Coagulation Effect of Potassium Perchlorate, Potassium Chlorate and Sodium Benzoate on Positive Silver Bromide Sol and of Potassium Sulfate on Positive Sols of Silver Halides

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The coagulation values of potassium perchlorate, potassium chlorate and sodium benzoate on positive silver bromide sol, and of potassium sulfate on positive sols of silver chloride, silver bromide and silver iodide *in statu nascendi* for various concentrations of the stabilizing ions have been determined. The experimental results were used for the discussion of the dependence of the coagulation values on the charge of the sol, the solubility of the compound formed between the stabilizing and the counter ion, the valency of the counter ion and the density of the charge at the surface of sol particles.

In a former paper[1] we described the coagulation effects of some monovalent anions on positive silver halide sols *in statu nascendi*. In the present paper we wish to discuss such effects of other monovalent anions (perchlorate, chlorate and benzoate) on positive silver bromide sol, and of bivalent sulfate ion on positive sols of silver bromide, silver chloride and silver iodide sols *in statu nascendi*. We chose these anions on account of their very different solubility in the presence of the stabilizing ion (Ag^+). Thus the solubility of silver perchlorate amounts to 4,08 $M/1$ (25^0C), of silver chlorate to 0,52 $M/1$ (in cold water), of silver benzoate to 0,011 $M/1$ (25^0), and of silver sulfate to 0,025 $M/1$ (20^0)[2]. As shown by previous investigations[1, 3], this solubility is one of fundamental factors influencing the coagulation processes. On the other hand we wished to determine the influence of the valency of negative counter ions on the coagulation value.

EXPERIMENTAL

The 10-minutes tyndallometric values (turbidity) in green light were determined for the investigated system by means of a Pulfrich Photometer in connection with a Zeiss Nephelometer. The silver halide sols were prepared in the usual way[1, 4] by mixing the solutions of the precipitating components (silver nitrate and potassium halide) in the presence of a neutral electrolyte (in our case $KClO_4$, $KClO_3$, C_6H_5COONa and K_2SO_4, respectively). The concentration of the potassium halide component was the same for all investigated systems ($2 \times 10^{-4}N$), whilst the concentration of silver nitrate was in one series of systems constant, but different in different series (up $1 \times 10^{-2}N$ to $2,5 \times 10^{-4}N$). The silver nitrate solutions were always of greater concentration than the potassium halide solution so that the resulting sols were positive[5]. The concentration of the added electrolyte was systematically varied in the critical coagulation region[6]. The tyndallometric values obtained served for the construction of the so-called 10-minutes concentration tyndallograms[7, 8] which give — by extrapolating the turbidity value to zero — critical coagulation values. Figure 1 shows the silver bromide sol coagulation values of univalent perchlorate, chlorate and benzoate ions as a function of the concentration of the stabilizing ion (Ag^+), Figure 2 shows the same effect of the sulfate ion for silver chloride, silver bromide and silver iodide sol *in statu nascendi*.

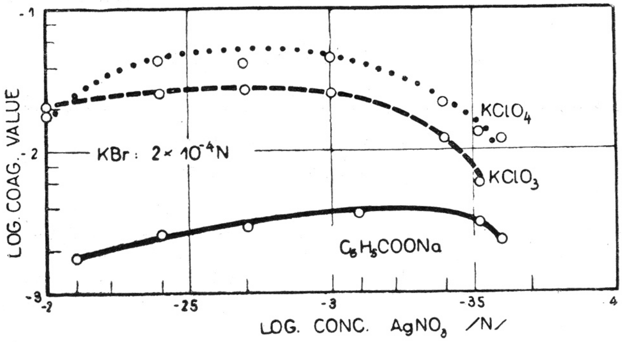

Fig. 1. Coagulation values of chlorate-, perchlorate- and benzoate-ion for positive silver bromide sols in presence of various concentrations of silver nitrate

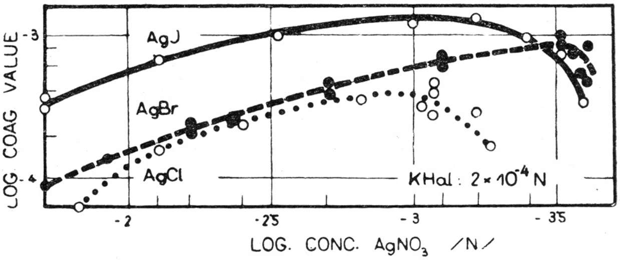

Fig. 2. Coagulation values of sulfate-ion for silver iodide, silver bromide and silver chloride sols in presence of various concentrations of silver nitrate

