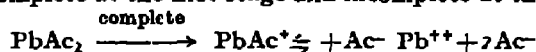


STUDIES IN THE BEHAVIOUR OF BI-UNIVALENT SALTS IN AQUEOUS SOLUTION. PART III. LEAD ACETATE

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Cells of the type $Hg_x \text{ Pb}_y \mid PbAc_2(c) \text{ HAc}(c_1) \parallel \text{salt bridge} \parallel Pb(NO_3)_2(c) \mid Hg_x \text{ Pb}_y$ were studied earlier and the dissociation constant of $PbAc^+ \rightleftharpoons Pb^{++} + Ac^-$ was shown to be 3.1×10^{-3} . Study of cells of the type $Hg \mid Hg_2Ac_2 \mid PbAc_2(c) \text{ HAc}(c_1) \parallel \text{Salt bridge} \parallel NaAc(2c) \text{ HAc}(c_1) \mid Hg_2Ac_2 \mid Hg$ showed that lead acetate dissociated into two stages. By combining the results of the study of the above two types of cells it was possible to calculate the two equilibrium constants. The value of $k_1(PbAc_2 \rightleftharpoons PbAc^+ + Ac^-)$ was found to be 3.0×10^{-2} and that of $k_2(PbAc^+ \rightleftharpoons Pb^{++} + Ac^-)$ to be 3.7×10^{-3} . Study of the cells of the type in which there is no liquid junction potential $Pb_x \text{ Hg}_y \mid PbAc_2(c) \text{ HAc}(c_1) \mid Hg_2Ac_2 \mid Hg$ showed that the calculated values of k_1 and k_2 were correct and the salt bridges had been able to eliminate liquid junction potential effectively.

In a previous communication (this *Journal*, 1952, 29, 169) the dissociation of lead acetate was assumed to be complete at the first stage and incomplete at the second stage as shown,



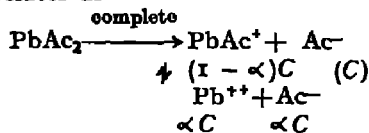
and the dissociation constant of $PbAc^+ \rightleftharpoons Pb^{++} + Ac^-$ calculated. It was also mentioned that further work was in progress. In the present work cells of the types

- (A) $Hg_x \text{ Pb}_y \mid PbAc_2(c) \text{ HAc}(c_1) \parallel \text{salt bridge} \parallel Pb(NO_3)_2(c) \mid Pb_y \text{ Hg}_x$ and
 (B) $Hg \mid Hg_2Ac_2 \text{ PbAc}_2(c) \text{ HAc}(c_1) \mid Pb_x \text{ Hg}_y$ have been studied.

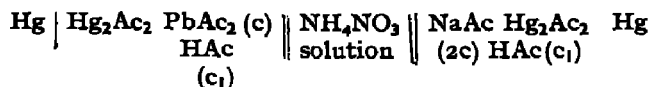
Cells of Type (A)

Preparation and use of reversible $Hg \mid Hg_2Ac_2 \text{ MAc}$ electrode was reported by Larson and McDougal (*J. Phys. Chem.*, 1937, 41, 493). Their method for the preparation of the half element was followed. In all the cells studied the concentration (g. mol./litre) of sodium acetate was twice the concentration (g. mol./litre) of lead acetate solution. Acetic acid was added both to sodium acetate and lead acetate solution used in the cell and the concentration of acetic acid in the two solutions was the same. The readings for the same concentration cell with different concentrations of acetic acid was extrapolated to zero concentration of the acid as in the previous work (*loc. cit.*). The bridge used was of the same type. In case of every cell four bridges 10N, 8N, 5N and 4N were used. From these, as done in the previous work, the mean E.M.F. was calculated and used for extrapolation. The mean E.M.F. values and the extrapolated values are given in Table I (30°).

If lead acetate dissociates as



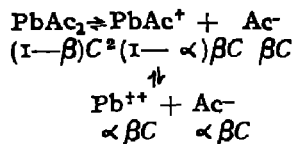
the concentration of the acetate ion is given by $(1 + \alpha) C$ g. ions/litre and E.M.F. of the cell



extrapolated to zero concentration of acetic acid will be given by

$$E_2 = \frac{RT}{F} \log \frac{2 \times f^- \text{ of } Ac^- \text{ ion in sodium acetate}}{(1 + \alpha) \times f^- \text{ of } Ac^- \text{ ion in lead acetate}}$$

