Studies on the Purities of Precipitate and Crystal. IV. The Investigation or Presumption of Solubility by Co-precipitation Phenomena

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Preparation of pure substance and mechanism of co-precipitation phenomena have long been studied in the fields of analytical and general chemistry.

The colloidal precipitates which are easily soiled by the adsorption of foreign ions become larger particles when formed under suitable conditions, and the adsorption of foreign ions will be decreased. Larger crystals of soluble salts are soiled by the occlusions on inner surfaces, and when they are made small by some method, for example, by the rapid cooling of hot saturated solution,(1) their occlusions will be decreased.

Therefore, the pure substances which show little adsorption or occlusion will be obtained by a suitable procedure; namely, by making particles of some definite size.

Dr. Takio Katô (Prof. of Faculty of Engineering, Tôhoku University) forecasted as follows(2):— " Particles of slightly soluble salts are

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(1) T. Ôsawa, *Chem. Anal. & Reag., Japan*, **7**, 256 (1948). (part I).

(2) T. Katô, *ibid.*, **7**, 248 (1948).

fine, while soluble salts form bigger particles. In conclusion, there will be definite relations between adsorption or occlusion of foreign ions by precipitates and solubilities at their formation. The size of pure precipitate or crystal, in other words, their solubilities will be smaller than potassium chloroplatinate (10^{-1} mol/l. at room temp.), but greater than barium sulfate (10^{-5}). Thus, the substances, having about 10^{-3} mol/l. solubility, or formed under the condition of about 10^{-3} mol/l. solubility will be almost pure."

As to this point, I have obtained almost the same conclusion with chromate of barium, potassium⁽¹⁾ and lead, that is, on the relation between acidity or solubility and coprecipitations of Cl^-, SO_4^{--} and K^+. And all pure substances will be obtained by the formation under a definite condition, the solubility being about 2×10^{-4} mol/l. (20°).

If the relations above mentioned were right, the solubilities of substances might be presumed from these relations. And according to the present research on the oxalates, it is concluded by the author that the solubility of zinc oxalate would be greater than that generally used.

Co-precipitation of Ferric Ions by Oxalates

The opinion⁽³⁾ of the present author on the relations between co-precipitations of ferric ions and solubilities of oxalates has been published⁽³⁾ and several opinions have already been reported by some authors. A part of these is shown in Table 1. These are mg. mol of irons in 1.0000 g. of oxalates, precipitated under a definite condition concerning temperature, foreign ions, addition velocity, direction of addition, aging, stirring, washing, drying etc.

Table 1

Oxalates	Solubilities,⁽⁴⁾ mol/l.	Temp., °C.	Authors	(A)	(B)
Ba	3.8×10^{-4}	18	F. Kohlrausch	$0.13\underline{5}$	$0.19\underline{3}$
Sr	$2.5\times$ 〃	〃	F. K. & Rose	$0.13\underline{0}$	$0.18\underline{3}$
Cd	$1.7\times$ 〃	〃	F. Kohlrausch	$0.12\underline{1}$	$0.17\underline{9}$
Cu	$1.6\times$ 〃	25	Schöfer		$0.17\underline{4}$
Ag	$1.1\times$ 〃	18.5	F. Kohlrausch	$0.06\underline{5}$	$0.10\underline{7}$
Ca	4.3×10^{-5}	18	〃	$0.15\underline{8}$	$0.45\underline{9}$
Zn	$4.1\times$ 〃	17.2	〃	$0.10\underline{4}$	$0.11\underline{6}$
Pb	$5\ \times10^{-6}$	18	〃	$0.26\underline{3}$	$0.44\underline{1}$

The determination of co-precipitated irons was made as follows: — Oxalate ions were decomposed by permanganate solution, excess of manganese dioxide by 3% hydrogen peroxide solution, and after being concentrated, iron was determined colorimetrically with potassium thiocyanide solution.

As another method, after the sample had been treated with permanganate, excess of manganese dioxide and iron were reduced in the reductor of liquid zinc amalgam, and titrated with permanganate standard solution.

(A) is mg. mol of irons in 1.0000 g. of oxalates. Oxalates were formed under 0.625 cc./min. add. velocities, washed five times with 50 cc. distilled water and dried at 90° for 5 hours. The same conclusion was obtained with oxalates dried at 105° for 2 hours. Nitrates of each metallic ions were used, when oxalates were found to be purer than those when acetates were used.

(B) is irons in oxalates, separated after the formation by filtration, transferred to another filter paper, pressed on both sides with five sheets of 9 cm. filter paper. and dried at 90° for 5 hours. The determination of purity was made by the same way as before. When oxalates were separated by suction only, the same relation as (B) was obtained. The silver oxalate was precipitated in the dark room.

$$Ba>Sr>Cd>Cu>Ag<Ca>Zn<Pb$$

$$Zn<Ca<Pb$$

Presumption for the Solubility of Zinc Oxalate

From Table 1, except zinc oxalate, it is known that the regular relations are held between solubilities of oxalates and co-precipitations of ferric ions by oxalates, which are analogous to those of barium chromate and calcium oxalate.⁽¹⁾⁽⁵⁾ The transition point of adsorption and occlusion of foreign ions is about 2×10^{-4} mol/l. at room temperature. For example, magnesium oxalate (1.3×10^{-3} mol/l.) and uranyl oxalate (2.1×10^{-2}) are not pure on account of occlusion, and cerium oxalate (1.6×10^{-7}) or lead oxalate (5×10^{-6}) is not so pure as copper oxalate (1.6×10^{-4}) or silver oxalate (1.1×10^{-4}) on account of adsorption.

