CCCXCIV.—*The Ternary Systems Copper Acetate–Acetic Acid–Water and Lead Acetate–Acetic Acid–Water at 25°.*

By Karl Sandved.

In connexion with a study of the relation between lead chloride and lead acetate in aqueous solution, the system lead acetate–acetic acid–water was examined, and also, for the sake of completeness, the system copper acetate–acetic acid–water. The results form the subject of the present communication.

The acetate–acetic acid–water systems investigated previously are of the same general type (Sodium salt: Dukelski, *Z. anorg. Chem.*, 1909, **62**, 114; Dunningham, J., 1912, **101**, 431. Ammonium salt: Ruth Sugden, J., 1926, 960. Silver salt: Knox and Will, J., 1919, **115**, 853), all obeying the following two rules: (1) The solubility of the acetate is depressed on addition of acetic acid, as would be expected from the classical solubility laws ; (2) acid acetates occur in the solid phase at a certain concentration of acetic acid.

Of the systems described in the present communication, the copper acetate system conforms completely to these rules, whereas the lead acetate system shows a totally different behaviour. The exceptional complexity of lead acetate solutions has frequently been described. A complete investigation of the ternary system lead acetate–acetic acid–water throws some light upon the constitution of these solutions, and provides data bearing on the existence or non-existence of acid lead acetates, which have not hitherto been described.

EXPERIMENTAL.

Copper Acetate–Acetic Acid–Water at 25°.

The following neutral and acid salts have been described: $Cu(C_2H_3O_2)_2$ (Tilden, J., 1884, **45**, 266), $Cu(C_2H_3O_2)_2,H_2O$ (Gerhardt, *J. Pharm.*, 1845, **9**, 50), $Cu(C_2H_3O_2)_2,5H_2O$ (Wöhler, *Pogg. Ann.*, 1836, **37**, 166; Astre, *J. Pharm. Chim.*, 1893, **28**, 542), $Cu(C_2H_3O_2)_2,2HC_2H_3O_2,H_2O$ (Villiers, *Compt. rend.*, 1877, **85**, 1236).

The mixtures were shaken in a thermostat at 25° ± 0·05°. The equilibria were completely established in 5 to 6 hours, except in solutions containing more than 90% of acetate, which required about 24 hours. The solid was allowed to settle, and the clear solution was drawn off and analysed. The solid was then rapidly drained on a Buchner funnel and analysed, the composition of the dry solid being found by Schreinemakers's method (*Z. physikal. Chem.*, 1893, **11**, 81). Copper was estimated by electrolytic deposition from dilute sulphuric acid solution (see Fischer, *Z. angew. Chem.*, 1907, **20**, 134), whilst the total acetic acid was estimated by distillation with phosphoric acid, as described by Dukelski (*loc. cit.*).

The copper acetate used was the purest obtainable from British Drug Houses, Ltd. Estimations of copper and acetic acid were in accord with the formula $Cu(C_2H_3O_2)_2,H_2O$. The anhydrous acetate was prepared by heating the monohydrate for 5 hours at 95—100° (Angel and Harcourt, J., 1902, **81**, 1385; Tilden, *loc. cit.*). Analysis then gave Cu, 34·9, 34·8, 34·9, 34·91, 34·9 (mean, 34·9) [Calc. : Cu, 35·0%]. This anhydrous copper acetate was employed for solutions corresponding to the extreme right side of the diagram.

The experimental results are in Table I, and Fig. 1 shows the corresponding graph, constructed according to Lodočnikow's method (*Z. anorg. Chem.*, 1926, **151**, 181). If, in order to show more clearly the varying composition of the saturated solutions, the scale is increased ten times (see right-hand ordinates), the broken line in Fig. 1 is obtained. It is seen that three compounds are capable of existence, *viz.*, (1) $Cu(C_2H_3O_2)_2,H_2O$ (marked 1 in the figure); (2) $Cu(C_2H_3O_2)_2,HC_2H_3O_2,H_2O$ (marked 2); (3) $Cu(C_2H_3O_2)_2,HC_2H_3O_2$ (marked 3).

