Coagulation Effects of Sodium Pyrophosphate on Silver Halide Sols *in Statu Nascendi*

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The effects of electrolytic coagulation of hydrophobic sols of silver halides *in statu nascendi* by aqueous solutions of sodium pyrophosphate have been investigated.

The precipitation system $AgNO_3$-$Na_4P_2O_7$ shows one maximum. The height of this maximum depends strongly on the concentration of the lattice forming ions. When nitric acid is added and the concentration of $AgNO_3$ is held constant the maximum shifts to higher pyrophosphate concentrations.

The precipitation system $AgNO_3$ — K-halide — $Na_4P_2O_7$ gives a precipitation curve with three different but very distinct separated maxima. The first maximum appears at high pyrophosphate concentration when the pH value exceeds 9 and consists probably of a mixed system of silver oxide and silver halide. The second maximum is the pure silver pyrophosphate which appears at the same place as when no halide component is present. The third is the silver halide maximum effected by the coagulation of the silver halide sol by means of pyrophosphate ions. The critical coagulation concentration shows the value which is characteristic for tetravalent counter ions. Other effects (e. g. the reversal of charge, the sequence of the coagulation value for different silver halide sols, the effect of sol concentration etc.) also prove the tetravalent character of pyrophosphate ion as counter ion. When nitric acid is added the dissociation equilibria of pyrophosphate ion change and the coagulation concentration takes higher values.

Gelatin was used for the differentiation of crystallisation and coagulation processes in investigated systems.

INTRODUCTION

The coagulation effects of tetravalent counter ions were often — owing to their variety — very interesting subjects of research. According to the Schulze-Hardy rule the critical coagulating concentration of tetravalent counter ions is extraordinary low. Further, the ions of higher valency cause the reversal of the charge of sols. The sols of reversed charge may also be coagulated but with the other ion of the added electrolyte. All the mentioned phenomena give us characteristic precipitation curves on which it is possible to distinguish various maxima and minima[1].

We intend to describe in this paper our experiments with positive silver halide sols when the coagulation has been accomplished by the tetravalent pyrophosphate ions. In this case the precipitation curve will be more compli-

cated since besides the silver halide sol, the silver pyrophosphate may be formed. On the other hand the pyrophosphate ion hydrolyses very strongly and causes at higher concentrations the alcaline reaction of the media making possible the formation of another slightly soluble salt — the silver oxide. Only under suitable experimental conditions it will be possible to obtain the precipitation curve with discernable maxima and minima.

EXPERIMENTAL

The experimental technique used in these investigations was the same as described previously[2]. The turbidities were determined by means of a Pulfrich photometer with a Zeiss nephelometer. The pH values were measured with the Macbeth apparatus with glass electrode. The charge of the sol was determined qualitatively in a simple electrophoretic cell by means of a slit ultramicroscope.
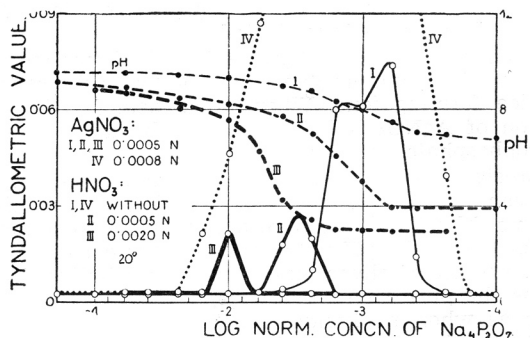

Fig. 1. Concentration tyndallograms. Precipitation maxima of the system $AgNO_3 - Na_4P_2O_7$. The effect of the concentration of $AgNO_3$ and of the added nitric acid on the size and the position of these maxima. Dashed curves represent corresponding pH values.

Since by mixing of silver nitrate and sodium pyrophosphate solutions the slightly soluble silver pyrophosphate may be formed, we investigated first this precipitation system. The results are given on Figure 1. The precipitation maximum formed depends very strongly on the concentration of silver nitrate and shifts by addition of nitric acid towards higher concentrations of sodium pyrophosphate. The corresponding pH curves are drown in the same diagram.

Figure 2 shows the coagulation effect of $Na_4P_2O_7$ on silver bromide sol *in statu nascendi* without HNO_3 and with 0,0005 N to 0,0020 N HNO_3. Each precipitation curve shows three maxima and three minima. The first maximum at high concentrations of sodium pyrophosphate is independent of the HNO_3 added. In this concentration region the pH value lies between 9 and 10. The second maximum appears nearly at the same concentrations as shown on Figure 1. The third maximum is very sensitive to the addition of nitric acid. Its limits—both the stabilisation limit (B) and the coagulation limit (A) — shift considerably to higher pyrophosphate concentrations when HNO_3 is added. The larger the concentration of added nitric acid the greater is the shifting of the limits.

