SOME ALIPHATIC MONOCARBOXYLATE COMPLEXES OF BIVALENT METALS IN AQUEOUS SOLUTION. PART III. LEAD ACETATO COMPLEXES AND LEAD PROPIONATO COMPLEXES

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Bjerrum's method for determining the values of successive constants in step equilibria has been shown to be unsuitable in cases where the ligand is charged. Suitable modifications have been introduced to adapt Bjerrum's method in cases of charged ligand, taking into account the activity coefficients of the ions present in the solution, calculated by the application of the "Debye-Hückel limiting law" from the value of the ionic strength of the solution mixture.

The p_Hs of aqueous solution mixtures of lead acetate and nitric acid at different concentrations after attainment of equilibrium have been determined, and the data utilised to calculate the thermodynamic dissociation constants, K_1 and K_2, for the two successive equilibria,

$$PbA_2 \rightleftharpoons PbA^+ + A^- \text{ and } PbA^+ \rightleftharpoons Pb^{2+} + A^-$$

(where, A stands for acetate or propionate ion), applying Bjerrum's method modified as above. The inapplicability of the Debye-Hückel limiting law to electrolyte solutions at finite concentrations has also been properly considered, and ingenious corrections have been made in finding the value of K_1 and K_2, which are 31.2×10^{-3} and 3.31×10^{-3} at 31-34.5° respectively for lead acetate and 51.1×10^{-3} and 4.57×10^{-3} at room temperature (21-30°) for lead propionate.

A complex of the type MA_2, where M is a bivalent metal ion and A is any ligand, may dissociate in aqueous solution in two stages, viz.,

$$MA_2 \rightleftharpoons MA + A \qquad \ldots \qquad \ldots \qquad (A)$$

$$MA \rightleftharpoons M + A \qquad \ldots \qquad \ldots \qquad (B)$$

The first and second dissociation constants of lead acetate are therefore given by

$$K_1 = \frac{a_{MA} a_A}{a_{MA_2}} = k_1 \cdot \frac{f_{MA}.f_A}{f_{MA_2}} \qquad \ldots \qquad \ldots \qquad (1)$$

and

$$K_2 = \frac{a_M.a_A}{a_{MA}} = k_2 \cdot \frac{f_M.f_A}{f_{MA}} \qquad \ldots \qquad \ldots \qquad (2)$$

where k_1 and k_2 are the classical concentration constants given by·

$$k_1 = \frac{c_{MA} c_A}{c_{MA_2}} \qquad \ldots \qquad \ldots \qquad (3)$$

and

$$k_2 = \frac{c_M c_A}{c_{MA}} \qquad \ldots \qquad \ldots \qquad (4)$$

Bjerrum ("Metal Ammine Formation in Aqueous Solution", P. Haase and Son, 1941) has developed a method of evaluating the successive mass action constants in step equilibria like (A) and (B) ; the method, however, is admirably suitable in cases where the ligand 'A' is a neutral molecule like NH_3, but not at all accurate in cases where the ligand 'A' is a charged ion like CH_3COO^- or $C_2H_5COO^-$.

Bjerrum defines formation function $\bar{n}$ in any solution mixture containing MA_2 and a strong acid as the average number of ligands per M^{2+} ion given by the following expressions,

$$\bar{n} = \frac{c_{MA}{}^{2+} + 2c_{MA_2}{}^{2+}}{c_M{}^{2+} + c_{MA}{}^{2+} + c_{MA_2}{}^{2+}}$$

$$= \frac{k_1c_A + 2c_A{}^2}{k_1k_2 + k_1c_A + c_A{}^2} \qquad \cdots \qquad \cdots \qquad (5)$$

Experimentally Bjerrum prepared two or more solution mixtures with different amounts of MA_2 and a strong acid keeping the total volume constant, and then determined for every such solution mixture, using some suitable method, the "free" ligand concentration, 'x', and $\bar{n}$ from the equation,

$$\bar{n} = \frac{\text{total ligand} - \text{free ligand}}{\text{total metal}} = \frac{2C - x}{C} \qquad \cdots \qquad (6)$$

'x' being the concentration of the ligand (not attached to the metal ion) present in the solution in the base form 'A' and in the acid form 'HA' ($x = c_A + c_{HA}$). Thus obtaining the values of $\bar{n}$ and c_A for any two solution mixtures, two simultaneous equations will be obtained from equation (5), the solution of which will give the values of 'k_1' and 'k_2'.

In cases where 'A' is neutral,

$$K_1 = k_1 \frac{f_{MA}{}^{2+} \cdot f_A}{f_{MA_2}{}^{2+}} = k_1$$

for solutions of low ionic strengths, since $f_A = 1$, and "$f_M{}^{2+} = f_{MA_2}{}^{2+}$" by the Debye-Hückel limiting law.

Similarly, $\qquad K_2 = k_2 \frac{f_M{}^{2+} \cdot f_A}{f_{MA_2}{}^{2+}} = k_2.$

Evidently in such cases, the classical concentration constants and the thermodynamic constants are very nearly the same and, hence, the former can be regarded as constants, independent of the ionic strengths. Therefore equation (5), which is essentially a stoichiometric equation involving the classical constants 'k_1' and 'k_2', remains valid for two solutions of different ionic strengths *if the ligand is neutral*. Hence, the values of 'k_1' and 'k_2' can be obtained more or less accurately by solution of simultaneous equations, as indicated above.

If, however, the ligand is a charged ion like CH_3COO^- and $C_2H_5COO^-$, the thermodynamic constants, 'K_1' and 'K_2', and classical constants, 'k_1' and 'k_2', have got very different values and, in fact, 'k_1' and 'k_2' cannot be regarded as constants for different

solution mixtures of varying ionic strengths. Equation (5) cannot therefore be employed to obtain the values of 'k_1' and 'k_2' even if we know the corresponding values of $\bar{n}$ and c_A, if 'A' is a charged ligand.

There is a further objection to use equation (6) if c_A has to be determined from p_H measurements, *whether or not the ligand is charged*. Equation (6) is a stoichiometric equation and 'x' is a stoichiometric concentration term. To evaluate 'x' we need know c_{HA} and c_A, given by the expressions :

c_{HA} = H$^+$ ions used up for the formation of undissociated HA

= total H$^+$ ions initially present (*i. e.* total acid) − H$^+$ ions left at equilibrium

$$c_{HA} = C_a - c_H{}^+ \qquad \ldots \qquad \ldots \qquad (7)$$

$$c_A = K_a \cdot \frac{c_{HA} \cdot f_{HA}}{a_H{}^+ \cdot f_A} \qquad \ldots \qquad \ldots \qquad (8)$$

where K_a is the thermodynamic dissociation constant of HA. From the p_H measurements, we can find the value of $a_H{}^+$ and not $c_H{}^+$. If 'A' is neutral, $f_A = 1$ but $f_{H}{}^+$ is unknown. If, however, 'A' is a monovalent anion, $f_{HA} = 1$ since HA is neutral, but $f_A{}^-$ remains unknown. In either case, equation (8) cannot be applied to determine c_A. Bjerrum, however, has not taken these facts into consideration and has virtually put the activity coefficients equal to 1, which is not justified, even for very dilute solutions.