It is found that α becomes negative. So the first stage of dissociation cannot be neglected. Taking the dissociation according to the scheme,



the E.M.F. of the cells $\text{Pb}_x\text{Hg}_y \mid \text{Pb}(\text{NO}_3)_2(c) \parallel \text{bridge} \parallel \text{PbAc}_2(c) \text{HAc}(c_1) \mid \text{Pb}_x\text{Hg}_y$ extrapolated to zero concentration of acetic acid and studied in Part II of this series (this *Journal*, 1952, 29, 169) will be given by

$$E_1 = \frac{RT}{2F} \log \frac{f_{\text{Pb}^{++}} \text{ in lead nitrate}}{\alpha \beta f_{\text{Pb}^{++}} \text{ in lead acetate}}$$

and that of the cells of type (A) in this paper and extrapolated to zero concentration of acetic acid will be given by

$$E_2 = \frac{RT}{F} \log \frac{2 \times f_{\text{Ac}^-} \text{ in sodium acetate}}{(1+\alpha)\beta f_{\text{Ac}^-} \text{ in lead acetate}}$$

From the values of E_1 and E_2 and using methods similar to that described in Part II of the series (*loc. cit.*) it was possible to calculate α and β on the basis of the assumptions that (a) the activity coefficient of chloride and acetate ions in two of its salts having the same ionic strength is the same, and (b) the activity coefficients of potassium and chloride ions in solutions of potassium chloride are the same. In Table II the values of α , β , etc. have been calculated on the basis of dissociation in two stages. The equilibrium constants are calculated as follows:

$$\begin{aligned} k_1 &= \frac{a_{\text{PbAc}^+} \times a_{\text{Ac}^-}}{a_{\text{PbAc}_2}} = \frac{(1-\alpha)\beta C f_{\text{PbAc}^+} (1+\alpha)\beta C \cdot f_{\text{Ac}^-}}{(1-\beta)C} \\ &= \frac{(1-\alpha^2)\beta^2 C f_{\text{PbAc}^+} f_{\text{Ac}^-}}{(1-\beta)} \end{aligned}$$

Here the activity of both the monovalent ions *i.e.*, PbAc^+ and Ac^- has been taken to be equal to that of chloride ion at the same ionic strength. Column 7 gives the values for k_1 .

$$\text{Further } k_2 = \frac{a_{\text{Pb}^{++}} \times a_{\text{Ac}^-}}{a_{\text{PbAc}^+}} \text{ which reduces itself to } k_2 = \frac{1+\alpha}{1-\alpha} \cdot \alpha\beta C f_{\text{Pb}^{++}}. \text{ Values of } k_2 \text{ are}$$

given in Table II.

The values of k_1 and k_2 are 3.0×10^{-2} and 3.7×10^{-2} respectively. The value of k_2 obtained here (3.7×10^{-2}) is very nearly its value found (3.1×10^{-2}) on the basis of complete dissociation of lead acetate into PbAc^+ and Ac^- (this *Journal*, 1952, 29, 174). The dissociation constant k_1 ($\text{PbAc}_2 \rightleftharpoons \text{PbAc}^+ + \text{Ac}^-$) is about ten times higher than k_2 . This coupled with the fact that the value of k_2 in the paper referred to has been obtained by extrapolation to zero concentration of lead acetate explains the cause of the closeness of the two values obtained on the basis of two different pictures.

TABLE I

Conc. of HAc.	Mean E. M. F.	Extrapolated E. M. F.	Conc. of AcOH.	Mean E. M. F.	Extrapolated E. M. F.	Conc. of AcOH.	Mean E. M. F.	Extrapolated E. M. F.
PbAc ₂ =0.01M.			PbAc ₂ =0.04M.			PbAc ₂ =0.075M.		
0.005M	0.0151 volt		0.0075M	0.0239		0.010 M	0.0292	
0.0075	0.0146	0.0144 volts	0.010	0.02405	0.0236	0.0125	0.02945	0.0286
0.010	0.0151		0.0125	0.02410		0.0150	0.0296	
0.0125	0.0153		0.0150	0.02405		0.0175	0.02955	
PbAc ₂ =0.02 M.			PbAc ₂ =0.05M.					
0.005 M	0.0195		0.010 M	0.02565				
0.0075	0.0194	0.0185	0.0125	0.0266	0.0249			
0.010	0.01895		0.0150	0.02585				
0.0125	0.01885		0.0175	0.02560				
PbAc ₂ =0.03M.			PbAc ₂ =0.06 M.					
0.0075 M	0.0214		0.010 M	0.02825				
0.010	0.0216	0.0209	0.0125	0.02790	0.0264			
0.0125	0.0216		0.0150	0.02755				
0.0150	0.0221		0.0175	0.02745				

