

**452.** *The Effect of Peptising Agents on the Crystal Growth of Insoluble Metal Salts. Part II.*<sup>1</sup> *The Reduction of Particle Size of Crystalline Insoluble Metal Salts (and Sol Formation) by Surface-active Agents.*

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The effect of macromolecules and colloidal electrolytes on the precipitation of crystalline insoluble metal salts from supersaturated solutions has been studied. The rate of fitting of the coagulated sol micelles into an ordered crystal structure is decreased more than the actual rate of coagulation: the appearance of the new phase of supersaturated solution is retarded, and the average particle size is reduced. The particle mass varies as an exponential function of the reciprocal of the concentration of peptiser. The results are best explained by the theory that peptisation occurs by adsorption of the added agent as a protective film round the sol micelles from which the crystals grow.

THIS paper extends a previous study<sup>1</sup> on the effect of organic acid peptising agents on the crystal growth of insoluble metal salts from supersaturated solution; the effect of addition of surface-active macromolecules and colloidal electrolytes has been investigated in greater detail.

#### EXPERIMENTAL

*Materials.*—Gelatins were supplied by the British Gelatine Works. The "Photographic" variety was freed from electrolytes and amino-acids by treatment with ion-exchange resins. The "free acidities" (*i.e.*, carboxyl groups including amino-acids formed by hydrolysis) expressed as c.c. of N-solution per 100 g. were: "Photographic" 14.9; "Coignet" 24.4; "Spa" 40.4 (cf. ref. 2).

Polysaccharides were supplied by B.D.H. Ltd. (of >95% purity).

Anionic and cationic colloidal electrolytes were prepared as described previously.<sup>3</sup>

Polyethylene glycol derivatives were supplied by General Metallurgical Co. Ltd.; polyethylene oxide derivatives by Dr. R. Matalon (for preparation see ref. 4).

*Techniques.*—An aqueous solution of the reacting cation (at 20°) was added to an equal volume of the reacting anion solution containing the required concentrations of peptising agent.

<sup>1</sup> Part I, Packter, *J.*, 1956, 2393.

<sup>2</sup> Matalon and Packter, *J. Colloid Sci.*, 1955, 10, 46.

<sup>3</sup> Packter, *ibid.*, 1956, 11, 150.

<sup>4</sup> Schulman, Matalon, and Cohen, *Discuss. Faraday Soc.*, 1956, 11, 117.

*Sol Stability.*—The stability of the supersaturated metal-salt systems was determined as described earlier,<sup>1, 5</sup> and the effects of the additives were followed up to the peptisation ratio.

*Average Particle Size.*—The precipitate was left to grow for 24 hr. at 20°. In the systems investigated in this work, the addition of peptising agent generally led to a fully deflocculated metal-salt sol or a suspension of average particle size within the range  $<0.05$ – $5 \mu$ : the average crystal diameter ( $d_c$ ) (by weight) of the primary particles was been determined on the unfiltered deflocculated system, by the centrifugal sedimentation methods of Martin<sup>6</sup> and Jacobsen.<sup>7</sup>

*Average Particle Weight.*—The mean weight ( $m_c$ ) of the primary particles will be given by the relation,  $m_c = C\rho d_c^3$ , where  $\rho$  is the specific gravity, and  $C$  is a shape factor.

## RESULTS

*Stability.*—We have shown previously<sup>1, 5</sup> that mixing the two reacting solutions generally causes an induction period ( $t$ ) before the rapid onset of turbidity. This period  $t$  varies with the concentration ( $C_p$ ) of peptiser, according to the general relation

$$\log_{10} t = F(C_p - \bar{C}_p)/C_s \dots \dots \dots (1)$$

where  $C_p = \bar{C}_p$  at  $t = 1$  sec., and  $F$  is a constant.

$C_p$  and  $C_s$  are generally expressed in g.-equiv. per l.  $F$  is always positive irrespective of whether the final crystal size of the metal-salt "deposit" is increased or reduced. If  $C_p/C_s = (C_p^*/C_s)_t$  at  $t = 24$  hr.,  $(C_p^*/C_s)_t$  is called the "peptisation ratio."