In the present investigation, the above method of Bjerrum has been modified to overcome the difficulties pointed out, and to make it suitable for the determination of the thermodynamic constants, 'K_1' and 'K_2', where the ligand is a charged ion. Here a new approach has been made to the problem of determining the above thermodynamic constants by noting the p_H of a set of solution mixtures, each containing in a definite volume of solution, either (*a*) a definite amount of MA$_2$ (in this case PbAc$_2$ or Pb Prop$_2$) and varying amounts of a strong acid (in this case nitric acid) or (b) a definite amount of a strong acid and varying amounts of MA$_2$, after the attainment of equilibrium. The activity coefficients of reacting ions have been calculated as follows.

In the following calculations we shall assume that the strong acid added is HNO$_3$, that the ligand is a monovalent anion A$^-$ (the ligand involved in the present case is acetate or propionate ion) and that both HNO$_3$ and M(NO$_3$)$_2$, formed by reaction between MA$_2$ and HNO$_3$ in solution, are completely dissociated.

Now, equation (7) can be written as,

$$c_{HA} = C_a - c_H{}^+ = C_a \qquad \ldots \qquad \ldots \qquad (7a)$$

since $c_H{}^+$ is negligible compared to C_a for our solution mixtures. Equation (8) then reduces to the form (8a).

$$a_A{}^- = \frac{K_a C_a}{a_H{}^+} \qquad \ldots \qquad \ldots \qquad (8a)$$

since $f_{HA} = 1$, HA being neutral. An approximate value of $\bar{n}$ can be found out from equation (6) by putting $c_A{}^- = a_A{}^-$ [$a_A{}^-$ being evaluated by equation (8a) from the

experimental p_H value]. This does not entail a serious error as long as the ionic strength of the solution is low.

Equation (5) can be reduced to the form,

$$\frac{c_A^{-2}(2-\bar{n})}{\bar{n}} = k_1 \frac{c_A^-(\bar{n}-1)}{\bar{n}} + k_1 k_2 \qquad \ldots \qquad \ldots \quad (5a)$$

Putting the value of $\bar{n}$ from (6) we have

$$c_A^{-2} \cdot \frac{x}{2C-x} = k_1 c_A^- \cdot \frac{C-x}{2C-x} + k_1 k_2 \qquad .. \quad (5b)$$

If we use solution mixtures of low ionic strengths, 'c_A^-' may be put equal to 'a_A^-' and 'k_1' and 'k_2' can be regarded as approximately constants. Now $c_A^{-2} \cdot x/(2C-x)$, if plotted on the y-axis, against $c_A^- \cdot (C-x)/(2C-x)$, on the x-axis, we get a nearly straight line curve, the slope of which is 'k_1' and the intercept on the y-axis is $k_1 k_2$. The resulting plots shown in Figs. 1 and 3 are not, in fact, good straight lines, but we can draw a straight line best fitting the points in each case. As is to be expected, some of the points (for which the ionic strength is high) fall much beyond this straight line. The values of 'k_1' and 'k_2', obtained from the slope and intercept of the curves, may be regarded as approximte average values of the two above quantities over the range of low ionic strengths used.

Now, there are two alternative methods for calculating the ionic strength 'μ' and, hence, the activity coefficients of the different ions present. The first method starts from the value of 'k_2' and the second one starts from the value of 'k_1'.

Method (a).—Since any solution mixture is electrically neutral, we have

$$2c_M^{2+} + c_{MA}^+ + c_H^+ = c_{NO_3}^- + c_A^- \qquad \ldots \qquad \ldots \quad (9)$$

or, $\quad 2c_M^{2+} + c_{MA}^+ \approx C_a + a_A^- \qquad \ldots \qquad \ldots \quad (9a)$

since $c_{NO_3}^-$ = total nitric acid concentration C_a, c_H^+ is negligible compared to other quantities on the left hand side of equation (9), and $c_A^- \approx a_A^-$.

Now, solving equation (4) and the electroneutrality equation (9a), we can get the approximate values of c_M^{2+} and c_{MA}^+, since the other quantities are known. We can now know the ionic strength 'μ' approximately from the relation (10) by inserting these values therein.

$$\mu = \tfrac{1}{2}(4c_M^{2+} + c_{MA}^+ + c_H^+ + c_{NO_3}^- + c_A^-) \approx \tfrac{1}{2}(4c_M^{2+} + c_{MA}^+ + C_a + a_A^-) \qquad \ldots \quad (10)$$

Then, since the solution mixtures used are of low ionic strengths, we can know approximate values of the activity coefficients of the ions present by application of the Debye-Hückel limiting law in the following way :

$$f_{H^+} = f_A^- = f_{MA}^+ = f_1 = \text{antilog} \, (-0.51 \sqrt{\mu}) \qquad \ldots \qquad \ldots \quad (11a)$$

and,

$$f_M^{2+} = f_2 = f_1^4 = \text{antilog} \, (-4 \times 0.51 \sqrt{\mu}) \qquad \ldots \qquad \ldots \quad (11b)$$

(0.51 being the Debye-Hückel constant at the temperature of the experiment).

Method (b).—By inserting the relation (12),

$$C = c_{MA_2} + c_{MA}^+ + c_M^{2+} \qquad \ldots \qquad \ldots \qquad \ldots \quad (12)$$

in the electro-neutrality equation (9a), we get (9b).

$$2C \approx 2c_{M_{12}} + c_{M^+} + C_A + a_{A^-} \qquad \dots \qquad \dots \quad (9b)$$

Solving (3) and (9b), we can get $c_{M_{12}}$ and c_{M^+} and then we can get $c_M{}^{2+}$, using relation (12). Using these values of c_{M^+} and $c_{M_A^+}$, we can calculate the ionic strength 'μ' from equation (10) and, hence, 'f_1' and 'f_2' by equations (11a) and (11b).

By comparing the values for the first twelve solutions (No. 1 to 12) in the case of lead acetate in Table II, it will be observed that the corresponding values of c_{M^+} and c_{M^+}, calculated by two independent methods (a) and (b), fairly agree with each other, differing mostly in the second significant figure. The last two values of c_{M^+} for solution numbers 11 and 12, calculated by method (b) in Table II, are, however, inaccurate because as ($c_{M_{12}} + c_{M^+}$) approaches C, the difference c_{M^+} (vide equation 12) would involve comparatively large error, the values of c_{M^+} and $c_{M_{12}}$ being rather erroneous.

By comparing the corresponding values of c_{M^+} and $c_{M_A^+}$ for the last seventeen solutions (No. 13 to 29) in Table II, we, however, find that there is no such good agreement as in the case of the first twelve solutions. But in any case we are interested in knowing the values of c_{M^+} and $c_{M_A^+}$ only to calculate 'μ', 'f_1' and 'f_2'. In spite of the disagreement, mentioned above, it will be seen that both the methods, (a) and (b), yield quite concordant values of 'μ'. The values of 'f_1' and 'f_2', calculated from these values of 'μ' by equations (11a) and (11b), will therefore also be concordant. We may add that accurate values of 'c_{A^-}', recalculated from equation (8b), are practically identical in both methods (vide Table II) :

$$c_{A^-} = \frac{K_a C_a}{a_{H^+} f_1} \qquad \dots \qquad \dots \qquad .. \quad (8b)$$

The values of 'c_{A^-}', 'f_1' and 'f_2' alone are required in the subsequent calculations, and the concordance of these in the two independent methods of calculation is a sufficient guarantee for the accuracy of later evaluations.

