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Original Scientific Paper

Methorics of the Precipitation Processes. XXIII. Flocculation and Charge Reversal of AgI Colloid in the Presence of Large Organic Ions and Electrolytes*

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Flocculation and charge reversal of AgI colloid in the presence of large organic ions bromophenolblue (BPB) and rhodamine B (Rhd B) has been investigated in aqueous or alcoholic medium. The kinetics of particle growth was followed tyndallometrically. By spectrophotometric measurements the adsorption isotherms were determined.

The flocculation mechanism is proposed on the basis of flocculants' action on surfaces either of the same or opposite charge. The flocculation and charge reversal of AgI sol in the presence of dyes were found to be simultaneous processes.

A AgI sol stabilized by BPB was flocculated in the presence of neutral electrolytes.

INTRODUCTION

Since Picton and Linder¹ and Freundlich² started the examination of the precipitation effects of electrolytes and organic substances on colloid systems and postulated some general principles of the flocculation theory, the problem has not yet been solved. Fajans^{3,4}, Schulek and Pungor^{5,6} developed the theory of adsorption indicators, which is in very close relation with the flocculation action of these dye-indicators, while La Mer and coworkers^{7,8,9} have developed the theory of flocculation, subsidence and refiltration. The flocculation phenomena were presented by La Mer using the filtration velocity of colloidal dispersions of the silica and the phosphate slimes in the presence of high polymers and polyelectrolytes.

Nowadays some authors started to use La Mer's definition of flocculation and to respect the distinction between flocculation and coagulation. It seems fully justified that the distinction between flocculation (mainly stereospecific) and coagulation (mainly coulombic) interaction should be recognized. In this respect it is interesting to investigate the interaction between organic dyes and AgI colloid.

Earlier^{10,11,12} we examined some flocculation phenomena of AgI in the presence of organic ions (sodium fluoresceinate and others). In this paper another organic dye bromophenol blue (BPB) is used to show the flocculation,

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reversal of charge and stabilization of the AgI colloid. This study is a kinetic one, although some stages indicate an approach to quasi equilibrated states. Also the systems in question are neither at the starting nor final states quite strictly definable.

EXPERIMENTAL

Materials

The chemicals used were of Analar grade from »Merck« — Darmstadt. The silver nitrate, and potassium iodide were standardized potentiometrically and by Fajans' method. The dyes used were bromophenol blue (BPB) and rhodamine B (Rhd B). The solutions were prepared with bidistilled water.

Methods

The precipitation systems were prepared using the technique *in statu nascendi* described earlier¹³ and *in situ* — this means that a certain time after the main precipitating components had been mixed, the flocculating or coagulating components were added. Tyndallographic values were measured by a Pulfrich photometer connected with a Zeiss tyndallogram. In order to estimate the adsorbed amounts of dyes on silver iodide the precipitates (colloid systems) have been centrifuged in a Janetzky centrifuge for 5 minutes at 10 000 r.p.m., 15 minutes after the systems had been prepared. For determination of dye concentration in supernatant solution after centrifuging a Pye Unicam spectrophotometer SP-1800 was used. The particle charge was determined by ultramicroscopic electrophoresis.

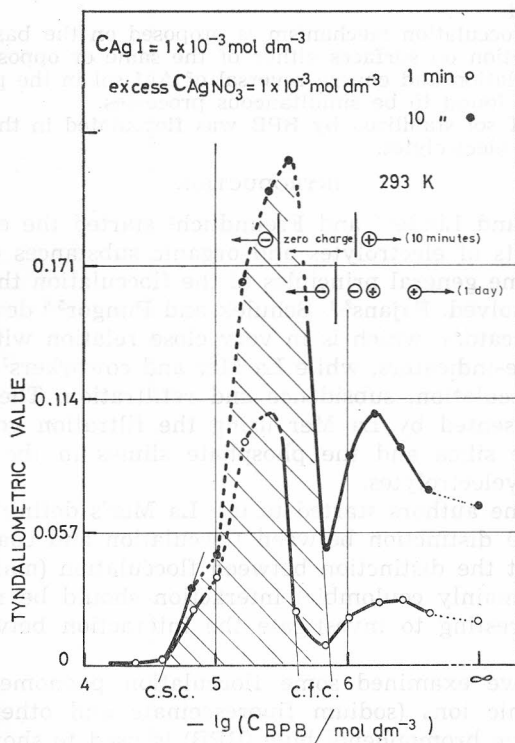


Figure 1. The concentration tyndallogram for system: AgNO₃ (in excess) — KI — BPB (gradient concentrations). Tyndallographic values measured 1 and 10 minutes after mixing of the precipitating components *in statu nascendi*. Particle charge was measured 10 minutes and 1 day after.

