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Note

Coulombic Retardation Effect of »Neutral« Electrolytes on Formation of Barium Sulfate Crystallites (Reversal of Schulze-Hardy Rule)

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The formation of precipitates by mixing the diluted solutions of barium nitrate and sodium sulfate (with sulfate in excess) and in presence of various concentrations of potassium, magnesium, and lanthanum nitrate, was followed tyndallometrically. It was found that there are critical concentrations of counter ions of the same order as with Schulze-Hardy rule but of opposite effect: at higher concentrations there was a distinct retardation in the formation of particles. The effect may be explained as the result of coulombic interactions in the formation of ion pairs or complexes between sulfate and counter ions causing either a slower embriation, or a hindrance of direct growth, and/or a retardation of the aggregation of growing nuclei into larger crystallites.

The charge effect of neutral counter ions upon the coagulation of hydrophobic sols (the Schulze-Hardy rule) is well established not only for preformed sols but also for sols *in statu nascendi*¹⁻⁶. To our knowledge, the inversion of ionic charge effect has never been reported. In this case there exist critical concentrations of mono-, di-, and tri-valent ions above which the systems are more stable and below which precipitation occurs. Such an effect may be of great interest in the elucidation of the mechanism of precipitation. The inverse Schulze-Hardy rule may be of special importance for systems which do not tend to form stable primary particles. We have repeatedly pointed out^{7-10,11-15} the difference in the characteristics of the precipitation phenomena of barium sulfate and silver halides, which appears in spite of their solubilities being similar (K_{sp} for $BaSO_4$ and $AgCl$ is approximately the same).

Figs. 1—4 demonstrate this inversion effect. Fig. 1 shows the change in turbidities of seven systems, all containing the same concentrations of barium nitrate and sodium sulfate and varying concentrations of added neutral electrolyte.

Turbidity was measured with a Zeiss tyndallometer in connection with a Pulfrich photometer using a blue, a green and a red filter. Chemicals used were of analytical reagent quality and were not purified further: barium nitrate (Carlo Erba S. A., Milano); ethanol abs. (Kemika, Zagreb), potassium nitrate (Laphoma, Skopje), magnesium nitrate (Pliva, Zagreb) and lanthanum nitrate (E. Merck, Darmstadt).

The resulting solutions from which the precipitates were formed were of ionic compositions as indicated in the legend. The average particles size

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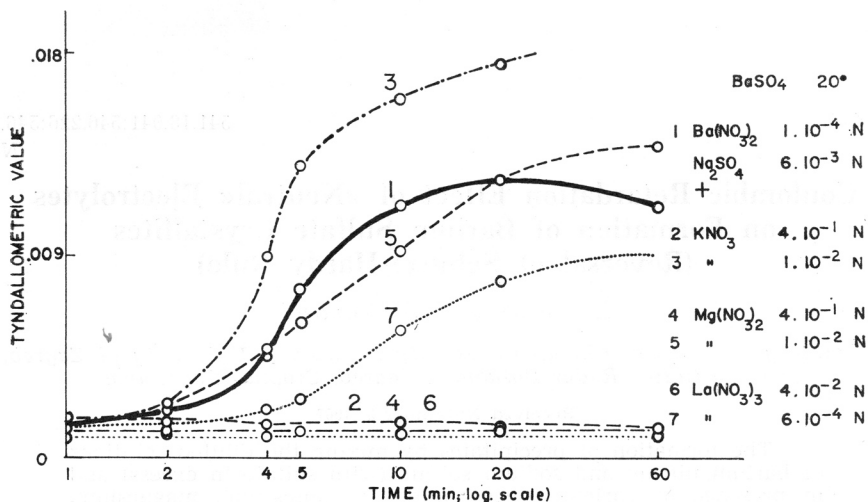


Fig. 1. Plot of turbidities (tyndalometric value) against time (min) after mixing of barium nitrate ($1 \times 10^{-4}N$) and sodium sulfate ($6 \times 10^{-3}N$) solutions in presence of potassium, magnesium, and lanthanum nitrate (concentrations indicated in the legend).

of all systems shown in Fig. 1 were determined by means of dispersity quotients^{16,7,17}. The results are given in Fig. 2. Systems with higher concentrations of corresponding electrolytes exhibited no measurable excess turbidity within one hour. The systems without foreign electrolyte or in presence of lower concentrations of each electrolyte showed high turbidities and consisted of particles larger than 200 μ .