DISCUSSION

All the systems demonstrated in Figures 1 and 2 show an increase of coagulation values with increasing concentration of the stabilizing ion in the vicinity of the equivalency of the reacting components. This effect may be explained by the increase of the charge of the sol particles, as stated previously[1, 8, 9]. It is necessary to point out that this effect with sulfate ion is more pronounced than it is usually with bivalent counter ions which show an almost linear relationship in this region, i. e. independent from the concentration of the stabilizing ion.

The chlorate and perchlorate curves in Figure 1 show in the middle region of $AgNO_3$-concentrations a constant coagulation value. We suppose that the surface of the sol particles in this region is saturated with adsorbed stabilizing ions, and therefore the coagulation values remain constant. At higher concentrations of $AgNO_3$ the coagulation values decrease again. This effect is probably due to the additive action of the nitrate ion as a second counter ion; so we have here a coagulation effect of a pair of ions.

The benzoate curve (Fig. 1) and the sulfate curves (Fig. 2) do not show the linear region for coagulation values. The coagulation values decrease with increasing $AgNO_3$ concentration immediately after reaching the maximum. The chlorate and perchlorate curves (Fig. 1) show a decrease in coagulation values at higher $AgNO_3$ concentrations after passing the linear region. We believe that besides the additivity of the counter ions, the solubility of the compound »Ag-counter ion« plays an important rôle in the mentioned regions. These compounds may be precipitated at higher concentrations of silver nitrate so that the solid phase consists in these cases of a mixed system: silver halide and the compound formed between the silver ion and the counter ion. The coagulation values must be influenced by this effect.

In a previous paper we discussed the influence of the solubility for acetate, propionate, butyrate and valeriate anions. Now it is possible to say more about this problem. If we plot in a diagram the solubilities of the compounds consisting of potential determining ion (Ag^+) and the counter ion *versus* the maximal coagulation values (from diagrams in this paper 1 and 2, and from diagram 1, 2 and 5 in a previous paper[1]) we obtain the curve shown in Figure 3. It is evident from this diagram that the coagulation value increases with increasing solubility of the compound composed of the potential determining ion and the counter ion. If we plot logarithmically the coagulation values *versus* solubilities the relationship is quite linear excepted the value for benzoate ion.

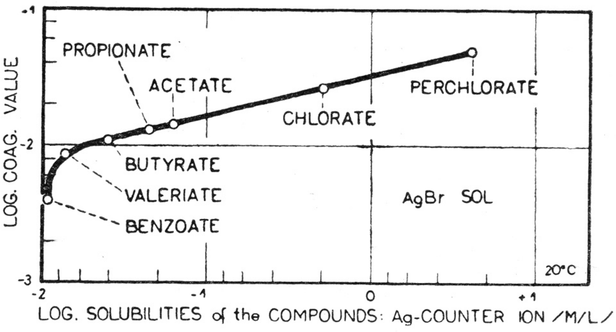

Fig. 3. Plot of the coagulation values of the perchlorate-, chlorate-, acetate-, propionate-, butyrate-, valeriate- and benzoate-ion for silver bromide sols versus the solubilities of the silver compounds of the same ions

The coagulation value of sulfate-ion is about 10 times smaller than the coagulation value of the butyrate-ion for silver bromide sol *in statu nascendi* (compare Fig. 2 in this paper with the Fig. 5 in the previous paper[1]). The solubilities of silver sulfate and of the silver butyrate are the same (0,25 *M*/1)[2], so that in this case the solubility cannot be the chief factor influencing the coagulation value. It is obvious that the valency of the counter ions (SO_4^{--} and $C_3H_7COO^-$) is responsible for the great difference in coagulation values. Thus we can consider this result as a proof of the validity of the Schulze-

Hardy rule for positive silver halide sols *in statu nascendi* in the same manner as it was shown for the negative sols[9].

The sequence of the curves for the coagulation effect of the sulfate ion on different silver halide sols shows that for the coagulation of the silver iodide sol we need the highest concentration of sulfate ion, and for silver chloride sol the lowest. The values for silver bromide sol are in the middle region. This effect is in accordance with the density of the charge on the surface of the sol particles[4]; which is the greatest on silver iodide sol, and the smallest on silver chloride sol[10].

