25. *Physico-chemical Studies of Complex Formation involving Weak Acids. Part III. Conductometric and Potentiometric Titrations of Metallic Acetates.*

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PREVIOUS work (Part II; J., 1931, 2831) has shown that metallic acetates may, according to the p_H at which their respective hydroxides become precipitable, undergo appreciable hydrolysis in solution and yet be capable of ionisation in a modified form. In this communication, further evidence as regards the extent of the hydrolysis and ionisation of typical acetates is advanced, and an attempt is made to account for the solubility of lead sulphate in solutions of ammonium and alkali acetates.

EXPERIMENTAL.

I. *Potentiometric and Conductometric Titrations of Metallic Acetates with Sodium Hydroxide.*

Since the work on acetate solutions (*loc. cit.*) revealed that appreciable proportions of them must exist in solution in a basic condition, potentiometric and conductometric titrations of lead, copper, beryllium, aluminium, and thorium acetates were carried out, a solution of the same acetate concentration being used for each pair of titrations. The p_H values were measured at room temperature, 18—20°, but the conductometric titrations were performed at 25° as described by Britton and German (J., 1930, 1949). The solutions were prepared as previously described (Part II), and 100 c.c. were employed for each titration. The sodium hydroxide solution was $0{\cdot}1N$, and the metallic acetate solutions *ca.* $0{\cdot}01N$. Sufficient data to show the variations that occurred in the thorium, aluminium, and beryllium titrations are given in Tables I (i), I (ii), and II respectively, the p_H values being recorded in col. 3 and the specific conductivities in col. 4. Table III refers to potentiometric titrations of solutions of the acetates of copper and lead with alkali, and also of copper sulphate and lead nitrate. During the addition of $0{\cdot}0975N$-sodium hydroxide to 100 c.c. of $0{\cdot}005M$-lead acetate the specific conductivity increased in a linear manner until 9·6 c.c. of alkali had been added, κ at 0 c.c. being $5{\cdot}29 \times 10^{-4}$ mho, and at 9·0 c.c. $8{\cdot}19 \times 10^{-4}$ mho. In the conductometric titration of $0{\cdot}00507M$-copper acetate by $0{\cdot}0882N$-sodium hydroxide, a linear increase in conductivity occurred until the stoicheiometric end-point was reached, *viz.*, from $5{\cdot}56 \times 10^{-4}$

mho at 0 c.c. to 7·47 × 10^{-4} at 11·0 c.c. The curves corresponding to the various titrations are shown in Fig. 1.

Potentiometric Titrations.—There was a marked delay in the precipitation from these dilute acetate solutions, and for the lead, copper, aluminium, and thorium solutions the point at which visible precipitation began was somewhat indefinite. The intensity of

FIG. 1.

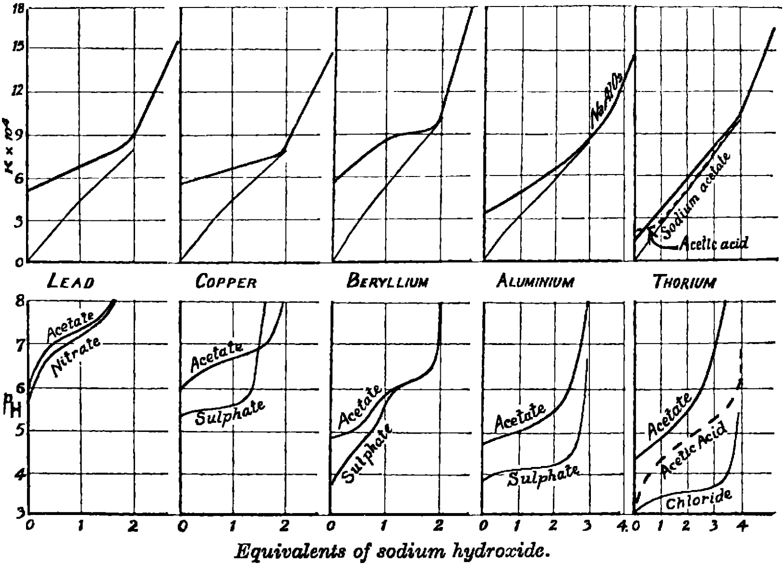


TABLE I.

(i) Electrometric titrations of 100 c.c. of 0·003184M-thorium acetate with 0·1266N-sodium hydroxide.