We have found that the  $F$  values for peptisation by macromolecules are generally 2–10 times less than those for peptisation by the corresponding monomer, while the  $(C_p^*/C_s)_t$  values are larger. When, on the other hand,  $C_p$  and  $C_s$  values are expressed in moles per l., the values of the constant  $F$  may be  $>10,000$  times greater than those for the corresponding monomer.

*Size of Deposited Particles.*—The crystallinity of many insoluble metal salts is markedly reduced when they are deposited in the presence of surface-active additives. Particles of colloidal size (deposited from solution) are in turn stabilised against coagulation and subsequent aggregation,<sup>8-10</sup> and concentrated insoluble metal-salt sols are formed.<sup>11-13</sup>

We have followed the variation of the particle size  $d_c$ , and of particle mass  $m_c$ , of such sols with concentration ( $C_p$ ) of the peptising agent. As  $C_p$  is increased,  $d_c$  falls continuously from  $d_0^*$  to below  $0.05 \mu$ , i.e.,  $m_c$  is reduced while  $N_c$  (the crystal number) is increased. For all the systems examined,

$$\log_{10} (N_c/N_0) = \log_{10} (M_c/M_0) = \log_{10} (d_c^3/d_0^3) = F'(C_p/C_s) \dots \dots (2)$$

where  $N_c = N_0$ ,  $M_c = M_0$ , and  $d_c = d_0$  at  $C_p = 0$ .  $F'$  is a negative constant, equal to the value of  $\log_{10} (M_c/M_0)$  at  $C_p/C_s = 1$ .

For the series of additives examined,  $-F'$  values were generally equal between  $0.3$  and  $0.8F$ .

The effect of all the peptising agents studied extends up to  $C_p$  values far beyond those that lead to minimum surface tension of the supersaturated solution.

*Factors determining  $F'$  Values.*— $F'$  values in turn depend on the sol concentration, the structure of the peptising agent, and the solubility of the precipitated salt.

(a) *Variation with sol concentration.* For any system of metal-salt and peptising agent,  $-F'$  falls markedly with increasing  $C_s$  values, according to a relation<sup>5</sup> of the type

$$-F' = \alpha(1/c_s)^m \dots \dots \dots (3)$$

where  $\alpha$  and  $m$  are constants. Some typical results are in Table 1.

\* The particle size ( $d_c$ ) of crystalline insoluble metal salts is generally  $>1 \mu$ .

<sup>5</sup> Packter and Matalon, *Discuss. Faraday Soc.*, 1955, **18**, 161.

<sup>6</sup> Martin, *Ind. Eng. Chem. Anal.*, 1939, **11**, 471.

<sup>7</sup> Jacobsen and Sullivan, *Ind. Eng. Chem.*, 1946, **18**, 360.

<sup>8</sup> Odén, *Arkiv Kemi, Mineralog., Geol.*, 1926, **9**, 1.

<sup>9</sup> Kolthoff and Rosenblum, *J. Amer. Chem. Soc.*, 1934, **56**, 1264, 1658.

<sup>10</sup> Kolthoff and Eggertsen, *ibid.*, 1940, **62**, 2125.

<sup>11</sup> Tabor and Salvinien, *Bull. Soc. chim. France*, 1944, **11**, 431.

<sup>12</sup> Coribet and Hamdiken, *J. Chim. phys.*, 1954, **51**, 18.

<sup>13</sup> Moillet and Curie, "Surface Activity," Chapter 7, Spon Ltd., London, 1951.

