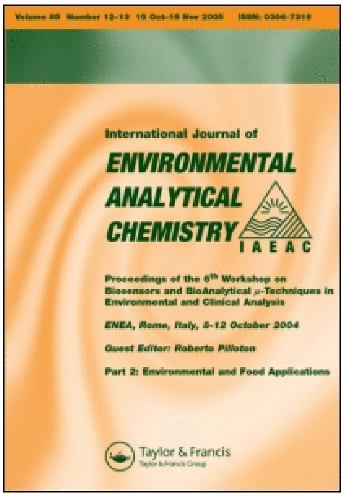

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Environmental Coordination Chemistry: Binary Systems Comprising Some Bivalent Cations and Monocarboxylates in Aqueous Solution. Ionic Medium Effects on Equilibrium Constants

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ENVIRONMENTAL COORDINATION CHEMISTRY: BINARY SYSTEMS COMPRISING SOME BIVALENT CATIONS AND MONOCARBOXYLATES IN AQUEOUS SOLUTION. IONIC MEDIUM EFFECTS ON EQUILIBRIUM CONSTANTS

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The molar single activity coefficients associated with propionate ion (Pr) have been determined at 25°C and ionic strengths comprised between 0.300 and 3.00 M, adjusted with $NaClO_4$, as background electrolyte. The investigation was carried out potentiometrically by using a second class Hg/Hg_2Pr_2 electrode. It was found that the dependence of propionate activity coefficients as a function of ionic strength (I) can be assessed through the following empirical equation: $\log y_{Pr} = -0.185\ I^{3/2} + 0.104\ I^2$. Next, simple equations relating stoichiometric protonation constants of several monocarboxylates and formation constants associated with 1:1 complexes involving some bivalent cations and selected monocarboxylates, in aqueous solution, at 25°C, as a function of ionic strength were derived, allowing the interconversion of parameters from one ionic strength to another, up to I = 3.00 M. In addition, thermodynamic formation constants as well as parameters associated with activity coefficients of the complex species in the equilibria are estimated. The body of results shows that the proposed calculation procedure is very consistent with critically selected experimental data.

Keywords: Activity coefficients; formation constants; medium effects

INTRODUCTION

The scarcity of quantitative studies dealing with weak interactions among ions in aqueous solution and the difficulty in distinguishing these interactions from those arising through ionic medium effects may be the reason for the lack of an

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adequate treatment concerning the ionic strength dependence of activity coefficients and hence of equilibrium constants, including protonation of ligands and thermodynamic stability of metal ion complexes. The associated equilibria are of fundamental importance in any area where a knowledge of the chemical form of an element is a prime requirement, as in "real life" systems (*e.g.*, environmental systems, biological fluids, food extracts) and in research including radioactive waste disposal, assessment of metal-dependent side effects of pharmaceuticals, the bioavailability of metal ions from foods and the use of metal complexes to suppress microorganism's activity.[1–3]

Mostly in view of the aforementioned requirements some progress has been attained regarding the search of procedures allowing interconversion of equilibrium parameters from an ionic strength to another one as well as the estimation of thermodynamic equilibrium constants (*i.e.*, at zero ionic strength).[3–8] All these data are particularly important for the speciation of metal complexes under prevailing environmental conditions.[8,9]

In the absence as yet of a comprehensive theory that can answer the fundamental questions concerning the dependence of equilibrium constants on ionic strength, it is of considerable interest to find equations (even empirical ones) that would allow equilibrium constants, measured at a given ionic strength (I), to be calculated for any other one.

In a previous work from this laboratory,[10] following the reasoning of Uemasu and Umezawa[11] and Capone *et al.*,[12] the molar single ion activity associated with the hydrogen, Cu^{2+}, Cd^{2+} and Pb^{2+} ions have been determined in aqueous solution, at 25°C and ionic strengths (I) comprised between 0.100 and 3.00 M, adjusted with $NaClO_4$. The investigation was carried out potentiometrically by using proton-sensitive glass, copper, cadmium and lead ion-selective electrodes. Empirical equations relating the molar activity coefficients of the aforementioned ions with I were established.[10] In the present work, by using a similar approach,[10] the molar activity coefficients of propionate ion were determined, also in aqueous solution, at 25°C, I = 0.300–3.00 M ($NaClO_4$). Subsequently, by employing the present data in connection with those previously obtained,[10] very simple equations have been derived, making feasible the interconversion of stability constants of 1:1 binary complexes involving some bivalent metal ions and monocarboxylates (aliphatic and aromatic) in so far as changes in ionic strength are concerned; moreover, thermodynamic constants and parameters associated with activity coefficients associated with the mentioned complex species are estimated, via extrapolation of linear relationships. The predictive power of the developed procedure has been evaluated by comparing the calculated constants with the corresponding ones, critically selected from the literature.[13]

It is worth noting that carboxylates are the largest single class of complexing donor groups in the environment and are present either as a result of degradative processes involving naturally—occuring bioorganic substances or through biological and chemical oxidations of terminal groups of hydrocarbon derivatives.[8,14]