FIG. 1.

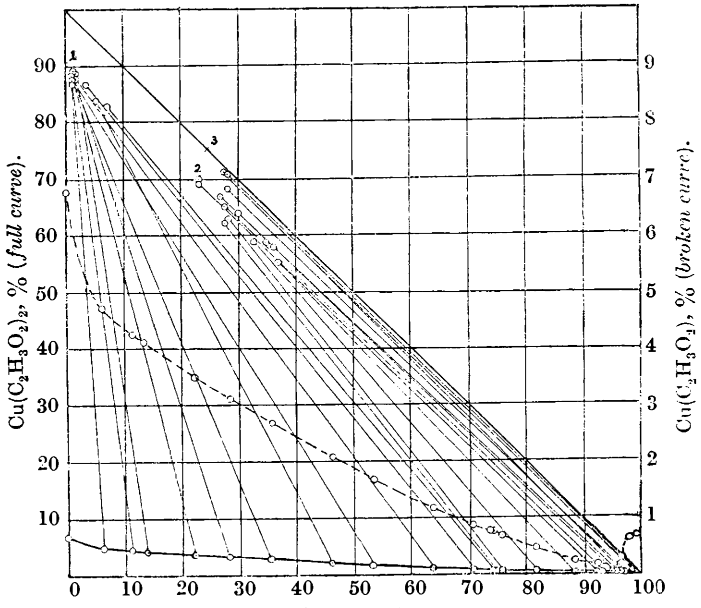


TABLE I.

The Ternary System $Cu(C_2H_3O_2)_2$–$HC_2H_3O_2$–H_2O at 25°.

Liquid.		Wet solid.		Liquid.		Wet solid.	
%CuAc$_2$.	%HAc.	%CuAc$_2$.	%HAc.	%CuAc$_2$.	%HAc.	%CuAc$_2$.	%HAc.
6·79	—	76·02	0·09	0·69	75·74	62·95	28·12
4·73	6·18	88·32	0·82	0·48	81·60	58·87	32·57
4·27	11·14	86·70	1·03	0·25	88·46	65·11	27·96
4·16	13·65	89·31	1·04	0·22	92·17	55·45	36·97
3·49	22·35	87·85	1·64	0·21	93·33	63·87	29·96
3·12	28·43	88·62	1·57	0·20	94·94	59·04	34·81
2·68	35·53	87·53	0·94	0·21	95·26	66·68	26·67
2·10	46·08	83·70	5·10	0·17	95·40	35·94	58·09
1·70	53·35	88·00	1·81	0·23	95·66	69·01	23·30
1·18	63·67	88·31	0·93	0·23	96·37	71·50	27·49
0·89	70·81	86·60	3·45	0·31	97·20	68·25	28·10
0·79	74·06	82·90	7·20	0·71	98·77	70·91	28·31
0·77	74·42	62·10	27·59	0·71	98·91	70·58	28·01

The ternary invariant point between (1) and (2) lies at 0·79% $Cu(C_2H_3O_2)_2$ and 74·06% $HC_2H_3O_2$, and that between (2) and (3) at

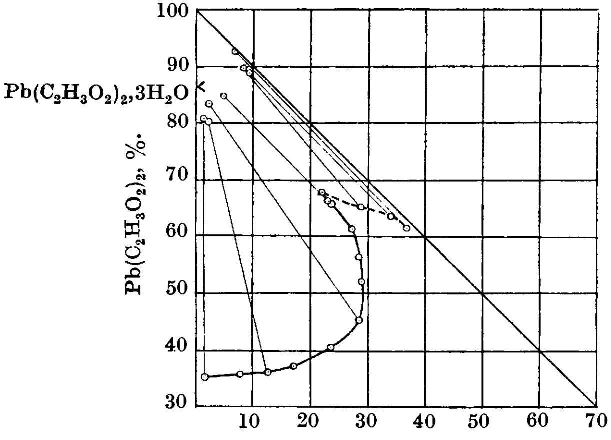
0·17% $Cu(C_2H_3O_2)_2$ and 95·40% $HC_2H_3O_2$. The solubility of copper acetate in water at 25° is 6·79%.

