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The Preparation Of Stable Silver Sulphide Sols and The Investigation Of The Flocculation Effects Of Different Technical Polymers and Salts On These Sols

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The Preparation Of Stable Silver Sulphide Sols and The Investigation Of The Flocculation Effects Of Different Technical Polymers and Salts On These Sols

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SUMMARY

In this work, silver sulphide sols were prepared by the reaction between dilute silver nitrate and sodium thiosulfate solutions. For this purpose, solutions were mixed in various proportions. Their stability were determined by plotting the absorbance values measured at definite time intervals versus time. The mixtures were prepared in two series as follows:

(A) Those in which silver nitrate was in excess as compared to silver thiosulfate.

(B) Those in which sodium thiosulfate was in excess as compared to silver nitrate.

In the cases where reagent concantrations were almost the same it was noted that sols were not stable. They were only stable when different concentrations are used and the most stable silver sulphide sol is obtained when the molar concentration ratio of $Na_2S_2O_3$ to $AgNO_3$ is 1,25 or greater. These are type (B) sols. It was found also that the ratios of concentrations influence the duration of sol formation. Shaking had no effect on such sols.

The stabilizing effect of nitrate ions was observed in the sols where the amount of silver nitrate was more than of sodium thiosulfate. Both sols are negatively charged. The flocculating effect of anionic, cationic and non-ionic polymers and aluminium nitrate, barium nitrate salts on the sols on mentioned above were investigated. Aluminium and barium salts had a negligible effect on the (A) type sols. On the other hand, the non-ionic polymers had the most flocculating effect when shaken for five minutes at 170 rpm. (rotasyon per minute). In (B) type sols, aluminium and barium salts act as strong flocculating agents. Anionic, cationic and non-ionic polymers had no flocculating effect on these sols when agitated.

The flocculating effect was determined from the curves obtained between the absorbances versus time at definite wavelength. It was conculuded that these sols differed from each other by their stability and flocculation with electrolytes. Micrographs might also show that their particles size and shapes also where different.

INTRODUCTION

The purpose of their study is to estimate in what way the properties of sols are affected by the reagent ratio during the formation of silver sulfide sols prepared by the reaction between dilute thiosulfate and silver nitrate solutions. The ratios used were divided in two groups.

$$\text{(A) type sols } \frac{Na_2S_2O_3}{AgNO_3} < 1, \text{ (B) type sols } \frac{Na_2S_2O_3}{AgNO_3} > 1$$

After the preparation of samples from two types sols, the ratios yielding the most stable sols were studied spectrophotometrically. The comparation of the particles were made with electron microscopic studies. It is of interest to investigate the effects of some salts and industrial polymers on the sols. Dependidg on the concentration ratios, the time for the formation of sols was determined by plotting the absorbances against time.

In a previous study the effect of same organic solvents on the stability of type (A) sols was investigated. [1]

EXPERIMENTAL

Material and apparatus

The reagents in the preparation of silver sulphide sols were Merck products.

The chemicals used as flocculation agents were

Nalco DC 4094 anionic polymer	$M \approx 3{,}0x10^6$
Nalco SC 8109 cationic polymer	$M \approx 3{,}0x10^6$
Prosifloc XN–100 non-ionic polymer	$M \approx 1{,}3x10^6$

Pure $Al(NO_3)_3$ and $Ba(NO_3)_2$ salts. (Merck).

From the analysis performed and the IR spectrum recorded it was found that Nalco DC 4094 anionic polymer was polyacrylic acid, Nalco SC 8109 cationic polymer was the copolymers of maleic acid-styrene and that Prosifloc XN–100 non-ionic polymer was polyacrylamide of 70 % purity. [2] Water used in the preparation of the solutions was distilled over potassyum permanganate. The absorbance measurements were carried out by means of a Bausch-Lomb Spectronic Spectrometer 100. For shaking the sols Kottermann apparatus was used.

The preparation of stable sols

The above mentioned chemicals were mixed in the order and concentration of:

$$\frac{N}{1000}\ AgNO_3,\ H_2O,\ \frac{N}{10}\ NaNO_3,\ \frac{N}{1000}\ Na_2S_2O_3\ .$$

in various proportions at (18 ± 1) °C. The total volume being 4,2 ml. During the experiments, distilled water was added to make the total volume 4,2 ml. After the preparation of the mixtures absorbances were immediately read in the definite time intervals. From these measurements the maximum absorption was found to be at 450 nm.

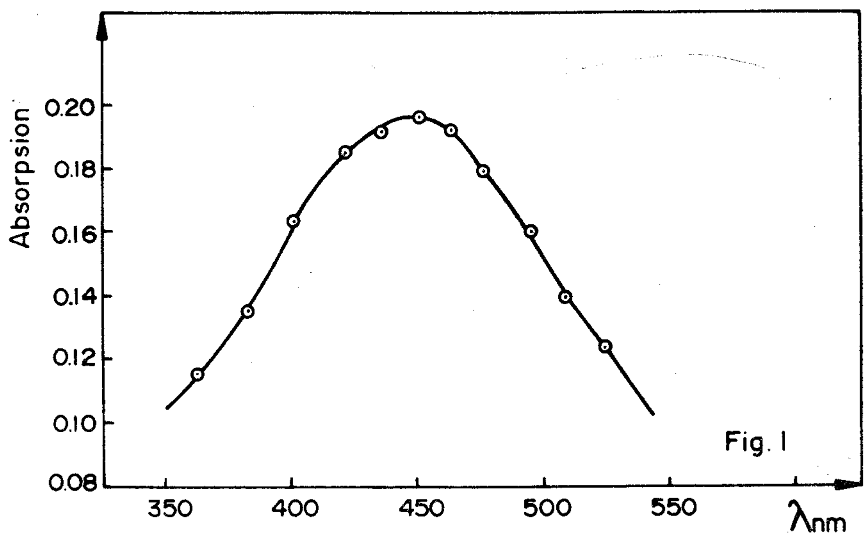

Fig. 1. The choice maximum wavelength in sol 4 type (B).