It will be seen from Table IV, that the agreement between the corresponding values of $c_{Pb^{2+}}$ and $c_{PbProp.^+}$, calculated by the two different methods (a) and (b), is quite satisfactory in all cases, excepting in a few, where there is a little difference in the second significant figure. Nevertheless, the values of 'μ', 'f_1' and 'f_2', calculated from the data in both tables, are satisfactorily concordant, and the recalculated value of 'c_{A^-}' are almost identical.

After determining a more accurate value of 'c_{A^-}' from (8b), we can find out more accurate value of 'x' ($x = c_{A^-} + c_{HA} = c_{A^-} + C_a$). Equation (5b) is an accurate relation for every solution mixture, though 'k_1' and 'k_2' may not be constants for different solution mixtures. Inserting (1) and (2) in (5b) we have

$$c_{A^-}{}^2 \frac{x}{2C - x} \cdot f_1{}^2 f_2 = K_1 c_{A^-} \cdot \frac{C - x}{2C - x} \cdot f_2 + K_1 K_2 \ .$$

or $$Y = K_1 X + K_1 K_2 \qquad \dots \qquad \dots \qquad \dots \quad (5c)$$

where, $$Y = c_{A-}{}^{2} \cdot \frac{x}{2C - x} f_1{}^2 f_2 \text{ and } X = c_{A-} \cdot \frac{C - x}{2C - x} f_2.$$

The terms 'K_1' and 'K_2' in (5c) are real thermodynamic constants, and therefore the plot of 'Y' on the y-axis and 'X' on the x-axis, using the more accurate values of 'x' and 'c_{A-}', should give a straight line curve, the slope of which gives the value of 'K_1' and the intercept of the y-axis that of "K_1K_2".

EXPERIMENTAL

Stock solutions of lead acetate (A.R.), lead propionate (prepared as given below) and nitric acid (A.R.) were prepared, in which lead was determined gravimetrically as lead sulphate and the acid by titration with a standard alkali solution. All solutions and dilutions were made with conductivity water.

Lead propionate was prepared by digesting finely powdered litharge in propionic acid (distilled and collected at 141°) on a water-bath. The resulting syrupy liquid on cooling gave a sticky white solid mass, which changed to white flakes on repeated extraction with anhydrous ether, when the excess propionic acid went in the ether layer. It was dried in vacuum and analysed. [Found: Pb (as sulphate), 59.15. Calc. for Pb $(C_2H_5COO)_2$: Pb, 58.66%].

In preparing solution mixtures in these experiments such volumes of parent stock solutions were accurately measured, which on dilution to 10 c.c. gave the desired initial molar concentration C for lead acetate or lead propionate and C_a' for nitric acid. After keeping the mixtures in a closed room for 3 hours, the p_H values were determined, using equation (13) from the E.M.F. (E) values at room temperature ($t°$) measured by a Leeds and Northrup K_2-type potentiometer. $0.1N$ Calomel and quinhydrone electrodes, bridged by saturated KCl solution, were used in all p_H determinations of lead acetate solution mixtures.

$$p_H = \frac{0.3625 - 0.00068 (t - 25) - E}{0.0591 + 0.0002 (t - 25)} \qquad \dots \qquad \dots \quad (13a)$$

Saturated calomel and quinhydrone electrodes bridged by saturated KCl solution were used in all p_H determinations of lead propionate solution mixtures.

$$p_H = \frac{0.4552 - 0.00009 (t - 25) - E}{0.0591 + 0.0002 (t - 25)} \qquad \dots \qquad \dots \quad (13b)$$

(Kohlhoff and Laitinen, "p_H and Electrotitration", John Wiley, 2nd ed., p. 92).

The E.M.F. reading for each solution was repeated in duplicate in all cases, and in many cases in triplicate, using each time a solution mixture independently prepared from the same stock solutions, or sometimes from different stock solutions, and in all cases the readings gave p_H values agreeing within $\pm$ 0.01 p_H units.

TABLE I

Soln. No.	C.	C_a.	$t°$.	p_H.	$a_A- \times 10^3$. (Eq. 8a) ($K_a = 1.80 \times 10^{-5}$).	$*a_A - . \dfrac{C-x}{2C-x} \times 10^3$.	$*a_A^{-1} . \dfrac{x}{2C-x} \times 10^3$.
1	0.01	0.015	34.5	3.60	1.08	-1.67	0.0048
2	0.0125	,,	31.8	3.86	1.96	-1.08	0.0213
3	0.015	,,	34.5	4.06	3.10	-0.80	0.0146
4	0.020	,,	,,	4.28	5.15	-0.039	0.0269
5	0.022	,,	,,	4.36	6.19	$+0.222$	0.0356
6	0.025	,,	,,	4.43	7.34	$+0.706$	0.0430
7	0.044	,,	,,	4.68	12.92	$+3.453$	0.0776
8	0.066	,,	,,	4.83	18.26	$+6.053$	0.1123
9	0.088	,,	,,	4.92	22.47	$+8.196$	0.1365
10	0.110	,,	,,	4.99	26.40	$+10.14$	0.1615
11	0.132	,,	,,	5.02	28.28	$+11.37$	0.1567
12	0.154	,,	,,	5.07	31.74	$+13.04$	0.1803
13	0.01	0.0012	32.4	5.51	6.99	$+1.071$	0.0339
14	,,	0.003	31.0	5.08	6.492	$+0.315$	0.0385
15	,,	0.005	,,	4.80	5.68	-0.41	0.0370
16	,,	0.007	,,	4.57	4.68	-0.94	0.0307
17	,,	0.009	,,	4.37	3.80	-1.48	0.0257
18	,,	0.011	,,	4.22	3.28	-2.47	0.0269
19	,,	0.013	,,	3.98	2.23	-2.45	0.0159
20	,,	0.015	,,	3.79	1.66	-3.32	0.0137
21	0.1	0.006	,,	5.43	29.10	$+11.45$	0.181
22	,,	0.008	,,	5.32	30.06	$+11.48$	0.214
23	,,	0.010	33.2	5.19	27.87	$+10.68$	0.181
24	,,	0.012	,,	5.13	29.15	$+10.80$	0.220
25	,,	0.014	,,	5.06	28.92	$+10.51$	0.2285
26	,,	0.015	32.2	5.02	28.27	$+10.23$	0.221
27	,,	0.030	,,	4.66	24.68	$+7.70$	0.229
28	,,	0.045	,,	4.39	19.88	$+5.17$	0.190
29	,,	0.060	,,	4.19	16.72	$+3.16$	0.174

* 'x' has been calculated from relation $x = a_A - + C_a$.

'C' and 'C_a' denote respectively the molar concentration of PbAc$_2$ and of HNO$_3$.