RESULTS

Usually, the concentration of silver iodide sol was constant, and the concentration of flocculant was changed successively. Experimental results of tyndallographic, spectrophotometric and electrophoretic measurements are presented graphically in Figures 1—6 and tabulated.

Figure 1 presents the typical concentration tyndalogram for concentration of $10^{-3} \text{ mol dm}^{-3} \text{ AgI}$, and excess concentration of $10^{-3} \text{ mol dm}^{-3} \text{ AgNO}_3$, being the same for the other examined sol concentrations. It is shown that the reversal of charge takes place in the concentration of BPB smaller than the critical flocculation concentration (c.f.c.). The c.f.c. and the critical stabilization concentration (c.s.c.) are related to the sol concentration as it is shown in Figure 2, where the region of flocculation and the zero charge region are presented. If the concentration of AgI is greater, more of BPB is needed for the flocculation and the stabilization of sol particles.

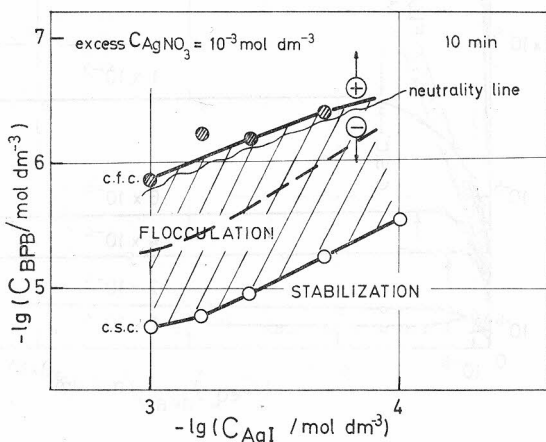


Figure 2. Flocculation region for various concentrations of AgI sol (excess concentration of AgNO_3 is constant).

In Figure 3 the adsorption isotherms are presented as $(c_o - c_{eq})$ versus c_{eq} . Figure 4. presents adsorption isotherms as $(c_o - c_{eq})$ versus c_o . The symbols used:

- c_o = initial concentration of BPB
- c_{eq} = equilibrium concentration of BPB residual in supernatant solution after centrifugation
- $c_o - c_{eq} = c_{ads}$ = adsorbed amount of BPB
- $(c_o - c_{eq})_{max} = c_{ads,max}$ = maximum adsorbed amount of BPB obtained from the limiting value of the adsorption isotherm
- $c_{ads,max}/c_{sol}$ = maximum adsorbed amount of BPB per unit mass of adsorbent (sol AgI).

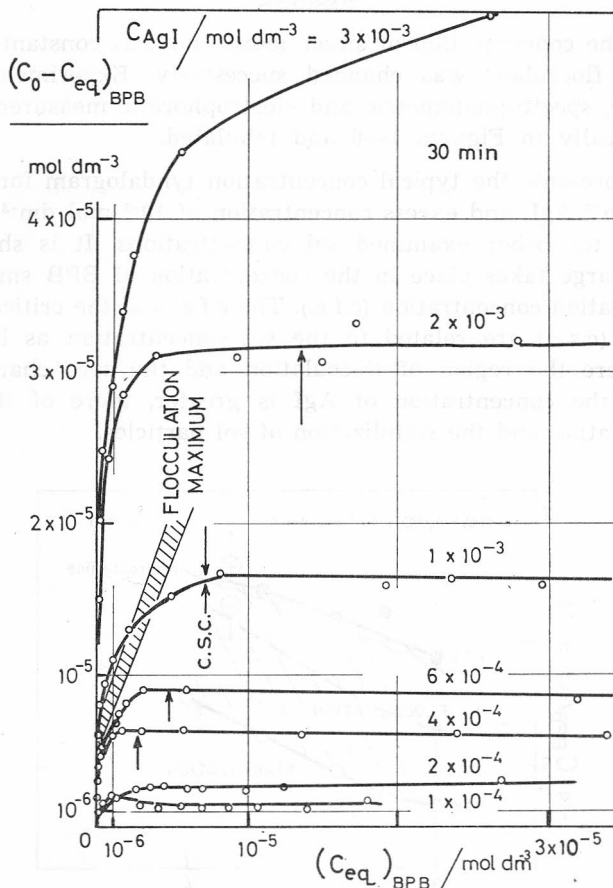


Figure 3. Adsorption isotherms at different sol concentrations. Adsorbed amount of BPB as a function of equilibrium concentration of BPB residual in supernatant solution after precipitation and centrifugation.

