

Ion Association in Solutions of Nickel Malonate and n-Butyl Malonate

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Potentiometric measurements at low concentration and at a series of constant ionic strengths from 0.03 to 0.2 M have been made in solutions containing nickel ions and malonate or n-butylmalonate ions. Both the thermodynamic and "concentration" association constants for the formation of NiA have been calculated in an attempt to determine the parameters of the Debye-Hückel activity coefficient expression.

A large number of studies of ionic equilibria in solution have been made in the presence of relatively high concentrations of "neutral" or inert electrolyte. It is assumed that the ions in excess do not interfere with the ions under study and that activity coefficients remain constant. These are included in the equilibrium expression yielding an equilibrium quotient valid only at the ionic strength used. Not only is there some doubt about the assumptions involved in this treatment, but it suffers from a number of disadvantages which make it desirable to obtain thermodynamic equilibrium constants for the association of oppositely charged ions.¹

In the present work, the association between nickel and malonate ions has been studied at low concentrations, arranged so as to limit the number of complexes to one, and at a series of constant ionic strengths in order to determine the best activity coefficient expression to be used in the calculation of the thermodynamic association constant. A similar study has been made with nickel and n-butylmalonate ions so that the effect on the ion size parameter \bar{a} of increasing the size of the anion could be examined.

EXPERIMENTAL

Grade-A glassware and A.R. reagents were used where available. Malonic acid was recrystallized from 1:1 ether+benzene mixture containing 5% petr. ether (60-80) and dried *in vacuo* at 40-50° (analysis: found H, 4%; C, 34.84%; calc. H, 3.87%; C, 34.62%). n-Butylmalonic acid was prepared by hydrolysis of the diethyl ester followed by ether extraction and recrystallization from the same solvent mixture (analysis: found H, 7.70%; C, 52.55%; calc. H, 7.55%; C, 52.49%). Sodium perchlorate solutions were prepared from the recrystallized material and analyzed on an ion-exchange resin column of Amberlite IR 120.

E.m.f. measurements were made with a glass electrode in cells of the type,

glass electrode/solution under study/AgCl/Ag, (1)

using a Pye potentiometer and a Vibron electrometer (E.I.L. model 33B) as a null indicator; readings were reproducible to ± 0.1 mV. Each cell, maintained at 25° in a thermostat, contained a pair of glass electrodes (E.I.L. type GG33) and a pair of Ag/AgCl electrodes so that any irregularity in the behaviour of a glass electrode was immediately detectable. At low concentrations the electrodes were standardized by two methods: (i) using hydrochloric acid solutions and the activity data given by Robinson and Stokes,² and (ii) by making additions of carbonate-free sodium hydroxide to malonic acid solution containing

known amounts of potassium chloride. From the known dissociation constants of malonic acid,³ the hydrogen-ion activities were calculated. Subsequent additions of nickel chloride solution could then be made. At constant ionic strength, the electrode system was standardized with mixtures of hydrochloric acid and sodium perchlorate. Calibration curves of e.m.f. against $\log [H^+]$ showed excellent linearity and unknown $\log [H^+]$'s could be obtained with an accuracy of ± 0.003 . Nitrogen was bubbled through the cell during each titration which consisted in making small additions of either sodium hydroxide or nickel chloride solution to the other components in the cell. Ionic strengths were maintained at the required values to within $\pm 1\%$.

RESULTS AND DISCUSSION

The concentration of hydrogen ions in cell (1) is given by

$$-\log [H^+] = (E - E^\circ + k \log [Cl^-] + (k' + k) \log f_1)/k',$$

where E represents the e.m.f., f_1 the activity coefficient, $k = 2.3026 RT/F$, and k' the modified value of k for the glass electrode. The thermodynamic dissociation constants of n-butyl malonic acid $k_1 = [H^+][HA^-]/f_1^2/[H_2A]$ and $k_2 = [H^+][A^{2-}]/f_2/[HA^-]$ were obtained from measurements on solutions containing the acid, sodium hydroxide, and potassium chloride. Concentrations of ionic species were evaluated using equations for total acid $T_a = [H_2A] + [HA^-] + [A^{2-}]$, and electroneutrality $[H^+] + [Na^+] + [K^+] = [Cl^-] + [HA^-] + 2[A^{2-}]$. The ionic strength $I = [H^+] + [Na^+] + [Cl^-] + [A^{2-}]$, and activity coefficients were obtained from the Davies equation⁴

$$-\log f_z = Az^2\{I^{1/2}/(1 + I^{1/2}) - 0.2I\}. \quad (2)$$

At less than half-neutralization, a graphical solution suggested by Speakman⁵ was employed for k_1 which was then introduced at higher pH for the evaluation of k_2 by successive approximations of I using a high-speed DEUCE computer. The values are given in table 2. At constant ionic strength, activity coefficients are omitted and the corresponding dissociation constants for both acids, written as k'_1 and k'_2 are given in table 2.