Using the experimental data absorbances are plotted against time. In these figures, the curves are parallel to the abscissa which indicate the stability of sols. The curves with negative slope indicate flocculation rates and the curves with positive slope denote the turbidity of the sols, hence the increase of sensitivity toward the flocculation. Fig. 2a, Fig. 2b.

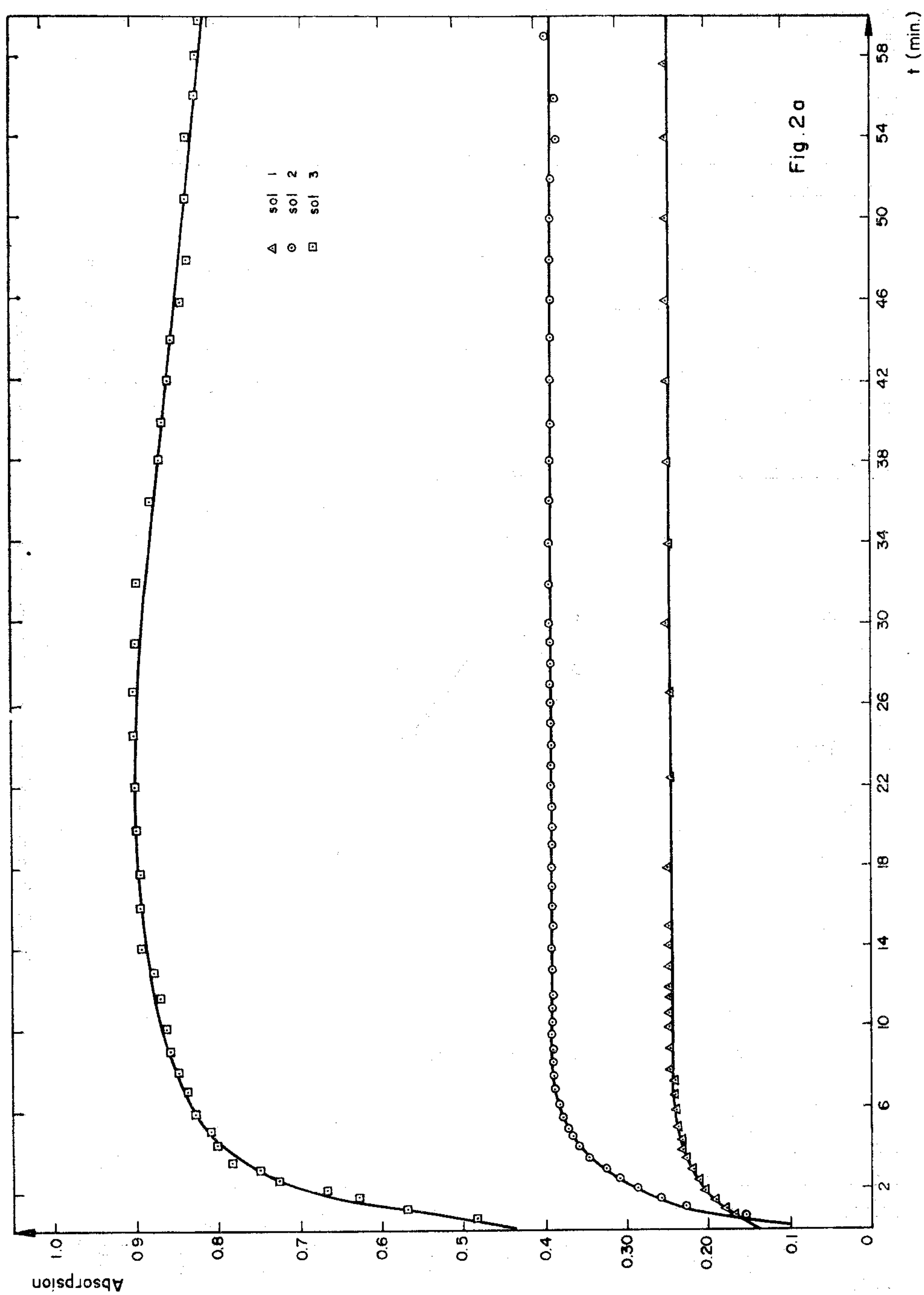

Fig. 2a. The effect of reactive concentrations on stability in type (A) Sols.