NaOH, c.c.	NaOH, equivs.	p_H.	$\kappa \times 10^4$.	Equivs. of OH. (a).	Equivs. of OH. (b).
0	0	4·31	1·27	2·90	—
2·5	1·0	4·88	3·44	2·66	1·71
4·0	1·6	5·21	4·70	2·60	2·13
5·0	2·0	5·47	5·50	2·62	2·36
6·0	2·4	5·79	6·27	2·72	2·61
7·5	3·0	6·75	7·73	3·04	3·03
9·0	3·6	8·69	8·92	—	—

(ii) Electrometric titrations of 100 c.c. of 0·003567M-aluminium acetate with 0·1266N-sodium hydroxide.

0	—	4·69	3·58	1·57	—
2·0	0·71	4·90	4·50	1·92	1·19
3·0	1·07	4·99	5·02	2·13	1·65
4·0	1·42	5·12	5·55	2·29	2·00
5·0	1·78	5·25	6·13	2·48	2·32
6·0	2·13	5·57	6·93	2·51	2·44
7·0	2·49	6·29	7·70	2·57	2·56

TABLE II.

Electrometric titrations of 100 c.c. of 0·00675*M*-beryllium acetate with 0·1266*N*-sodium hydroxide.

NaOH,				Equivs. of	κ_{NaOAc},	$\kappa_{diff.}$,	$\kappa_{Be(OAc)_2}$,	
c.c.	equivs.	p_H.	$\kappa \times 10^4$.	OH, (*a*).	$\times 10^4$.	$\times 10^4$.	(*A*).	(*B*).
0	0	4·82	5·62	0·90	—	—	—	—
1·0	0·19	4·92	6·23	0·97	1·18	5·05	5·58	4·96
2·0	0·38	5·09	6·84	0·98	2·18	4·66	5·54	4·70
3·0	0·56	5·27	7·48	1·01	3·11	4·37	5·50	4·20
4·0	0·75	5·50	8·09	1·04	4·11	3·98	5·45	3·73
5·0	0·94	5·79	8·51	1·10	5·02	3·49	5·42	3·23
6·0	1·13	5·96	—	1·24				
8·0	1·50	6·15	9·02	1·57				
9·0	1·69	6·45	—	1·73				

TABLE III.

Potentiometric titrations (quinhydrone electrode) of 0·005*M*-solutions of 100 c.c. of copper acetate, copper sulphate, lead acetate, and lead nitrate with *N*/10-sodium hydroxide.

	p_H Values.							
Equivs. NaOH added	0	0·1	0·25	0·75	1·00	1·25	1·50	1·75
Copper acetate	5·98	6·15	6·30	6·55	6·62	6·72	6·86	7 22
Copper sulphate	5·33	5·37	5·40	5·47	5·56	5·74	7·67	9·71
Lead acetate	5·93	6·36	6·80	7·04	7·45	7·82	8·32	8·94
Lead nitrate	5·57	6·00	6·60	6·80	7·26	7·75	8·32	8·93

the colloidal suspensions increased as the alkali was added, but almost stoicheiometric amounts of alkali were necessary to cause coagulation.

During the precipitation of a hydroxide or basic salt of a metal from a solution of one of its salts with a strong mineral acid, the hydrogen-ion concentration is largely determined by the concentration of hydroxyl ions with which the particular solid phase enters into equilibrium. Fig. 1, however, shows that the acetate radical has an important effect on the p_H values set up in each titration, with the exception of that of lead acetate. By comparing the p_H range corresponding to the titrations of acetates of the weak bases copper, beryllium, aluminium, and thorium by alkali, with that corresponding to the neutralisation of acetic acid of the same concentration (given as a broken line in Fig. 1), it is seen that the hydrogen-ion concentrations prevailing at different points of the precipitation reactions must be attributed to particular stages of the equilibria involving acetic acid and acetate ions. This is only possible if the metallic acetate solutions are appreciably hydrolysed throughout the reactions. The p_H of these solutions would thus be governed by the relationship $p_H = p_K + \log[OAc']/[HOAc]$.

The lead nitrate and copper sulphate curves were obtained by means of quinhydrone and are similar to those of Britton (*ibid.*, p. 2148) with the oxygen electrode, but in the latter case the p_H values during precipitation of copper are now seen to be about 0·2 p_H unit too high. The p_H curve of lead acetate is slightly higher than that of the nitrate. Fig. 1 shows that a sudden increase in p_H occurred after the addition of 1·5 equivs. of alkali, indicating the formation of the basic acetate, $3Pb(OH)_2,Pb(OAc)_2$.

