

Notes

Repeptization of AgI-Flocs

Kruyt and Klompé (1) describe how they redisperse isoelectric AgI coagula by adding excess I^- ions. AgI flocs formed in electrolyte coagulation can also be redispersed with excess I^- , but there are circumstances where simply washing away the coagulating salt is enough to bring about the repeptization of AgI flocs. This makes the AgI hydrosol an interesting model system for a study of the conditions for repeptization, especially since so much is known already about the coagulation of this colloid.

Fresh precipitates are generally easier to redisperse than old ones (2-4). This indicates that an aggregate of colloidal particles is not in equilibrium. There are irreversible, temperature-dependent (1) aging processes in coagula. Therefore the interpretation of repeptization phenomena in terms of the interaction between the primary particles in an aggregate is impossible unless the data are obtained in experiments with a shorter time scale than the aging time of the flocs. Kruyt and Klompé indicate that at least some of the aging mechanisms run on a time scale of the order of minutes. This makes the interpretation of most earlier work on repeptization (5-8) dubious since these experiments involved the sedimentation of flocs and had time scales of the order of hours.

We adapted the optical method for the study of coagulation rates (9, 10) to the study of repeptization (Fig. 1). The degree of coagulation in a sol could thus be measured long before settling of the flocs occurs. By suddenly diluting the intermicellar electrolyte after only a short period of coagulation (t) we could switch to repeptization conditions. In most of our experiments t was only a little longer than the Smoluchowski half-life time of the coagulating colloid (10). Beer's law held for stable AgI sols as well as for these sols in given states of aggregation. Therefore the optical extinction after $5\times$ dilution (B_t) could be compared with the calculated values $B_{ft} = 0.2 B_f$ and $B_{st} = 0.2 B_s$ for no repeptization and complete repeptization, respectively. In Fig. 1 the effects of dilution with H_2O and with $0.1 M KNO_3$ are compared. The effects of variations in sol concentration, in coagulant, in degree of dilution, and in age of the aggregate can be studied by this method and extra agents can be introduced to promote or hinder redispersion.

AgI sols were prepared by slowly adding $0.04 M AgNO_3$ to a slight excess of equally concentrated KI solution. Sols were routinely aged, either for two weeks at room temperature or for 64 hours at $80^\circ C$, and then diluted (approximately $4\times$) so that their extinction was between 0.5 and 1 at $\lambda = 800 nm$ in 10-mm cuvettes. We observed that without aging there is a steady increase in the extinction of the sols with time, accompanied by a decreasing stability against added electrolytes

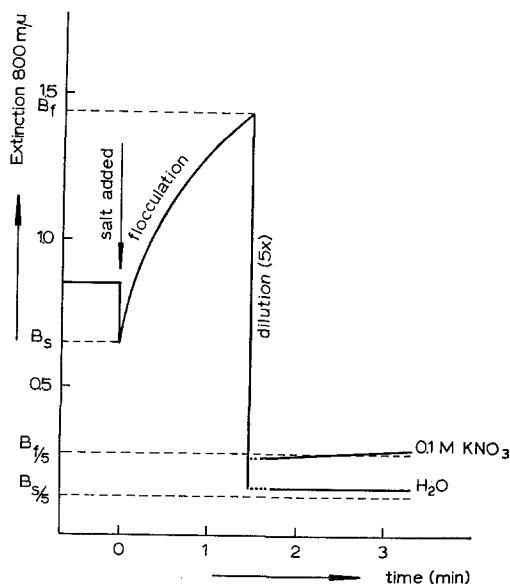


FIG. 1. Optical extinction (B) vs. time during the coagulation and the repeptization of an AgI hydrosol. Dilution with H_2O and with $0.1 M KNO_3$ results in different degrees of aggregation (B_t).

(*cf.* reference 11). In such changing sols repeptization was considerably less complete than in the same colloids under the same conditions but after aging. The aged sols were used without further treatment. pI varied between 4 and 5. All experiments were carried out at room temperature ($20^\circ \pm 2^\circ C$).

In order to compare B_t , B_{ft} , and B_{st} we introduce the number D , defined as $D = (B_{ft} - B_t) / (B_{ft} - B_{st})$. Somewhat loosely one might call D the degree of repeptization: at $D = 1$ there is

complete reeptization. $D = 0$ means that all aggregates remain intact upon dilution. By centrifugation we established that the variations in D as they were obtained in our experiments correspond to variations in the state of aggregation.

After coagulation with $0.115 M KNO_3$ and dilution with water the reeptization was nearly complete ($D = 0.9$). Neither changes in pI at the different stages of coagulation and/or dilution, nor the degree of dilution, nor the original sol concentration affected the reeptizability of flocs in our (short t) experiments. There was a slight effect of the salt concentration during coagulation. With constant $B_{f,t}$ and $B_{s,t}$, D changed from 0.9 to 0.8 as the concentration during coagulation increased from 0.10 to $0.15 M KNO_3$, i.e., from just below to well above the coagulation threshold of the sols. Details on the experiments can be found elsewhere (12).