EXPERIMENTAL

Materials and Solutions

Distilled, de-ionised water and grade "A" glassware were used throughout. All chemicals employed were of analytical reagent grade. Propionic acid, sodium propionate and sodium chloride stock solutions were standardized potentiometrically with standard sodium hydroxide, hydrochloric acid and silver nitrate solutions, respectively. Stock solutions of sodium perchlorate were analysed by evaporating and drying to constant mass at 120°C. Mercurous propionate was prepared by mixing, in aqueous solution, the corresponding nitrate with excess of sodium propionate. The resulting precipitate was filtered through a sintered glass funnel, washed with deionized water until nitrate free and then dried in a desiccator, over calcium chloride, under reduced pressure, at room temperature to constant mass. A white powder was obtained as the final product. Metallic mercury was treated sequentially with 5% nitric acid, deionized water, 3% sodium hydroxide, deionized water, 3% nitric acid and deionized water. After drying with a filter paper it was distilled by following the conventional procedure. The mercurous propionate indicator electrode was prepared as follows: mercurous propionate (0.6 g) and metallic mercury (0.2 g) were mixed in a agate mortar and the material was crushed until a homogeneous gray solid is obtained. Pure powdered graphite (0.19 g) was then added and the crushing process was continued until perfect homogeneization was attained. Part of the resulting solid was transferred to a press mold, being compressed at 20,000 pounds/sq. inch, for about 30 seconds. The black pellet (1.5 mm thickness, 13 mm o.d. and 0.6 g mass) was fixed at one end of a glass tube (13 mm o.d., 80 mm length) with a silicone-rubber glue ("Rhodiastic", Rhône-Poulenc, France) and allowed to dry for 48 hours. Sufficient metallic mercury was then introduced into the tube to produce a small pool upon the inner pellet surface; electrical contact was established through a platinum wire plunged into the mercury pool and a subsequent conductor cable. The resulting electrode is schematized in Figure 1.

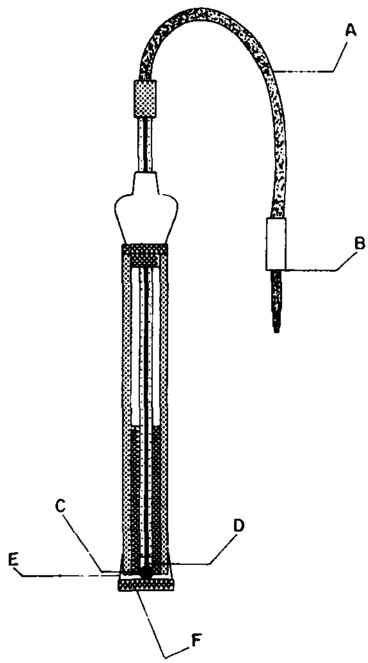

FIGURE 1 Mercurous propionate electrode. A: conductor cable; B: banana plug; C: metallic mercury; D: Pt wire; E: silicone glue; F: sensor pellet (graphite/Hg_2Pr_2/Hg).

Instruments

The emf values are read to the nearest 0.1 mV with a "Metrohm" mod. 670 Titroprocessor. The reference electrode was a "Metrohm" Ag/AgCl double junction, model 6.0726.100. A thermostated titration cell (25.0 ± 0.1°C) was employed. Volume measurements (± 0.001 ml) were performed with "Metrohm" model 665 automatic burettes. All experiments were performed in a thermostated room (25 ± 1°C).

Potentiometric Cell

The following cell was used,

$$\begin{array}{l|l:l:l|l}
 & [NaCl]_{(aq.)} = & & [HPr]_{(aq.)} = xM & \\
Ag/AgCl & = 0.010\ M & [NaClO_4]_{(aq.)} = & [NaPr]_{(aq.)} = xM & (graphite- \\
 & [NaClO_4]_{(aq.)} = & = 1\ M & [NaClO_4]_{(aq.)} = & -Hg_2Pr_2)\ |\ Hg\ |\ Pt\ + \\
 & = (1 - 0.010)\ M & & = (1 - x)\ M &
\end{array}$$

where Pr stands for propionate ion and x was comprised in the (2.57–12.1). 10^{-2} M range. No flow of chloride ions from the reference electrode into the

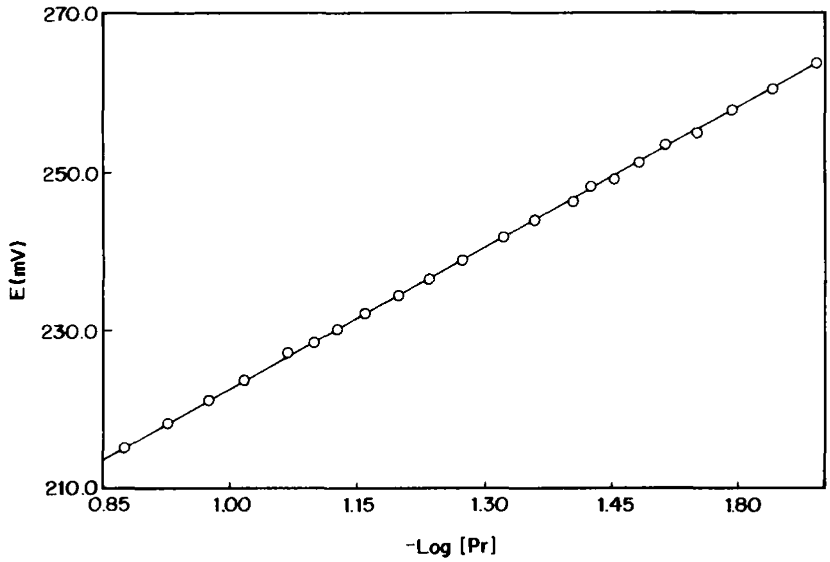

FIGURE 2 Calibration graph for the propionate-sensitive electrode. I = 0.500 M; t = 25°C; S = 58.9 mV/dec. Only about one-tenth of the experimental values, chosen at random, have been plotted.

test solution could be detected during the measurements. A typical E *vs* $-\log[Pr]$ plot for the above mentioned cell is shown in Figure 2.

