

# On the Accuracy of Stability Constants of Carboxylate Complexes from Potentiometric Measurements of Central Ion Concentrations

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The influence of the liquid junction potential,  $E_j$ , and varying activity coefficients,  $\gamma$ , on the values of stability constants obtained from emf measurements of central ion concentrations is discussed. It is found both experimentally and theoretically that  $\beta_1$  is quite insensitive to errors in  $E_j$  and to non-constant  $\gamma$  whereas  $\beta_2$  may be substantially changed thereby. The choice of expression for  $E_j$  in carboxylate systems is discussed. It is also suggested that  $\beta$  values should be calculated using different assumptions about the value of  $E_j$  in order to obtain better estimates of the uncertainties in the numerical values of equilibrium constants.

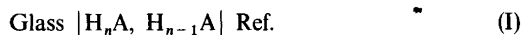
In an aqueous solution of two electrolytes A and B the mean activity factors will vary when the composition of the solution is changed from one of pure A to one of pure B at constant ionic strength. The variations often follow Harned's rule.<sup>1</sup> Since composition changes must necessarily be made in complexation studies the principle of specific interactions of ions<sup>2</sup> is used in the design of the electrolyte background employed to reduce activity coefficient and liquid junction potential changes. Thus the concentration of the anion of the medium is kept constant when the complex formation between mainly cationic species is studied and *vice versa*. The success of this approach to damp activity changes was demonstrated by Biedermann and Sillén.<sup>3</sup> They also provided evidence showing that the medium effects upon an ion from changes in the composition of the ions of opposite charge could be expressed by the relation  $\lg \gamma_B = k[A]$ .  $\gamma_B$  is the activity coefficient of ion B,  $k$  is a constant and  $[A]$  the concentration of an ion exchanged in the medium.

For exchanges made at constant equivalent con-

centration there is now ample evidence<sup>4,5</sup> indicating that the above relation is also followed when the charges on A and B are of the same sign. The  $k$  values are small and neglect of activity coefficient variations will be a main concern only in studies of weak complex formation where large concentrations of the ligand must be used. For the same reason the values of the stability constants of the higher complexes will in general be effected. These remarks are also pertinent to the influence of a neglect of liquid junction potentials when the emf method is used.

## STUDIES ON CARBOXYLATE BUFFERS

In two recent studies<sup>6,7</sup> the complex formation between  $\text{Pb}^{2+}$  and aliphatic dicarboxylic acids,  $\text{H}_2\text{A}$ , has been investigated by central ion measurements. Since the complexation is of moderate strength with the dicarboxylate ion and the protonated complexes are weak, it was felt necessary to estimate and correct for the effects mentioned in the introduction. This has been attempted by measurement of the cell



$$E = E^\circ - g \ln a_{\text{H}} - E_j \quad (1)$$

The experimental details of this measurement and those to be described later can be found in Refs. 6 and 8. The ionic medium employed was 1 M  $\text{Na}(\text{ClO}_4)$  and the activity scales chosen so that  $\gamma \rightarrow 1$  when the composition of the equilibrium solution  $\rightarrow 1$  M  $\text{NaClO}_4$ .  $E_j$  is the liquid junction potential and  $g = RTF^{-1}$ .  $[\text{H}_n\text{A}]^*$  etc. represent the formal concentrations of the components of the buffer. The ratio  $[\text{H}_n\text{A}]^*/[\text{H}_{n-1}\text{A}]^*$  was kept con-

stant in each run and  $E$  was measured as a function of the total concentration of the buffer. An approximate hydrogen ion concentration,  $h$ , can be found from eqn. (1) putting  $y_{H^+} = 1$  and then inserted together with  $[OH^-]$  into the expression

$$\phi = ([H_n A]^* - h + [OH^-])([H_{n-1} A]^* + h - [OH^-])^{-1} \quad (2)$$

The approximate nature of the concentrations of  $H^+$  and  $OH^-$  is not serious since they are small compared to the concentrations of the buffer components. For a  $N$ -basic acid we have

$$[H_n A]^* + [H_{n-1} A]^* = \sum_0^N [H_m A] = [A]_{tot} \quad (3)$$

$$n[H_n A]^* + (n-1)[H_{n-1} A]^* = \sum_0^N m[H_m A] + h - [OH^-] \quad (4)$$

so that eqn. (2) can be written

$$\phi = \left( \sum_0^N (1+m-n)[H_m A] \right) \left( \sum_0^N (n-m)[H_m A] \right)^{-1} \quad (5)$$