TABLE 1. *Variation of  $-F'$  with sol concentration.*

System	$-F'$ at sol molarity stated						
	1/200	1/280	1/400	1/600	1/800	1/1000	1/2000
Ag <sub>2</sub> CrO <sub>4</sub> -gelatin (pH 3.6) .....	<0.1		0.3			0.65	
Ag <sub>2</sub> CrO <sub>4</sub> -Na <sub>4</sub> ethylenediamine-NNN'N'-tetra-acetate (pH 8.0) .....	0.7		1.8			8.6	64.0
Cu pyridine thiocyanate-gelatin (pH 6)			<0.05	0.10	0.30		
PbI <sub>2</sub> -agar agar (pH 7; 30°) .....	6	19	90				

(b) *Variation with structure of the peptising agent.* Typical results for the peptising power (as measured by  $-F'$ ) of series of colloidal electrolytes and macromolecules for different metal-salt systems at 20° are presented in Table 2.

TABLE 2. *Variation of  $-F'$  with the nature of the peptising agent.*

m/400-Ag salts				m/600 Cu pyridine thiocyanite			
Peptising agent	pH	$-F'$		Peptising agent	pH	$-F'$	
		Chromate	Oxalate				
Gluconate .....	8.0	<0.01	<0.01	Gelatins :			
Citrate .....	8.0	0.032	0.01	Coignet .....	6.1		0.15
Na <sub>4</sub> edta <sup>a</sup> .....	8.0	0.32	0.11	Photogr. ....	6.1		0.10
				Starch .....	7.0		<0.05
Gelatins :				Gum tragacanth .....	7.0		<0.05
Coignet .....	3.6	0.60	0.30	Agar .....	7.0		0.50
Photogr. ....	3.6	0.50	0.25				
Spa .....	3.6	0.80	0.30				
				m/200-Pb salts			
Starch <sup>b</sup> .....	7.0	<0.05	n.d. <sup>e</sup>	Peptising agent	pH	Basic chromate	$-F'$ Iodide
Gum tragacanth <sup>c</sup> ...	7.0	0.16	..	Sucrose <sup>d</sup> .....	—	<0.05	<0.05
Alginate <sup>e</sup> .....	7.0	0.4	..	Dextrin <sup>d</sup> .....	—	<0.05	<0.05
Agar (at 30°) <sup>d</sup> .....	7.0	3.2	..	Starch <sup>d</sup> .....	—	0.05	0.04
				Methylcellulose .....	—	0.10	0.30
C <sub>12</sub> H <sub>25</sub> SO <sub>4</sub> Na .....				Gum tragacanth ...	7.0	3.0	2.8
Na oleate .....				CMC <sup>g</sup> .....	7.0	5.0	5.0
Cetyl pyridinium bromide				Agar (at 30°) .....	7.0	0.5	1.0
HO·[(CH <sub>2</sub> ) <sub>2</sub> O·(CH <sub>2</sub> ) <sub>2</sub> ] <sub>10</sub> OL <sup>f</sup>		0.016	0.010				
				m-600-Ca oxalate			
				Peptising agent	pH	$-F'$	
				Gelatin, photogr. ....	3.6		0.05
				Agar .....	7.0		0.20
				H <sub>p</sub> ·[O·CH <sub>2</sub> ·CH <sub>2</sub> ] <sub>n</sub> ·OH <sup>h</sup>	7.0		0.90
				H <sub>p</sub> ·[O·CH <sub>2</sub> ·CH <sub>2</sub> ] <sub>n</sub> ·OH <sup>h</sup>			
				<i>n</i> = 10 .....		n.d. <sup>e</sup>	0.006
				<i>n</i> = 15 .....		..	0.007
				<i>n</i> = 23 .....		..	0.008
				HO·[(CH <sub>2</sub> ) <sub>2</sub> O·(CH <sub>2</sub> ) <sub>2</sub> ] <sub>n</sub> OL <sup>f</sup>			
				<i>n</i> = 5 .....		..	0.04
				<i>n</i> = 10 .....		..	0.06
				<i>n</i> = 20 .....		..	0.04

<sup>a</sup> edta = ethylenediamine-NNN'N'-tetra-acetate. <sup>b</sup> Equiv. wt. = 90, *i.e.*, one HO-CO<sub>2</sub>H group per gluconic acid residue. <sup>c</sup> Equiv. wt. = 100, *i.e.*, as in (b). <sup>d</sup> Equiv. wt. = 2000, *i.e.*, one free SO<sub>4</sub> group per 10 galactose units (Packter, *J. Phys. Chem.*, 1955, **59**, 1140. <sup>e</sup> n.d. = not determined. <sup>f</sup> L = laurate. <sup>g</sup> CMC = carboxymethylcellulose. <sup>h</sup> Hp = heptyl. [Equiv. wt. = (mol. wt.)/*n*.]