Figure 3 shows the effects with the silver iodide sol. Under the same experimental conditions as in the preceding figure, the second maximum disappears, so that only the first and the third maxima are developed. We suppose that the disappearance of the silver pyrophosphate maximum is caused by the
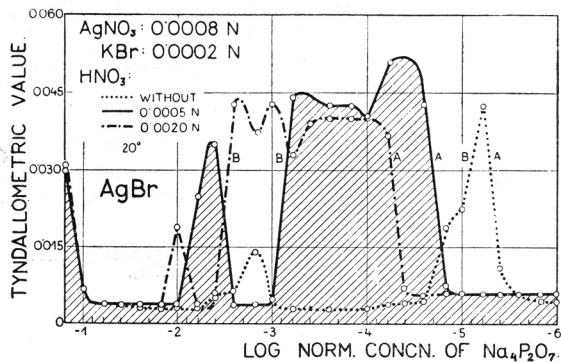

Fig. 2. Concentration tyndallograms. Precipitation curves of the system: silver nitrate — potassium bromide — sodium pyrophosphate — (nitric acid), 10 minutes after mixing the reacting components.

complex binding of Ag^+ by I^-. If there is an excess of Ag^+ in the solution the maximum appears again. Figure 4 shows that when the concentration of $AgNO_3$ in such a system reaches the value of 0,0015 N, a strongly marked silver pyrophosphate maximum is developed.

Fig. 5 gives the results with the silver chloride sol. Also in this case it is possible to distinguish three maxima although the third appears rather effaced.
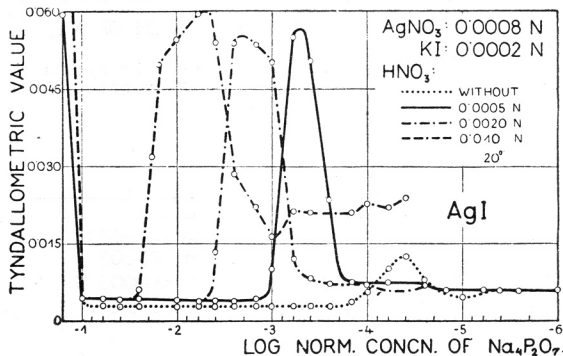

Fig. 3. Concentration tyndallograms. Precipitation curves of the system: silver nitrate — potassium iodide — sodium pyrophosphate — (nitric acid), 10 minutes after mixing the reacting components.

If gelatin is added to the described systems the third maximum dissapears entirely, whilst the first maximum develops after some hours. The silver pyrophosphate maximum develops completely as without addition of gelatin. If KBr is present the pyrophosphate maximum is considerably reduced. All these effects are given on Figure 6.
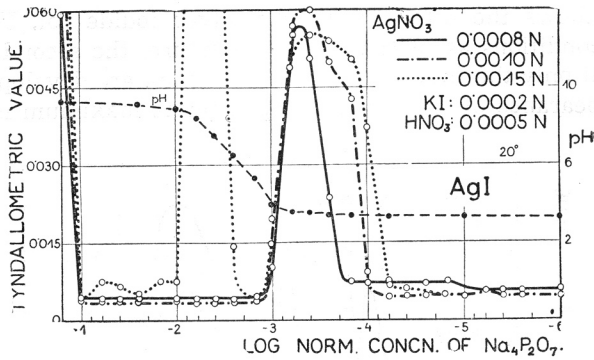
Fig. 4. The effect of various concentrations of AgNO₃ on the precipitation curve of the system AgNO₃ — KI — Na₄P₂O₇ — HNO₃.
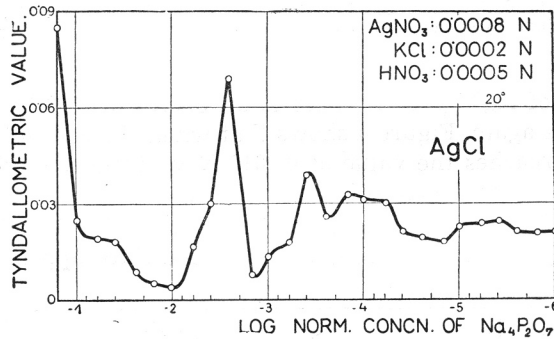

Fig. 5. Concentration tyndallogram. Precipitation curve of the system silver nitrate — potassium chloride — sodium pyrophosphate — nitric acid, 10 minutes after mixing the reacting components.
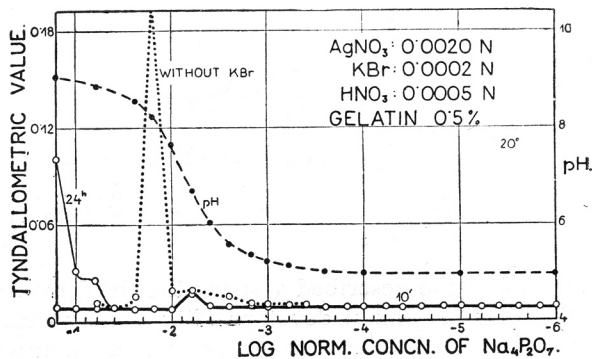

Fig. 6. The effect of gelatin on the precipitation of silver pyrophosphate and silver bromide in the presence of pyrophosphate ions.