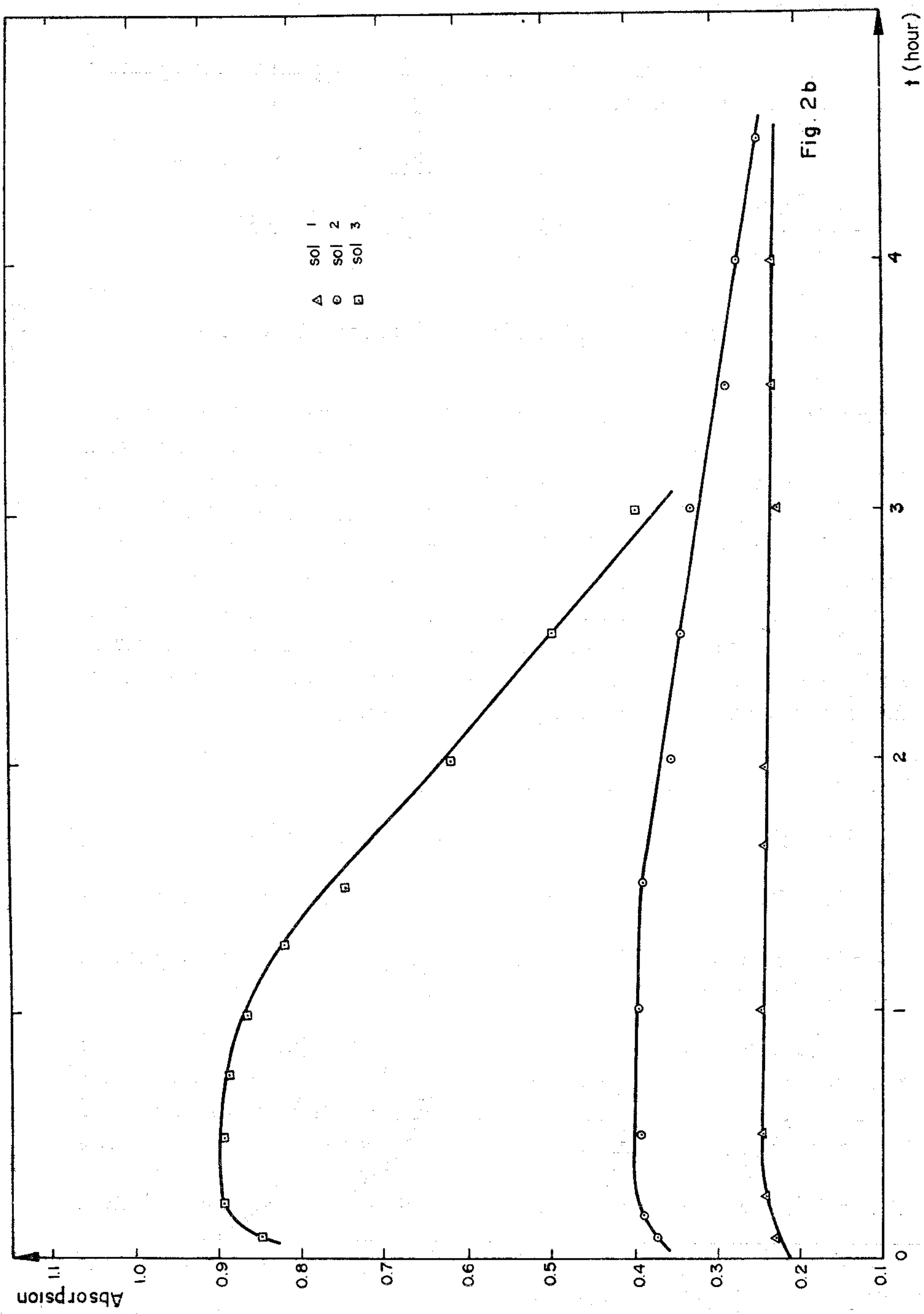

Fig. 2b. The effect of reactive concentrations on stability in type (A) sols.

The study of (A) type sols

In one of the series, sols were prepared by using the following molar ratios and their stabilities were investigated.

	Sol 1	Sol 2	Sol 3
$\frac{Na_2S_2O_3}{AgNO_3}$	0,05	0,10	0,60
Cons. of sols $\left(\frac{M}{1}\right)$	$0{,}24 x 10^{-4}$	$0{,}50 x 10^{-4}$	$0{,}12 x 10^{-3}$

As seen in Fig. 2b the third sol is not stable. Approximatly 30 minutes after the formation of sol, flocculation starts and is rapidly completted. Sol 2 also did not have a good stability. An initial flocculation was observed in approximately 90 min., but not as rapid as in sol 3. Sol 1 was stable. This stability could be clearly seen by the parallelism the absorbance versus the time curve with the abcissa. For this sol the molar concentration of silver nitrate is 20 times greater than that of sodium thiosulfate, since there are more nitrate and silver ions in the medium. As the sol having the nitrate ions in excess was the most stable the effect of these ions on the stability was also investigated.

The effect of nitrate ions on stability of (A) type sols

The third sol that is not stable was prepared by adding $\frac{N}{10}$ $NaNO_3$ in varying amounts (0,1–0,8) mls. keeping the total volume of the mixture at 4,2 mls. Their stability was checked by plotting the absorbances against time. Fig. 3a, Fig. 3b.

Since the curves are parallel to the abcissa they show that the nitrate ions increase the stability of this sol. From the measurements carried out with varying sodium nitrate concentrations it was conduded that the most proper concentration of sodium nitrate which increases the stability of the sols was about $5x10^{-3}$ $\frac{M}{1}$. This concentration corresponds to the minimum of the curve if Fig. 3b. In the preparation of sols of type (A), this value is used for the amount of $NaNO_3$.