TABLE II

Solution No. (as per Table I)	Method of calculation.	$c_{MA^+} \times 10^3$.	$c_{M^{2+}} \times 10^3$.	'μ'.	$*c_{A^-} \times 10^3$. (Eq. 8b)	$\dagger Y \times 10^3$.	$\dagger Y \times 10^3$.
1	(a)	3.16	6.46	0.02254	1.24	−0.05674	0.00213
	(b)	3.36	6.36	0.02244	1.24	−1.018	0.00231
2	(a)	5.23	5.86	0.01281	2.27	−0.6952	0.00399
	(b)	6.19	5.39	0.02235	2.26	−0.688	0.00397
3	(a)	7.48	5.31	0.02341	3.61	−0.5556	0.00724
	(b)	8.09	5.01	0.02312	3.60	−0.5564	0.00724
4	(a)	10.87	4.64	0.02479	6.02	−0.1512	0.01321
	(b)	11.14	4.51	0 02466	6.01	−0 1530	0.01321
5	(a)	12.39	4.45	0.02559	7.26	−0 0473	0.01751
	(b)	11.77	4 71	0.02590	7.26	−0.0408	0.01736
6	(a)	13.97	4.18	0.02651	8.63	+0.2130	0.02115
	(b)	13.09	4.63	0.02697	8 64	+0.2060	0 02105
7	(a)	20.83	3 54	0.03145	15.48	+1.582	0.03654
	(b)	20.31	3.81	0.03173	15.48	+1.576	0.03621
8	(a)	26.80	3.23	0.03649	22.21	+2.750	0.05036
	(b)	26.21	3.53	0.03679	22.22	+2.740	0.05025
9	(a)	31.33	3.07	0 04054	27.66	+3.658	0.0595
	(b)	31.45	3.01	0 04048	27.65	+3.655	0 0592
10	(a)	35.49	2.95	0.04434	32.85	+4.413	0.0683
	(b)	35.71	2.85	0.04425	32.85	+4.416	0.0681
11	(a)	37.45	2.91	0.04618	35.38	+4.928	0.0650
	(b)	41.76	0.76	0.04404	35.17	+5.021	0.06612
12	(a)	41.05	2.84	0.04957	40.07	+5 510	0.07295
	(b)	44.97	0 89	0.04763	39.85	+5 598	0.07392
13	(a)	5.03	1.58	0.00977	7.63	+0.502	0.0229
	(b)	5.73	1.23	0.00942	7.61	+0.51?	0.02301
14	(a)	5.66	1.91	0.01139	7.15	−0.0885	0.0252
14	(b)	5.29	2.10	0.01159	7.61	−0.0702	0.0247
15	(a)	6.02	2.33	0.01301	6.31	−0.536	0.0219
	(b)	5.00	2.84	0.01352	6.33	−0.562	0.02308
16	(a)	6.02	2.83	0.01451	5.24	−0.839	0.0184
	(b)	4.86	3.41	0.01509	5.24	−0.849	0.0182
17	(a)	5 93	3.43	0.01622	4.29	−1.161	0.0149
	(b)	4.56	4.12	0.01692	4.30	−1.149	0.0146
18	(a)	6.10	4.09	0.01837	3.75	−1.831	0.0154
	(b)	3.82	5.23	0.01951	3.76	−1.772	0.0149
19	(a)	5.12	5.05	0.02027	2.57	−1.674	0.00858
	(b)	3.56	5.84	0.02107	2.57	−1.634	0.00835
20	(a)	4.56	6.05	0.02271	1.93	−2.116	0.00702
	(b)	2.66	7.00	0.02366	1.94	−2.136	0.00705
21	(a)	30.48	2.31	0.03741	35.50	+5.283	0.0845
	(b)	30.48	2.31	0.03741	35.40	+5.273	0.0838
22	(a)	33.20	2.43	0.04049	37.00	+5.103	0.0963
	(b)	29.15	4.46	0.04252	37.24	+5.001	0.0948
23	(a)	32.71	2.58	0.04045	34.30	+4.772	0.0812
	(b)	31.04	3.42	0.04129	34.39	+4.731	0.0805
24	(a)	35.75	2.70	0.04385	36.30	+4.626	0.0960
	(b)	29.32	5.92	0.04707	36.46	+4.47½	0.0921
25	(a)	37.25	2.83	0.04574	36.20	+4.405	0.0973
	(b)	29.18	6.87	0.04979	36.55	+4.239	0.0938
26	(a)	37.44	2.91	0.04617	35.40	+4.276	0.0929
	(b)	29.66	6.81	0.05008	35.70	+4.121	0.0894
27	(a)	46.41	4.13	0.05880	31.90	+2.817	0.0826
	(b)	30.66	12.01	0.06669	32.40	+2.632	0.0771

TABLE II (contd.)

Solution No.	Method of calculation.	$c_{MA}+ \times 10^3$.	$c_{M^{2+}} \times 10^3$.	'μ'	$c_A- \times 10^3$..	X × 10³.	Y × 10³.
28	(a)	53.12	5.88	0.07076	26.40	+1.683	0.0593
	(b)	33.67	15.61	0.08049	26.97	+1.557	0.0553
29	(a)	60.74	7.99	0.08471	22.90	+0.852	0.0478
	(b)	34.89	20.92	0.09764	23.40	+0.767	0.0433

* K_a = 1.75 × 10⁻⁵ (Harned and Owen, "The Physical Chemistry of Electrolytic Solutions", 2nd ed., p. 580).

† 'X' represents $c_A- \cdot \dfrac{C-x}{2C-x} f_1$ and 'Y' represents $c_A-^2 \dfrac{x}{2C-x} f^2 f_2$ where, 'f_1' and 'f_2' are calculated from the value of 'μ' by equations (11a) and (11b) and $x = c_A- + C_a$.