Procedure

Isomolar HPr-NaPr buffer solution, made up to the desired ionic strength value with $NaClO_4$, was successively added (in 0.300 ml. increments) to a known volume of $NaClO_4$ solution of identical ionic strength, in the potentiometric cell. After each addition the emf of the cell was measured. In all cases equilibrium was easily reached (the criterion was to achieve constant emf values within ± 0.2 mV during 3 minutes, for $I \leq 1.0$ M values, and $\pm$ 0.1 mV during 1.5–2 minutes, when $I > 1.0$ M).

Convention

This work is based on some principles previously established by several authors:[15–18]

1. The emf for a cell of the type used in this work is defined by:[16–18]

$$E = (E_i^{0'})_0 - S \log a_i + X_i [i] \qquad (1)$$

where:

$E_i^{0'}$ = sum of all constant terms that contribute to the total measured emf, (mV).
$a_i = y_i[i]$ = individual activity of an ion or neutral substance, i(mol.dm^{-3}).
[i] = molar concentration of an ion or a neutral substance, i(mol.dm^{-3}).
y_i = molar activity coefficient of i.
$(E_i^{0'})_0$ = limiting value of $E_i^{0'}$ when $\log y_i = 0$ (mV).
S = experimental value obtained for the coefficient of the logarithmic term of the electrode potential (mV/decade).
X_i = term of proportionality between liquid junction potential (E_J) and [i] (mV.mol^{-1}.dm^3).

2. Within the considered concentration range, Nai is a strong electrolyte,
3. At constant temperature (t), maintaining constant and high enough 1 values, y_i will be constant,[16]
4. The straight line obtained by plotting E − S log [i] *vs.* [i] (at constant I) within certain [i] range can be extrapolated for smaller [i] values (that is, $E_i^{0'}$ and X_i are valid, at least, for the entire O-[i] range[16–18]),
5. For electrolytes (and non-electrolytes) mixtures, it is preferable to use empirical equations (with extrathermodynamic but experimental and practical meaning) instead of theoretical ones.[15]

Calculation Methods

Molar activity coefficients of propionate ion

Equation (1) as applied to the potentiometric cell used in this work is:

$$E = (E_{Pr}^{0'})_0 - S \log y_{Pr} - S \log[Pr] + X_{Pr} [Pr] \qquad (2)$$

If it is considered (for each fixed I value) that:

$$E_{Pr}^{0'} = (E_{Pr}^{0'})_0 - S \log y_{Pr} = \text{constant} \qquad (3)$$

We shall have:

$$E = E^{0'}_{Pr} - S \log [Pr] + X_{Pr} [Pr] \tag{4}$$

From enough experimental (E, [Pr]) pairs of values $E_{Pr}{}^{0'}$, S and X_{Pr} parameters (corresponding to each fixed I value) can be determined by using the multiple linear regression method. From the calculated X_{Pr} it is possible to find $E_{Pr}{}^{0'}$ values corresponding to each experimental [Pr] value by employing Eq. (4). For this particular case X_{Pr} was found to be negligible for the range of [Pr] concentrations used, *i.e.*, $E_J \simeq 0$, even for $I = 0.300$ M.

For the calculation of log y_{Pr} values the following expression was used,[15]

$$\phi_{Pr} = \log y_{Pr} = (aI^{1/2} + bI + CI^{3/2} + \text{---}). \tag{5}$$

where a, b, c, --- are empirical parameters.

From (3) and (5):

$$E^{0'}_{Pr} = (E^{0'}_{Pr})_0 - S\,(aI^{1/2} + bI + cI^{3/2} + \text{---}) \tag{6}$$

By employing an adequate statistical program[19] and from enough ($E_{Pr}{}^{0'}$, I) pairs, one can determine all parameters of Eq. (6) and, therefore, the mathematical relationship between y_{Pr} and I.

Other Equilibrium Parameters

For the equilibrium $H^+ + A^- \Leftrightarrow HA$ corresponding to a given monocarboxylic acid, in aqueous solution, the thermodynamic protonation constant is defined as,

$$^{T}K_H = \frac{[HA]}{[H][A]} \cdot \frac{y_{HA}}{y_H \cdot y_A} = K_H \frac{y_{HA}}{y_H \cdot y_A} \tag{7}$$

where charges are omitted for simplicity. From (7):

$$\log {}^{T}K_H = \log K_H + \log y_{HA} - \log y_H - \log y_A \tag{8}$$

Making $\phi_i = \log y_i$, Eq. (8) turns to:

$$Y = \log K_H - \phi_H - \phi_A = \log {}^{T}K_H - \phi_{HA} \tag{9}$$

From sufficient $\mathbf{K_H}$, ϕ_H, ϕ_A and **I** values, log $^{T}\mathbf{K_H}$ and ϕ_{HA} may be estimated, through linear relationships.