Since lead hydroxide is precipitated in the vicinity of p_H 6—7 (see Fig. 1), it might be expected that considerable combination of acetic acid with lead hydroxide would be possible, and consequently that in the titration the concentration of acetate ions compared with that of free acetic acid would be fairly great. As the p_H of 0·005*M*-lead acetate solution is 5·93, it follows that [OAc′]/[HOAc] is 15·9; and therefore, if all the acetate in the unhydrolysed basic acetate were ionised, the extent of hydrolysis would be approximately 6%. In the course of the reaction with 0·25 equiv. of alkali, this free acetic acid was neutralised, for the p_H rose to 6·8, a value which corresponds to [OAc′]/[HOAc] = 99/1.

Copper hydroxide, being precipitable initially at p_H 5·3 under ordinary conditions, comes more within the influence of the acetate ion–acetic acid equilibrium, and thus we find in Fig. 1 that the hydrolysed acetic acid causes p_H values to be set up that are well above 5·3.

The p_H values, 4·31 and 4·69, of the solutions of thorium and aluminium acetates were much higher than those at which precipitation normally begins, *viz.*, at 3·5 and 4·1 respectively, yet no precipitation occurred. The equation shows that there must have been 2·6 and 1·1 mols. respectively of acetic acid to each acetate ion. Some idea of the nature of the unhydrolysed basic acetate complexes may be obtained from the last two cols. of Table I. The figures represent the number of equivalents of hydroxide groups attached to the metal, *i.e.*, the number of equivalents of acetic acid with which thorium and aluminium have failed to combine. In arriving at the estimates given in col. (*a*), we have assumed that the sodium hydroxide reacted to form sodium acetate, which ionised completely, and that the basic acetate thereby produced remained in solution in the form of some hydrolysed acetic acid and a more basic acetate which underwent complete ionisation as far as its acetate content was concerned, thus: $Th(OH)_x(OAc)_{4-x} \longrightarrow Th(OH)_x^{\cdot\cdot\cdot\cdot(4-x)} + (4-x)OAc'$.

The ratio [OAc′]/[HOAc] would be equal to

$$\frac{[OAc']_{NaOAc} + C_{(\text{total basic acetate})} - [HOAc]_{(\text{hydrolysed})}}{[HOAc]_{(\text{hydrolysed})}}$$

As $[OAc']_{NaOAc}$, the concentration of acetate ions from the sodium acetate, and *C*, that of the basic acetate solution (in equivs.), are both known, it is possible to calculate the number of equivs. of acetic acid that were set free by hydrolysis, and therefore to find the composition of the basic complex. In col. (*b*), the other extreme was assumed, *viz.*, that the basic portion left in the solution at any stage of the titration only hydrolyses to supply the acetic acid and that the acetate ions required by the ratio [OAc′]/[HOAc] come only from the sodium acetate, the actual basic complex being incapable of ionisation. The truth lies between these two extremes, for the conductometric titration curves show that the basic acetates left in solution contribute some conductivity to the solutions and must therefore ionise to some extent. Hence the numbers of the basic groups in the basic complexes must fall somewhere between the numbers given in the two columns (*a*) and (*b*).

In the titration of beryllium acetate the solution remained perfectly clear until 1 equiv. of alkali had been added and a p_H of 5·9 attained. A similar behaviour was observed by Britton (J., 1925, **127**, 2121), using the quinhydrone electrode, with beryllium sulphate solutions, from which precipitation began at p_H 5·7 : the curve labelled " Sulphate " refers to a solution of the sulphate of the same concentration as that of the acetate. The sections of the acetate and sulphate curves corresponding to precipitation by the second equivalent of alkali are coincident. This is the only instance in the precipitation reactions studied in which the acetate anion was not without marked effect on the hydrogen-ion concentration at which precipitation occurred.

The p_H variations during the addition of the first equivalent of alkali are of interest. The amounts of hydrolysed acetic acid have been calculated on the basis of the assumptions used in col. (*a*) of Table I, and from these the composition of the unhydrolysed beryllium basic acetate has been ascertained for the different stages of the reaction. The number of equivalents of hydroxide (OH) in combination with each atom of beryllium is given in col. (*a*) in Table II. It is significant that the composition of the basic complex should range from $Be(OAc)_{1\cdot1}(OH)_{0\cdot9}$ to $Be(OAc)_{0\cdot9}(OH)_{1\cdot1}$ in the clear solutions before precipitation began. Although the basic beryllium acetate solutions were appreciably ionised, as shown by conductivity measurements, it is probable that they were not completely dissociated, and consequently the compositions given above cannot be exact. Nevertheless, they show that about 1 equiv. of acetic acid fails to combine with beryllium hydroxide. This would be expected from the fact that 1 equiv. of sulphuric acid in beryllium sulphate is in a state of feeble combination so that the p_H's of normal and basic beryllium sulphate solutions at comparable concentrations are 3·8 and 5·7. Acetic acid, in combining completely (actually 99%) with a metallic base, necessitates the production of a p_H value by the salt above $p_H = 4{\cdot}73 + 2$, *i.e.*, p_H 6·73. Clearly this is not possible with beryllium hydroxide, and thus it appears that beryllium acetate cannot exist, as such, in solution, but must exist as a basic complex together with much free acetic acid (see, however, Sidgwick and Lewis, J., 1926, 2538).