TABLE II

Conc.	μ in lead acetate soln.	$\beta(1-\alpha) f_{Ac}$	$\beta(1-\alpha)$	$\alpha\beta$	β	α	k_1^*	k_2^{**}
0.1 M	0.01624	1.0105	1.1457	0.312	0.9337	0.3743	2.972×10^{-2}	4.000×10^{-3}
0.02	0.02828	0.82775	0.97017	0.2072	0.7629	0.2716	3.308	3.617
0.03	0.0396	0.72696	0.87375	0.1659	0.7078	0.2344	3.364	3.651
0.04	0.0517	0.63929	0.7815	0.147	0.634	0.2318	2.740	3.905
0.05	0.063	0.59225	0.73755	0.1300	0.6075	0.2139	2.890	3.931
0.06	0.0735	0.5518	0.69507	0.1154	0.5796	0.1991	2.902	3.783
0.075	0.0882	0.49797	0.63843	0.0878	0.5506	0.15048	2.999	3.064

$$* \text{Mean value of } k_1 = 3.0 \times 10^{-2} \quad *k_1 = \frac{(1-\alpha^2)\beta^2 C f_{PbAc}^+ f_{Ac-}}{(1-\beta)}$$

$$** \text{Mean Value of } k_2 = 3.7 \times 10^{-3} \quad **k_2 = \frac{1+\alpha}{1-\alpha} a_{Pb^{++}}$$

Cells of Type (B)

With a view to obtaining some more insight, cells of the type Hg | Hg₂Ac₂PbAc₂ (c) HAc (c₁) | Pb_x Hg_y were studied. The two half cells were filled with the same solution. Here, there is no liquid junction. The two half cells filled with the same solution were joined through a bridge containing the same solution. In lead acetate solution acetic acid had to be used and E.M.F. for zero concentration of acetic acid was found by extrapolation. The experiments were all done in duplicate and they generally agreed within 0.1 m.v. In very few cases the difference was about 0.2 m.v. The experimental data are given in Table III. In column 4 of the same table are given the extrapolated E.M.F. values for zero concentration of acetic acid.

The E.M.F. (extrapolated to zero concentration of acetic acid) of the cells of this type is given by the equation

$$E = E_0 - \frac{RT}{2F} \log a_{Pb^{++}} \times a_{Ac}^-$$

TABLE III
(30°)

Conc. of lead acetate.	Conc. of acetic acid.	E.M.F. (volt)	Extrapolated E.M.F. (volt)	$\beta(1+\alpha)Cf_{Ac^-}$	$\alpha\beta Cf_{Pb^{++}}$	$\frac{RT}{2F} \log a_{Pb^{++}} a_{Ac^-}$	E_o
0.01 M	0.005 M	0.8326	0.8320	0.01010	0.001827	0.20198	0.6202
	0.010	0.8330					
	0.015	0.8336					
	0.020	0.8338					
0.02 M	0.010	0.81815	0.8175	0.0164	0.00207	0.1876	0.6299
	0.015	0.81845					
	0.020	0.81850					
	0.025	0.81880					
0.03 M	0.010	0.8095	0.80875	0.02180	0.002265	0.1790	0.6298
	0.015	0.8102					
	0.020	0.8104					
	0.025	0.8106					
0.04 M	0.015	0.8039	0.8030	0.02557	0.002436	0.1730	0.6291
	0.020	0.8043					
	0.025	0.80470					
	0.030	0.80495					
0.05 M	0.020	0.7796	0.7990	0.02961	0.002546	0.1694	0.6296
	0.030	0.8001					
	0.040	0.8003					
	0.050	0.8011					
0.06 M	0.020	0.7970	0.7965	0.03311	0.002527	0.1667	0.6298
	0.030	0.79715					
	0.040	0.7989					
	0.050	0.7970					
0.075 M	0.020	0.7928	0.7920	0.03735	0.002220	0.1623	0.6291
	0.030	0.7925					
	0.040	0.7930					

Mean value of $E_o = 0.6296$

On the basis of two stage dissociation it has been shown that $a_{Pb^{++}} = \alpha\beta Cf_{Pb^{++}}$ and $a_{Ac^-} = (1+\alpha)\beta Cf_{Ac^-}$. So the equation is reduced to

$$E = E_o - \frac{RT}{2F} \log \alpha\beta^2 (1+\alpha) C^2 f_{Pb^{++}} f_{Ac^-}$$

The values of α and β calculated on the basis of (i) two stages of dissociation, (ii) elimination of liquid junction potential by the salt bridge, (iii) activity coefficient of an ion being the same in two different solutions of the same ionic strength and (iv) activity coefficient of acetate ion being equal to that of chloride ion in solutions of the same ionic strength, are given in Table II. With these values of α and β , E_o has been calculated and is given in Table III. The mean value of E_o is 0.6296. The difference from the mean does not exceed 0.6 m.v. This is an ample justification for the correctness of all the assumptions made by us.