Similarly, for the equilibrium $Me^{2+} + A^- \Leftrightarrow MeA^+$ of a divalent metallic cation with a monocarboxylate, the thermodynamic formation constant is defined as:

$$^{T}\beta_{I} = \frac{[MeA]}{[Me]\,[A]} \cdot \frac{y_{MeA}}{y_{Me} \cdot y_{A}} \tag{10}$$

and,

$$Y = \log \beta_{I} - \phi_{Me} - \phi_{A} = \log {}^{T}\beta_{I} - \phi_{MeA} \tag{11}$$

where β_1 is a stoichiometric formation constant.

Starting from sufficient **(Y, I)** pairs, we can calculate log $^{T}\beta_1$ and ϕ_{MeA} values, also via linear relationships, as will be shown along this work.

RESULTS AND DISCUSSION

Experimental data and estimates of molar activity coefficients for propionate ion, along with the corresponding estimates for other ions, from previous work,[10] are shown in Table I. The best fit of Eq. (6) to the ($E_{Pr}^{0'}$, **I**) of that Table led to the following equation:

$$E_{Pr}^{0'} = 162.0 - 59.0\,(-0.185\,I^{3/2} + 0.104\,I^{2}) \tag{12}$$

and, so,

TABLE I Parameters Associated With the HPr-NaPr-$NaClO_4$ Aqueous System, Along With Related Data.[10] t = 25.0 ± 0.1°C.

	*Propionate**			y_i‡			
I (M)	$E_{Pr}^{0'}$ *(mV)*	*S (mV/dec)*†	y_{Pr}	H^+	Cu^{2+}	Cd^{2+}	Pb^{2+}
0.100	–	–	–	0.748	0.497	0.665	0.747
0.300	163.4	59.5	0.953	0.689	0.388	0.416	0.616
0.500	164.5	58.9	0.913	0.695	0.374	0.373	0.554
0.900	166.4	60.7	0.844	–	–	–	–
1.00	–	–	–	0.811	0.460	0.416	0.516
1.20	167.6	56.8	0.806	0.886	0.532	0.479	0.532
1.50	168.4	54.0	0.784	1.03	0.689	0.642	0.587
1.60	–	–	–	1.09	0.757	0.721	0.614
1.80	168.6	55.5	0.777	1.22	0.924	0.933	0.687
2.00	–	–	–	1.37	1.14	1.24	0.788
2.10	168.3	51.9	0.786	–	–	–	–
2.40	167.7	52.8	0.815	1.75	1.79	2.41	1.12
2.50	–	–	–	1.86	2.02	2.88	1.24
2.70	165.8	54.1	0.866	–	–	–	–
3.00	163.7	55.1	0.943	2.60	3.74	7.80	2.26

*-Present work.
†-Calculated by linear regression from (E, log[Pr]) pairs. In all cases, correlation coefficients (R) higher than 0.999 were obtained.
‡-From Ref.[10].

$$\phi_{Pr} = -0.185\ I^{3/2} + 0.104\ I^2, (\sigma = 0.52) \tag{13}$$

where σ stands for the standard error of estimate. Among the various types of tested equations none fitted so perfectly to the experimental data as did this one. From Table I it can be seen that the S values vary randomly with ionic strength, just as already found for well-established electrodes.[10]

In a previous work[10] similar relationships between ϕ_i and **I** were found, *i.e.*,

$$\phi_{H}{}^{+} = -0.542\ I^{1/2} + 0.4511\ I, (\sigma = 1.01) \tag{14}$$

$$\phi_{Cu}{}^{2+} = -1.249\ I^{1/2} + 0.912\ I, (\sigma = 0.63) \tag{15}$$

$$\phi_{Cd}{}^{2+} = -0.829\ I^{1/2} + 0.448\ I^{3/2}, (\sigma = 1.32) \tag{16}$$

$$\phi_{Pb}{}^{2+} = -0.404\ I^{1/2} + 0.117\ I^2, (\sigma = 2.03) \tag{17}$$

Stoichiometric protonation constants for propionic acid, critically selected from the literature,[13] coupled with present and previously estimated parameters, ϕ_H and ϕ_{Pr}, allowed the calculation of the associated log $^T\mathbf{K}_H$ and ϕ_{HPr} values, through Eq. (9); for this particular case $\phi_A = \phi_{Pr}$ and $\phi_{HA} = \phi_{HPr}$. It was found that a straight line can be nicely fitted to the (**Y**, $\mathbf{I}^{0.5}$) points, giving log $^T\mathbf{K}_H$ and ϕ_{Pr} as intercept and slope, respectively. The values found are displayed in Table II.

Equation (9) was also tested for eleven other monocarboxylic acids (aliphatic and aromatic, with and without additional functional groups) by assuming $\phi_{Pr} = \phi_A$. The results are shown in Table II. Our study has been restricted to only twelve monocarboxylates due to the paucity of critically selected values from the literature.[13] Very good agreement is observed between literature and calculated log $^T\mathbf{K}_H$ values; this seems to be more than fortuitous, mainly when the chemical differences among the considered acids are taken into account. The results are somewhat surprising and very gratifying.