TABLE I

$c_{\text{sol}}/\text{mol dm}^{-3}$	$c_{\text{ads.max}}/c_{\text{sol}}$
3×10^{-3}	1.8×10^{-2}
2×10^{-3}	1.6×10^{-2}
1×10^{-3}	1.6×10^{-2}
6×10^{-4}	1.5×10^{-2}
4×10^{-4}	1.55×10^{-2}
2×10^{-4}	1.3×10^{-2}
1×10^{-4}	1.3×10^{-2}

(excess concn of AgNO_3 10^{-3} mol dm^{-3} ; adsorption measured after 30 minutes)

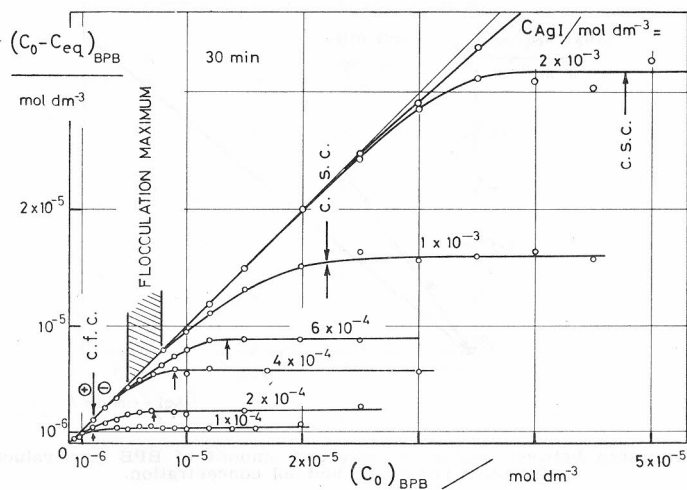


Figure 4. Adsorption isotherms for the same conditions as in Figure 3. Adsorbed amount of BPB as a function of initial concentration of BPB.

The c.f.c. and c.s.c. are denoted by arrows. The flocculation maximum is denoted for sol concentration of 10^{-3} mol dm $^{-3}$. It is shown that the concentration of BPB at maximum flocculation is about one half of c.s.c. This phenomenon is observed for all examined sol concentrations. The Langmuir type isotherms show the limiting value dependent on sol concentration.

The ratio $c_{\text{ads.max}}/c_{\text{sol}}$ has the constant value for the examined concentrations of positively charged sol amounting to about 1.5×10^{-2} (Table I). When we took negatively charged AgI (conc. of AgI 10^{-3} mol dm $^{-3}$, excess conc. of KI 10^{-4} mol dm $^{-3}$) and tried to flocculate it in the presence of BPB, the ratio became 2×10^{-3} . The experiments performed with positively charged sols in an alcoholic medium (30% EtOH) show about the same flocculation phenomena and a slightly stronger adsorption due to the different dispersity of AgI particles. The adsorption measurements resulted 2×10^{-2} for the ratio $c_{\text{ads.max}}/c_{\text{sol}}$. Systems prepared by the technique *in situ*, when BPB was added to the AgI sol aged 10 seconds or 3 hours, showed similar flocculation phenomena and the adsorption isotherms are the same within the limits of experimental errors.

From these results we can see that the adsorption is related to the sol concentration, and is slightly influenced by changes of the mediums' dielectric constant. The adsorption per unit mass is not dependent on the sol concentration; it is changed by the character of surface, *i.e.*, the positively or negatively charged AgI colloid, respectively. Consequently the plot of $(c_0 - c_{\text{eq}})_{\text{max}}$ versus c_{sol} gives the straight line presented in Figure 5. Adsorption was measured 30 minutes and 1 day after preparing the systems. In the present paper the surface areas were not measured, and the sol concentration, *i.e.* the amount of AgI sol precipitated, was presumably taken to be related to the whole area that was available to the dye.