TABLE III

Soln. No.	*C.	*Ca.	t°.	p_H.	$a_A- \times 10^3$ (Eq. 8a) (K_a =1.35×10⁻⁵).	$a_A- \dfrac{C-x}{2C-x} \times 10^3$	$a_A-^2 \dfrac{x}{2C-x} \times 10^3$
1	0.006	0.010	22.0	3.733	0.72	−2.23	0.0037
2	0.007	,,	,,	4.043	1.48	−2.49	0.0095
3	0.008	,,	,,	4.183	2.06	−2.12	0.0129
4	0.009	,,	,,	4.323	2.84	−2.11	0.0200
5	0.010	,,	22.7	4.445	3.76	−2.27	0.0312
6	0.015	,,	,,	4.712	6.96	−1.04	0.0629
7	0.020	,,	,,	4.858	9.73	+0.13	0.0921
8	0.030	,,	,,	5.05	15.15	+2.10	0.1656
9	0.040	,,	,,	5.13	18.22	+4.14	0.1810
10	0.050	,,	,,	5.22	22.39	+5.83	0.2401
11	0.055	,,	,,	5.25	24.02	+6.63	0.2583
12	0.060	,,	,,	5.27	25.14	+7.36	0.2617
13	0.065	,,	,,	5.29	26.32	+8.05	0.2685
14	0.070	,,	22.7	5.30	26.94	+8.64	0.2601
15	0.075	,,	,,	5.33	28.85	+9.38	0.2909
16	0.080	,,	,,	5.35	30.20	+10.03	0.3060
17	0.085	,,	,,	5.36	30.96	+10.56	0.3042
18	0.090	,,	,,	5.38	32.38	+11.20	0.3228
19	0.01	0.0015	22.0	5.59	7.88	+0.46	0.0548
20	0.01	0.0025	,,	5.34	7.35	+0.10	0.0530
21	0.01	0.0035	,,	5.17	6.99	−0.36	0.0538
22	,,	0.0045	,,	5.02	5.05	−0.47	0.0303
23	,,	0.0050	22.7	4.928	5.72	−0.45	0.0378
24	,,	0.010	,,	4.432	3.65	−2.10	0.0286
25	,,	0.011	21.6	4.346	3.29	−2.49	0.0272
26	,,	0.012	,,	4.193	2.53	−2.09	0.0170
27	,,	0.013	,,	4.130	2.37	−2.75	0.0186
28	,,	0.014	,,	4.022	1.98	−2.83	0.0.52
29	,,	0.015	22.7	3.887	1.54	−2.77	0.0180
30	0.04	0.003	21.0	5.70	20.34	+5.97	0.1705
31	,,	0.004	,,	5.59	21.01	+6.81	0.2007
32	,,	0.005	,,	5.49	20.84	+5.45	0.2070
33	,,	0.006	,,	5.40	20.35	+5.17	0.2033
34	,,	0.007	,,	5.33	20.19	+4.89	0.2099
35	,,	0.008	,,	5.26	19.67	+4.63	0.2045

* C denotes molar conc. of Pb(prop)₂ and C_a, that of HNO_3.

TABLE IV

The symbols used in the table headings and their evaluations are same as in Table II.

Soln. No. (as per Table.III)	Method of calculation.	$c_{MA}+ \times 10^3$	$c_{M^{2+}} \times 10^3$	'μ'	$*c_{A^-} \times 10^3$ (Eq. 8b)	$X \times 10^3$	$Y \times 10^3$
1	(a)	1.05	4.83	0.01554	0.83	−1.907	0.00265
	(b)	1.20	4.76	0.01548	0.83	−1.910	0.00265
2	(a)	2.10	4.69	0.01627	1.70	−1.911	0.00590
	(b)	2.23	4.63	0.01612	1.70	−1.909	0.00559
3	(a)	2.86	4.60	0.01666	2.35	−1.527	0.00752
	(b)	3.35	4.36	0.01642	2.35	−1.533	0.00757
4	(a)	3.86	4.49	0.01733	3.26	−1.578	0.01176
	(b)	4.15	4.35	0.01719	3.26	−1.583	0.01180
5	(a)	4.99	4.38	0.01813	4.33	−1.757	0.01835
	(b)	4.73	4.52	0.01838	4.34	−1.763	0.01841
6	(a)	8.71	4.12	0.02107	8.12	−1.078	0.03617
	(b)	8.20	4.38	0.02134	8.13	−1.079	0.03608
7	(a)	11.75	3.99	0.02372	11.48	−0.445	0.05166
	(b)	11.10	4.32	0.02405	11.50	−0.449	0.05152
8	(a)	17.58	3.83	0.02902	18.24	+0.453	0.08904
	(b)	15.25	4.95	0.03010	18.30	+0.434	0.08802
9	(a)	20.71	3.75	0.03196	22.12	+1.571	0.09310
	(b)	20.35	3.94	0.03216	22.15	+1.564	0.0931
10	(a)	25.01	3.69	0.03608	27.59	+2.248	0.1202
	(b)	23.33	4.53	0.03692	27.63	+2.221	0.1189
11	(a)	26.68	3.67	0.03769	29.75	+2.594	0.1275
	(b)	25.02	4.50	0.03852	29.80	+2.566	0.1262
12	(a)	27.83	3.65	0.03778	31.22	+2.951	0.1273
	(b)	27.10	4.02	0.03916	31.24	+2.938	0.1268
13	(a)	29.03	3.64	0.03995	32.75	+3.267	0.1285
	(b)	28.99	3.67	0.03999	32.78	+3.267	0.1289
14	(a)	29.67	3.63	0.04056	33.67	+3.576	0.1244
	(b)	31.39	2.78	0.03972	33.54	+3.608	0.1247
15	(a)	31.61	3.62	0.04247	36.23	+3.814	0.1368
	(b)	32.26	3.30	0.04215	36.16	+3.829	0.1368
16	(a)	32.98	3.61	0.04381	38.00	+4.061	0.1416
	(b)	33.65	3.28	0.04348	38.00	+4.079	0.1425
17	(a)	33.76	3.60	0.04456	39.11	+4.307	0.1403
	(b)	35.60	2.68	0.04364	38.39	+4.350	0.1412
18	(a)	35.31	3.58	0.04595	41.05	+4.531	0.1472
	(b)	36.75	2.82	0.04520	40.93	+4.564	0.1478
19	(a)	5.10	2.14	0.01152	8.78	−0.152	0.0383
	(b)	6.36	1.51	0.01089	8.77	−0.149	0.0389
20	(a)	5.21	2.33	0.01220	8.29	−0.427	0.0369
	(b)	6.22	1.83	0.01171	8.26	−0.408	0.0370
21	(a)	5.39	2.55	0.01304	7.87	−0.730	0.0365
	(b)	5.97	2.26	0.01325	7.86	−0.727	0.0366
22	(a)	4.14	2.76	0.01224	7.14	−0.832	0.0325
	(b)	7.31	1.12	0.01067	7.24	−0.810	0.0331

TABLE IV (contd.)

Soln. No.	Method.	$c_{MA^+} \times 10^3$.	c_M^{2+}.	$_r\mu$.	$*c_A^- \times 10^3$.	$X \times 10^5$.	$Y \times 10^3$.
23	(a)	4.98	2.87	0.01359	6.46	−0.638	0.0246
	(b)	6.25	2.24	0.01296	6.44	−0.634	0.0280
24	(a)	4.86	4.39	0.01803	4.21	−1.628	0.0168
	(b)	4.85	4.40	0.01805	4.21	−1.628	0.0168
25	(a)	4.75	4.77	0.01906	3.81	−1.846	0.0157
	(b)	4.47	4.91	0.01920	3.81	−1.841	0.0155
25	(a)	4.02	5.25	0.01977	2.93	−1.471	0.00937
	(b)	4.50	5.02	0.01955	2.93	−1.477	0.00944
27	(a)	4.06	5.65	0.02101	2.77	−1.913	0.0103
	(b)	3.85	5.76	0.02113	2.76	−1.894	0.0101
28	(a)	3.68	6.15	0.02213	2.33	−1.998	0.00846
	(b)	3.44	6.27	0.02225	2.33	−1.994	0.00844
29	(a)	3.13	6.70	0.02323	1.83	−1.841	0.00585
	(b)	3.06	6.74	0.02328	1.83	−1.925	0.00606
30	(a)	17.61	2.86	0.02620	24.18	+2.74	0.0951
	(b)	20.80	1.27	0.02461	24.10	+2.81	0.0985
31	(a)	19.03	2.99	0.02800	25.21	+2.44	0.1124
	(b)	19.77	2.62	0.02763	25.16	+2.45	0.1225
32	(a)	19.62	3.11	0.02895	25.09	+2.24	0.1145
	(b)	19.58	3.13	0.02897	25.06	+2.24	0.1139
33	(a)	19.89	3.23	0.92958	24.55	+2.09	0.0905
	(b)	19.69	3.33	0.02963	24 54	+2.09	0.1105
34	(a)	20.49	3.35	0.03054	24.37	+1.90	0.1123
	(b)	19.47	3.86	0.03105	24.46	+1.88	0.1190
35	(a)	20.71	3.48	0.03115	23.85	+1.76	0.1084
	(b)	19.62	4.03	0.03170	23.88	+1.74	0.1078

* Using $K_a = 1.33 \times 10^{-5}$ (Harned and Owen, "Physical Chemistry of Electrolytic Solutions", 2nd ed., p. 580).

