DISPERSOIDOLOGICAL STUDY OF SILVER SALTS IN AQUEOUS ETHYL ALCOHOL, ACETONE AND PROPIONE SOLUTIONS. I.

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On the Complex(1) Solubility and on the Dispergation of an AgI-Precipitate in Aqueous Ethyl Alcohol and Acetone Solutions of KI.

Historical Introduction and Subject of Investigations. The colloidal synthesis of silver salts which are practically insoluble in an aqueous dispersion medium, was the subject of the classical investigations of

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(1) By "complex solubility" P.P. von Weimarn designates the solubility of substance AB in solutions of substance AX or BY, with which AB forms complex molecules; the complex molecules become decomposed on the dilution of the solutions by the dispersion medium. In these cases of dissolution, crystals of substance AB are the solid phase (saturating substance).

A. Lottermoser⁽¹⁾; who also established that e.g. for the cases of dispergation of an AgI-precipitate in *aqueous* KI solutions of progressively increasing concentrations,⁽²⁾ the dispergation curves have a maximum point (see Curve A, Fig. 2).

The stability of colloidal solutions of silver salts is explained by Lottermoser (l.c.) by the adsorption of ions; owing to this adsorption the disperse particles acquire electrical charges which hinder coagulation.

P.P. von Weimarn⁽³⁾ ascribes the causes of stability of these colloidal solutions to kinetic processes taking place on the surfaces of the disperse particles and in the dispersion medium; these processes are closely connected with the formation of complex molecules (e.g. AgI, KI).

On the ground of his investigations embracing the colloidal synthesis in mixtures of alcohols and water, of various salts (amongst them of AgI, AgBr, AgCl, silver-citrate and silver-tartrate) P.P. von Weimarn⁽⁴⁾ had arrived at a series of conclusions, of these the two following are of special importance for the present investigations.

(1) Ability for complex-formation increases with decrease in the dielectric constant of the dispersion medium. For instance, in the aqueous ethyl alcohol solutions, the dielectric constant decreases with increase of the concentration of alcohol; therefore, with a certain⁽⁵⁾ *constant* concentration of substance AX (or BY) in the solution, owing to increase in the complex-formation, the complex solubility of substance AB increases simultaneously with increase of the concentration of alcohol (e.g. $BaSO_4$ in an alcoholic-aqueous BaI_2 solution; AgI in an alcoholic-aqueous KI solution, etc.). These correlations are represented schematically in Fig. 1.

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(1) Lottermoser, *J. prakt. Chem.*, **72–73** (1905), 39 and 374; *Koll.-Zeitschr.*, **1** (1906), 11; *Z. physik. Chem.*, **60** (1907), 451; *Koll.-Zeitschr.*, **2** (1907), Suppl. I, IV; *Z. physik. Chem.*, **62** (1908), 359; *Koll.-Zeitschr.*, **3** (1908), 31; *Z. physik. Chem.*, **70** (1910), 239; *Koll.-Zeitschr.*, **5** (1909), 78; *Koll.-Zeitschr.*, **36** Erg. (1925), 230; *Collegium* (1925), 573; *Z. angew. Chem.*, **39** (1926), 347.

(2) Lottermoser, *Z. physik. Chem.*, **62** (1908), 376.

(3) P.P. von Weimarn, *J. Russ. Chem. Soc.*, **40** (1908), 1785; *Koll.-Zeitschr.*, **4** (1909), 123; "Kolloides und kristalloides Lösen und Niederschlagen," **2** (1921), Kyoto.

(4) P. P. von Weimarn, *News of the Ural Mining Institute*, **1** (1918–1919), Part III, 38; *Koll.-Zeitschr.*, **28** (1921), 99; **32** (1923), 147. For more details see P.P. von Weimarn's paper referred to in Footnote (1) in the next page.

(5) With weaker concentrations of substance AX or BY, the solubility of substance AB decreases according to the Nernst-Noyes' law. For more details, see P. P. von Weimarn's paper referred to in Footnote (1) in the next page.

(2) Increase in complex-formation and complex solubility of substance AB, when the concentration of alcohol in the alcoholic-aqueous solutions of substance AX (or BY) is increased, has an influence on the stability of colloidal solutions, in narrowing the region of concentrations of substance AX (or BY) within the limits of which the existence of a colloidal solution of substance AB is possible.