The adsorption isotherms derived from spectrophotometric measurements followed the Langmuir's equation. Similar results of dye adsorption among

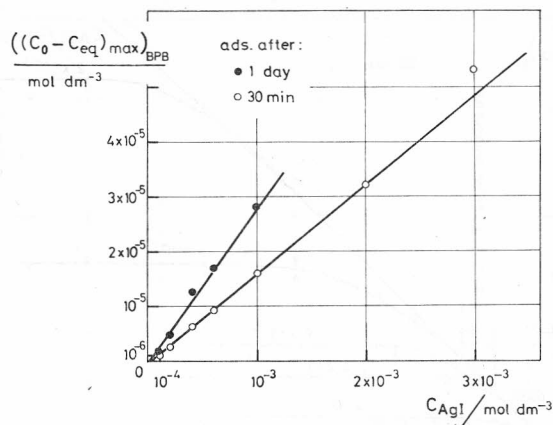


Figure 5. Relationship between maximum adsorbed amount of BPB (the values taken from adsorption isotherms) and sol concentration.

others were published by Padday^{14,15} and Herz and Helling^{16,17} for some cyanine dyes adsorbed on silver halide surfaces.

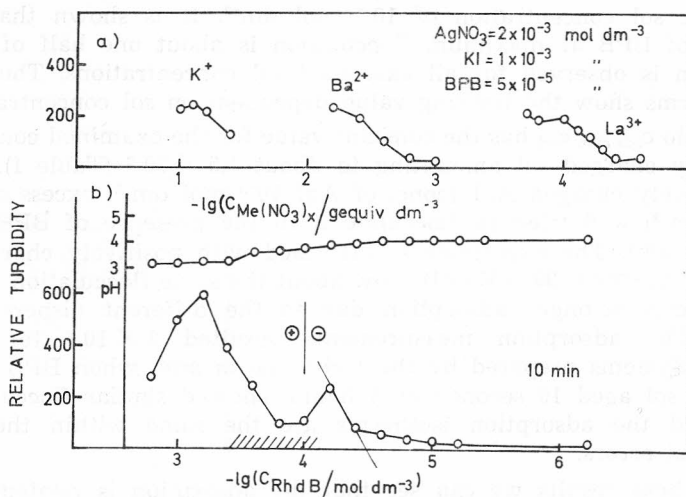


Figure 6. Four-component system:

- a) (AgNO_3 (in excess) — KI — BPB) — constant concentrations, and K, Ba, La-nitrates — changed concentrations. Coagulation action of electrolytes following Schulze-Hardy rule.
 b) (AgNO_3 (in excess) — KI — BPB) — constant concentrations, and Rhd B — changed concentrations. Flocculation action of Rhd B and reversal of charge.

It is interesting to see the behaviour of particles of AgI sol stabilized by BPB against neutral electrolytes (K, Ba, La-nitrates) and the flocculating agent (Rhd B). For this purpose some experiments were performed and the results presented in Figure 6 part a) for coagulation in the sense of Schulze-Hardy rule; part b) shows the flocculation of such negatively stabilized sol in the presence of positive Rhd B. Such a complex precipitation system can

be treated as mixed type of the coagulation — flocculation phenomena. On the basis of tyndallometric and electrophoretic measurements the supposed type of »sandwich« particles is: $\text{AgI}^+ / \text{Dye}^- / \text{Dye}^+$.

DISCUSSION

The terms coagulation — flocculation are very much used in literature, but not always quite clear defined. The coagulation is mainly caused by coulombic interaction and according to B. Težak¹⁰ is due to the formation of ion pairs between stabilizing ions adsorbed and the counter ions within the methorical layer. The flocculation is mainly caused by adsorption and defined by La Mer^{18,19} as a rapid and specific precipitation process, meaning to form a floc, *i. e.* producing a network of flocs of the porous structure which permits a rapid rate of filtration.