In solutions containing nickel chloride, organic acid, and sodium hydroxide, the concentrations of ionic species were calculated using equations for the total acid,

$$T_a = [H_2A] + [HA^-] + [A^{2-}] + [NiA],$$

total metal

$$T_m = [Ni^{2+}] + [NiA],$$

and electroneutrality

$$[H^+] + [Na^+] + 2[Ni^{2+}] = 2T_m + [HA^-] + 2[A^{2-}].$$

The ionic strength

$$I = \frac{1}{2}\{6T_m - 4T_a + [Na^+] + [H^+] + 4[H_2A] + 5[HA^-] + 8[A^{2-}]\},$$

and the association constant

$$K = [NiA]/[Ni^{2+}][A^{2-}]f_2^2$$

was obtained by successive approximations using the activity coefficient expression (2). Table 1 shows the good constancy of K for each anion. The value for nickel malonate is in excellent agreement with $126(\pm 4) \times 10^2$ from hydrogen electrode measurements.⁶ From similar experiments at constant ionic strength, the concentration

equilibrium constants K' were calculated and these are given in table 2. We may write $K = K'f_2^{-2}$, and introducing the activity coefficient expression in the form,

$$\log f_z = -Az^2I^{\frac{1}{2}}/(1+B\alpha I^{\frac{1}{2}}) + \beta I,$$

where A and B are Debye-Hückel constants and β is an adjustable parameter, we obtain

$$\alpha = \log K + 2\beta I, \quad (3)$$

where

$$\alpha = \log K' + 4.072I^{\frac{1}{2}}/(1 + 0.329\alpha I^{\frac{1}{2}}).$$

TABLE 1.—E.M.F. MEASUREMENTS AT LOW CONCENTRATIONS

$10^3 T_a$	$10^3 T_m$	$10^3 [\text{Na}^+]$	$10^5 [\text{H}^+]$	$10^2 I$	$10^4 [\text{A}^{2-}]$	$10^3 [\text{MA}]$	$10^{-2} K$
NICKEL MALONATE							
4.269	4.428	6.026	5.647	1.694	1.431	1.742	129
4.254	4.590	6.005	5.904	1.737	1.367	1.748	130
4.247	4.670	5.995	6.047	1.759	1.333	1.751	131
4.240	4.750	5.985	6.181	1.780	1.303	1.754	131
3.784	4.474	5.218	6.634	1.710	1.124	1.465	124
3.777	4.555	5.209	6.762	1.733	1.102	1.467	124
3.771	4.637	5.200	6.867	1.755	1.085	1.469	124
3.765	4.451	5.191	7.002	1.778	1.063	1.471	124
mean $K = 127 (\pm 3) \times 10^2$							
NICKEL n-BUTYL MALONATE							
5.214	5.177	6.916	1.626	1.879	4.024	1.359	26.5
5.195	5.158	7.262	1.163	1.844	5.027	1.605	26.6
5.176	5.139	7.607	0.838	1.811	6.130	1.844	26.9
5.157	5.120	7.948	0.593	1.788	7.479	2.061	26.3
5.060	4.165	6.391	1.875	1.612	3.563	1.048	26.3
5.041	4.149	6.741	1.280	1.584	4.704	1.276	26.2
5.022	4.134	7.089	0.902	1.558	5.928	1.505	26.5
4.985	4.104	7.778	0.446	1.525	8.933	1.912	26.6
mean $K = 26.5 (\pm 0.2) \times 10^2$							

TABLE 2.—EQUILIBRIUM CONSTANTS AT CONSTANT IONIC STRENGTHS

$10^3 k'_1$	$10^6 k'_2$	$10^{-2} K'$
NICKEL MALONATE		
0	1.40	2.07
0.03	1.99 \pm 0.03	3.70 \pm 0.06
0.05	2.04 \pm 0.10	4.15 \pm 0.05
0.10	2.22 \pm 0.01	5.24 \pm 0.08
0.15	2.22 \pm 0.01	6.25 \pm 0.08
0.20	2.41 \pm 0.02	6.73 \pm 0.03
NICKEL n-BUTYL MALONATE		
0	0.96 \pm 0.01	1.11 \pm 0.03
0.03	1.29 \pm 0.02	2.27 \pm 0.02
0.05	1.42 \pm 0.01	2.56 \pm 0.03
0.10	1.55 \pm 0.01	3.15 \pm 0.10
0.15	1.62 \pm 0.01	3.67 \pm 0.04
0.20	1.66 \pm 0.03	4.04 \pm 0.04

It is possible to obtain values for β and the ion-size parameter, \bar{a} , from plots of α against I for a series of \bar{a} . Such plots are shown in fig. 1 and 2 and are linear only for certain values of \bar{a} . Fig. 1 covers the range $\bar{a} = 0$ to 20 Å for nickel n-butyl