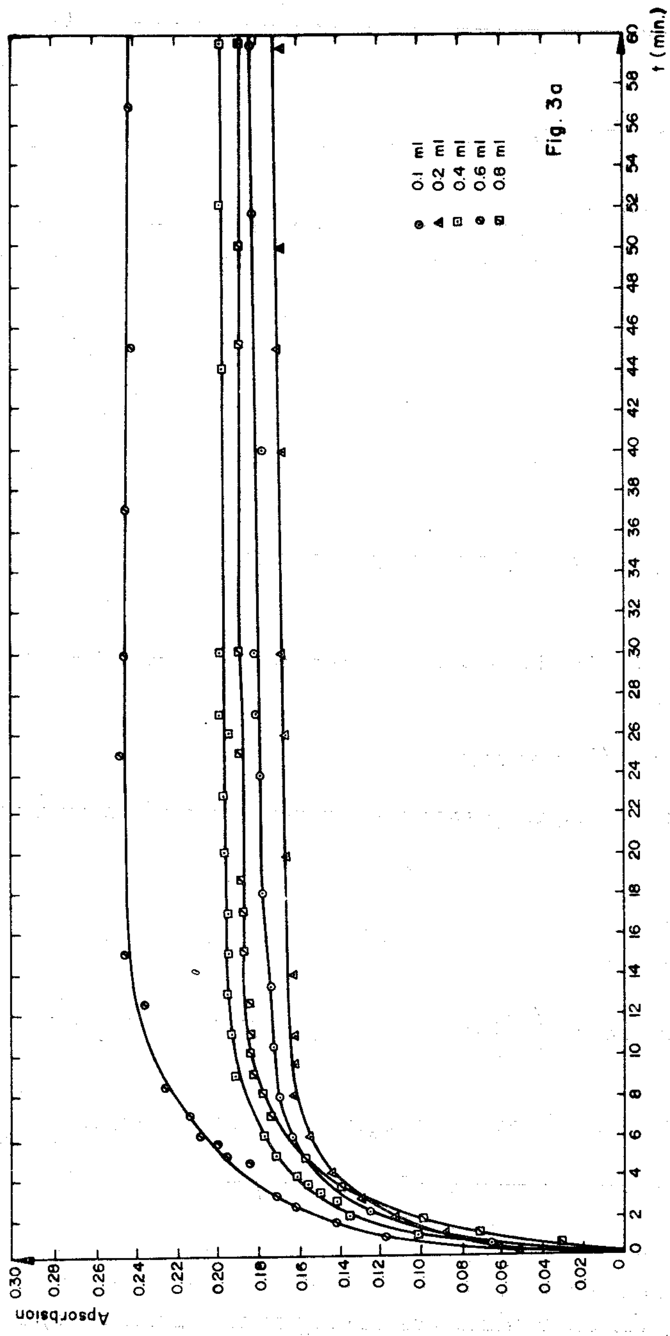

Fig. 3a. The effect of sodium nitrate on the stability in type (A) sols.

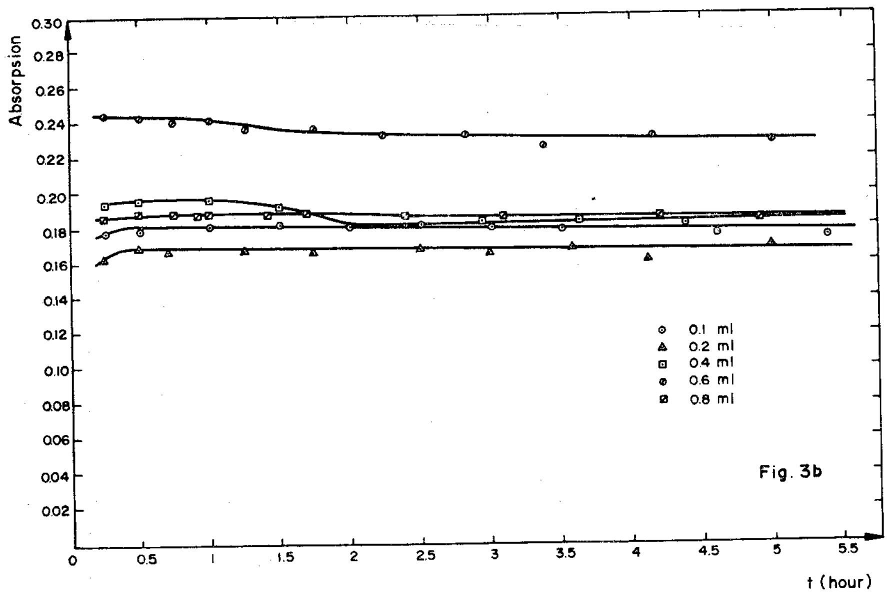

Fig. 3b. The effect of sodium nitrate on the stability of sol 3 type (A).

The study of (B) type sols

In these sols, the reagents are mixed in the following proportions:

	Sol 4	Sol 5	Sol 6
$\frac{Na_2S_2O_3}{AgNO_3}$	1,25	1,87	3,75
Conc.of sols $\left(\frac{M}{1}\right)$	$1{,}90 \times 10^{-4}$	$1{,}90 \times 10^{-4}$	$0{,}95 \times 10^{-4}$

These sols were found to be significantly stable. As the $\frac{Na_2S_2O_3}{AgNO_3}$ ratio increases, the amount of thiosulfate ions in the medium increased in accordancc. This stability can clearly be seen from the curves, Fig. 4. These curves also show the time of the formation of sols. This time corresponds to the time where the absorbance gets constant. Among the samples, the sol 6 which has the higest concentrations ratio, formed