Tables I and III show for lead acetate and lead propionate solution mixtures respectively the experimentally determined p_H values of the functions

$$a_{A^-}. \frac{C-x}{2C-x} \times 10^3 \qquad \text{and} \qquad a_{A^-}^{-2}. \frac{x}{2C-x} \times 10^3,$$

so that equation (5b) can be represented graphically; this has been done in Fig. 1 for lead acetate solution mixtures, in which the circles represent data from Table I for the first 12 solution mixtures (No. 1 to 12) in which 'C_a' is constant and 'C' varying, and the triangles represent those for the last seventeen solution mixtures (No. 13 to 29) in which 'C' is constant and 'C_a' varying. A straight line, best fitting the majority of the points, has been drawn, and the values of 'k_1' and 'k_2' have been calculated from the slope and the intercept of this straight line, as already explained. These values are $k_1 = 13.20 \times 10^{-3}$ and $k_2 = 2.20 \times 10^{-3}$. It will be seen that some of the triangular points fall much beyond the straight line, drawn in Fig. 1. The points which spread themselves over a rather wide region in the first graph (Fig. 1), will all be observed to fall practically on a single straight line in Figs. 2A and 2B, in which data corrected from a consideration of ionic strengths have been used.
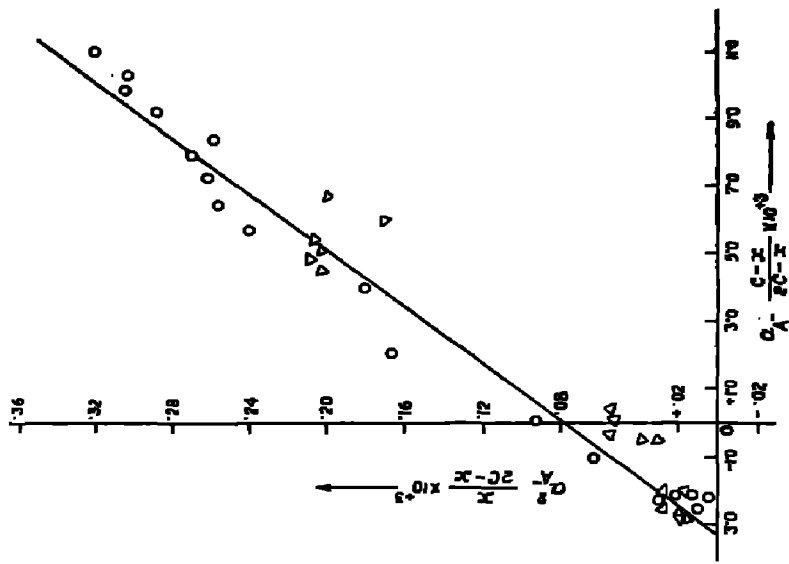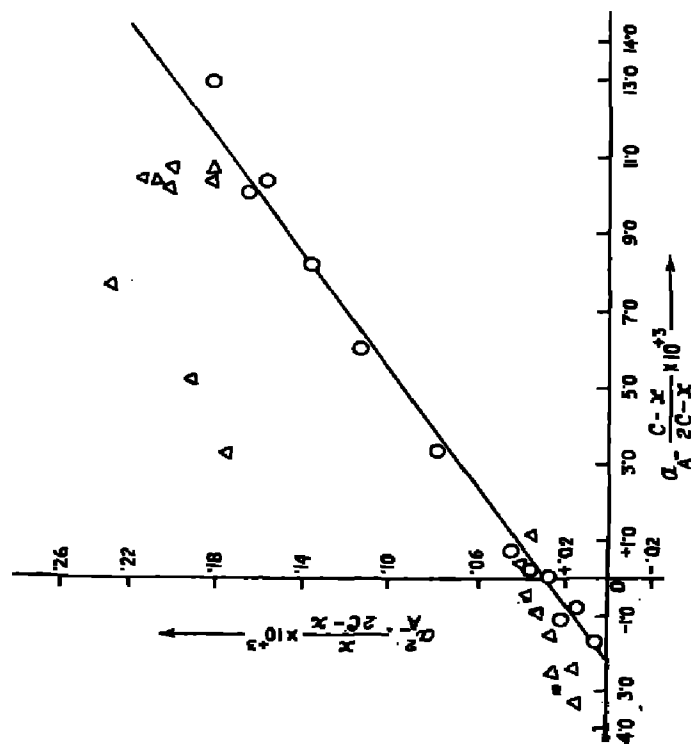
FIG. 3

FIG. 1

(Ordinate has been magnified 50 times as compared to abscissa).

Equation (5b) has been represented graphically in the case of lead propionate solution mixtures in Fig. 3, using data from Table III. Here the circles represent data for the solution mixtures from No. 1 to No. 18 (Table III) in which C_a is constant and C varying, and triangles represent those for the mixtures from No. 19 to No. 35 (Table III) where 'C' is constant and C_a varies. The slope and intercept on the ordinate of the straight line curve obtained, give the values of k_1 and k_2 as $k_1 = 23.6 \times 10^{-3}$ and $k_2 = 3.30 \times 10^{-3}$. These values may be regarded as the average values of these quantities over the range of ionic strengths employed. The first six triangular points have fallen much beyond the best fitting straight line, but it will be seen later that after making necessary corrections from a consideration of the activity coefficients of the ions, even these points come very close to the mean straight line representing equation (5c).