DISCUSSION

Our experimental results show that the silver halide sols *in statu nascendi* —· when coagulated with sodium pyrophosphate — give characteristic »precipitation spectra«. The maxima are of a different kind. The first maximum is very probably a mixed system consisting of silver oxide and silver halide. It is, however, interesting to note, that this maximum doesn't appear when no halide ions are present in the solution although pH has reached the value at which the solubility product of silver oxide is exceeded. It seems that pyrophosphate ions inhibit its formation. If halide ions are added the maximum appears always at the same place; likewise when gelatin is added, but then after a longer time. All these effects prove its complex character. The silver pyrophosphate maximum is a crystallisation maximum. The experimental records on Figures 1 and 6 serve as basis for this statement*.

The third maximum is the silver halide maximum developed under the influence of pyrophosphate ions. This maximum shows all properties of hydrophobic precipitation systems if coagulated by tetravalent counter ions. The critical coagulation concentration in the neutral media amounts for the silver bromide to $\sim 3 \times 10^{-6}$ N and for the silver iodide sol to $\sim 5 \times 10^{-5}$ N. For the silver chloride sol it was not possible to determine the exact value, because the maximum was not sufficiently pronounced. The mentioned values agree in order entirely with critical coagulation concentration of tetravalent counter ions. The sequence of values for different silver halide sols agrees with those previously determined[3].

An analogue shift of the stabilisation limit (Figure 2, B) if nitric acid is added could be found in coagulation of negative silver halide sols with Th^{4+} ions. But the large shifting of the coagulation limit (Fig. 2, A) is characteristic for coagulation effects of pyrophosphate ions. It is possible to explain this effect as a consequence of the change in the dissociation equilibria of pyrophosphate ions under the influence of added nitric acid.

An increase of the concentration of potential determining ion (Ag^+) causes a lowering of the critical coagulation values. Such effect we could establish already earlier, especially with trivalent counter ions[4].

The electrophoretic measurements showed that the positive silver halide sols change under the influence of pyrophosphate ions their charge. This effect of reversal of charge as mentioned is a general property of tetravalent counter ions.

The investigations described prove that the coagulation effects of pyrophosphate ions on silver halide sols although very complex can be explained and that these effects are in full agreement with our results published previously.

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* Compare the discussion in our paper: »Über komplexe Fällungserscheinungen der Silberphosphat-Sole *in statu nascendi*«, *Kolloid-Z.* in press.

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IZVOD

Koagulacioni efekti natrijeva pirofosfata na solovima srebrnih halogenida
in statu nascendi

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Ispitivan je utjecaj natrijeva pirofosfata na koagulaciju pozitivnih solova srebrnih halogenida *in statu nascendi*.

Najprije su istraženi uvjeti, pod kojima se taloži srebrni pirofosfat bez prisutnosti halogenida. Rezultati su prikazani na sl. 1, gdje se vidi položaj i veličina taložnih maksimuma uz različite koncentracije $AgNO_3$ kao i utjecaj dodane dušične kiseline.

Slike 2, 3, 4 i 5 pokazuju taložne krivulje sistema srebrni nitrat — kalijev bromid (jodid ili klorid) — natrijev pirofosfat uz različite dodatke dušične kiseline. Na taložnoj se krivulji razabiru tri izrazita maksimuma. Prvi maksimum (kod najviših koncentracija pirofosfata) vjerojatno nastaje zbog taloženja miješanih sistema, koji se sastoje od srebrnog oksida i srebrnog halogenida. Drugi maksimum ima kristalizacioni karakter i nalazi se na istom mjestu gdje i čisti srebrni pirofosfat. Treći je maksimum koagulacioni maksimum srebrnih halogenida. Pirofosfatni ion pokazuje sve efekte, koje smo mogli utvrditi i kod drugih četverovalentnih protuiona pri koagulaciji solova srebrnih halogenida *in statu nascendi*. Ti se efekti očituju, na pr., kod vrijednosti kritične koncentracije koagulacije, prenabijanja sola, odnosa kritičnih koncentracija za solove različitih srebrnih halogenida i dr. Naročito je izrazit utjecaj dodatka dušične kiseline kako na stabilizacionu, tako i na koagulacionu granicu tog maksimuma. Taj je utjecaj posljedica promjene u disocijacionim ravnotežama pirofosfatnog iona.

Sl. 6 pokazuje utjecaj želatine na iste taložne sisteme. Pokusi sa želatinom poslužili su za diferenciranje maksimuma s obzirom na njihov kristalizacioni i koagulacioni karakter.

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