The pentahydrate described by Wöhler and by Astre (*locc. cit.*) is not stable as a solid at 25°. Fig. 1 shows, moreover, that the acid salts obtained are not of the same type as that described by Villiers (*loc. cit.*), for no acid salt is indicated containing more than 1 mol. of acetic acid to 1 mol. of copper acetate.

Lead Acetate–Acetic Acid–Water at 25°.

Numerous basic and neutral lead acetates are mentioned in the literature, whereas no acid compound has been identified (Gmelin-Kraut, "Handbuch," 1924). Sakabe (*Mem. Coll. Sci. Kyoto*, 1914, **1**, 57) has investigated the system lead oxide–acetic acid–water, but his data do not go beyond 19·28% of free acid. Moreover, his figures do not agree either with the results of the present work or with those obtained by Jackson (*J. Amer. Chem. Soc.*, 1914, **36**, 2346) for the system lead acetate–lead oxide–water. Thus Sakabe found the solubility of lead acetate to be about 6·5%, whereas the true solubility is about six times as high. Further, Sakabe employed ignited lead oxide for his experiments and probably true equilibria were not attained owing to the inactivity of the oxide.

FIG. 2.



The lead was estimated as sulphate according to the recognised method. For the estimation of acetic acid, an excess of *N*/5-sulphuric acid was added to the solution, which was then diluted with twice its volume of alcohol and titrated with *N*/5-sodium hydroxide (free from carbon dioxide) and phenolphthalein. (The addition of alcohol produced a very sharp end-point.) Boiled water only was used, and all flasks were fitted with tight glass stoppers. In order to check the method, titrations were carried out with pure lead acetate from the British Drug Houses : the alkali required for back titration was always equivalent to the amount of acid added. Anhydrous lead acetate was prepared by heating the trihydrate at 130°. Three estimations of lead in the dried product gave 63·7, 63·7, 63·7 [Calc. : Pb, 63·7%].

As may be seen from Table II and Fig. 2, the solubility of lead acetate increases on addition of acetic acid, at first rather slowly, but from 20% acetic acid very sharply. The maximum percentage of acetic acid is at 28·99%, which consequently is the highest possible content of acetic acid in presence of lead acetate trihydrate as a solid at 25°, owing to the high solubility of the latter. By dissolving the trihydrate in glacial acetic acid, a point was finally reached corresponding to 67·90% $Pb(C_2H_3O_2)_2$ and 22·01% $HC_2H_3O_2$, marked * in Table II. Anhydrous lead acetate was used for the extreme part of the diagram; it dissolved very slowly in concentrated acid, 2 days being necessary for the attainment of constant values. The solution always showed a slight turbidity, which rendered separation of the two phases impossible at the highest concentrations of acid. This part of the curve, being less trustworthy, has been drawn as a broken line in Fig. 2, but it nevertheless shows that anhydrous lead acetate is still present as a solid and that no acid compounds can be prepared in this way. In order to check this result, the anhydrous salt and glacial acetic acid were boiled together for 5 hours, but the high viscosity and density of the solution prevented the separation of the solid from the liquid. The appearance of the solution was not perceptibly altered after 3 weeks, and it was quite impossible to effect any crystallisation in this highly supersaturated solution. It may be emphasised that these experiments do not definitely prove the non-existence of acid lead acetates. The velocity of reaction in such viscous systems is so depressed that true equilibria may not be reached.

TABLE II.