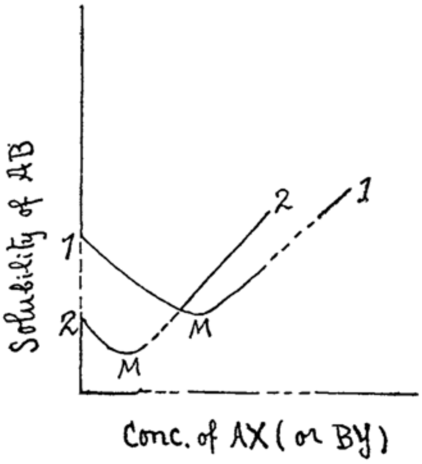
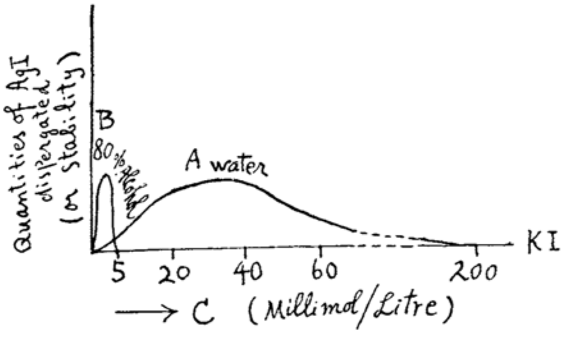


Fig. 1.

(After P.P. von Weimarn. Curve 1 M 1-dispersion medium, water; curve 2 M 2-dipersion medium, e.g. 80% alcohol).

These correlations in the case of AgI and KI are shown schematically in Fig. 2.

For a clear understanding of the stability of colloidal solutions in presence of complex-formation, P.P. von Weimarn in his recent paper⑴ has especially stressed the great importance of quantitative investigations of complex solubility, of adsorption and of other variables. Prof. P.P. von Weimarn was kind enough to suggest to me a quantitative study of the following:



(Curve A, after A. Lottermoser; Curve B, after P. P. von Weimarn.)

Fig. 2.

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(1) P.P. von Weimarn, "The influence of solubility, adsorption, complex-formation and solvation, upon the stability of the colloidal state." This paper will appear in the course of this year, in *Kolloidchemische Beihefte.*

1. The dispergation of *precipitates*(1) of different dispersities of AgI, AgBr, AgCl etc. in KI, KBr, KCl etc. ethyl alcoholic aqueous solutions with a progressively increasing concentration of alcohol.
2. The complex solubilities of the same substances.
3. The adsorption of the above-named dispergators.
4. The dispersoidal synthesis of practically insoluble silver salts, in aqueous acetone and propione (diethyl ketone) solutions.

The dielectric constants of acetone and propione are smaller than that of ethyl alcohol (ethyl alcohol, 26.5; acetone, 20.7 and propione, 17.0). Moreover, no investigations have been carried out up to the present upon the colloidal synthesis of practically insoluble silver salts in aqueous acetone and propione solutions.

Up to the present the author has completed the determination of the complex solubility of AgI(2) in aqueous ethyl alcohol and acetone solutions of KI,(3) as well as determining the AgI dispergation curves for these solutions.

Experimental Part.

§ 1. Complex Solubility, and the Dispergation Curve of AgI in Aqueous Ethyl Alcohol Solution of KI. An extremely pure AgI-precipitate was prepared for the experiments. It did not show traces of any admixtures ($AgNO_3$ or KI) even when tested by the most sensitive qualitative reactions. In order to reach such a high state of purity the AgI precipitate was washed during ten days with large amounts of water. Further the precipitate was thoroughly washed with ethyl alcohol and dried at 130°C. Micro-and ultramicroscopical investigations of this precipitate showed its polydispersity. A part of the crystals composing the precipitate were of colloidal dimensions, but the degree of their dispersity was not high. The size of other crystals of this AgI-precipitate was above the colloidal; nevertheless they were so small that only seldom could the regularity of their shape be established by microscopic examination under maximum magnification.

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(1) Colloidal synthesis of practically insoluble silver salts in statu nascendi (by the double decomposition reaction) was the subject of P.P. von Weimarn's investigations (l.c.). P.P. von Weimarn will continue these researches, especially with aqueous solutions of propyl and butyl alcohols.