Table II shows the values of 'μ', 'X' and 'Y' for lead acetate solution mixtures calculated by both methods (a) and (b). 'Y' and 'X', calculated by method (a), have been plotted in Fig. 2A and those calculated by method (b) in Fig. 2B. The circles and triangles in Figs. 2A and 2B refer to solution No. 1 to 12 and 13 to 29 respectively (Table I) as in the case of Fig. 1. It will be seen that in both the plots 2A and 2B, the triangles lie in a straight line, almost parallel to another, passing through the circles, the two straight lines being very near to each other. These two straight lines should theoretically coincide, but as the values of 'μ', 'f_1' and 'f_2' used are not quite accurate, the straight lines are separated a little from each other ; it must, however, be pointed out that in the graphs 2A and 2B the ordinate has been magnified one hundred times as compared to the abscissa, and this also magnifies the separation between the two straight lines. If, however, we draw a mean straight line in between the two sets of points, this will fit in both sets of data better and obviously, the slope

FIG. 2B   FIG. 2A

$X \rightarrow$ $X \rightarrow$

(The ordinate magnified 100 times of abscissa).
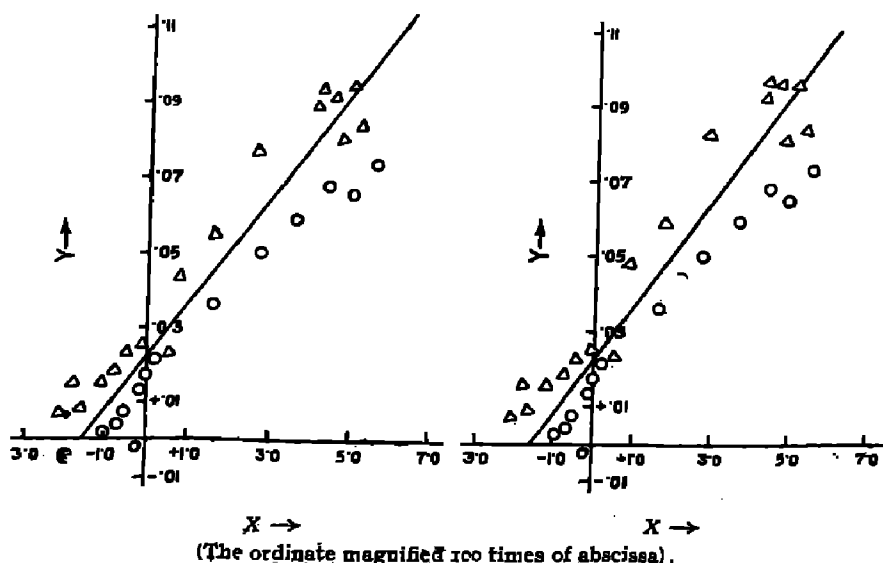
of this mean straight line more correctly represents 'K_2' and its intercept on the y-axis gives K_1K_2 more accurately than any of the two individual straight lines.

The values of 'K_1' and K_2', thus obtained from the mean straight line in Fig. 2A, and those obtained from the mean straight line in Fig. 2B, have been found to be identical, viz., $K_1 = 14.6 \times 10^{-3}$ and $K_2 = 1.55 \times 10^{-3}$, in both cases ; these are not, however, the final values (vide Discussion). The values of 'μ', 'X' and 'Y' for lead propionate solution mixtures recorded in Table IV, calculated by methods (a) and (b), are plotted in Figs. 4A and 4B respectively. The circles in the plot refer to solutions No. 1 to 18 (Table III) and the triangles to solutions No. 19 to 35 (Table III) as in Fig. 3.

FIG. 4B

FIG. 4A
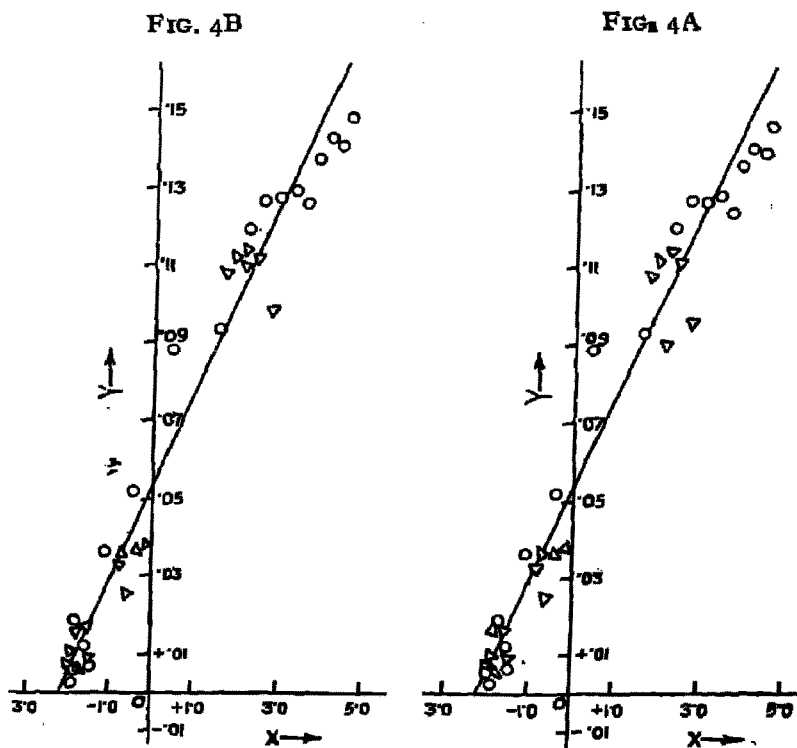
.(The ordinate magnified 100 times of abscissa).

It will be seen that the points, which spread themselves over a rather wider region in Fig. 3, all condense into a very narrow strip on the two sides of the mean straight line in Figs. 4A and 4B, even though the scale of the ordinate has been doubled in the latter case. The distance of the individual points from the mean straight line in the Figs. 4A and 4B will not appear to be unduly large, if we consider that the ordinate is hundred times magnified compared to the abscissa. It will be seen by comparison that the straight line curves in Figs. 4A and 4B are identical in slope, and both cut the y-axis at the same point. So these two straight lines are identical, and evidently both the curves will give

identical values of K_1 and K_2. The values of the thermodynamic dissociation constants obtained from the graphs are $K_1 = 24.6 \times 10^{-3}$ and $K_2 = 2.20 \times 10^{-3}$ These are not, however, the final values (*vide infra*).

DISCUSSION

The values of 'K_1' and 'K_2', obtained in the above way, however, are not independent of ionic strengths, since 'f_1' and 'f_2', calculated from the Debye-Hückel limiting law, are erroneous due to the inapplicability of the law itself in the cases of solutions with even moderately low ionic strength. The values of 'K_1' and 'K_2', obtained graphically taking data from a series of solution mixtures with different ionic strengths, as done here, can be regarded as containing a mean error corresponding to a mean ionic strength taken over the range of ionic strengths used. This can be substantiated in the following way.

The value of 'K_2', obtained here in the case of PbAc$^+$ complex, is 1.55×10^{-3} and therefore $pK_2 = 2.8097$. The mean value of 'μ', obtained from its values calculated by method (b) in Table II, is 0.03521 and therefore $\sqrt{\mu}_{\text{mean}} = 0.1876$. The plot of $pK_2 = 2.8097$ against $\sqrt{\mu}_{\text{mean}} = 0.1876$, is a point on the straight line curve representing $pK / \sqrt{\mu}$-plot in Part I of this paper (this *Journal*, 1958, 35, 276; Fig. 3). In that figure the point so plotted has been shown by the mark ⊙.* If μ_{mean} is taken from the values of 'μ' calculated by method (a) in Table II, then also we get a nearly identical point which has not been shown in the graph.