Similarly, Eq. (18), below, was used for the calculation of log $^T\beta_1$ and ϕ_{MeA} associated with several Me(II)-monocarboxylate systems:

$$Y = \log \beta_l - \phi_{Me} - \phi_{Pr} = \log {}^T\beta_l - \phi_{MeA} \tag{18}$$

TABLE II Estimates of log $^{T}K_H$ and ϕ_{HA} for Some Monocarboxylic Acids. Aqueous Solution. t = 25.0°C.

Acid	*I* Range (M)*	*n†*	*log $^{T}K_H$* This work	*log $^{T}K_H$* Literature[13]	*$\phi_{HA}/I^{0.5}$*	*R^2*	*$\sigma.10^3$*
formic	0.1–3	4	3.74 ± 0.01	3.745 ± 0.007	0.134	0.9952	7
acetic	0.1–3	5	4.77 ± 0.01	4.757 ± 0.002	0.035	0.9875	3
propionic	0.1–3	5	4.86 ± 0.00	4.874 ± 0.001	0.051	0.9886	3
butyric	0.1–3	3	4.78 ± 0.00	4.819 ± 0.001	0.021	0.9812	4
isobutyric	0.1–3	4	4.84 ± 0.01	4.849	0.043	0.9800	5
lactic	0.1–2	4	3.85 ± 0.00	3.860 ± 0.002	0.055	0.9961	2
glycolic	0.1–2	4	3.80 ± 0.00	3.832 ± 0.001	0.053	0.9808	4
benzoic	0.1–1	3	4.18 ± 0.00	4.202 ± 0.003	0.044	0.9885	3
furoic	0.1–2	3	3.16 ± 0.00	3.167 ± 0.007	0.010	0.9991	1
pyruvic	0.1–2	4	2.43 ± 0.00	2.49 ± 0.1	0.121	0.9986	2
phenylacetic	0.1–3	3	4.27 ± 0.00	4.310 ± 0.003	0.049	0.9961	3
mandelic	0.1–2	3	3.36 ± 0.01	3.40 ± 0.01	0.042	0.9791	10

*-Adjusted with $NaClO_4$.
†-Number of (log K_H, I) pairs used; taken from Ref. 13.

By plotting **Y** *vs.* **I**, very good linear relationships are obtained for all systems considered in this work; some examples are given in Figures 3 to 5. The calculated values for log $^{T}\beta_1$ and (ϕ_{MeA}/I) are displayed in Table III. Again, the set of formation constants used is limited by the paucity of reliable data for all bivalent cations other than Cu^{2+}, for which the gap is less pronounced. Within the restricted database available a very good agreement is generally found between the literature data and the corresponding ones, calculated through application of Eq. 18, in so far as log $^{T}\beta_1$ values are concerned.

As can be seen in Table III and Figures 3 to 5, equation (18) was tested, for most of the considered systems, by putting $\phi_{Me} = \phi_{Cu}$, ϕ_{Cd} or ϕ_{Pb}. The overall conclusion is that the effectiveness of the ion-selective electrodes in giving good estimates of y_{Me} follows the order Cu > Cd > Pb; it is noteworthy that this same order prevails concerning the reliability of the aforementioned electrodes for analytical purposes.[20]

This work was based on the relatively small number of available critical protonation and stability constants for carboxylates and their Me^{2+} complexes.[13] The full test for the presently proposed calculation procedure requires the development of the largest possible database of reliable stability constants and associated protonation constants.

An inherent advantage of the proposed methodology is that through linear relationships, reliable estimates of thermodynamic constants can be obtained, via extrapolation. There are a number of techniques for estimating thermodynamic stability constants;[21–23] these are more commonly obtained by extrapo-

TABLE III Estimates of log $^T\beta_1$ and ϕ_{MeA} for Several Me^{+2}-Monocarboxylates Complexes. Aqueous Solution. t = 25.0°C.