The use of eqn. (5) will be illustrated with acetic acid as an example. Then  $N=n=1$  and  $\phi = [HA]/[A]$ . The protonation constant,  $\beta_1$  of the acid is defined by

$$\beta_1 = [HA][A]^{-1} y_{HA} y_A^{-1} a_H^{-1} \quad (6)$$

Eqns. (1), (5), and (6) yield

$$E - E^\circ + g \ln \phi = g \ln \beta_1 + g \ln (y_A y_{HA}^{-1}) - E_j \quad (7)$$

In Fig. 1 the left hand side of eqn. (7) has been plotted as a function of  $[A]_{tot}$  for various buffer ratios. Straight lines are obtained which have a common intercept within 0.1 mV. From the intercept the protonation constant at infinite dilution in the medium can be calculated.  $\beta_1 = 3.91 \times 10^4 \text{ M}^{-1}$  obtained for acetic acid agrees very well with the value found by Ahrlund.<sup>9</sup> An iterative procedure must be used for diprotic acids.

It has been observed that the slopes of the lines representing eqn. (7) can be expressed as linear functions of  $[H_n A]$  and  $[H_{n-1} A]$ , i.e.

$$g \ln (y_{H_{n-1} A} y_{H_n A}^{-1}) - E_j = k_n [H_n A] + k_{n-1} [H_{n-1} A] \quad (8)$$

The linearity is in agreement with the Guggenheim and Setchenow relations for activity coefficients<sup>10</sup> and the linearized form of Henderson's equation.<sup>11</sup>

The values of the coefficients,  $k_m$ , in eqn. (8) obtained for acetic acid and the series of dicarboxylic acids from oxalic to adipic acid were in reasonable agreement with the values estimated from Henderson's equation for the charged species. The coefficients for the acids were in the range  $1-2 \text{ mVM}^{-1}$ . It was therefore concluded that the observed effects mainly arose from variations in the liquid junction potential and that the activity coefficients could be considered as invariant. A correction term  $E_j = \sum_0^N k_m [H_m A]$  would then be

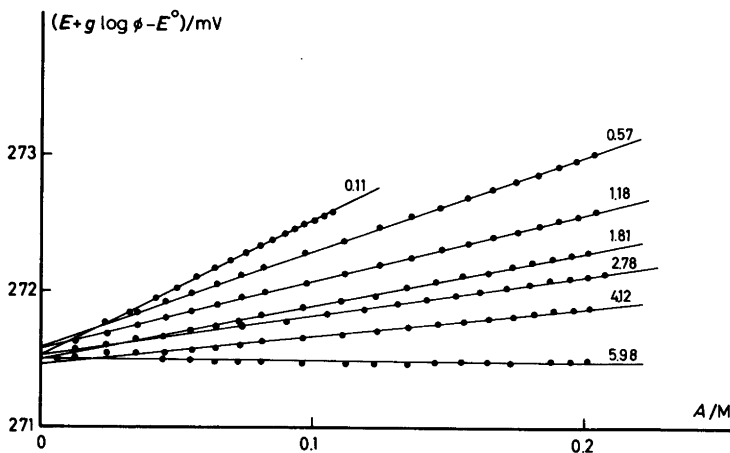


Fig. 1. The experimental values of  $E + g \log \phi - E^\circ$  [see eqn. (7)] in the acetate system plotted against  $A$  at different values of the quotient  $[HA]^*/[A]^*$ . In this figure  $g = 59.16 \text{ mV}$ .

applicable to the emf of other electrodes as well. A similar correction has been applied by Sandell,<sup>12</sup> who demonstrated that in this way the stability constants calculated from central ion measurements were brought into better agreement with those from ligand measurements.

When data obtained for benzoic and some other aromatic acids were treated in the way described above, it was found that some of the coefficients were considerably greater than expected for a pure liquid junction potential. It must therefore be concluded that changes in the activity coefficients and/or dimerisation of the acids occur.