High  $-F'$  values, corresponding to marked peptising properties, are observed when the additive possesses two essential structural features, *viz.*, a polar grouping through which adsorption may occur on to the surface of the sol particle, and a lyophobic section.

Both polypeptides and polysaccharic acids are effective peptising agents for silver salts, while polysaccharic acids and non-ionic detergents are suitable for lead salts.

The order of  $-F'$  values for peptisation of silver-salt systems follows inversely that of the "gold numbers" for peptisation of gold sols.<sup>15, 16</sup>

(c) *Variation with solubility of the peptised salt.* We have compared the  $F'$  values for the peptisation, by the same surface active agent, of series of crystalline salts of the same cation but different solubility. No correlation has been observed between  $F'$  values and the metal-salt solubility, either when the former have been compared for systems at constant sol concentration,

<sup>15</sup> Packter, unpublished work.

<sup>16</sup> Paul, Szper, and Szper, *Kolloid Z.*, 1938, **82**, 43.

<sup>16</sup> Williams and Chang, *J. Phys. Chem.*, 1951, **55**, 719.

or at constant supersaturation (cf. refs. 1 and 5). It appears that the peptising effects of a particular additive on a metal salt are determined by interaction with the whole molecule of the metal salt, and are not related to interaction of the metal cation with the peptising agent.

*Colloidal Sol Formation.*—It follows from equation (2) that, for any system of metal salt and peptising agent system,  $\log_{10} d_c^3 = \log_{10} d_o^3 + F'C_p/C_s$ .

In those systems where  $d_o$  is low, and  $-F'$  is high, the particle size of the material deposited from solution may fall to  $d_c^* = 0.01 \mu$ , the lower size limit for colloidal systems.

If  $d_c = d_c^*$  at  $C_p = C_p^*$ , we may define the term  $(C_p^*/C_s)_d$  as the peptisation ratio for size reduction (cf. ref. 5).

We have only verified relation (2) down to  $d_c$  values of ca.  $0.05 \mu$ ; but if we assume that it is obeyed down to  $d_c = d_c^*$ , it follows that

$$(C_p^*/C_s)_d = [3 \log_{10} (0.01/d_o)]/F' \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$(C_p^*/C_s)_d$  then varies inversely as  $\log_{10} d_o^3$  and  $F'$ . Generally, the  $(C_p^*/C_s)$  values with the sol concentration and the nature of the peptising agent for a particular system of metal salt and peptising agent are in the same relative order as the concentrations required for deflocculation alone,<sup>14</sup> i.e., the factors that enhance deflocculation lead to reduction of size at higher concentrations of peptising agent.

#### DISCUSSION

Polypeptides, polysaccharic acids, and polyhydroxylic non-ionic colloidal electrolytes are all good modifiers of crystal size; and their addition reduces the particle size of the deposits from supersaturated solutions of insoluble metal salts.

Stable sols (of average particle size  $<0.1 \mu$ ) may be prepared from "colloidal" insoluble metal salts by precipitation from supersaturated solutions in presence of suitable deflocculating agents,<sup>11-14</sup> or by actual dispersion of the dried precipitate. Certain "crystalline" insoluble metal salts may also be prepared as particles of size  $<0.1 \mu$ , by precipitation from very concentrated highly supersaturated solutions, but the complete deflocculation of these systems would require correspondingly large amounts of peptiser. The experiments described in this work suggest that a satisfactory method for preparing stable sols of many crystalline insoluble metal salts is to mix more dilute reacting solutions in presence of a peptising agent that reduces the particle size of the material deposited as well as acting as a deflocculant.