In the early history of coagulation — flocculation experiments Freundlich² already has shown that organic substances have lower critical concentrations needed for the precipitation of colloids than the inorganic salts. Usually, according to the Schulze—Hardy rule against negatively charged sols the c.c.c. for monovalent inorganic cation are about 10^{-1} g-equiv. dm^{-3} , for bivalent cation 2×10^{-3} g-equiv. dm^{-3} and for trivalent cation 4×10^{-5} g-equiv. dm^{-3} , while the c.f.c. for BPB was found to be from 3×10^{-7} to 2×10^{-6} mol dm^{-3} and for c.s.c. 3×10^{-6} to 2×10^{-5} mol dm^{-3} depending on sol concentration (or surface of adsorbent that needs to be covered by dye molecules in the flocculation process). Therefore, it is reasonable to assume that the flocculation action is mainly due to the stereospecific adsorption of flocculant. It does mean that in general accordance with the explanations of La Mer, we may assume that the flocculation is caused by specific steric forces (adsorption) and inclusions in precipitate, therefore, of some kinds of molecules within the methorical layer. The attractive forces that cause flocculation are due to the chemical, stereochemical and physical structure of flocculant from one side, and the properties of the surface one the other side; thus, the role of charge may be in many cases quite unimportant. The reversal of charge characterizes the flocculation also, and the zero charge is usually reached before the flocculation maximum. Thus we can represent the mechanism of flocculation with rising BPB concentration (Figure 1):

(1) sensitization occurs at small amounts of BPB, involving coulombic interaction, coagulation, neutralization and reversal of charge; this is the region of the first maximum at about 10^{-6} mol dm^{-3} of BPB;

(2) flocculation action occurs at higher concentrations of BPB and involves the stereospecific interaction of silver iodide particles of reversed charge with dye molecules of the same charge as the surface is. When the amount of BPB in the methorical layer is exhausted by adsorption in relationship to the concentration of kinetic species in the bulk solution, the particles were driven together and flocculated;

(3) at still higher concentrations of BPB a flocculation maximum is reached which is the result of very fast formation of flocs as sponge-like particles;

(4) further addition of flocculant saturates the surface with BPB molecules and no more such molecules can be attracted to the surface. The molecules accumulate at higher concentration in the methorical layer than that in the

bulk of solution; the result is the stabilization or peptization of such a system²⁰.

By changing the sol concentration the corresponding change of c.f.c. and c.s.c. takes place.

Adsorption measurements give the isotherms of the Langmuir type. The curves show the limiting values which are strongly dependent on the sol concentration. Up to the top of the flocculation maximum all BPB from solution is adsorbed; $c_{eq} = 0$. In the flocculation maximum one half of surface is usually covered. By higher concentration of flocculant the adsorbed amount is increased reaching a constant value at c.s.c.; that means the completely covered surface characterizes the stabilization.

CONCLUSION

A mechanism of the flocculation process is proposed using the example of positively and negatively charged AgI sol precipitated in the presence of BPB. The experimental data and the explanations are in general agreement with the flocculation theory of La Mer⁷ and in complete accordance with the interpretation of coagulation and flocculation phenomena already published^{10,20,21}.

The maximum amount adsorbed per unit mass of adsorbent possesses a constant value, which changed only if the character of surface is changed.

It is generally proposed that the flocculation process is usually composed first of the neutralization of charge, and than the stereospecific adsorption of the ions on the surface of either the same or opposite charge. The maximum flocculation takes place when 1/2 of the surface is covered, while the stabilization is reached when the whole surface is covered with adsorbed ions or molecules. The maximum adsorbed amount of BPB *versus* sol concentration shows a straight line.

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SAŽETAK

Metorika precipitacionih procesa. XXIII. Flokulacija i prenabijanje sola AgI u prisustvu velikih organskih iona i elektrolita**Đ. Težak, M. Jedovnický i B. Težak*

Flokulacija i prenabijanje sola AgI ispitivani su u nazočnosti velikih organskih iona bromfenol plavog (BPB) i rodamina B (Rhd B) u vodenom ili alkoholnom mediju. Kinetika rasta čestica praćena je tindalometrijski. Adsorpcijske izoterme dobivene su na temelju spektrofotometrijskih mjerenja.

Flokulacijski mehanizam predložen je na osnovi djelovanja flokulanta na suprotno ili isto nabijene površine sola AgI. Nađeno je da su procesi flokulacije i prenabijanja sola AgI u priststvu organskih iona simultani. Maksimalna adsorbirana količina BPB na količinu sola daje konstantnu vrijednost.

Solovi AgI stabilizirani bojom BPB, flokulirani su rodaminom B ili koagulirani elektrolitima.

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