Me^{2+}	*Ligand*	ϕ_{Me} *used in Eq. (18)*	*I* Range (M)*	*n†*	*log* $^T\beta_1$ *This work*	*log* $^T\beta_1$ *Literature.*[13]	ϕ_{MeA}/I	R^2	$\sigma.10^3$
Cu	acetate	ϕ_{Cu}	0.1–2.0	3	2.19 ± 0.02	2.21 ± 0.03	0.264	0.9924	20
Cu	propionate	ϕ_{Cu}	0.1–3.0	3	2.21 ± 0.01	2.22	0.324	0.9998	10
Cu	methoxyacetate	ϕ_{Cu}	1.0–3.0	3	2.55 ± 0.01	–	0.390	0.9996	8
Cu	pyruvate	ϕ_{Cu}	0.1–2.0	3	2.52 ± 0.02	(2.2)‡	0.595	0.9993	20
Cu	pyruvate	ϕ_{Pb}	0.1–2.0	3	2.35 ± 0.02	(2.2)‡	0.389	0.9989	20
Co	acetate	ϕ_{Cu}	0.5–2.0	3	1.26 ± 0.01	1.38 ± 0.09	0.313	0.9999	2
Co	acetate	ϕ_{Cd}	0.5–2.0	3	1.32 ± 0.00	1.38 ± 0.09	0.313	0.9999	2
Ni	acetate	ϕ_{Cu}	0.5–2.0	3	1.33 ± 0.01	1.43	0.294	0.9997	5
Ni	acetate	ϕ_{Cd}	0.5–2.0	3	1.38 ± 0.01	1.43	0.266	0.9996	5
Zn	acetate	ϕ_{Cu}	0.1–3.0	4	1.56 ± 0.00	1.58 ± 0.01	0.428	0.9999	2
Zn	acetate	ϕ_{Cd}	0.1–2.0	3	1.57 ± 0.01	1.58 ± 0.01	0.290	0.9995	8
Zn	acetate	ϕ_{Pb}	1.0–3.0	3	1.58 ± 0.01	1.58 ± 0.01	0.315	0.9999	4
Cd	acetate	ϕ_{Cu}	0.1–3.0	4	1.93 ± 0.00	1.93	0.381	0.9996	6
Cd	acetate	ϕ_{Cd}	0.1–2.0	4	1.91 ± 0.00	1.93	0.304	0.9998	4
Pb	acetate	ϕ_{Cu}	1.0–3.0	3	2.65 ± 0.01	2.68	0.315	0.9999	4
Pb	acetate	ϕ_{Pb}	1.0–3.0	3	2.73 ± 0.03	2.68	0.230	0.9994	8
Pb	lactate	ϕ_{Cu}	1.0–3.0	3	2.78 ± 0.03	2.78	0.365	0.9984	20
Hg	formate	ϕ_{Cd}	1.0–3.0	3	3.59 ± 0.01	(3.51 ± 0.14)‡	0.245	0.9998	4
Hg	formate	ϕ_{Cu}	0.5–3.0	3	3.33 ± 0.04	(3.51 ± 0.14)‡	0.100	0.9800	20
Hg	propionate	ϕ_{Cd}	1.0–3.0	3	4.50 ± 0.01	(4.38 ± 0.14)‡	0.292	0.9998	6
Hg	propionate	ϕ_{Pb}	1.0–3.0	3	4.34 ± 0.01	(4.38 ± 0.14)‡	0.165	0.9980	4
Hg	propionate	ϕ_{Cu}	1.0–3.0	3	4.50 ± 0.01	(4.38 ± 0.14)‡	0.260	0.9994	8
Hg	butyrate	ϕ_{Cd}	0.1–1.0	3	4.12 ± 0.00	(3.99 ± 0.13)‡	0.156	0.9996	2
Hg	butyrate	ϕ_{Cu}	0.1–1.0	3	4.02 ± 0.01	(3.99 ± 0.13)‡	0.178	0.9999	2

* - Adjusted with $NaClO_4$.
† - Number of (log β_1, I) pairs used; taken from Ref. 13.
‡ - Doubtful value, according to Ref. 13.