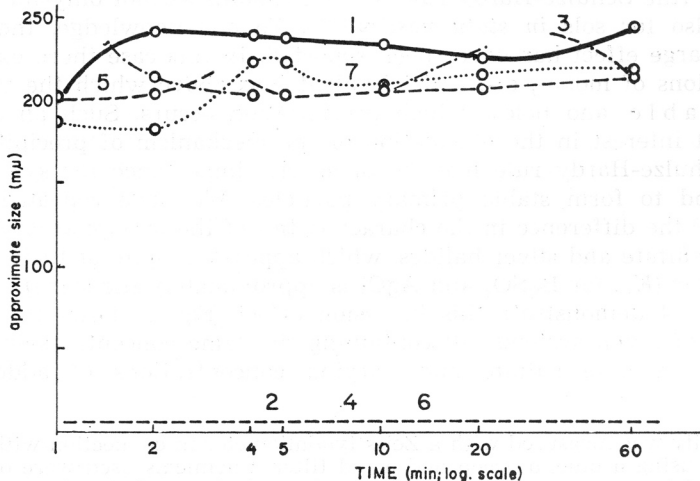


Fig. 2. Plot of approximate size of the particles of the systems represented in Fig. 1. against time (min).

If the precipitation experiments were carried out in a wider range of concentrations of foreign ions, the systems revealed the existence of critical concentrations of potassium, magnesium, and lanthanum ion but the effect was opposite¹⁸ to the usual coagulation phenomena, as it is shown in Fig. 3.

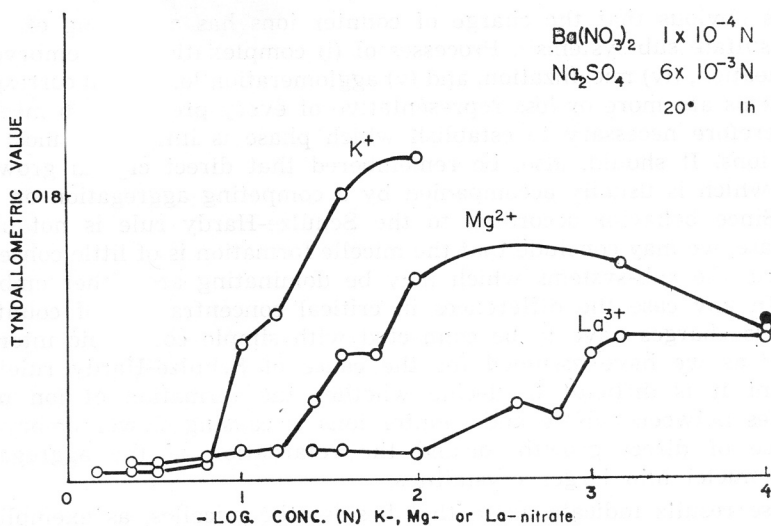


Fig. 3. Plot of turbidities against concentration of potassium, magnesium and lanthanum nitrate (logarithmic scale) for the precipitating system of barium nitrate ($1 \times 10^{-4} \text{ N}$) and sodium sulfate ($6 \times 10^{-3} \text{ N}$); 1 hour after mixing of reacting components.

Fig. 4 shows that the same effect is also observed if higher concentrations of barium sulfate are employed. Fig. 4 shows turbidities 1 and 20 minutes after mixing of precipitating components.