Conductometric Titrations.—The thin line in each of the diagrams of Fig. 1 represents the contribution made to the specific conductivity of the solutions by the sodium acetate formed. The broken line in the thorium diagram represents the neutralisation of an acetic acid solution of the same equivalent concentration. The curves corresponding to the reaction of the metallic acetates with alkali increasingly resemble the "sodium acetate" line as one passes from lead to thorium, this being the order of the respective hydroxide precipitation p_H's, with the exception of beryllium, which is anomalous. The thorium, aluminium, copper, and beryllium curves touch the sodium acetate lines near the stoicheiometric end-point, but the lead curve does not do so. The p_H curve for this metal indicates that high p_H's occurred long before the theoretical end-point was reached; it is therefore probable that the reaction of the alkali with the precipitated basic acetate in the region of the end-point was slow, so that the solution contained a little unattacked alkali which thus gave rise to a higher conductivity. The fact that the aluminium and thorium curves lie near the sodium acetate line shows that the solutions contained much free acetic acid, and also that the basic metallic acetates left in solution were ionising, though only to a small extent (*vide supra*).

Fig. 1 shows that, after the stoicheiometric amount of alkali had been added to the aluminium acetate, the subsequent increase in specific conductivity only assumed the steep linear gradient (due to excess of sodium hydroxide) after an extra equivalent of alkali had been added. This reaction with 4 equivs. of alkali provides further confirmation of the existence of $NaAlO_2$ in solution (see also Britton, J., 1925, **127**, 2121; Robinson and Britton, J., 1931, 2817).

The specific conductivities corresponding to the reaction of lead acetate with the first equivalent of alkali are those of soluble basic lead acetate and sodium acetate. A series of basic solutions containing from 0·39 to 0·98 equiv. of hydroxide were made by boiling the required quantities of litharge and acetic acid under reflux until dissolution had been effected. After addition of sodium acetate and water in amounts corresponding to various points of the titration, their specific conductivities were determined at 25°. These were in complete agreement with those obtained in the titration.

An attempt was made to analyse the section of the beryllium acetate conductometric curve produced during the addition of the first equivalent of alkali. The specific conductivity of the 0·00675*M*-solution corresponds to an equivalent conductivity of 41·65 mho. Taking $\Lambda_\infty = 83{\cdot}8$, we find that $\alpha = 50\%$ app., but the potentiometric curve indicates that beryllium acetate exists in solution as Be(OH)(OAc). If the latter ionises completely to $BeOH^{\cdot}$ and OAc', the presence of the acetate ions would almost entirely suppress the ionisation of the acetic acid, thereby reducing its conductivity to a small amount, and also it would explain why $\alpha = 50\%$, the important assumption being that the mobility of the beryllium ion is equal to that of $Be(OH)^{\cdot}$. Nothing, however, is known on this point. It was considered that the conductivity of beryllium acetate solutions might possibly be due to the ionisation of the basic complex that they appear to contain, and not to any great extent to the hydrolysed acetic acid. Hence the neutralisation of this free acetic acid should not affect the conductivity of the basic beryllium acetate, unless its removal impaired the stability and ionisation of the basic complex; so, on subtraction of the specific conductivity due to the sodium acetate alone from the observed conductivity, the remaining portion should be that of basic beryllium acetate. On this assumption, the values so obtained should be approximately equal to the specific conductivities of the original beryllium acetate when corrected for the slightly increased dilution. Such differences are given in Table II and are not in accord with κ of beryllium acetate, corrected for slight increases in dilution, in col. (*A*). It is remarkable that they are similar to the specific conductivities recorded in the last column, (*B*), which are those of solutions of beryllium acetate having the same acetate content as the basic solutions of the titration and at the same dilution. No satisfactory explanation has yet been found, but further work is being done on the complex nature of solutions of beryllium salts.