Liquid.		Wet solid.		Liquid.		Wet solid.	
$\%PbAc_2$.	%HAc.	$\%PbAc_2$.	%HAc.	$\%PbAc_2$.	%HAc.	$\%PbAc_2$.	%HAc.
35·50	1·61	80·80	1·35	61·48	27·10		
35·62	7·82			65·84	23·62	84·63	4·87
36·08	12·56	80·05	2·39	66·48	22·98		
37·10	17·04			*67·90	22·01		
40·58	23·58			65·09	28·90	89·85	8·05
45·39	28·55	83·39	2·73	63·55	34·00	88·70	9·28
52·10	28·99			61·50	36·77	92·61	6·81
56·50	28·41						

Discussion.

The abnormal behaviour of lead acetate solutions has been long known. Measurements of electrolytic conductivity (Noyes and Whitcomb, *J. Amer. Chem. Soc.*, 1905, **27**, 747) and of *E.M.F.* (Conrad, Diss., Göttingen, 1903) indicate a low concentration of free lead ions in these solutions : according to Noyes and Whitcomb the degree of dissociation in *N*-solution is about 17%.

These results are in agreement with the changes which occur when lead salts and acetates are brought together. The increased solubility of lead sulphate in ammonium acetate (Carius, *Annalen*, 1863, **125**, 87) is explained by Noyes and Whitcomb as due to the formation of un-ionised lead acetate by metathesis; and a similar assumption was made by Fox (J., 1909, **95**, 878) to account for the solubility of lead sulphate in alkali acetate solutions.

Several other authors have maintained, however, that various other factors, besides the low degree of dissociation, have to be considered in such solutions. White (*Amer. Chem. J.*, 1904, **31**, 4; 1906, **35**, 218) explains the increased solubility of lead chloride in lead acetate solutions, as well as the type of double compound isolated, by assuming complex ions to be present in the solution. (The author hopes to publish the results of a phase-rule study of this system.)

Further evidence on the existence of complex ions has been given by Blomberg (*Chem. Weekblad*, 1914, **11**, 1030; *Z. Elektrochem.*, 1915, **21**, 438), Conrad (*loc. cit.*), and Labendzinski (Diss., Breslau, 1904). By postulating the equilibria

$$\begin{aligned}
&(1)\ 2Pb(C_2H_3O_2)_2 \rightleftharpoons Pb(C_2H_3O_2)^{\cdot} + Pb(C_2H_3O_2)_3{}' \\
&(2)\ Pb(C_2H_3O_2)^{\cdot} \rightleftharpoons Pb^{\cdot\cdot} + C_2H_3O_2{}' \\
&(3)\ Pb(C_2H_3O_2)_3{}' \rightleftharpoons Pb(C_2H_3O_2)^{\cdot} + 2C_2H_3O_2{}'
\end{aligned}$$

Blomberg is able to account for the abnormal solubility data as well as for the electrochemical measurements referred to previously.

As shown by Hill (*J. Amer. Chem. Soc.*, 1917, **39**, 218), the conditions are altogether different when acetic acid is used instead of alkali acetates; thus, the solubility of lead chloride increases slightly on addition of small amounts of acetic acid, and then falls regularly on further additions (see Herz and Martin, *Z. anorg. Chem.*, 1924, **140**, 339). Hill points out that the theory of metathesis predicts an increase of solubility and therefore can hardly be valid; he suggests, furthermore, that the grounds for these anomalies lie in deviations from the mass-action law. Experiments carried out in connexion with the present work show that the solubility of lead sulphate is depressed in a similar way on addition of acetic acid.

It seems evident, however, that these facts do not by any means disprove Noyes and Whitcomb's hypothesis. All the data available on lead acetate solutions show that this salt, even when regarded as a ternary electrolyte, is more extensively dissociated than acetic acid. Hence the equilibrium $PbCl_2 + 2HC_2H_3O_2 \rightleftharpoons Pb(C_2H_3O_2)_2 + 2HCl$ will give very small amounts of lead acetate in the solution. The slight formation of lead acetate is, however, probably the cause of the increased solubility on the first part of Hill's curve.

