735	0.752	0.718	0.718	0.739	0.761	0.727	0.736	0.772	0.726	0.733	0.748
0.300	0.688	0.756	0.831	0.710	0.733	0.687	0.686	0.721	0.756	0.700	0.712	0.693	0.698	0.707	0.727
0.400	0.666	0.755	0.856	0.693	0.721	0.665	0.664	0.713	0.763	0.682	0.698	0.673	0.680	0.689	0.713
0.500	0.649	0.757	0.883	0.681	0.715	0.649	0.649	0.712	0.781	0.670	0.692	0.657	0.665	0.676	0.704
0.600	0.637	0.763	0.914	0.673	0.711	0.636	0.635	0.712	0.796	0.661	0.686	0.646	0.655	0.667	0.698
0.700	0.626	0.772	0.952	0.667	0.711	0.625	0.624	0.715	0.817	0.654	0.683	0.636	0.646	0.660	0.696
0.800	0.618	0.783	0.992	0.662	0.709	0.617	0.616	0.721	0.841	0.650	0.684	0.629	0.640	0.654	0.692
0.900	0.610	0.795	1.036	0.659	0.712	0.609	0.608	0.728	0.869	0.646	0.684	0.622	0.634	0.649	0.690
1.000	0.604	0.809	1.084	0.657	0.715	0.603	0.602	0.735	0.894	0.645	0.689	0.617	0.630	0.645	0.689
1.200	0.593	0.840	1.190	0.654	0.721	0.592	0.591	0.754	0.959	0.643	0.697	0.608	0.623	0.640	0.691
1.400	0.586	0.876	1.310	0.655	0.732	0.584	0.582	0.778	1.033	0.644	0.708	0.602	0.618	0.637	0.692
1.500	0.583														
1.600	0.580	0.916	1.447	0.657	0.744	0.578	0.576	0.804	1.115	0.647	0.722	0.598	0.617	0.636	0.697
1.800	0.576	0.960	1.600	0.662	0.761	0.574	0.572	0.832	1.202	0.652	0.738	0.595	0.615	0.636	0.702
2.000	0.573	1.009	1.777	0.668	0.779	0.570	0.567	0.863	1.300	0.658	0.756	0.593	0.614	0.637	0.708
2.100	0.572														
2.400	0.570														
2.500	0.569	1.147	2.312	0.688	0.832	0.564	0.559	0.947	1.576	0.678	0.808	0.593	0.618	0.644	0.729
2.700	0.569														
3.000	0.569	1.316	3.044	0.714	0.896	0.561	0.553	1.051	1.941	0.705	0.874	0.595	0.622	0.652	0.747
3.500	0.572					0.560	0.548			0.738	0.952	0.600	0.629	0.662	0.766
3.600	0.573														
4.000	0.577					0.560	0.544			0.779	1.052	0.608	0.641	0.673	0.785
4.200	0.579														
4.500	0.583					0.561	0.540					0.616	0.651	0.683	0.800

I (mole.l^{-1})	$f_\pm(KCl)$	$f_-(HCO_3^-)$	$f_\pm(KNO_3)$	$f_-(NO_3^-)$	$f_\pm(KH_2PO_4)$	$f_-(H_2PO_4^-)$	$f_\pm(MgCl_2)$	$f_+(Mg^{2+})$	$f_\pm(FeCl_2)$	$f_+(Fe^{2+})$	$f_\pm(CaCl_2)$	$f_+(Ca^{2+})$	$f_\pm(MnCl_2)$	$f_+(Mn^{2+})$
0.001	0.965													
0.002	0.954													
0.005	0.930													
0.006	0.925										0.856	0.733		
0.010	0.904													
0.015	0.888										0.795	0.637		
0.020	0.872	0.876												
0.030	0.854										0.734	0.542		
0.040	0.836	0.843												
0.050	0.818													
0.060	0.808	0.821									0.667	0.454		
0.080	0.789	0.803												
0.100	0.770	0.790	0.739	0.709	0.731	0.694								
0.150	0.744										0.579	0.351		
0.200	0.718	0.746	0.663	0.612	0.653	0.594								
0.300	0.688		0.614	0.548	0.602	0.527	0.528	0.311	0.520	0.297	0.518	0.294	0.518	0.294
0.400	0.666	0.704	0.576	0.498	0.561	0.473								
0.500	0.649		0.545	0.458	0.529	0.431								
0.600	0.637	0.682	0.519	0.423	0.501	0.394	0.488	0.286	0.475	0.264	0.472	0.259	0.471	0.258
0.700	0.626		0.496	0.393	0.477	0.363								
0.800	0.618	0.667	0.476	0.367	0.456	0.336								
0.900	0.610		0.459	0.345	0.438	0.314	0.476	0.290	0.456	0.255	0.455	0.253	0.452	0.248
1.000	0.604	0.654	0.443	0.325	0.421	0.293								
1.200	0.593		0.414	0.289	0.393	0.260	0.474	0.303	0.450	0.259	0.448	0.256	0.444	0.249
1.400	0.586		0.390	0.260	0.369	0.232								
1.500	0.583	0.636					0.480	0.325	0.452	0.272	0.448	0.265	0.442	0.254
1.600	0.580		0.369	0.235	0.348	0.209								
1.800	0.576		0.350	0.213	0.332	0.191	0.490	0.355	0.456	0.286	0.453	0.280	0.445	0.266
2.000	0.573	0.627	0.333	0.194										
2.100	0.572						0.505	0.393	0.465	0.307	0.460	0.297	0.450	0.278
2.400	0.570						0.521	0.436	0.475	0.330	0.470	0.320	0.457	0.294
2.500	0.569	0.619	0.297	0.155										
2.700	0.569						0.543	0.495	0.490	0.364	0.484	0.350	0.468	0.317
3.000	0.569		0.269	0.127			0.569	0.569	0.508	0.405	0.500	0.386	0.481	0.344
3.500	0.572		0.246	0.106										
3.600	0.573						0.630	0.762	0.549	0.504	0.539	0.477	0.509	0.402
4.000	0.577													
4.500	0.583						0.708	1.057	0.598	0.637	0.587	0.603	0.544	0.480