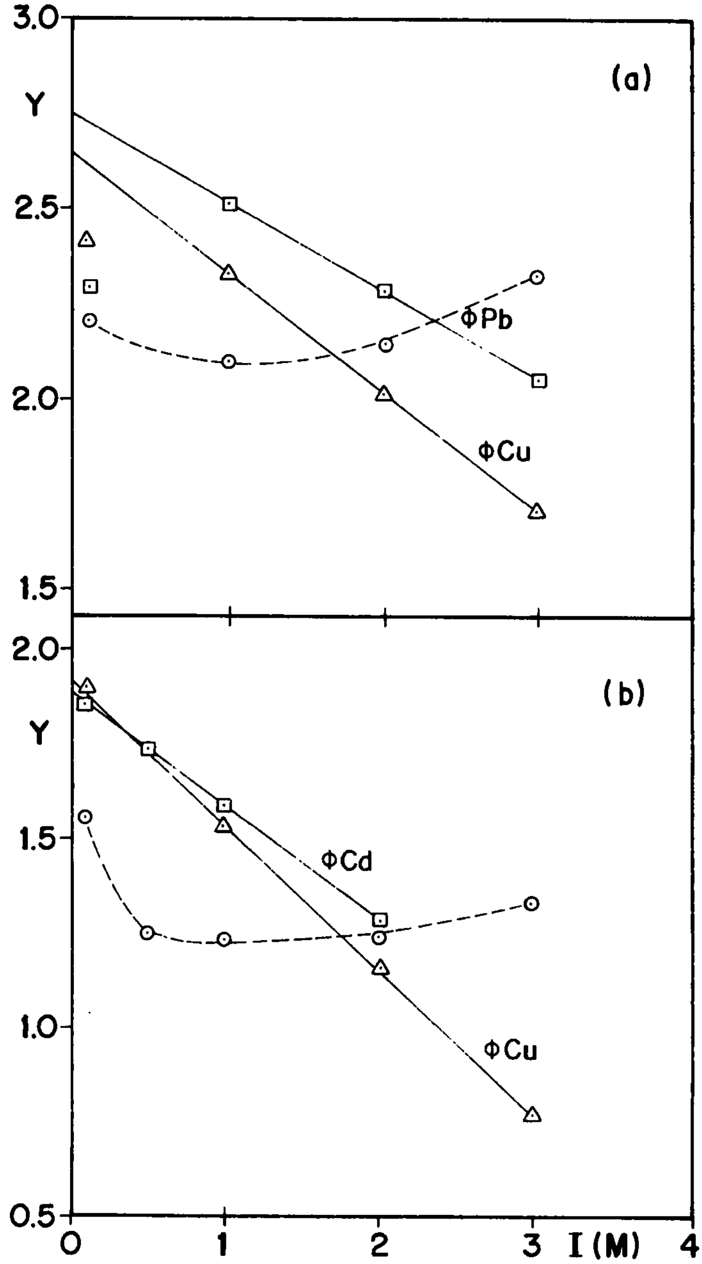

FIGURE 3 Me^{2+}-Acetate Systems. (a) Pb^{2+}: (b) Cd^{2+}. Open circles: $Y = \log \beta_1$. Open squares and triangles: $Y = \log \beta_1 - \phi_{Me} - \phi_{Pr}$. The ϕ_{Me} used for each correlation is indicated inside the Figure. The open circles are joined by a dotted line just for better visualization.

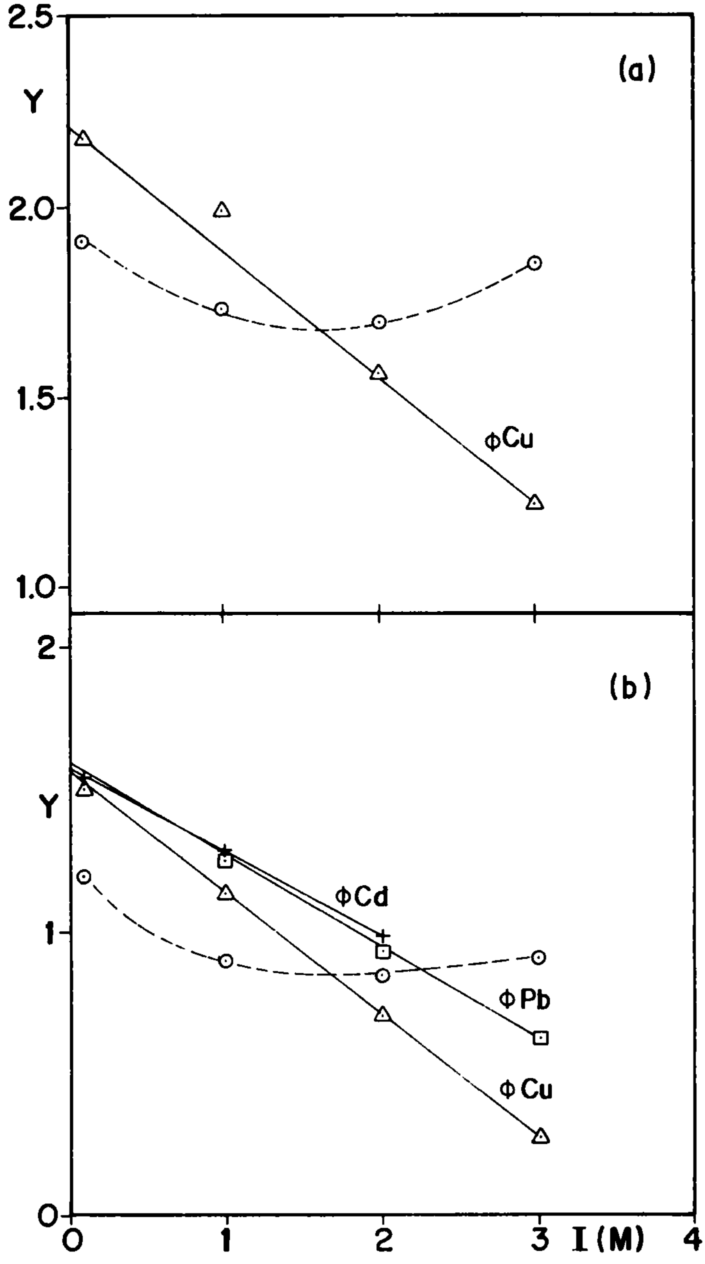

FIGURE 4 Me^{2+}-Monocarboxilates Systems. (a) Cu^{2+}—propionate; (b) Zn^{2+}—acetate. Open circles: $Y = \log \beta_1$. Crosses, open squares and triangles: $Y = \log \beta_1 - \phi_{Me} - \phi_{Pr}$. The ϕ_{Me} used for each correlation is indicated inside the Figure. The open circles are joined by a dotted line just for better visualization.