The dimerisation of carboxylic acids has been much debated and it is hardly likely that the arguments can be settled from thermodynamic measurements alone.<sup>13</sup> This can be seen if the  $\phi$ -function is used. One would then have

$$\phi = ([\text{HA}] + [\text{HA}_2] + 2[\text{H}_2\text{A}_2])([\text{A}] + [\text{HA}_2])^{-1} \quad (9)$$

Assuming constant activity coefficients and introducing the equilibrium constants  $K_1$  and  $K_2$  of the reactions  $\text{HA} + \text{A} \rightleftharpoons \text{HA}_2$  and  $2\text{HA} \rightleftharpoons \text{H}_2\text{A}_2$  eqn. (10) is obtained from eqn. (9)

$$\phi = h\beta_1(1 + K_1[\text{A}] + 2K_2[\text{HA}])(1 + K_1[\text{HA}])^{-1} = h\psi \quad (10)$$

A combination of eqns. (1) and (10) leads to

$$E - E^\circ + g \ln \phi = g \ln \psi - E_j \quad (11)$$

In cases where  $K_1$  and  $K_2$  are small,  $\ln \psi$  is approximately

$$\ln \psi \approx \ln \beta_1 + K_1[\text{A}]^* + (2K_2 - K_1)[\text{HA}]^* \quad (12)$$

A plot of the left hand side of eqn. (11), where  $\phi$  is calculated from eqn. (2), as a function of  $[\text{A}]_{\text{tot}}$  should at a constant buffer ratio then give a

straight line as is observed in Fig. 1. One is thus faced with a situation where activity coefficient and liquid junction potential changes, and dimerisation lead to the same type of deviation from a horizontal line for a plot of  $E - E^\circ + g \ln \phi$  as a function of the total concentration of the buffer. When  $K_1$  and  $K_2$  have comparatively large values, as appears to be the case for aromatic acids, eqn. (12) is no longer valid. Calculations on models show, however, that deviations from a linear relationship become significant only if a very broad range in  $[\text{HA}]/[\text{A}]$  and  $[\text{A}]_{\text{tot}}$  is investigated.

For the most thoroughly investigated system, acetic acid-acetate ion, Danielsson and Stenius,<sup>14</sup> and Persson<sup>15</sup> concluded that the observed effects are mainly due to changes in activity coefficients and liquid junction potentials. Farrer and Rossotti<sup>16</sup> made an attempt to compensate for these variations and obtained values for  $K_1$  and  $K_2$ . Indirect evidence for and against dimerisation has been obtained in complexation studies.<sup>15,17</sup> It appears plausible that the course of the plots of eqn. (7) cannot be solely attributed to  $E_j$  for the following reasons: (i) the emfs of cells without a liquid junction<sup>15</sup> cannot be explained by the simple  $\text{H} + \text{A} \rightleftharpoons \text{HA}$  equilibrium (ii) the coefficients in eqn. (8) are different from those,  $k_{\text{HA(H)}}$  and  $k_{\text{A(OH)}}$  from measurements of cell (I) with an excess of  $\text{H}^+$  or  $\text{OH}^-$ . See Table 1 for experimental results. It may be noted that  $k_{\text{A(OH)}}$  is close to the values estimated from the Henderson equation.

Activity coefficient changes also seem to be present.  $k_{\text{HA(H)}}$  is definitely observed to be  $\neq 0$  and the most reasonable cause is variations of the activity coefficients. This is further corroborated by measurements on the cell



where  $\text{HB}-\text{B}$  is a buffer present at a constant concentration. It is chosen so that there is virtually

Table 1. Experimental values of the coefficients from eqn. (8) in  $\text{mVM}^{-1}$ .  $k_{\text{HA(H)}}$  and  $k_{\text{A(OH)}}$  refer to results from cell (I) with an excess of  $\text{H}^+$  or  $\text{OH}^-$ .