II. *Reaction of Sodium Acetate with Metallic Acetates.*

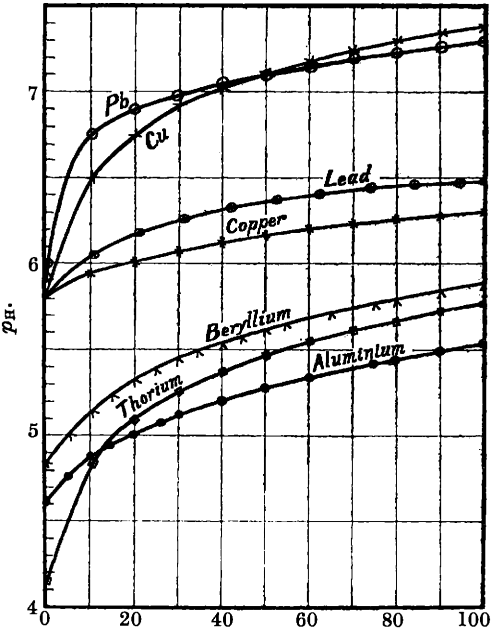
Britton (J., 1926, 269) found that sodium acetate could be added to zirconium chloride or thorium chloride solutions without producing a precipitate even though the p_H values at which the respective hydroxides usually begin to separate were considerably exceeded. Despite this, the p_H values established when various amounts of sodium acetate were added in excess revealed that very little acetic acid had remained in combination with the zirconium hydroxide.

The p_H of a solution of sodium acetate of concentration c is equal to $9{\cdot}4 + \frac{1}{2}\log_{10}c$ (Britton, "Hydrogen Ions," 2nd edtn., 1932,

p. 186), though neutralisation of 1% of its alkali causes the p_H to fall to 6·73. It would be expected, *a priori*, that sodium acetate would cause precipitation when added to solutions of salts of metallic bases, *e.g.*, thorium, aluminium, and tervalent iron, that are precipitated below p_H 6. The tendency, however, is for sodium acetate to hold such weak bases in solution at p_H values well above those at which they are normally precipitated. In order to study the condition under which typical weak bases are retained in sodium acetate solutions, the p_H values were measured with the quinhydrone electrode of acetate solutions to which varying amounts of sodium acetate were added. Details of the solutions used are given in Table IV, together with a few typical p_H data. The variations in hydrogen-ion concentration are represented in Fig. 2; the two curves, labelled Pb and Cu, refer to the experiments in which more concentrated sodium acetate solutions were used, some of the relevant observations being recorded in the right-hand sections of Table IV (i and ii).

FIG. 2.

Acetates of Pb, Cu, Be, Al, Th, titrated with NaOAc.



Sodium acetate, c.c.

Had the metallic acetates not been appreciably hydrolysed, the addition of sodium acetate would have set up p_H values in the vicinity of p_H 7 at least. It should also be remembered that sodium acetate itself may have a considerable effect in promoting the hydrolysis of salts of weak bases. The well-buffered curves in Fig. 2 show that much acetic acid was liberated. As before, it is possible to calculate the ratio [OAc′]/[HOAc] which is responsible for the establishment of each p_H value, but unless [OAc′] is known the percentage of acetic acid hydrolysed cannot be computed. The two extremes, however, have been calculated by the method previously adopted and are given in the columns headed I and II. When concentrated solutions of sodium acetate are used, the concentrations of acetate ions originating from the basic acetate become of negligible magnitude and so render the hydrolysis estimated by method II approximately correct.

TABLE IV.

(i) Titration of 100 c.c. of 0·0101*M*-lead acetate by (*a*) *x* c.c. of 0·096*N*-sodium acetate; (*b*) *y* c.c. of 1·340*N*-sodium acetate.

x.	p_H.	I.	II.	*y*.	p_H.	II.
0	5·85	—	—	0	5·85	—
21·05	6·19	6·7	3·5	20·0	6·90	9·0
42·1	6·34	7·2	4·9	40·0	7·05	12·4
63·2	6·41	8·2	6·3	60·0	7·13	15·8
84·25	6·46	9·2	7·5	80·0	7·22	17·2
105·8	6·50	10·1	8·5	100·0	7·29	18·3

(ii) Titration of 100 c.c. of 0·0099*M*-copper acetate by (*a*) *x* c.c. of 0·1011*N*-sodium acetate; (*b*) *y* c.c. of 2·029*N*-sodium acetate.