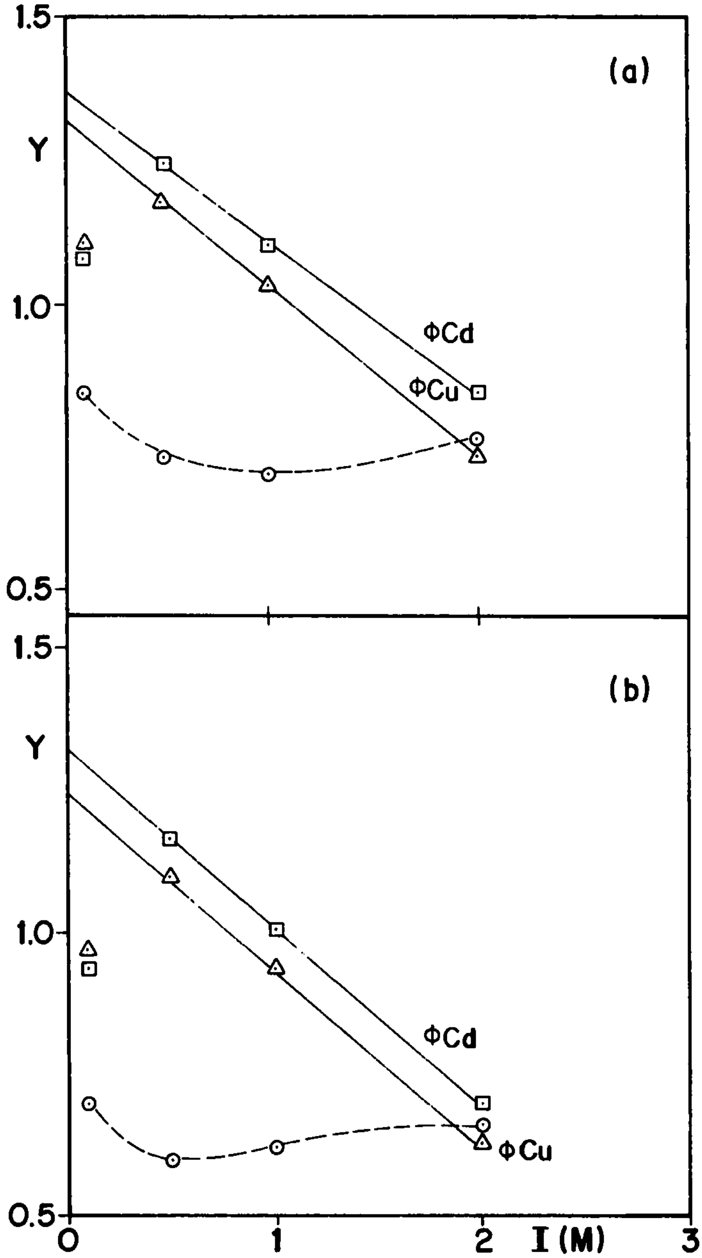

FIGURE 5 Me^{2+}-Acetate Systems. (a) Ni^{2+}; (b) Co^{2+}. Open circles: $Y = \log \beta_1$. Open triangles and squares: $Y = \log \beta_1 - \phi_{Me} - \phi_{Pr}$. The ϕ_{Me} used for each correlation is indicated inside the Figure. The open circles are joined by a dotted line just for better visualization.

lating stoichiometric constants, determined at several ionic strengths, to infinite dilution. Plots of log β_1 (or log K_H) against I, I^2, $I^{1/2}$, $I^{1/3}$, $I^{2/3}$, etc. are sometimes extrapolated by eye or by using complex functions such as the right-hand side of Eq. (19),

$$\log {}^T\beta_l = \log \beta_l - \frac{AZ_+ \cdot Z_- \cdot I^{0.5}}{1 + aBI^{0.5}} - CI \tag{19}$$

against **I** or $I^{0.5}$, where a, A, B and C are constants, some or all of which may be treated as adjustable parameters.[21,22] None of these extrapolations are very reliable, except in a few favourable cases (see, *e.g.*, Ref.[21]). The functions involving log β_1 (or log K_H) and ionic strength are markedly curved for most systems (*i.e.*, of the type shown in Figures 3 to 5) making extrapolations to **I** = 0 rather uncertain. In fact it has been shown that the deviation for values of ${}^T\beta_1$ obtained by using different extrapolation procedures may amount to several hundred percent.[22,23] Even with the more recent refinements concerning these extrapolations,[24] the error of estimated log ${}^T\beta_1$ can be very large, if values of stoichiometric constants are known only for **I** $\geq$ 0.5 M, except in circumstances where these values are properly distributed on the **I** scale, a situation that seldom occurs with the currently available experimental data. The thermodynamic stability constant for the Cu^{2+}-methoxyacetate system, for which the corresponding value has not yet been assigned,[13] was calculated in this work and is given in Table III.

Another gratifying feature of our procedure lies in the fact that its good predictive power is not limited only to systems for which specific ϕ_{Me} parameters are available: thus, good estimates of thermodynamic stability constants were obtained also for Co^{2+}, Ni^{2+}, Zn^{2+} and Hg^{2+} complexes. On the other hand, ϕ_A is available exclusively for propionate; in spite of this, protonation and formation constants in line with critically selected ones could be achieved for 12 monocarboxylates, other than propionate (Tables II and III). This lends some support to the assumption made in the first part of this work,[10] namely that similar ions should display closely related equilibrium parameters.

It seems worthwhile to point out that the presently proposed procedure for conversion of equilibrium constants—in so far as differences in ionic strengths are concerned—is quite distinct from that described in ref. 13, which is based mostly on estimation by chemical trends and free energy relationships, using the library of equilibrium data found in compilations. The general criteria and guidelines for data selection have been presented and discussed in detail.[8,13,14,25]

In some of the **Y** *vs.* **I** correlations it has been noted that one point moves away from the linear relationship built upon the remaining points, *e.g.*, the Y values corresponding to the acetates of Ni^{2+} and Co^{2+} at I = 0.100 M (Figure 5). This suggests that the associated β_1 values might be in error and these systems probably deserve reinvestigation. Studies on systems comprising other metal ions and ligands are currently in progress in this laboratory.

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