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IZVOD

Koagulacioni utjecaj kalijeva perklorata, kalijeva klorata i natrijeva benzoata na pozitivni sol srebrnog bromida, te kalijeva sulfata na pozitivne solove srebrnog klorida, bromida i jodida

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U ovom je radu ispitivan koagulacioni utjecaj kalijeva perklorata, kalijeva klorata i natrijeva benzoata na pozitivni sol srebrnog bromida *in statu nascendi,* te kalijeva sulfata na pozitivne solove srebrnog klorida, bromida i jodida *in statu nascendi.*

Na temelju dijagrama (sl. 1. i sl. 2.), kojima je prikazana ovisnost koagulacione vrijednosti spomenutih elektrolita o koncentraciji stabilizacionog iona (Ag^+), došli smo do ovih zaključaka:

1. Povećanjem koncentracije stabilizacionog iona povećava se koagulaciona vrijednost i kod jednovalentnih perklorat-, klorat- i benzoat-iona i kod dvovalentnih SO_4-iona, ali samo do neke granice; za perklorat i klorat ostanu koagulacione vrijednosti nakon toga konstatne, no onda se postepeno smanjuju; kod benzoata i sulfata koagulacione se vrijednosti smanjuju, čim su postignute maksimalne vrijednosti. Držimo, da je spomenuto smanjivanje koagulacionih vrijednosti klorata i perklorata pri porastu koncentracije stabilizacionog iona posljedica djelovanja protuiona (ClO_4^-, ClO_3^-) i NO_3-iona, dakle para iona; smanjivanje koagulacionih vrijednosti benzoata i sulfata najvjerojatnije je posljedica ne samo djelovanja protuiona ($C_6H_5COO^-$, odnosno SO_4^{--}) i NO_3-iona, nego i veoma male topljivosti spoja između stabilizacionog iona i benzoat-, odnosno sulfat-iona (Ag-benzoat kod 25°C topljiv 0,011 mol/1, Ag_2SO_4 kod 20°C topljiv 0,025 mol/1). Zbog navedene male topljivosti imamo kod većih koncentracija stabilizacionog iona kao čvrstu fazu ne samo srebrni

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halogenid, nego i srebrni benzoat, odnosno srebrni sulfat, što se mora odraziti i na koagulacionom efektu.

2. Usporedimo li koagulacione vrijednosti klorat-, perklorat- i benzoat-iona (sl. 1.) kod jednakih koncentracija stabilizacionog iona u srednjem koncentracionom području, vidimo, da su različite, iako se radi o jednakovalentnim ionima. I u ovom slučaju treba tražiti uzrok u različitoj topljivosti spoja između stabilizacionog iona (Ag^+) i protuiona (ClO_4^-, ClO_3^-, $C_6H_5COO^-$). U prilog toj tvrdnji navodimo dijagram (sl. 3.), gdje su na ordinatu nanesene koagulacione vrijednosti perklorata, klorata i benzoata, te acetata, propionata, butirata i valerijata, koje smo objavili u prethodnom radu[1], a na apscisu topljivosti spojeva između navedenih iona i stabilizacionog iona, t. j. Ag-perklorat,-klorat,-acetat,-propionat,-butirat i -valerijat.

3. Iz činjenice, da su koagulacione vrijednosti SO_4 iona manje od koagulacionih vrijednosti jednovalentnih perklorat-, klorat- i benzoat-iona, proizlazi, da i za anione vrijedi Schulze-Hardyjevo pravilo. Mogli bismo međutim pomisliti, da je spomenutu razliku uzrokovala različita topljivost spoja između navedenih iona i stabilizacionog iona. Izrazita se razlika vidi, međutim, između koagulacone vrijednosti SO_4-iona i butirat-iona (sl. 5. prethodnoga rada[1]) (koagulaciona je vrijednost SO_4-iona oko 10 puta manja), premda su topljivosti srebrnog benzoata i srebrnog butirata jednake (0,025 mol/l).

4. Koagulacioni je utjecaj SO_4-iona na solove srebrnih halogenida *in statu nascendi* različit. Uzrok je tome različita gustoća naboja na površini koloidnih čestica, o čemu se već prije diskutiralo u vezi s radovima s negativnim solovima[4].

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