0	5·84	—	—	0	5·84	—
20·0	6·01	10·0	5·4	20·0	6·75	19·4
40·0	6·14	11·4	7·9	40·0	7·02	20·8
60·0	6·21	13·0	10·1	60·0	7·18	21·6
80·0	6·28	13·9	11·5	80·0	7·30	21·8
100·0	6·32	15·3	13·1	100·0	7·39	22·2

(iii) Titration of 100 c.c. of 0·00678*M*-beryllium acetate by *x* c.c. of 0·100*N*-sodium acetate.

x	0	20	40	60	80	100
p_H	4·85	5·32	5·53	5·68	5·78	5·88
I	—	50·6	54·0	54·7	56·5	55·4
II	—	37·9	46·8	49·7	52·6	52·2

(iv) Titration of 100 c.c. of 0·00713*M*-aluminium acetate by *x* c.c. of 0·100*N*-sodium acetate.

x	0	20	40	60	80	100
p_H	4·61	5·00	5·21	5·34	5·45	5·54
I	—	67·6	71·4	75·0	75·8	76·1
II	—	50·2	61·9	68·8	71·2	72·4

(v) Titration of 100 c.c. of 0·00383*M*-thorium acetate by *x* c.c. of 0·100*N*-sodium acetate.

x	0	20	40	60	80	100
p_H	4·14	5·09	5·37	5·55	5·67	5·77
I	—	70·1	67·4	64·7	64·1	63·0
II	—	57·1	59·9	59·4	60·0	59·6

The tables show that the percentage hydrolysis increases with increasing concentration of sodium acetate, and also that the metallic acetates may be arranged in the order of increasing hydrolysis : lead, copper, beryllium, thorium, aluminium. With the exception of the last two, this is the order of their hydroxide p_H values. In view of the fact that the hydroxide p_H of beryllium is 5·7 and that of copper is 5·3, it might appear remarkable that beryllium acetate should undergo so very much more hydrolysis than that of copper. This is to be attributed to the exceptional property of beryllium of forming soluble basic salts, and in the light of the observations made in the previous section the fact that the hydrolysis should range from about 40 to 50% is particularly significant. The hydrolysis of both aluminium and thorium acetate in the presence of sodium acetate is much higher than 50%. The probable reason for the hydrolysis of the former being greater than that of the latter is that thorium hydroxide, being the less soluble, passes into a kind of colloidal suspension and adsorbs acetic acid more tenaciously than does the dispersed aluminium hydroxide or basic acetate.

Somewhat lower p_H values were recorded when an excess of sodium acetate was added to thorium sulphate. This indicated, on the basis of the assumptions made in method I, that the thorium acetate formed by metathesis was approximately 70% hydrolysed. By adding sodium acetate solution to one of aluminium sulphate precipitation was delayed but began at p_H 5·03, the hydrolysis then being 50—66·6%.

The above experiments show that sodium acetate, when added to solutions of metallic acetates, renders them basic, yet imparts enhanced stability to the resulting solutions. Whilst the possibility of hydrolysis in sodium acetate–lead acetate solutions has been overlooked, previous investigators (*e.g.*, Jaques, *Trans. Faraday Soc.*, 1910, **5**, 225) have attributed the stability to the formation of complex anions containing lead. For these reasons, the conductivities of solutions of (i) sodium acetate and lead acetate, and (ii) sodium acetate and copper acetate in various proportions were measured at 25°. Typical data are recorded in Table V, concentrations being given in mols./litre.

In the fourth columns are the observed specific conductivities; in the fifth, those of solutions of sodium acetate alone in the respective concentrations; in the sixth, those of the corresponding metallic acetate solutions; and in the seventh, the differences between the observed specific conductivities and those of the simple solutions of sodium acetate—these give the specific conductivities due to the metallic acetates in the mixtures, if the presence of the

TABLE V.

[NaOAc].	[Pb(OAc)$_2$].	$\frac{[\text{NaOAc}]}{[\text{Pb(OAc)}_2]}$.	$\kappa \times 10^3$.	NaOAc, $\kappa \times 10^3$.	Pb(OAc)$_2$, $\kappa \times 10^3$.	κ (Diff.) $\times 10^3$.
0·0169	0·00840	2·0	1·85	1·42	0·77	0·43
0·0288	0·00719	4·0	2·64	2·38	0·69	0·26
0·0378	0·00629	6·0	3·23	3·07	0·62	0·16
0·0449	0·00559	8·0	3·71	3·60	0·57	0·11
0·0505	0·00503	10·0	4·09	4·03	0·53	0·06

[NaOAc].	[Cu(OAc)$_2$].	$\frac{[\text{NaOAc}]}{[\text{Cu(OAc)}_2]}$.	$\kappa \times 10^3$.	NaOAc, $\kappa \times 10^3$.	Cu(OAc)$_2$, $\kappa \times 10^3$.	κ (Diff.) $\times 10^3$.
0·0169	0·00827	2·04	1·95	1·41	0·79	0·54
0·0290	0·00710	4·08	2·79	2·38	0·71	0·41
0·0381	0·00622	6·12	3·38	3·08	0·65	0·30
0·0452	0·00554	8·16	3·83	3·64	0·59	0·19
0·0509	0·00499	10·20	4·21	4·06	0·55	0·15

lead or copper acetate does not interfere with the ionisation of the sodium acetate. The effect on the specific conductivity caused by the repression of the hydrolysis of the sodium acetate by the acetic acid liberated from the acetate of the heavy metal is negligible.