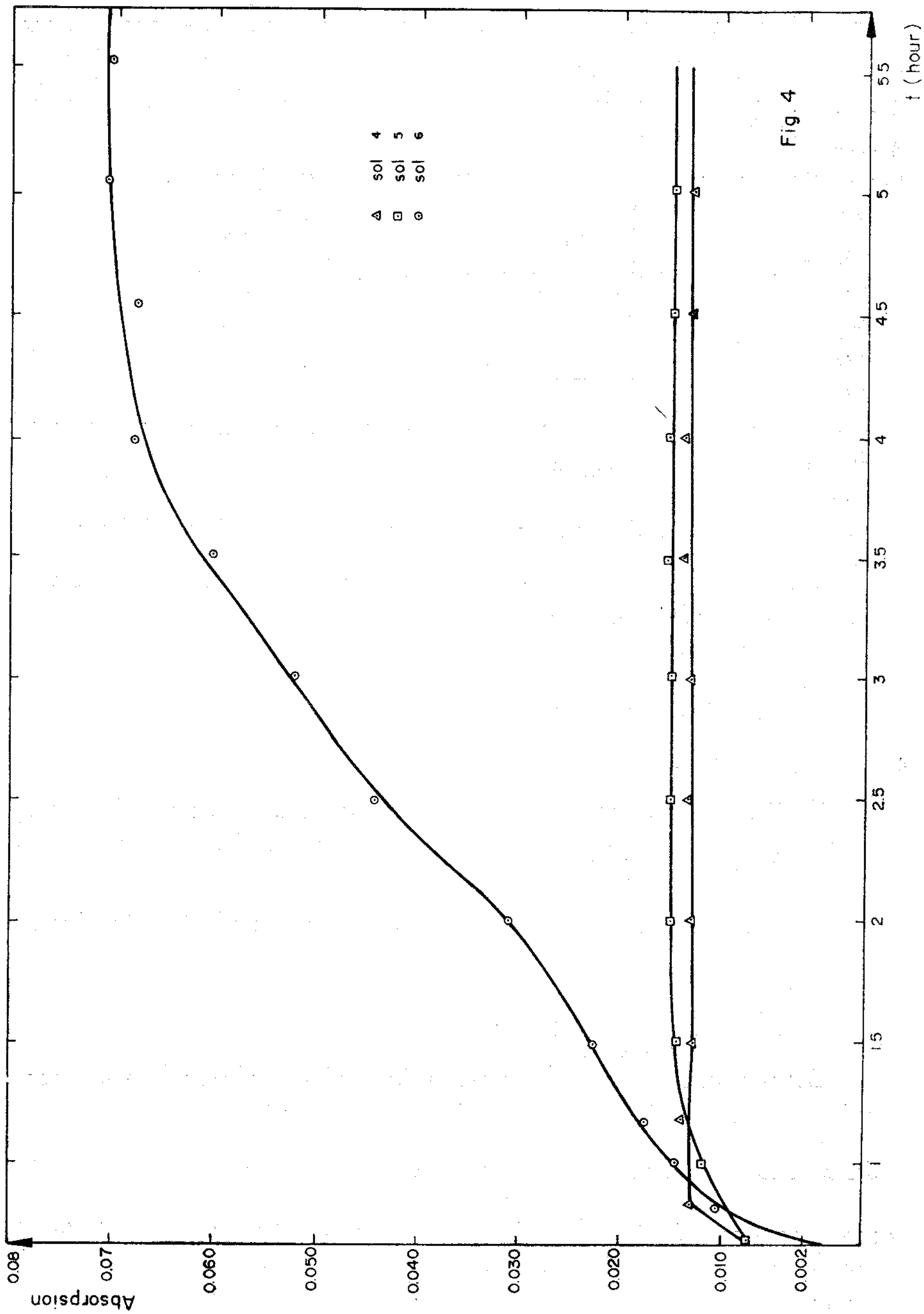

Fig. 4. The effect of reactive concentrations on stability and on the duration of formation in type (B) sols.

latest. This sol contains the higest amount of thiosulfate ions. As the ratio becomes greater, thiosulfate ions in the medium increases as well. In the same way, the time necessary for the formation of sols 4 and 5 is determined. Table 1.

Table 1. The time for the formation of (B) type silver sulphide sols as a function of ratios of concentrations.

Sol	Ratio of concentrations	~ Form. time (min)
4	1,25	42
5	1,87	82
6	3,75	245

The time the formation of the (A) type sols is quite short, approximately 5–10 mins. Fig. 2a.

Flocculation of the sols by polymer, salts and the effect of shaking

For the flocculation, the effect of shaking at different speed and duration was assayed at:

(a) 110 rpm
(b) 170 rpm
(c) 240 rpm
(d) 280 rpm

In the measurements with various speeds and durations of shaking it was observed that the most proper shaking for the type (A) sols is 170 rpm. which gives less duration Fig. 5.

Therefore, in the subsequent flocculation studies this speed and time parameters was used.

Flocculating effect of polymer

Stock solutions of 500 ppm for each kind of polymers were prepared. The flocculation effect of polymers was first tested on type (A) stable sol of $0{,}24 \times 10^{-4}$ $\frac{M}{1}$ concentration. Varying amounts of 50 ppm solution, between (0,1–0,8) mls. were added to the sols to make up the final volume of 4,2 mls. Since they did not have a flocculating effect, sol-polymer mixtures were shaken for 5 minutes at a speed of 170 rpm. Absorbance-concentration curves were plotted for the three polymers. Fig. 6.