Acid	$k_{\text{HA}}$	$k_{\text{HA(H)}}$	$k_{\text{A}}$	$k_{\text{A(OH)}}$	Medium ( $\text{NaClO}_4$ ) (M)
Acetic	1.4	2.6	-13.5	-7.2	1
Acetic	-	3.4 <sup>a</sup>	-	-2.9; -6.3 <sup>a</sup>	3
<i>p</i> -Hydroxybenzoic	-47	6.8	-25.3	-9.5 <sup>b</sup>	1
Benzoic	-	-	-	-3.2	3

<sup>a</sup> Ref. 15. <sup>b</sup> Benzoate ion.

no proton transfer from HB to A. The concentration of A was varied from 0 to 0.2 M. With B=borate or tris(hydroxymethyl)aminomethane, and A=acetate or benzoate it was found that  $E$  as a function of  $[A]$  could be represented by straight lines. Their slopes were different from  $k_{A(OH)}$ , which indicates that  $y_{B}y_{HB}^{-1}$  changes with  $[A]$  unless some quite unfamiliar species are postulated to form.

## MODELLING

*Modelling of the influence of varying liquid junction potentials and activity coefficients on calculated stability constants.* When the complexation of a metal ion,  $M^{z+}$ , is studied by central ion measurements, the correct value of  $E_j$  to be used is somewhat difficult to ascertain. This difficulty is enhanced when the ligand contains carboxylate groups due to the alleged dimerisation. Variations of the activity coefficients will further add to the uncertainty of the model proposed. An instructive case can be found in Ref. 18. In the actual case, calculations of the stability constants under various assumptions will provide an estimate of the uncertainties in these constants and hence in the proposed model. It is, however, instructive to obtain semi-quantitative information from a study of a simple case.

Let it be assumed to simplify matters that  $M^{z+}$  forms only the complexes  $ML$  and  $ML_2$  with the ligand  $L$ . The species present are thus  $M$ ,  $L$ ,  $ML$  and  $ML_2$ . The metal ion activity,  $a_M$ , is determined from potentiometric measurements

$$E = E^\circ + g \ln a_M + E_j; a_M = my_M; g = RT(zF)^{-1} \quad (13)$$

It is further assumed that the total concentration of the metal,  $M$ , is small compared to the total concentration of the ligand. The concentration of non-complexed  $L$ ,  $l$ , can therefore be considered as known. The relation between  $E$  and the composition of the solution is found from the equations

$$M = m + [ML] + [ML_2] \quad (14)$$

and

$$\beta_1 = [ML]m^{-1}l^{-1}y_1^{-1}; \beta_2 = [ML_2]m^{-1}l^{-2}y_2^{-1} \quad (15)$$

where  $y_1$  and  $y_2$  are combinations of the individual activity coefficients. Eqns. (13)–(15) yield

$$E = E^\circ + g \ln M + g \ln y_M - g \ln (1 + \beta_1 ly_1 + \beta_2 l^2 y_2) + E_j \quad (16)$$

Since it has been found experimentally that  $E_j$  and  $\ln y$  are linear functions of  $l$  and if in addition  $M$  is kept constant eqn. (16) can be written

$$E = E^{\circ'} - g \ln (1 + \beta_1 ly_1 + \beta_2 l^2 y_2) + kl \quad (17)$$

In this equation  $y_1$  and  $y_2$  are largely unknown and the value of  $k$  subject to some ambiguity. When solving eqn. (17) for the  $\beta$  values,  $y_1$  and  $y_2$  are given a value = 1 when the ionic medium method is used. The uncertainty in  $\beta$  caused thereby can be estimated as follows.

In the relation  $g \ln y = kl$  the constant  $k$  is generally less than  $20 \text{ mVM}^{-1}$ . This corresponds to moderate changes in  $y$  when  $l < 0.2 \text{ M}$  and the relation can therefore be written

$$y = 1 + p_1 l + p_2 l^2; p_1 = kg^{-1} \text{ and } p_2 = 0.5 p_1^2 \quad (18)$$

Inserting this into eqn. (17) yields

$$E = E^\circ - g \ln (1 + \beta_1 l + (\beta_2 + \beta_1 p_{11}) l^2 + (\beta_1 p_{12} + \beta_2 p_{21}) l^3 + \beta_2 p_{22} l^4) + kl \quad (19)$$

With  $k$  known eqn. (19) will yield stability constants,  $\beta'$ , which are related to the values at infinite dilution by

$$\beta'_1 = \beta_1 \text{ and } \beta'_2 = \beta_2 + \beta_1 p_{11} \quad (20)$$

$\beta_1$  is thus expected to be little effected by changes in the activity factors whereas the error in  $\beta_2$  (and higher  $\beta$ ) can be considerable. The values of  $\beta'_3$  and  $\beta'_4$  are so small that they can hardly be mistaken for real constants. However, varying activity coefficients could lead to a systematic trend in  $E_{\text{calc}}$  amounting to a few tenths of a millivolt. One should therefore be cautious to interpret small trends as indicating the formation of higher complexes.