Table I shows the influence of concentrations in the diluting solution on the degree of reeptization. In all these experiments coagulation was in $0.115 M KNO_3$. The coagulating sol was diluted to $5\times$ its volume with KNO_3 solutions of concentra-

tions C_d or with a glucose solution of 18.01 gm/l which is isotonic with $0.10 M KNO_3$ (13). Analogous results were obtained in coagulation and dilution with salt solutions containing other monovalent counterions for the negative AgI -sol. From Table I it follows that the changes in D are brought about by the changes in electrolyte concentration upon dilution, and not by the dilution process as such. That the glucose in Ih did not hinder redispersion in the same way as the KNO_3 in Id indicates that it is not the difference in osmotic value inside and outside an aggregate which causes reeptization (14), but that electrical (double layer) repulsion breaks the flocs. This is borne out more clearly by Table II, which shows the effects of counterion valency on the reeptization of AgI . Here the general procedure was as in Table I, but solutions of different salts were used for coagulation and for dilution. In Table II C_d is the concentration during coagulation; C_d is again the concentration of the diluting solution; \bar{C}_d is the average concentration of the dilute system. After coagulation with Ba or La nitrate the dilution either with water or with dilute KNO_3 fails to produce reeptization. The same was known already about oxides and sulfides (6, 7), so this seems to be a rather general rule. After coagulation with KNO_3 dilution with Ba or La nitrate solution (below the coagulation concentration) does cause reeptization. The experiments d-g in Table II show that the reeptization of a floc is governed by the counterions present at its formation, and that the final composition of the intermicellar liquid is of little consequence for the reeptization process.

Table III describes the effects of the age of flocs on their reeptizability. Here coagulation was again in $0.115 M KNO_3$, dilution with water ($5\times$) at a time t after the onset of coagulation. In these experiments $B_{s,t} = 0.085$. Analogous results were obtained at other salt concentrations

TABLE I
EFFECT OF ELECTROLYTE CONCENTRATION

	$C_d (M KNO_3)$	D
a	0-0.07	0.9
b	0.08	0.8
c	0.09	0.7
d	0.10	0.4
e	0.11	0.2 ^a
f	0.12	<0.1 ^a
g	0.13	<0.1 ^a
h	Glucose	0.9

^a Coagulation continues.

TABLE II
EFFECT OF COUNTERION VALENCY

	Salt	$C_d(M)$	$C_d(M)$	$\bar{C}_d(M)$	D
a	KNO_3	11.5×10^{-2a}	0	2.4×10^{-2}	0.9
b	$Ba(NO_3)_2$	16.7×10^{-4a}	0	3.3×10^{-4}	0.1
c	$La(NO_3)_3$	3.5×10^{-5a}	0	0.7×10^{-5}	0.1
d	$\left\{ \begin{array}{l} KNO_3 \\ Ba(NO_3)_2 \end{array} \right.$	11.5×10^{-2}	— 4.0×10^{-4}	$\left. \begin{array}{l} 2.4 \times 10^{-2} \\ 3.3 \times 10^{-4} \end{array} \right\}$	0.9
e	$\left\{ \begin{array}{l} KNO_3 \\ Ba(NO_3)_2 \end{array} \right.$	16.7×10^{-4}	— 3.0×10^{-2}	$\left. \begin{array}{l} 2.4 \times 10^{-2} \\ 3.3 \times 10^{-4} \end{array} \right\}$	0.1
f	$\left\{ \begin{array}{l} KNO_3 \\ La(NO_3)_3 \end{array} \right.$	11.5×10^{-2}	— 0.9×10^{-5}	$\left. \begin{array}{l} 2.4 \times 10^{-2} \\ 0.7 \times 10^{-5} \end{array} \right\}$	0.9
g	$\left\{ \begin{array}{l} KNO_3 \\ La(NO_3)_3 \end{array} \right.$	— 3.5×10^{-5}	3.0×10^{-2} —	$\left. \begin{array}{l} 2.4 \times 10^{-2} \\ 0.7 \times 10^{-5} \end{array} \right\}$	0.1

^a These gave the same rate of coagulation.

TABLE III
EFFECT OF FLOC AGE

	$t(\text{sec})$	B_t	D
a	105	0.10	0.9
b	550	0.18	0.7
c	1800	0.29	0.3

(e.g., a decrease $D = 0.85$ to $D = 0.05$ in 1800 sec at $0.143 M KNO_3$). In Table III the rise of B_t compared to the constant B_{st} is a direct indication that flocs which grow at the same rate and under the same circumstances become less reversible with time. It is possible that extrapolation to small t would make $D = 1$ in all cases. The time of contact and the closeness of the contacts determine the amount of aging in a floc and therefore its rezeptizability.

From the above we conclude that the AgI hydrosol can indeed be rezeptized by washing away the coagulating electrolyte. This is not an osmotic effect. It is brought about by the lowering of the counterion concentration. Since it is also quite sensitive to the valency of counterions, especially of those inside the floc structure, it is very likely that double layer repulsion is the driving force for this rezeptization.

Rezeptization is a very rapid, spontaneous process. On the time scale of our experiments its rate could not be measured. In our experiments we would reach high degrees of rezeptization only if the time scale of the experiment was short relative to that of aging processes in the flocs. If there have been doubts about the truly electrocratic nature of the colloids (mainly oxides and sulfides) which have been known to rezeptize easily, there is no reason to distrust the AgI-hydrosol in this respect. Therefore rezeptization should find a natural place in the description of electrocratic

colloids as the opposite process of coagulation (15).

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