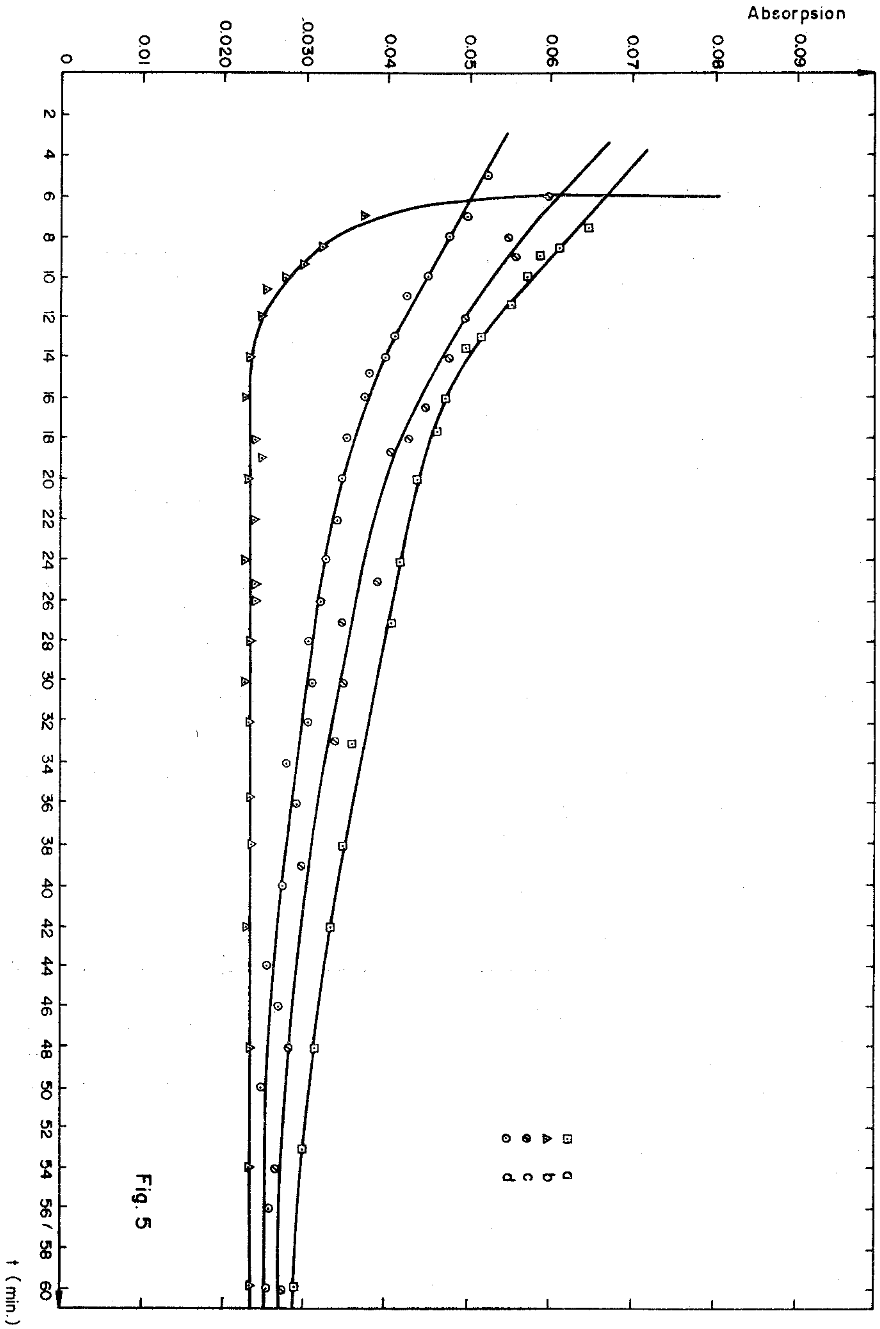

Fig. 5. The effect of shaking on type (A) sols.

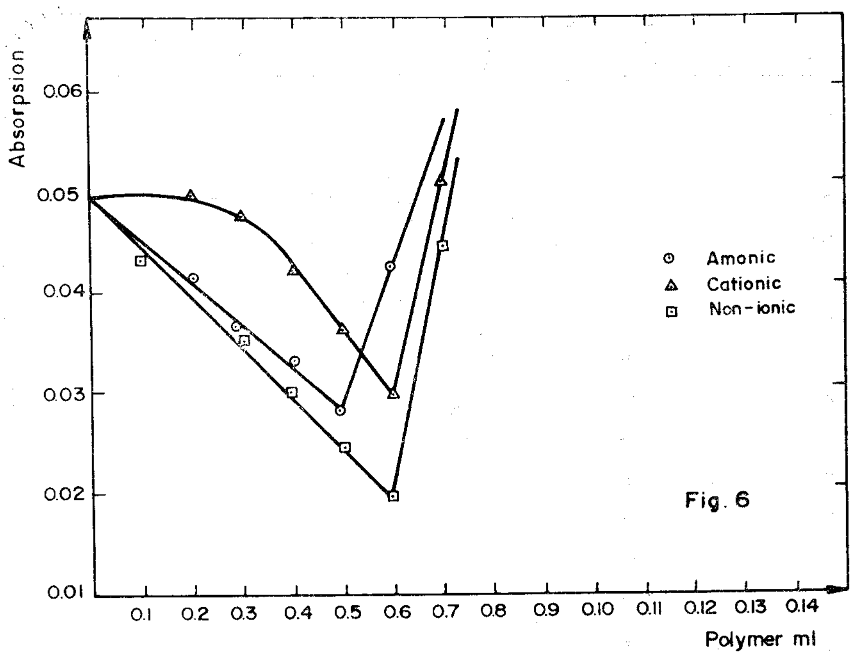

Fig. 6. The choice of proper amounts of polymers acting on the flocculation of type (A) sols.

Here it was conculuded that these polymers might be effective when shaken. The definite concentrations and among these polymers the non-ionic poylmers gives the lowest absorbance value for 7,0 ppm. in concentration. The non-ionic polymer is the most effective flocculating agent for these sols.

When the same measurements were carried out with stable sols of type (B) of 1,90x10^{-4} $\frac{M}{1}$ concentration, no flocculation was obtained with or without shaking at various speeds. It was found that an anionic polymer of approximately 8,0 ppm. in concentration increased the stability of this sol.

Flocculation of (A) type sols by salts

Flocculation effect of Aluminium Nitrate salt.

These effect was first investigated on (A) type stable sol having a concentration ratio of 0,05 and $0{,}24 \times 10^{-4} \frac{M}{l}$. Varying amount of $\frac{N}{100}$ aluminium nitrate solution, (0,04–0,15) mls. were added to the sols to make up the volume 4,2 mls. After 30 minutes, flocculation was not occured in the sol but a turbidity was observed.

Flocculation effect of Barium Nitrate salt

The flocculation effect of barium nitrate salt on (A) type sols investigated by similar studies. Concentration was taken as $\frac{N}{10}$ and the amounts added to the sol were changed between (0,02–0,13) mls. 30 minutes after the addition of salt absorbances were measured. These were plotted against the salt concentrations. Fig. 7.

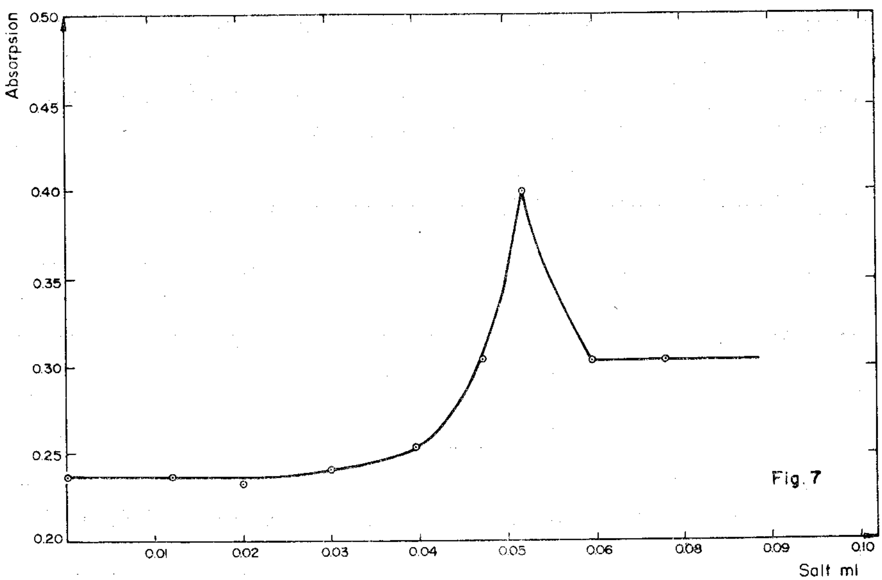

Fig. 7. The effect of barium nitrate on the flocculation of the sol.