The influence of a change in  $k$  on the values of  $\beta$  is found upon differentiation of eqn. (17) putting  $y_1 = y_2 = 1$ .

$$(1 + \beta_1 l + \beta_2 l^2) \Delta k = g (\Delta \beta_1 + l \Delta \beta_2) \quad (21)$$

From this equation it can be seen that if the complex formation is strong enough to allow  $ML_2$  and higher complexes to be present in considerable amounts, it is not possible to fully compensate a change in  $k$

Table 2. Stability constants of cadmium and lead benzoate complexes calculated using various expressions for the liquid junction potential (see text for further details). Three times the estimated standard deviation from the least-squares calculation is given within parenthesis.

$E_j$	$\beta_1/M^{-1}$	$\beta_2 \times 10^{-2}/M^{-2}$	$\sigma(E_{pb})/mV$	$\beta_1/M^{-1}$	$\beta_2 \times 10^{-2}/M^{-2}$	$\sigma(E_{cd})/mV$
(1) No Correction	73.4(1.0)	8.75(0.17)	0.09	10.9(0.5)	55.1(0.7)	0.02
(2) $6.8[HA] - 9.5[A^-]$	74.1(0.6)	7.59(0.10)	0.05	10.2(0.4)	43.5(0.5)	0.01
(3) (2) + $HA_2^-$	73.8(0.6)	7.78(0.11)	0.06	10.2(0.1)	44.9(0.7)	0.01
(4) $-25.4[A^-]$	74.8(0.1)	5.76(0.02)	0.01	9.10(0.03)	26.4(0.4)	0.01

by changes in the values of  $\beta$ . In this case the extension of the program LETAGROP by Ulmgren and Wahlberg to treat  $k$  as an adjustable parameter would be useful to find the best set of  $\beta_1$ ,  $\beta_2$ , and  $k$ . Their paper<sup>5</sup> should be further consulted for suggestions on the treatment of data in systems where uncertainties in the activity factors and liquid junction potentials are present.

When the complex formation is weak so that  $ML_2$  does not become predominant,  $\Delta k$  can be largely compensated for by the following changes in  $\beta$

$$\Delta\beta_1 = \Delta kg^{-1}; \Delta\beta_2 = \beta_1 \Delta kg^{-1} = \beta_1 \Delta\beta_1 \quad (22)$$

as can be seen from eqn. (21). In this case simultaneous refinement of  $k$ ,  $\beta_1$ , and  $\beta_2$  would tend to fail. It is also to be noted that  $\beta_2$  is much more sensitive to  $\Delta k$  than  $\beta_1$ .

The conclusions reached here were corroborated by calculations made on "theoretical" data with the program LETAGROP.<sup>19</sup>  $\Delta\beta_2$  was in general greater

than estimated by eqn. (22) which is not surprising in view of the term  $\beta_2 l^2$  in eqn. (21). A real case is shown in Table 2, where the result of a study of the complex formation between  $Pb^{2+}$ ,  $Cd^{2+}$  and the benzoate ion is presented.<sup>8</sup> The expressions for the  $E_j$  correction in eqn. (13) were obtained as follows;  $E_j(2)$  uses the coefficients  $k_{HA(H)}$  and  $k_{A(OH)}$  obtained from cell (I) with excess of  $H^+$  or  $OH^-$ ;  $E_j(3)$  includes the species  $HA_2^-$  with a stability constant determined from measurements of cell (I) using the corrections suggested by Farrer and Rossotti,<sup>16</sup> i.e.  $E_j(2)$ ;  $E_j(4)$  uses the coefficients  $k_{HA}$  and  $k_A$  obtained when the same data as used for finding  $E_j(3)$  were treated according to eqns. (7) and (8). In accordance with the predictions  $\beta_1$  is quite insensitive to the choice of  $E_j$  and  $\beta_2$  subject to large variations. It can also be observed that when the complexation is weak as for  $Cd^{2+}$ , the covariation between  $E_j$  and  $\beta$  in all cases leads to small  $\sigma(E_{cd})$ . This is no longer the case when the complexation becomes stronger, as for  $Pb^{2+}$ .