Comparison of the data in the last two columns reveals a rapid decrease in the specific conductivity with increase of sodium acetate until stages are reached where the contributions of the basic acetates almost vanish. In another series of more concentrated solutions containing lead acetate, the difference became zero when the respective concentrations of sodium acetate and lead acetate were 0·447*M* and 0·0672*M*, *i.e.*, 6·65 mols. of sodium acetate to 1 mol. of lead acetate. These experiments show that the ionisation of basic lead and copper acetates is profoundly influenced by the presence of sodium acetate, and although the existence of lead anions, $\text{Pb(OAc)}_3'$, is highly improbable, yet the correct interpretation of the results is not apparent. It seems that ionisation is repressed owing to the fact that p_{H} values which are higher than the respective hydroxide precipitation values are impressed on the basic acetates. This would tend to cause them to coalesce into aggregates that undergo comparatively little ionisation on account of the preponderance of acetate ions originating from the sodium acetate. In effect, the basic acetates might be expected to acquire the properties of a highly dispersed colloid and the particles would thus be either positively or negatively charged. On subjection to the electric current, electrophoretic migration would take place, which would be very much smaller than that of ions in a state of true solution. This would explain the failure of Noyes and Whitcomb (*J. Amer. Chem. Soc.*, 1905, **27**, 747) to observe any definite migration of the lead in ammonium acetate solutions of lead sulphate. In one experiment, however, they observed a comparatively slight migration in the direction of the anode.

III. *The Solubility of Lead Sulphate in Sodium Acetate Solutions.*

Solutions of lead acetate in sodium acetate were studied in more detail in view of their bearing on the solubility of lead sulphate in alkali and ammonium acetate solutions. Fox (J., 1909, **95**, 878) determined the solubility of lead sulphate in sodium acetate solutions of concentrations ranging from 0·88*M* to 4·15*N*, and his data show that the number of mols. of sodium acetate required to dissolve 1 mol. of lead sulphate rapidly fell from 35·9 to 10·0 with increasing concentration of sodium acetate. On the other hand, Jaques (*loc. cit.*) claims to have proved the existence of complex lead anions in much more dilute solutions by means of potential measurements of the lead electrode. We have measured the lead-ion concentrations (see Part II) of a number of lead acetate–sodium acetate solutions, and also of sodium acetate solutions containing (i) lead nitrate and potassium sulphate in exactly equivalent amounts and (ii) lead acetate and potassium sulphate in varying excess. The lead-ion concentrations of typical solutions used in these three sets of experiments are given in Tables VI, VII, and VIII respectively.

TABLE VI.

[NaOAc].	$[Pb(OAc)_2]$.	$\frac{[NaOAc]}{[Pb(OAc)_2]}$.	p_H.	Hydrolysis. I.	II.	$[Pb^{\cdot\cdot}] \times 10^4$.	Pb,% ionised.	$[Pb^{\cdot\cdot}][OH']^2 \times 10^{19}$.
—	0·0101	0	5·85	—	—	28·8	28·5	1·45
0·00912	0·00915	1·0	6·06	6·7	2·3	19·5	21·7	2·57
0·0167	0·00835	2·0	6·19	6·7	3·5	14·1	16·9	3·39
0·0230	0·00765	3·0	6·27	7·0	4·3	9·33	12·2	3·24
0·0284	0·00711	4·0	6·34	7·2	4·9	6·76	9·5	3·24
0·0331	0·00661	5·0	6·38	7·7	5·6	5·89	8·9	3·39
0·0372	0·00619	6·0	6·41	8·2	6·3	5·01	8·1	3·31
0·0407	0·00582	7·0	6·44	8·6	6·8	4·27	7·3	3·24
0·0492	0·00492	10·0	6·50	10·1	8·5	2·82	5·7	2·82
0·122	0·00918	13·3	6·76		6·2	1·07	1·17	3·55
0·223	0·00842	26·5	6·90		9·0	0·347	0·41	2·19
0·309	0·00777	39·8	6·97		11·4	0·169	0·22	1·48
0·383	0·00721	53·1	7·05		12·4	0·102	0·14	1·29
0·447	0·00673	66·4	7·09		14·5	0·0676	0·10	1·02
0·503	0·00631	79·7	7·13		15·8	0·0479	0·08	0·87
0·552	0·00594	92·9	7·19		16·1	0·0355	0·06	0·85
0·596	0·00561	106·2	7·22		17·2	0·0269	0·05	0·74
0·635	0·00532	119·4	7·26		17·6	0·0219	0·04	0·72
0·670	0·00505	132·7	7·29		18·3	0·0169	0·03	0·66

TABLE VII.