In the case of PbProp$^+$ complex, the value of K_2 obtained here is 2.20×10^{-3}, pK_2 being therefore equal to 2.6576 and $\sqrt{\mu}_{\text{mean}} = 0.1617$, obtained from the value of 'μ' recorded in Table IV; if this value of pK_2 is plotted against the above corresponding value of $\sqrt{\mu}_{\text{mean}}$ on the $pK_2 / \sqrt{\mu}_{\text{mean}}$ plot, shown in Fig. 2 in Part II of this paper (this *Journal*, 1958, 35, 282), the point will be seen to fall on the straight line curve representing $pK_2 / \sqrt{\mu}$ obtained from the data in Part II of this series (vide Fig. 2, Part II where the point under reference has been shown by ⊙ mark).*

It is quite obvious that the method of determining 'K_2' as described in Part I, is theoretically more sound and gives a more accurate value compared to the method described in Part III, since in the former method extrapolation to "$\sqrt{\mu} = 0$" is possible.

The method described in Part I for lead acetate and in Part II for lead propionate is incapable of giving the value of 'K_1', and the value of 'K_1', obtained by the method in Part III, is somewhat erroneous, as has already been indicated. A more accurate value of 'K_1' can, however be determined indirectly as follows, Though the individual values of 'K_1' and 'K_2' obtained in Part III are rather incorrect, it is expected that the ratio K_1/K_2, calculated from these values, are materially correct, as the same relative error occurs in both and comes from the same source, viz. the inapplicability of the Debye-Hückel limiting law to solutions with finite ionic strengths. Now, from this ratio K_1/K_2 and the correct value of 'K_2' from Part I, in the case of PbAc$^+$ complex and from Part II in the case of

*As the type signifying solar mark used by the authors is not available, the present sign has been used instead. Ed.

PbProp⁺ complex, we can find an accurate value of 'K_1' in either case. The values of 'K_1', obtained in this way, and those of 'K_2', found in Parts I and II, are given below together with the values obtained by previous workers by other methods, for comparison.

<div align="center">TABLE V</div>

Authors.	K_1.	K_2.	Reference.
	For PbAc₂ .		
Present	31.2×10^{-3} at $31.0 - 34.5°$	3.31×10^{-3} at $31.0 - 34.5°$	...
Aditya and Prasad	30.0×10^{-3}	3.7×10^{-3}	This *Journal*, 1953, **30**, 213.
Purkayastha and Sen Sarma	...	40.76×10^{-3} at $30°$	*Ibid.*, 1946, **23**, 31.
Edmond and Birnbaum	...	9.65×10^{-3} at $25°$ (mean value worked out from several values given)	*J. Amer. Chem. Soc.*, 1910, **62**, 2367.
Shin Suzuki	$K_1 K_2 = 2.1 \times 10^{-6}$ at $25°$		*J. Chem. Soc.*, Japan, Pure Chem. Sec., 1953, **74**, 531.
	For PbProp₂.		
Present	51.1×10^{-3} at room temp. (21-30°)	4.57×10^{-3} at room temp. (21-30°)	
Mohanty and Aditya	3.1×10^{-2} at $35°$	2.2×10^{-3} at $35°$	This *Journal*, 1955, **32**, 234.

The values of 'K_1' and 'K_2' for PbAc₂, obtained by the present authors, accord fairly well with those obtained by Aditya and Prasad by an independent and theoretically sound method. The values of 'K_2', obtained by Purkayastha and Sen Sarma and by Edmund and Birnbaum, are in our opinion erroneous for reasons already discussed in Part I of this paper. Shin Suzuki has determined the value of the constant for the equilibrium,

$$Pb^{2+} + 2HAc \rightleftharpoons PbAc_2 + 2H^+$$

to be 1.45×10^{-4} at $25°$. Dividing this by K_a^2, where K_a is the ionisation constant of acetic acid, we can have the value of $K_1 K_2$, the overall constant for the equilibrium $PbAc_2 \rightleftharpoons Pb^{2+} + 2Ac^-$, which comes out to be 2.1×10^{-6}, shown above as against our value, $K_1 K_2 = 1.07 \times 10^{-4}$. Shin Suzuki, however, has overlooked the intermediate step $Pb^{2+} + HAc \rightleftharpoons PbAc^+ + H^+$ and, hence, in our opinion his value is not dependable.

Mohanty and Aditya (*loc. cit.*) have determined the thermodynamic dissociation constants K_1 and K_2 of lead propionate in aqueous solution by the measurement of solubility of lead iodate in sodium propionate solution and, also by the measurement of E.M.F. of concentration cell of the type,

$$Pb_x \cdot Hg_y \mid Pb(NO_3)_2 \parallel \text{Salt bridge} \parallel NaPr.Pb(NO_3)_2 \mid Pb_x \cdot Hg_y$$

The mean values obtained are $K_1 = 3.1 \times 10^{-2}$ and $K_2 = 2.2 \times 10^{-3}$ at $35°$. These values, though of the same order as in the present work, are materially different in magnitude, being about half of those latter. A few experiments on the determination of freezing points of dilute lead propionate solutions by the present authors indicate that the values of K_1 and K_2, found in this paper, agree better with the freezing point data as compared to the values obtained by Mohanty and Aditya (*loc. cit.*). The details of the cryoscopic work will be published later.

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SOME ALIPHATIC MONOCARBOXYLATE COMPLEXES OF BIVALENT METALS IN AQUEOUS SOLUTION. PART IV. COBALT MONO-ACETATO COMPLEX

BY S. K. SIDDHANTA AND S. N. BANERJEE

The composition of the complex formed between Co^{2+} and acetate ions has been found to be $CoAc^+$ from a study of the equilibrium H^+ ion concentrations in mixtures of equimolecular cobalt nitrate and acetic acid solutions, by "Job's method of continued variation", using a new index property, viz., the increase of H^+ ion concentration.

The thermodynamic dissociation constant, K, for the equilibrium $CoAc^+ \rightleftharpoons Co^{2+} + Ac^-$ has been found out as 37.2×10^{-3} at $29.31°$, by the direct application of "law of mass action", taking into account the activity coefficients of the individual ions, calculated from the ionic strength of the mixture of cobalt nitrate and acetic acid solutions employing the "Debye-Hückel limiting law".

Thermodynamic dissociation constant, K, for the equilibrium, $(CoAc)^+ \rightleftharpoons Co^{2+} + Ac^-$

$$K = \frac{a_{Co^{2+}} \cdot a_{Ac^-}}{a_{CoAc^+}} = \frac{c_{Co^{2+}} \cdot c_{Ac^-}}{c_{CoAc^+}} \cdot \frac{f_{Co^{2+}} \cdot f_{Ac^-}}{f_{CoAc^+}}$$

has been determined by following the same procedure as adopted for lead acetato complex described in Part I of this series (this *Journal*, 1958, **35**, 269) from the determination of p_H of solution mixtures, containing a volume '$1-x$' of cobalt nitrate and 'x' of acetic acid, 'x' varying between 0.1 and 0.9, and both parent solutions being at concentration C. The composition of the complex formed has been determined as in the case of lead acetato complex (*loc. cit.*) by the application of "Job's method of continued variation", using the increase, 'Y', of