(2) On the complex solubility of $BaSO_4$ in alcoholic-aqueous solutions of BaI_2, $BaBr_2$ and $BaCl_2$, see the paper of P.P. von Weimarn and S. Ishii, which will appear in the course of this year, in *Kolloidchemische Beihefte.*

(3) I have also studied crystals of various complex compounds of AgI and KI; certain of these crystals proved to be sensitive to light. The results of this investigation will appear in my paper in the *Reports of the Imperial Industrial Research Institute of Osaka* (1931).

The experiments for the determination of AgI complex solubility in aqueous ethyl alcohol KI solutions were carried out as follows. About 3 gr. of AgI-precipitate and 100 c.c. KI-solution of a definite concentration were placed into a cylindrical glass vessel which after being carefully stoppered, was shaken for half an hour in a shaking machine. After shaking, the vessel containing the disperse system formed, was kept in a thermostat (20°C.) up to the time when complete precipitation of AgI disperse particles took place. The precipitation was regarded as completed when the supernatant solution no longer produced the Tyndall cone (in a dark room, under arc-lamp illumination). This solution, perfectly "optically void," was filtered and about 80 c.c. were taken for the determination of AgI and KI concentrations. After heating the solution in order to eliminate the alcohol, 300 c.c. water were added. The quantity of AgI (precipitated on the addition of water) was determined by gravimetric analysis; and that of KI in the filtrate by volumetric analysis according to Volhard. Complex solubilities, weaker than 1.10^{-4} mol per litre, were determined by tyndallimetry.

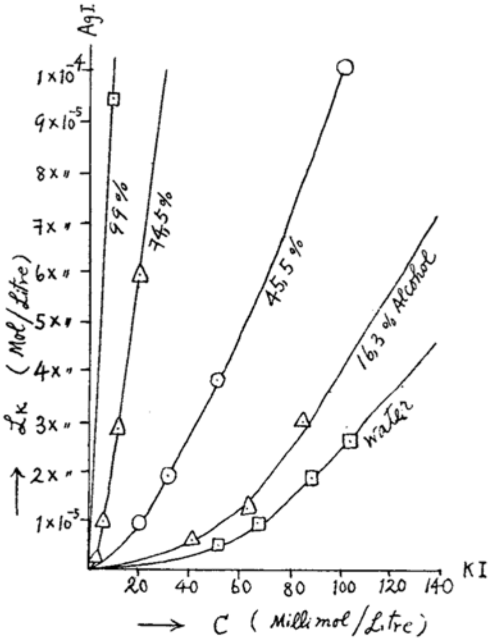

Fig. 3*a*.

In Figs. 3*a* and 3*b* are shown graphically the results obtained by the author (the coordinates for the curves in Fig. 3*a* are L_k, complex solubility in mol-liter, and *C*, concentration in millimol-liter of KI in the solution; for the curves in Fig. 3*b* they are LogL_k and $\sqrt{C}$; the concentration of alcohol is expressed by weight percentage).

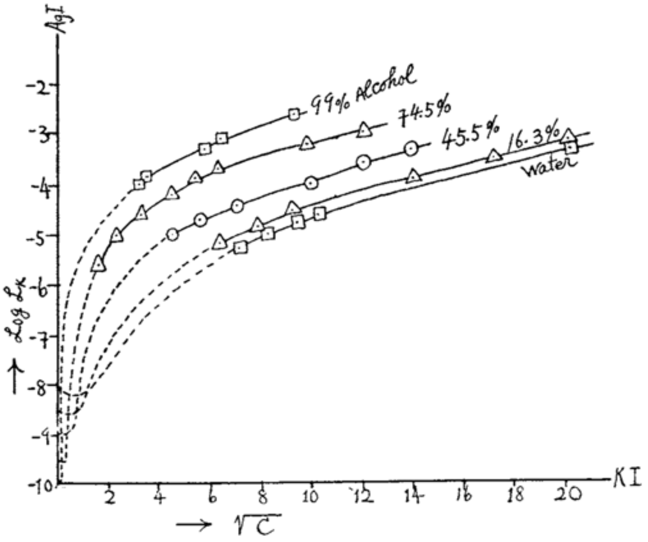

Fig. 3*b*.