When strong electrolytes such as alkali acetates are used instead of acetic acid, the conditions are evidently completely altered, and in this case the acetate ions will have to unite with the lead ions to a considerable extent. In the author's opinion, the increased solubility of sparingly soluble lead salts in solutions of alkali acetates is chiefly due to this combination of ions. It does not appear reasonable that this reaction leads to the formation of undissociated lead acetate only, as originally supposed by Noyes and Whitcomb, but rather to univalent ions $Pb(C_2H_3O_2)^{\cdot}$. By considering lead acetate as a binary electrolyte, it is possible to interpret more satisfactorily the results obtained from conductivity measurements. The degree of dissociation calculated on this assumption is about 70% in *N*-solutions, giving the maximum upper limit of this primary dissociation. The measurements by Conrad (*loc. cit.*) seem to show that the second dissociation takes place only to a slight extent.

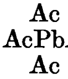
Fox (*loc. cit.*) gives the following solubilities of lead acetate in potassium acetate solutions at 25° :

$KC_2H_3O_2$,%	0	13·87	15·40
$Pb(C_2H_3O_2)_2$,%	35·90	38·05	36·91

Data for the solubility in sodium acetate solutions at 25° have now been obtained :

$NaC_2H_3O_2$,%	0	4·81	15·37	15·96
$Pb(C_2H_3O_2)_2$,%	35·75	35·23	43·28	38·85

If these figures are compared with those in Table II, it will be seen that alkali acetates and acetic acid have approximately the same effect upon the solubility of lead acetate. In the former case, however, the maximum solubility will be reached at a comparatively low concentration of alkali acetate due to changes in the solid phase It will be seen also that the first addition of sodium acetate causes the solubility to fall slightly, while an increase occurs on further addition. This fact seems to be satisfactorily accounted for by the theory of Blomberg (*loc. cit.*). The first quantity of sodium acetate will depress the dissociation of the $Pb(C_2H_3O_2)^{\cdot}$ ion (2), whereas at higher concentrations of acetate ions, and consequently of $Pb(C_2H_3O_2)^{\cdot}$ ions, the formation of complex ions, $Pb(C_2H_3O_2)_3'$, and undissociated molecules (1 and 3) will be predominant. In the case of acetic acid, the first effect due to the increase in acetate ions will naturally disappear, causing the solubility to increase continuously throughout the whole range.

The extraordinary solubility of lead acetate in acetic acid can hardly be accounted for in any other way than by assuming the occurrence of molecular changes. Differences in the thermodynamical and electrical properties of water and acetic acid (Webb, *J. Amer. Chem. Soc.*, 1926, **48**, 2263) scarcely suffice to explain deviations of the observed magnitude, nor does it seem that the basic character of lead acetate solutions can be of essential importance (Löfman, *Z. anorg. Chem.*, 1919, **107**, 241). Webb (*loc. cit.*) has pointed out that strong electrolytes, such as lithium iodide or nitrate, most probably are incompletely dissociated in glacial acetic acid. It seems therefore plausible to assume that complex salts of the type $x\text{HC}_2\text{H}_3\text{O}_2,y\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ would be almost undissociated in concentrated acetic acid solution. The failure to isolate any acid salts from these solutions points to a very high solubility of the complex compounds, as may be expected from the modern theories on solubility. A symmetrical combination of the type  $\text{Ac}\overset{\text{Ac}}{\underset{\text{Ac}}{\text{Pb}}}\text{Ac}$, in which the lead atom is entirely surrounded by acetate groups, will show in respect to its electrical and thermodynamical properties a close similarity to pure acetate groups, and hence have a special ability for penetrating a field built up by such groups.

Summary.

The two ternary systems copper acetate–acetic acid–water and lead acetate–acetic acid–water have been investigated at 25°. The first system belongs to the same type as the alkali acetate–acetic acid–water systems, whereas the second shows totally different properties, in accordance with the generally abnormal character of lead acetate solutions.

It is suggested that this abnormal behaviour is best accounted for by the assumption of molecular changes, and it is pointed out that the supposed non-validity of the mass-action law is insufficient to explain deviations of the observed magnitude.

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IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY,
LONDON, S.W. 7.
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