The increase of the absorbance values with the salt concentration indicates that a good flocculation did not occur.

Flocculation of (B) type sols by salts

Flocculation effect of Aluminium Nitrate and Barium Nitrate salts.

The experiments were carried out on stable sols having a ratio of 1,25 and a concentration of $1{,}90x10^{-4}$ $\frac{M}{1}$. For this purpose, different volumes of $\frac{N}{100}$ aluminium nitrate solution were added to the sol to make up the volume 4,2 ml $\frac{N}{10}$ barium nitrate solution. In each experiments, after 30 minutes, flocculation occured in both of salt but aluminium salts were more effective.

The coagulation value of Aluminium Nitrate on (A) and (B) types sols

The coagulation value of aluminium nitrate on (A) type sols was determined as 3,0 milimol per liter, where as on (B) type sols this value was $5{,}0x10^{-4}$ milimol per liter. These coagulating values are the proff of the stabilizing effect of the nitrate ions the silver sulphide sols obtained by sodium thiosulfate and silver sulphide reaction.

Simultaneous Flocculation Effect of Polymers with Salts

This effect was only investigated on the type (A). Stable sol having a reactive ratio of 0,05. The weak effect of aluminium nitrate salt chosen with the three polymers was observed again. In Fig. 8 the increase in absorbance show the presence of turbulance.

DISCUSSION

In type (B) 4,5,6 silver sulphide sols there is excess of thiosulfate ions, as it is apperent from the $\frac{Na_2S_2O_3}{AgNO_3}$ rations which is greater than 1. This suggests that the thiosulfate ion adsorption occured on the particle surface rendering it a negative charge which is countered by sodium ions. The sability of these sols increased with the increassing ratio.

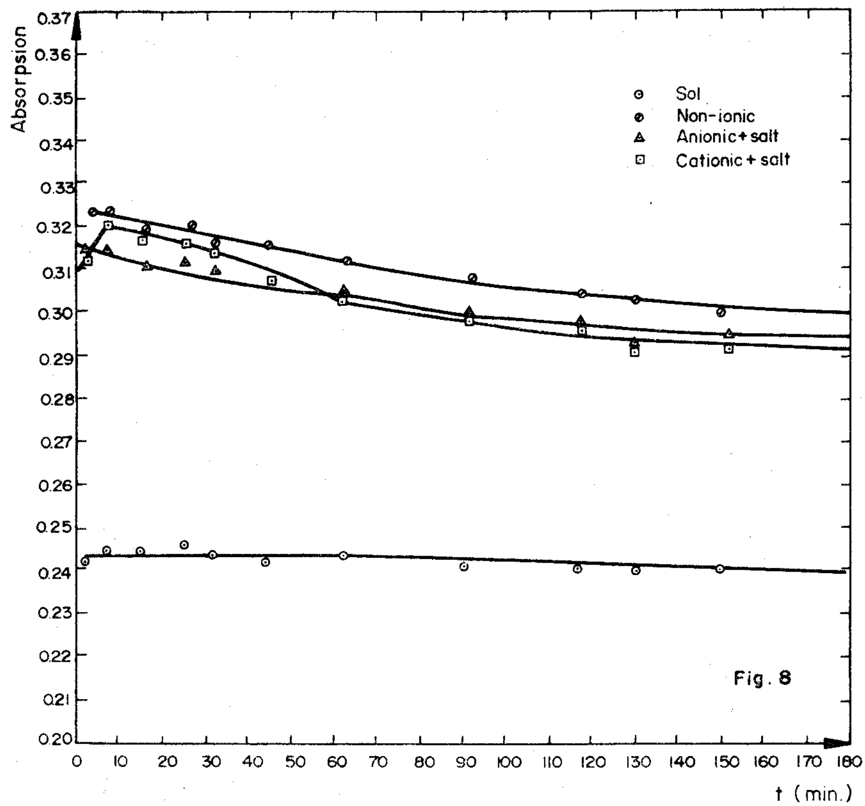

Fig. 8. The flocculation effect of aluminium nitrate together with polymers on type (A) sols.

In type (A) 1,2,3 silver sulphide sols there are no excess thiosulfate ions in the medium. Because it is the limiting reaction reagent. There are only an excess of nitrate ions in these solutions which are adsorbed on the particles and cause there negative chaıge. In order to increase the stability of these sols, the addition of nitrate ions have been tried and proved succesful. Among (A) type sols the more dilute one is the most stable. In comparing the different type of sols it is observed that (B) type sols are monodispersed spherocolloids and have a good stability whereas the (A) type sols are polydispersed have less stability and particles are greater than type (B). Fig. 9 and Fig 10 show the comparison of the two type sols.

In these sols of silver sulphide charged with different ions, there is also a difference as to their behavior towards the electrolytes. (e.g. type

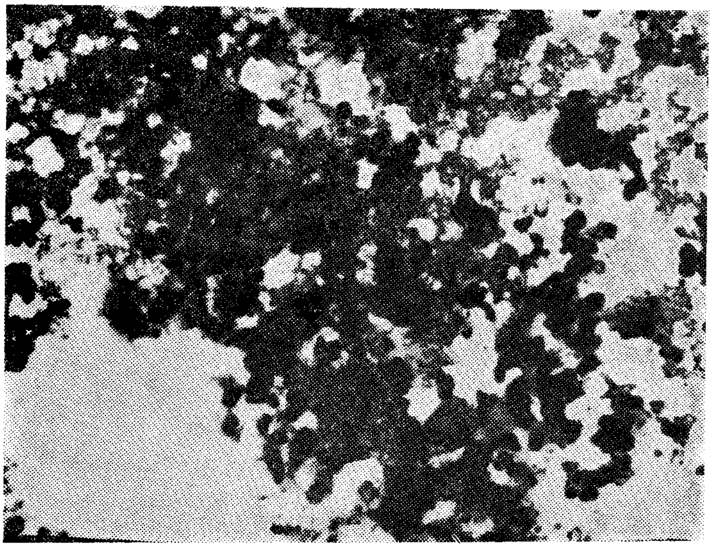

Fig. 9. Electronmicrograph taken from the type (A) stable sol with reactive ratio of 0,05. Mag. 110000.