Most studies on modification of crystal size of soluble metal salts by surface-active agents have led to the conclusion that it is due to (physical) adsorption of monolayers of the added agent on to the growing host crystal, generally through specific polar groups. This adsorption in turn reduces the rate of both nucleus formation and crystal growth.<sup>17, 18</sup> It seems reasonable to suggest that a similar mechanism will explain the effect of surface-active agents on the crystal size of insoluble salt precipitates or sols.\*

We suggest that such adsorption of added agents reduces the rates of both coagulation and fitting of the sol micelles to form the final crystal (cf. ref. 1). The latter process is apparently affected to a far greater extent (cf. refs. 21); and only a small number of micelles fit on to an ordered crystal structure in each of the particles deposited

\* Earlier workers<sup>19</sup> suggested that crystal growth and coagulation may be significantly affected by diffusion factors; and one might expect these to be especially important in the systems studied in the present work, where the addition of peptising agents may increase the viscosity appreciably. However, Collins and Leinweber<sup>20</sup> recently showed that the particle size of insoluble metal-salt precipitates, over a wide range of viscosity, is not appreciably modified by diffusion, since the rates of both "nucleus" formation and growth on to nuclei are equally affected by viscosity.

<sup>17</sup> Packter, *J. Phys. Chem.*, 1955, **59**, 1140.

<sup>18</sup> Buckley, "Crystal Growth," Chapter 10, Chapman & Hall, London, 1951; Bunn, *Proc. Roy. Soc.*, 1933, *A*, **141**, 567; Wells, *Discuss. Faraday Soc.*, 1949, **5**, 197; Geydal, *J. Amer. Chem. Soc.*, 1956, **78**, 1803.

<sup>19</sup> Valetton, *Z. Kryst.*, 1923, **59**, 335; van Hook and Bruno, *Discuss. Faraday Soc.*, 1949, **5**, 112.

<sup>20</sup> Collins and Leinweber, *J. Phys. Chem.*, 1956, **60**, 389.

<sup>21</sup> Abkin and Lipatov, *Trudy Moskov. Tekhnol. Inst.*, 1941, 108; Nathanson, *Doklady Akad. Nauk, S.S.S.R.*, 1950, **74**, 517.

from solution. The final number deposited will then be increased, and the average particle size will be reduced (cf. refs. 22). The particle size will then vary with the concentration of peptising agent according to the exponential relation,  $\log_{10} (d_c^3/d_o^3) = F'(C_p/C_s)$ , where  $F'$  is negative, and the values of  $-F'$  will be roughly equal to half those of  $F$ , the corresponding constant in the exponential relation between sol stability and peptiser concentration.

Although our present data are insufficient for a detailed quantitative analysis, the results are in general agreement with these concepts. With the fall in hydrophilic character of a polymer macromolecule, the peptising power may fall with reduced adsorption affinity; on the other hand, increased length of the hydrophobic groups associated with an anchored polar group will lead to enhanced steric or sheathing effects. Hence, as the molecular weight of a series of polymers of similar type increases,  $-F'$  will depend on two conflicting factors: for some materials,  $-F'$  increases with molecular weight, while for others it reaches an optimum for some particular chain length. On the other hand, the  $F$  values for increase in stability generally fall rapidly with lower overall polarity of the peptising agent.

The peptising power of certain materials may also be reduced by association or aggregation of molecules. For colloidal electrolytes, micelles are formed at low concentrations, while units of macromolecules may also cohere strongly at interfaces;<sup>23</sup> the latter effect may, for example, be the cause for the poor peptising properties of starches compared with that of methylcellulose.

*Conclusions.*—The addition of complex peptising agents to supersaturated solutions of insoluble metal salts reduces the particle size of the precipitate deposited.

The peptisation effects probably occur by adsorption of monolayers of the additive through polar groups on to the surface of the growing metal-salt particles.

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<sup>22</sup> Duke and Brown, *J. Amer. Chem. Soc.*, 1954, **76**, 1443; Packter, 2nd Internat. Congr. on Surface-Activity 1957.

<sup>23</sup> Sir Eric Rideal, *J. Polymer Sci.*, 1955, **16**, 531.

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