$[Pb(NO_3)_2]$.	$[K_2SO_4]$.	[NaOAc].	p_H.	$[Pb^{\cdot\cdot}] \times 10^5$.	$[Pb^{\cdot\cdot}][SO_4'']\times 10^7$.
0·02655	0·02655	0·960	7·64	0·74	1·96
0·02855	0·02855	0·731	7·53	1·35	3·85
0·03333	0·03333	0·682	7·47	1·91	6·37
0·03687	0·03687	0·538	—	1·55	5·71
0·03913	0·03913	0·445	—	1·78	6·96

TABLE VIII.

$[Pb(OAc)_2]$.	$[K_2SO_4]$.	[NaOAc].	p_H.	$[Pb^{\cdot\cdot}] \times 10^6$.	$[Pb^{\cdot\cdot}][SO_4'']$ $\times 10^7$.
0·00385	0·05769	0·780	7·79	1·45	0·84
0·00741	0·05556	0·752	7·73	2·82	1·57
0·01071	0·05357	0·725	7·70	4·17	2·23
0·01667	0·05000	0·676	7·60	8·32	4·16
0·02857	0·04286	0·580	—	8·32	3·57

Table VI shows that there is a progressive decrease in lead-ion concentration as the concentration of sodium acetate increases. This large diminution is surprising when it is considered that after the addition of 133 mols. of sodium acetate to lead acetate hydrolysis had only proceeded to 18%. The last column, which gives the ionic product, shows that the solubility product of lead hydroxide is in no case exceeded. By comparing these products with those referring to basic lead acetate solutions alone (see Part II), it will be noticed that the effect of the added sodium acetate was to stabilise the basic lead acetate by maintaining a lower ionic product. There is little except qualitative agreement between the authors' lead-ion concentration data and those of Jaques (*loc. cit.*), although our potentials were reproducible to within a millivolt. In col. 6 of Tables VII and VIII the products of the lead- and sulphate-ion concentrations were calculated on the assumption that fully ionised sodium sulphate existed in the solution. The first three solutions referred to in Table VII were clear when their lead-ion concentrations were determined, but the other two contained traces of lead sulphate. The first two solutions became cloudy after 5 hours' shaking, whilst definite precipitates were noted in the others. All the solutions in Table VIII were turbid, but in the last there was a definite precipitate. An attempt was made to determine the solubility product of lead sulphate electrometrically by using the lead electrode in the titration of lead nitrate with potassium sulphate solution. In the vicinity of the end-point, however, and after excess potassium sulphate solution had been added, the lead electrode behaved erratically and did not yield steady potentials; this also proved to be the case in solutions of potassium sulphate containing lead sulphate which had been allowed to stand.

The solubility product of lead sulphate, however, has been calculated to be $1{\cdot}83 \times 10^{-8}$ at 20° from published data (see Mellor, "A Comprehensive Treatise, etc.," Vol. 7, p. 808). Sehnal (*Compt. rend.*, 1909, **148**, 1394) gives a value four times as great for 18°. It will be seen from Tables VII and VIII that the value of $[Pb^{\cdot\cdot}][SO_4'']$ is larger than either of these values, even though in some cases the solutions were clear. It therefore appears that true equilibrium had not been obtained, and although shaking of the solutions tended to accomplish this, the precipitation of lead sulphate was only brought about very slowly. The p_H values given in Tables VII and VIII are dependent upon the ratio [OAc′]/[HOAc]. A 0·5M-sodium acetate solution would have $p_H = 9{\cdot}4 + \frac{1}{2}\log 0{\cdot}5 = 9{\cdot}29$. The lower values obtained indicated that there must have been some undissociated acetic acid in solution with which the acetate ions from the concentrated sodium acetate solution had come into equilibrium. These p_H's, together with the low lead-ion concentration, therefore support the contention that the dissolution of lead sulphate in sodium acetate is due to the formation of basic lead acetate and free acetic acid.

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