Therefore, the separation of lead or cerium in pure state from foreign ion will be established by increasing the solubility to about 2×10^{-4} mol/l.; for example it will be achieved by using $1.0\sim1.5$ *N* nitric acid⁽³⁾ as the solvent. Of course, if acidity of solution increases, then oxalates may become impure again. So it is forecasted that, perhaps, presumption of solubility will be possible by

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(3) T. Ôsawa, *J. Chem. Soc. Japan*, **71**, 191(1950). (part III).

(4) Seidell, "Solubil. inorg. & metal. org. comps." (1940).

(5) T. Ôsawa, *J. Chem. Soc. Japan*, **71**, 68(1950). (part II).

the use of this phenomenon.(6)

According to F. Kohlrausch(7) the solubility of zinc oxalate is 4.1×10^{-5} mol/l. at 18°. Therefore, according to the author's surmise, the quantity of co-precipitation of iron by zinc oxalate might be between calcium oxalate (4.3×10^{-5}) and lead oxalate (5×10^{-6}), but is found less than the case of calcium oxalate (Table 1).

From the viewpoint of relations between co-precipitation phenomena and solubilities, the solubility of zinc oxalate would be between silver oxalate (1.1×10^{-4}) and copper oxalate (1.6×10^{-4}), or between silver oxalate and calcium oxalate (4.3×10^{-5}), because the quantities of co-precipitated irons by zinc oxalate are nearer those of copper or silver oxalate rather than those of calcium or lead oxalate.

If the solubility of zinc oxalate is about 4.1×10^{-5} mol/l. (F. Kohlrausch), it seems to act on the acid solvents like lead or calcium oxalate. But the transition point of adsorption and occlusion in zinc oxalate is 0.009 *N* of nitric acid,(3) and is more similar to copper oxalate than to oxalate of lead or calcium. It is presumed, therefore, the solubility of zinc oxalate may be $1.1\sim1.6\times10^{-4}$ mol/l. at room temperature.

Determination of Solubility and Composition of Zinc Oxalate

The oxalate, prepared in a suitable solvent, was stirred with distilled water in a thermostat at 20° ± 0.05°, and its solubility was determined by titrating the soluble oxalate ions with the permanganate solution.

As to zinc oxalate, a sample was prepared by the following way:— The equivalents of zinc nitrate and ammonium oxalate were separately dissolved in 0.05 *N* nitric acid, which is a good solvent for zinc oxalate,(3) and zinc nitrate solution was stirred at 80°, and then ammonium oxalate was added in the direction of $C_2O_4^{--}\rightarrow Zn^{++}$ to prevent the formation of soluble oxalate complex. The precipitate washed ten times, and after digested in water with stirring to the equilibrium at 20° ± 0.05°, it was filtered by using Tôyo roshi No. 5c, No. 4 and platinium filter cone, and the filtrate was titrated with permanganate solution.

The titration was carried out under a definite condition; 5 cc. of 6 *N* sulfuric acid and 2 cc. of *N*/10 sodium oxalate standard solution were added for the end point correction etc. In Table 2, x is titres of *N*/10 $KMnO_4$ for 2 cc. $Na_2C_2O_4$ solution, 5 cc. of 6 *N* H_2SO_4 and 25 cc. distilled water.

In primary experiments, substances, which have $10^{-4}\sim10^{-6}$ mol/l. solubility, required about 7 hours to attain equilibrium with distilled water.

And, as expected, with zinc oxalate, greater values than that of F. Kohlrausch were found, but it was presumed that it might be due to the complex formation.

In Table 2, data marked * are for zinc oxalate determined by the following procedure. The composition of zinc oxalate was determined by the estimation of ZnO and C_2O_4, the former by means of ignition, and the latter by titration with permanganate solution.

Table 2

Stirring hours, hr. min.	*N*/10 $KMnO_4$ titres (means), cc.	*N*/10 $KMnO_4$ factor	x (means), cc.	Titres x, cc.	Solubility, mol/l.
5	$1.85\underline{0}$	0.929	$1.80\underline{0}$	$0.05\underline{0}$	0.9×10^{-4}
2.05	$1.86\underline{0}$	〃	$1{\cdot}79\underline{0}$	$0.07\underline{0}$	1.3 〃
7.00	$2.82\underline{0}$	〃	$2.74\underline{5}$	$0.07\underline{5}$	1.4 〃
7.35	$1.87\underline{6}$	〃	$1.80\underline{0}$	$0.07\underline{6}$	1.4 〃
16.53*	$3.22\underline{0}$	1.227	$3.17\underline{0}$	$0.05\underline{0}$	1.2 〃
70.00*	$1.95\underline{0}$	1.032	$1.89\underline{0}$	$0.06\underline{0}$	1.2 〃
72.00*	$1.95\underline{0}$	〃	$1.89\underline{0}$	$0.06\underline{0}$	1.2 〃
96.02	$2.82\underline{3}$	0.929	$2.74\underline{0}$	$0.08\underline{3}$	1.4 〃

The distilled water, used in the experiments, was prepared in this labolatory and its specific conductivity was found to be 3.6×10^{-6} $cm.^{-1}$ Ω^{-1}.