Another example is given in Table 3, which

Table 3. Stability constants of lead acetate complexes for various expressions of the liquid junction potential  $E_j = k_1[HA] + k_2[A]$ . In (8) and (9)  $k_1$  and  $k_2$  were included in the least-squares refinement.  $k_1$  and  $k_2$  have been taken from Table 1. Three times the estimated standard deviation from the refinements is given within parenthesis.

$E_j/mV$	$\beta_1 \times 10^{-2}/M^{-1}$	$\beta_2 \times 10^{-3}/M^{-2}$	$\beta_3 \times 10^{-3}/M^{-3}$	$\sigma(E_{pb})/mV$
(1) No correction	0.95(0.04)	1.37(0.06)		0.36
(2) $2.6[HA] - 7.2[A]$	0.99(0.02)	1.23(0.03)		0.17
(3) $2.6[HA] - 7.2[A]$	1.03(0.02)	1.06(0.05)	1.1(0.3)	0.10
(4) $1.4[HA] - 13.5[A]$	1.00(0.01)	1.11(0.01)		0.09
(5) $1.4[HA] - 13.5[A]$	1.02(0.01)	1.05(0.04)	0.38(0.02)	0.08
(6) (2) + $HA_2 + H_2A_2$	1.01(0.01)	1.28(0.02)		0.10
(7) (6) + $PbHA_2$	0.996(0.01)	1.27(0.01)	<sup>a</sup>	0.08
(8) $5.4[HA] - 13.6[A]$	1.020(0.004)	1.11(0.02)		0.03
(9) $-3.0[HA] - 11.9[A]$ + $HA_2 + H_2A_2$	1.002(0.006)	1.17(0.04)		0.05

<sup>a</sup>  $\beta(PbHA_2) = 1.1 \times 10^6 M^{-3}$ .

presents results for the lead–acetate system from titrations covering a broad range of buffer quotients,  $[HA]/a = 0.1, 1, \text{ and } 2$ . With the types of coefficients in Table 1, cases (1)–(5),  $\sigma(E_{Pb})$  is greater than 0.08 mV. Allowance for the dimerisation of acetic acid does not improve  $\sigma(E_{Pb})$ , cases (6)–(7). However, simultaneous refinement of the  $\beta$  values and the coefficients in  $E_j$  results in a substantial improvement in  $\sigma(E_{Pb})$ , cases (8)–(9).

Individual sets of coefficients in  $E_j$  for the glass and the amalgam electrodes seem to give the best result, a situation that is not unexpected if changes in activity coefficients occur. From measurements in only one buffer (or a narrow range of buffer quotients) this will hardly show up due to the partial interdependence between  $\beta$  and the coefficients in  $E_j$ .

## CONCLUSIONS

Liquid junction potentials and activity coefficient changes can have considerable effect on the numerical values of stability constants obtained from emf measurements of central ion concentrations as can be seen in Tables 2 and 3. Realistic estimates of the uncertainties in these constants can therefore be obtained only by a study of these influences. It will not be possible, in general, to derive simple expressions for finding them. Instead, one has to make calculations for a number of reasonable models with the least-squares program at hand and use the changes in the values of  $\beta$  as a measure of the uncertainties.

In complicated systems, for instance, when the ligand is the conjugate base of a di- or triprotic acid, the number of parameters in  $E_j$  will be great. Simultaneous refinement of these parameters and a large number of equilibrium constants can be anticipated to cause problems. Use of the  $E_j$  correction obtained from glass electrode measurements in buffers appears to yield good estimates of the  $\beta$  values in many systems. A better fit seems to be obtained by this correction than by the Farrer and Rossotti correction.<sup>16</sup> This result is probably partly fortuitous, since with a large  $E_j$  correction there is a smaller part of  $E - E^\circ$  in eqn. (17) to be accounted for by complex formation. In all probability results with the Farrer and Rossotti correction are more accurate than those obtained by the more common " $E_j = 0$ " correction. Large values of  $k$  obtained from buffers probably indicate association reactions in the ligand system and  $E_j$  values from such measurements would then tend to overestimate  $E_j$ .

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