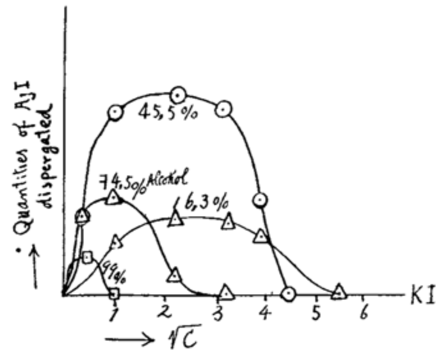

Fig. 4. (After one month)

The experiments on the dispergation of the AgI-precipitate in KI solutions were carried out as follows. A cylindrical glass vessel containing 1 gr. of AgI (powdered in an agate mortar) and 25 c.c. KI solution of a definite concentration was carefully stoppered and placed in a shaking machine for 20 minutes. The disperse system, obtained after shaking, was kept in a dark room. In Fig. 4 are represented graphically some of the results obtained by the author (the coordinates for the curves are $\sqrt{C}$ and quantities of AgI dispergated).

2. Complex Solubilities and the Dispergation Curves of AgI in Aqueous Acetone Solutions of KI. The same methods of investigation as those described in paragraph 1 have been employed. The results obtained are graphically represented in Figs. 5*a*, 5*b* and 6.

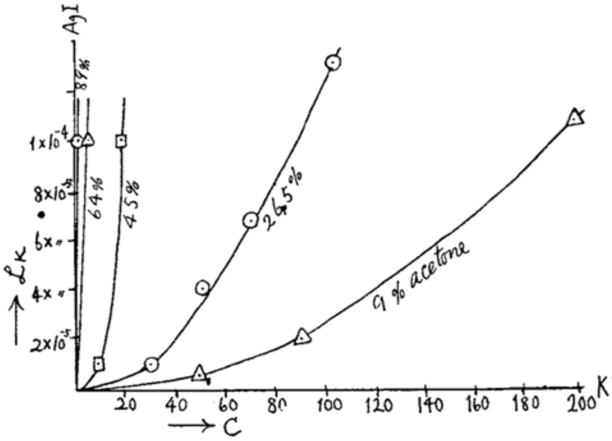

Fig. 5*a*.

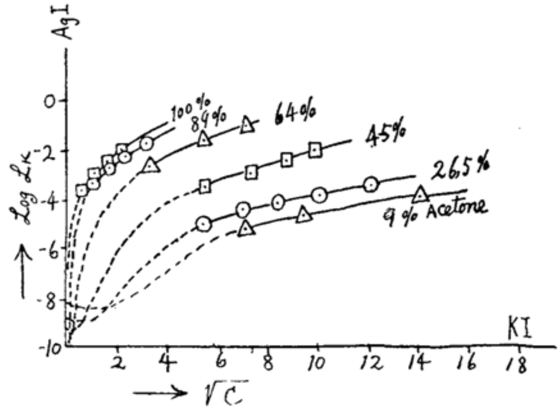

Fig. 5*b*.

When acetone is diluted with water, the strong fall in the complex solubility must correspond (see P. P. von Weimarn, Preface) to a strong increase of the dielectric constant in the acetone-aqueous mixtures, when the concentration of acetone is lowered. As is clear from the following Table such increase of the dielectric constant actually takes place.

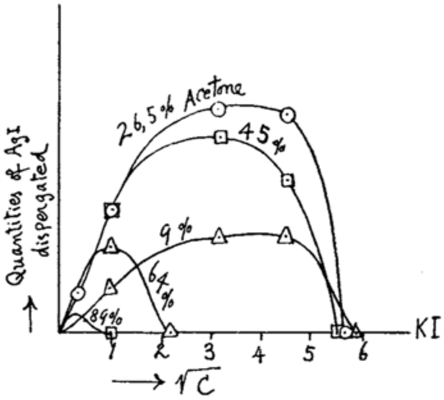

Fig. 6. (After one month)

Table 1.

Wt. % acetone	Dielect. const (19°C.)	Wt. % ethyl alcohol	Dielect. const. (20°C.)
0.	81.8	0.	81.9
25.0	67.7	—	—
50.0	51.2	50.0	49.4
80.0	32.2	80.0	34.1
100.0	20.7	100.0	26.5

Summary.

In this paper is given a graphical representation of quantitative data pertaining to:

1. The complex solubility of the AgI-precipitate in aqueous ethyl alcohol solutions of KI.
2. The dispergation process in the same solutions.
3. The complex solubility of the AgI-precipitate in aqueous acetone solutions of KI.
4. The dispergation process in the same solutions.

I wish to express here to Professor P.P. von Weimarn my sincere gratitude for suggesting the theme for these investigations.

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