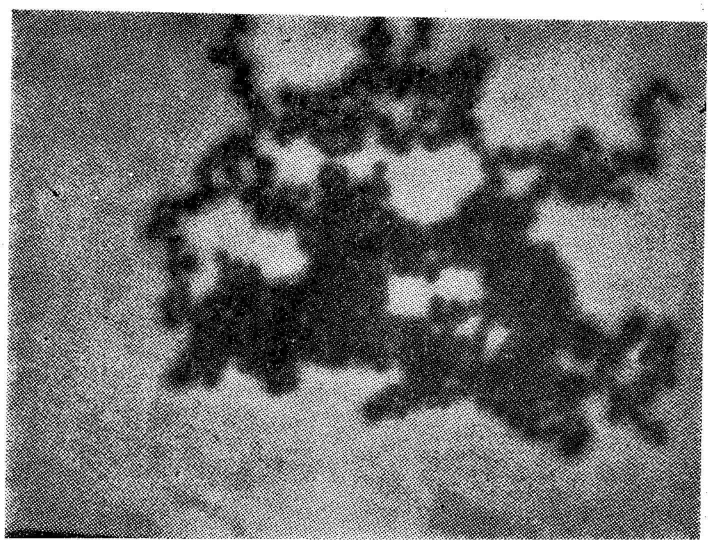

Fig. 10. Electronmicrograph taken from the type (B) stable sol with reactive ratio of 1,25. Mag. 110000.

(B) sols are charged with thiosulfate ions, type (A) sols are charged with nitrate ions.)

The flocculating effect of aluminium nitrate and barium nitrate salts are very weak in (A) type sols, because the excess of nitrate ions in the solutions prevent the dissociation of these salts. [3] The same salts show the normal coagulating effect on type (B) sols.

In case of the flocculating with polymers the (A) type sols are affected by non-ionic polymers but not by others which can be explained by the selective adsorption of he colloidal particles on the polymer. If a mixture of salt and polymer is used a flocculation is observed which is due to the polymer.

CONCLUSION

The properties of the silver sulphide sols obtained by the interaction of very dilute solutions of sodium thiosulfate and silver nitrate depend greatly on the ratios of concentrations of the reagents.

If the ratio of the equivalent concentrations of sodium thiosulfate and silver nitrate in the solution is about one, the sols formed is not stable. If this ratio is higer than one, the sols have a good stability and the stability increases with increasing ratio. The sols formed are monodispersed and the particles are spherocolloidal which are negatively charged by the adsorption of thiosulfate ions. They are affected by the salts but are not affected by the polymers such as Nalco DC 4094 anionic, Nalco SC 8109 cationic, Prosifloc XN–100 non-ionic.

When the value of this ratio is lower than one, the sols formed have aweaker stability. They are polydispersed with greater and irregular particles negatively charged by the adsorption of nitrate ions. These sols are very weakly by aluminium nitrate and barium nitrate. The non-ionic polymer Prosifloc XN–100 has a moderate flocculating effect on this type of sol.

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ÖZET

Bu çalışmada, gümüş sülfür solü, seyreltik gümüş nitrat ve sodyum tiosülfat çözeltileri arasındaki reaksiyonla hazırlandı. Bu amaçla reaktif çözeltileri değişik oranlarda karıştırıldı. Oluşan sollerin stabilite durumları belirli zaman aralıkları ile ölçülen absorbans değerleri ve zaman arasında çizilen grafikten saptandı. Karışımlar aşağıda verilen iki grupta hazırlandı.

(A) Gümüş nitratın tiosulfata nazaran fazla olduğu,

(B) Tiosülfatın gümüş nitrata nazaran fazla olduğu haller,

Reaktif konsantrasyonlarının biribirine yakın olduğu durumlarda sollerin stabl olmadıkları farklı konsantrasyonlarda stable olabildikleri saptandı. Bunlardan en stable gümüş sülfür solü, $Na_2S_2O_3/AgNO_3$ oranının 1,25 veya daha büyük olduğu zaman elde edildi. Reaktif oranının sollerin oluşma müddetinide etkilediği görüldü. Bu tip soller üzerinde çalkalamanın etkisi incelendi.

Gümüş nitrat konsantrasyonunun tiosülfata nazaran fazla alınarak hazırlanan sollerde nitrat iyonlarının stabilleştirici etkisi görüldü. Her iki tip sol negatif yüklüdür. Söz konusu soller üzerinde aliminyum nitrat ve baryum nitrat tuzlarının anyonik, katyonik ve non-ionik polymerlerin flokülan etkileri denendi. (A) tipi sollerde, aliminyum ve baryum tuzlarının etkisi fazla değildir. Polimerlerden de non-ionik polymerlerin 170 devir/dak. ve 5 dak. çalkalamalı olarak ve fazla flokülan etkisi görüldü. (B) tipi sollerde aliminyum ve baryum tuzları kuvvetli flokülandırlar. Anyonik, Katyonik ve non-ionik polymerlerin çalkalamalı olarak flokülan etkisi görülmedi. Flokülan etki, belirli dalga boyunda ölçülen absorbansla zaman arasında çizilen grafikten saptandı. (A) tipi ve (B) tipi sollerin stabilite ve flokülasyon bakımından farklı oldukları sonucuna varıldı. Her iki solden alınan mikrograflarda da tanecik büyüklüklerinin ve şekillerinin farklı olduğu görülmektedir.