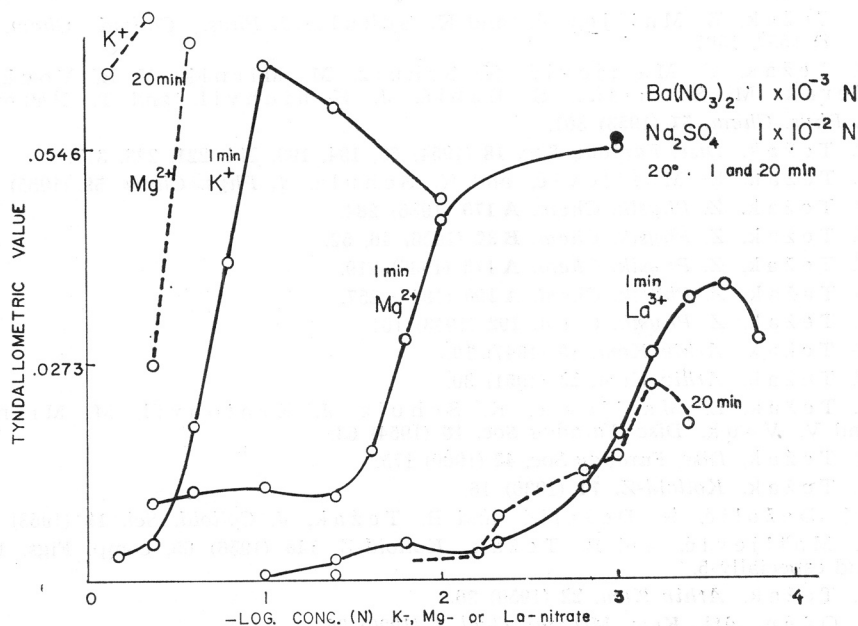


Fig. 4. Plot of turbidities against concentration of potassium, magnesium and lanthanum nitrate (logarithmic scale) for the precipitating system of barium nitrate ($1 \times 10^{-3} \text{ N}$) and sodium sulfate ($1 \times 10^{-2} \text{ N}$); 1 and 20 min. after mixing of reacting components.

It is obvious that the charge of counter ions has a striking effect upon barium sulfate sub-systems¹⁵. Processes of (i) complexation, (ii) embryonation, (iii) nucleation, (iv) micellization, and (v) agglomeration leading to corresponding sub-systems are more or less representative of every precipitation mechanism. It is therefore necessary to establish which phase is influenced most by the foreign ions. It should, also, be remembered that direct crystal growth is a process which is usually accompanied by a competing aggregation on various levels. Since behavior according to the Schulze-Hardy rule is not observed in this case, we may conclude that the micelle formation is of little consequence. Therefore, the sub-systems which may be dominating are either embryos or nuclei. In any case the differences in critical concentrations of counter ions of various charges have to be connected with simple coulombic interactions, similarly as we have assumed for the cause of Schulze-Hardy rule^{1,19,4}. At this point it is difficult to decide whether the formation of ion pairs or complexes between sulfate and counter ions is causing slower embryonation, hindrance of direct growth, or/and the retardation of the aggregation of growing nuclei into larger crystallites.

These results indicate again that besides the micelles, as exemplified by silver halides sols *in statu nascendi*, and Odén's primary particles of barium sulfate crystallites²⁰⁻²², there exist also aggregational units of lower level than primary particles.

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IZVOD

Kulonski efekt usporavanja »neutralnih« elektrolita na precipitaciju barium-sulfata (obrnuto Schulze-Hardyjevu pravilu)*B. Težak i B. Novosel*

Tindalometrijski je određivana precipitacija barium-sulfata dobivena miješanjem razrijeđenih otopina barium-nitrata i natrium-sulfata (u suvišku sulfata), a uz dodatak različitih koncentracija kalium-, magnezium- i lantanum-nitrata. Nađeno je da postoje kritične vrijednosti isto kao i kod Schulze-Hardyjeva pravila, ali obrnutog efekta: u višim koncentracijama postoji usporavanje formiranja čestica. Taj efekt se može protumačiti kao rezultat međusobnog kulonskog djelovanja sulfat-iona s protuionima u toku nastajanja ionskih parova ili kompleksa, što ujedno uzrokuje polaganiju agregaciju nukleusa u toku njihova rasta u veće čestice.

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