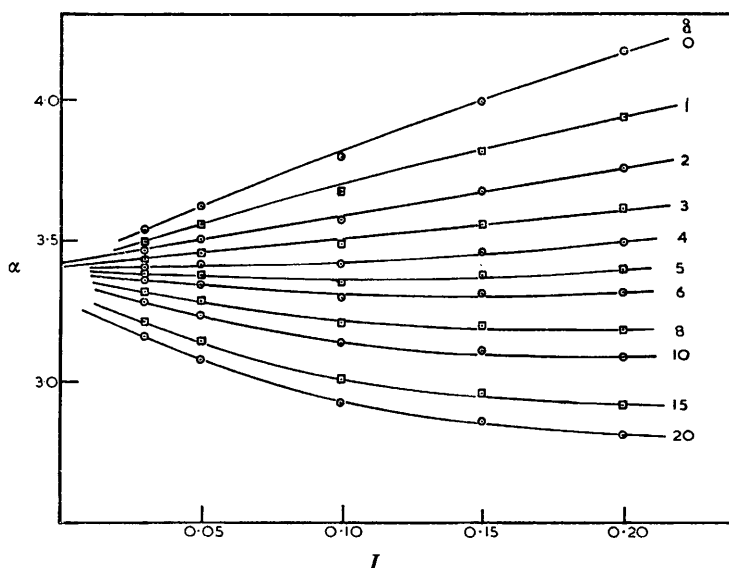


FIG. 1.—Nickel n-butyl malonate. Plots of α against I for various \bar{a} values.

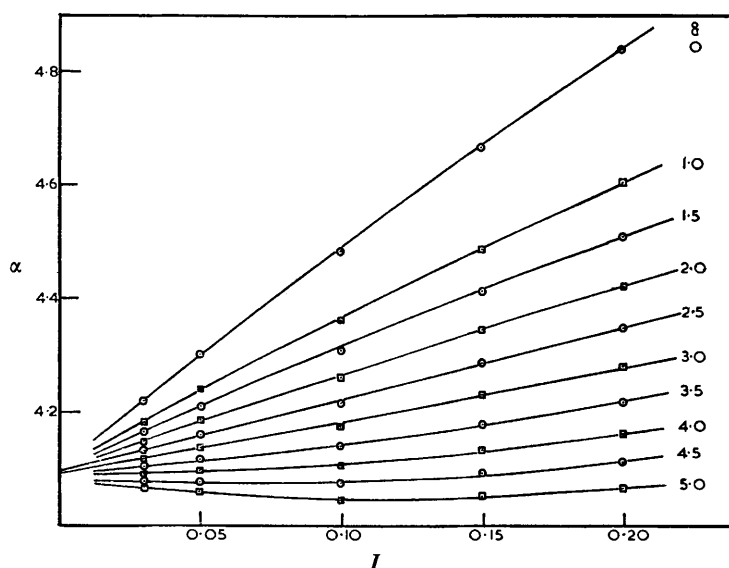


FIG. 2.—Nickel malonate. Plots of α against I for various \bar{a} values.

malonate, and fig. 2, 0 to 5 Å in steps of 0.5 Å for nickel malonate. In both systems, with $2 > \bar{a} > 3.5$, the plots are curved whereas eqn. (3) requires linearity for the correct choice of parameters; moreover, for closely similar \bar{a} values the lines should intersect on the α axis. The values obtained are for nickel malonate $\bar{a} = 2.5$

or 3.0, $\beta = 0.6$ or 0.4, and for nickel n-butyl malonate, $\bar{a} = 2.5$ or 3.0, $\beta = 0.6$ or 0.45. The close similarity suggests that the overall size of the anion is of less importance than the radius of the bonding atoms. The Davies equation corresponds to $\bar{a} = 3$ and $\beta = 0.4$. The extrapolated association constants at zero ionic strength are given in parentheses in table 2. They are in excellent agreement with the values in table 1 which were obtained using eqn. (2) for the activity coefficients of both uni- and bivalent ions.

These results provide evidence that in certain cases there is less uncertainty in the value of \bar{a} to be used in activity coefficient expressions than has hitherto been considered by some workers.⁷ Although there is always some doubt as to the exact form of the equation to be used for extrapolation purposes, for the divalent metal dicarboxylates at least, the results justify the use of the Davies equation.^{6, 8, 9}

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² Robinson and Stokes, *Electrolyte Solutions* (Butterworths, London, 1955).

³ Gelles and Nancollas, *Trans. Faraday Soc.*, 1956, **52**, 680.

⁴ Davies, *J. Chem. Soc.*, 1938, 2093.

⁵ Speakman, *J. Chem. Soc.*, 1940, 855.

⁶ Nair and Nancollas, *J. Chem. Soc.*, 1961, 4367.

⁷ Brown and Prue, *Proc. Roy. Soc. A*, 1955, **232**, 320.

⁸ McAuley and Nancollas, *J. Chem. Soc.*, 1961, 2215.

⁹ McAuley and Nancollas, *J. Chem. Soc.*, 1961, 4458.