Table 3

No.	Sample, g.	*N*/10 $KMnO_4$, cc.	ZnO, g.	Zn, %	C_2O_4, %
1	0.2036	17.50			46.41
2	0.2013	17.31			46.43
3	0.3455		0.1483	34.49	
4	0.2675		0.1149	34.50	
5	0.1980		0.0850	34.49	
6	0.1951	16.81			46.52
7	0.2472	21.29			46.50
8	0.2607	22.41			46.41
9	0.2265	19.49			46.46
			means ·········	34.49	46.46

(Chemical factor of *N*/10 $KMnO_4$ is 1.227.)

The theoretical percentage of Zn and C_2O_4 in various forms of zinc oxalate are as follows:—

Forms of Oxalate	Zn, %	C_2O_4, %
ZnC_2O_4 ···················	42.62	57.38
$ZnC_2O_4\cdot H_2O$ ···········	38.18	51.35
$ZnC_2O_4\cdot 2H_2O$ ·········	34.52	46.47
$(NH_4)_2Zn(C_2O_4)_2$ ······	23.56	63.45

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(6) T. Ôsawa, at meeting of Tohoku Branch, Chem. Soc. Jap., July, 1949.

(7) Landolt-Börnstein, "Physik. Chem. Tabellen," 3 auf. 584 (1905).

From above data, it is deduced that the samples used for the determination of solubilities in Table 2 are not oxalate complex, but $ZnC_2O_4 \cdot 2H_2O$. An investigation was made for other oxalates' solubilities with the same precedures. The results are as follows:—

Table 4

Oxalates	Authors	Temp., °C.	Solubilities reported, mol/l.	Hours equil. hr. min.	Solubility measured, mol/l.
Ba	F. Kohlrausch	18	3.8×10^{-4}	7.0	4.2×10^{-4}
Sr	〃 & Rose	〃	2.5 〃	7.45	3.2 〃
Cd	〃	〃	1.7 〃	7.0	1.9 〃
Cu	Schöfer	25	1.6 〃	2.0	1.55 〃
Ag	F. Kohlrausch	18	1.1 〃	52.0	0.7 〃
Ca	Aumerase	20	5.7×10^{-5}	70.0	5.9×10^{-5}
Pb	F. Kohlrausch	18	$5. \times10^{-6}$	7.0	$7. \times10^{-6}$

(20° ± 0.05°C)

Silver oxalate was decomposed easily and its solubility differed from F. Kohlrausch's, so the time of stirring seemed short, but the present author always obtained lower values in spite of more than 72 hours stirring. Other oxalates were almost of the same value even more than stirring times of Table 4. And some oxalate were determined by the same procedure and their composition were $CaC_2O_4 \cdot H_2O$, $SrC_2O_4 \cdot H_2O$ and $BaC_2O_4 \cdot H_2O$.

Summery

The solubility of zinc oxalate has been reported by Kunschert (7×10^{-5} mol/l. at 25°)(8) or F. Kohlrausch (4.2×10^{-5} at 18°),(9) but, from the viewpoint of the relations between solubility and co-precipitation phenomena, it would be greater than their values, perhaps about $1.1 \sim 1.6 \times 10^{-4}$ mol/l. at room temperature.

Measurements showed the solubility of zinc oxalate, of which composition was $ZnC_2O_4 \cdot 2H_2O$, to be 1.2×10^{-4} mol/l. at 20° ± 0.05°. This is almost the same with the result obtained by Scholder, Gadene and Niemann (1.36×10^{-4} mol/l. as 18°)(4) but further details are not clear.

By the relations between solubility and co-precipitation phenomena, a presumption or investigation of solubility may be possible; namely, it may be determined by the use of the transition point of adsorption and occlusion of foreign ions (about 2×10^{-4} mol/l. at 20°). Needless to say, the formation or treatment of precipitate should be done under the same condition. The study on a mechanism for the adsorption or Balarew's occlusion phenomena(10) is in progress.

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(8) Kunscheht, *Z. Anorg. Chem.*, **41**, 337 (1904).

(9) F. Kohlrausch, *Z. Physik. Chem.*, **12**, 234 (1893).

(10) Balarew, *Z. Anal. Chem.*, **101**, 161 (1935); **102**, 241, 408 (1935); **106**, 249 (1936); **107**, 289 (1936); *Z. Physik. Chem.*, **30**, (1935), etc.