

Methorics of the Coagulation Processes. XI.*
Coagulation Effect of Potassium Succinate, Potassium Fumarate
and Potassium Maleate on Positive Silver Bromide Sol.**

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The coagulation effect of potassium succinate, potassium fumarate and potassium maleate on positive silver bromide sol *in statu nascendi* has been determined. The coagulation values of these electrolytes depend on the concentration of the stabilizing ion, the solubility of the »stabilizing ion — counter ion« compounds and the concentration of hydrogen ions.

In the preceding papers¹ we discussed the coagulation effect on positive sols of silver halides *in statu nascendi* of such monovalent and bivalent anions (nitrate, perchlorate, chlorate and sulfate) that do not hydrolyse, and of such (acetate, propionate, butyrate and valerate) that do, but the hydrolysis has practically no influence on their coagulation effect. In this paper we shall consider some cases of succinate-, fumarate- and maleate-ions where the hydrolysis plays an essential role in the coagulation effect on sols of silver halides *in statu nascendi*.

RESULTS

The experimental technique used was the same as described previously^{1, 2}. The coagulation values of potassium succinate, potassium fumarate and potassium maleate were determined from 10-minutes concentration tyndallograms for concentrations of silver nitrate from $2 \times 10^{-3}N$ to $2,2 \times 10^{-4}N$ at a constant concentration of potassium bromide ($2 \times 10^{-4}N$) (pH from ~ 6 to 6.8) at 20°C. The logarithms of values thus obtained were plotted on the ordinate, and the logarithms of concentration of silver nitrate on the abscissa (Fig. 1).

The coagulation values of potassium succinate and potassium maleate were determined in the following systems: AgNO₃-KBr-HNO₃-potassium succinate, and AgNO₃-KBr-HNO₃-potassium maleate.

The concentrations of silver nitrate varied from series to series (2×10^{-3} , 8×10^{-4} , 4×10^{-4} and $2,5 \times 10^{-4}N$), but were constant in the same series; the concentration of potassium bromide was constant ($2 \times 10^{-4}N$). The concentration of HNO₃ was systematically varied so that pH had a value between 3 and 7, while the concentrations of the electrolyte (succinate or maleate) covered the region of critical coagulation². In that region the concentration of hydrogen ions was also measured by means of

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a pH-meter with glass electrode. By extrapolating the measured values, the pH values at the critical coagulation¹ concentration of the electrolyte were obtained (Fig. 2 and 3).

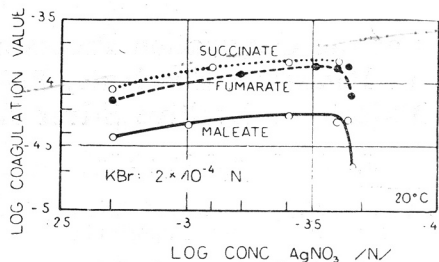


Fig. 1. Coagulation values of succinate, fumarate- and maleate-ion for silver bromide sol in presence of various concentrations of silver nitrate

The solutions of potassium salts of maleic and fumaric acid were prepared by neutralizing these acids with potassium hydroxide; the solution of potassium succinate was obtained by dissolving the salt in water.

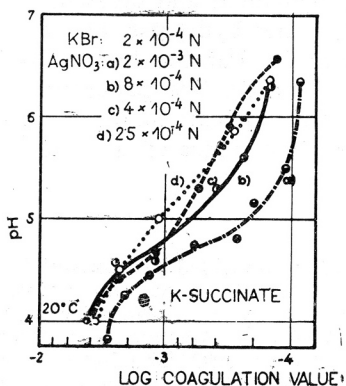


Fig. 2.

Fig. 2. Plot of the coagulation values of the potassium succinate versus concentration of hydrogen ions in presence of various concentrations of silver nitrate

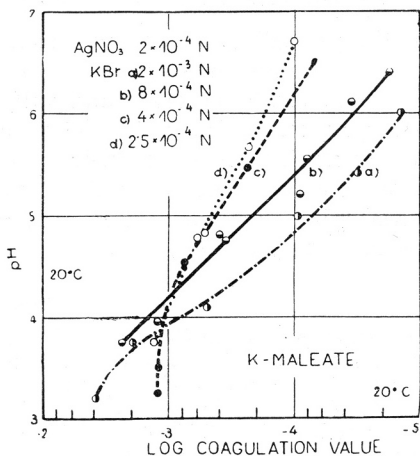


Fig. 3.

Fig. 3. Plot of the coagulation values of the potassium maleate versus concentration of hydrogen ions in presence of various concentrations of silver nitrate. (Added in proof: In this figure the symbols KBr and AgNO_3 should be interchanged)

DISCUSSION

Fig. 1 shows the dependence of coagulation values of potassium succinate, potassium fumarate and potassium maleate on positive silver bromide sol *in statu nascendi* in dependence on the concentration of silver nitrate. The coagulation effect of bivalent succinate-, fumarate- and maleate-ion is the same as that of bivalent sulfate-ion¹ with regard to the increase of coagulation values in the vicinity of the equivalency of the reacting components (AgNO_3 and KBr) with increasing concentration of the stabilizing ion (Ag^+) as well as with regard to the gradual decrease of coagulation values in the field of larger concentration of silver nitrate. Such behaviour is natural¹, because in

this case we deal with bivalent anions, as, for example, the sulfate ion, while the solubility of the compound « stabilizing ion — counter ion », is smaller than the solubility of silver sulfate. The solubilities³ are: Ag-succinate $6 \times 10^{-4} M/1$, (20°C), Ag-fumarate $3,9 \times 10^{-4} M/1$, (30°C), Ag-maleate $3,6 \times 10^{-3} M/1$, (30°C), and Ag-sulfate $2,5 \times 10^{-2} M/1$, (20°C).

If we compare the coagulation values of potassium succinate, potassium fumarate, and potassium maleate for equal concentrations of stabilizing ions (Ag^+) (Fig. 1), we see that such values for potassium succinate and potassium fumarate differ very slightly, while the analogous values of potassium maleate change perceptibly. The reason for it can be found in the solubility of « stabilizing ion — counter ion » compounds. While the solubility of Ag-succinate and Ag-fumarate slightly differ, the solubility of Ag-maleate is about ten times greater, and accordingly, its coagulation effect is also greater⁴.

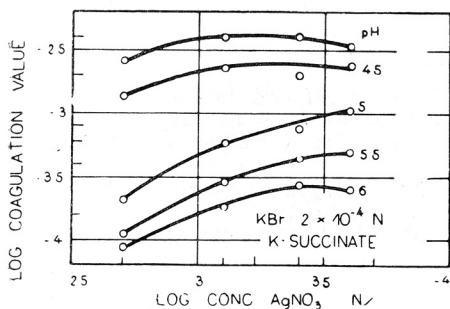


Fig. 4. Coagulation values of potassium succinate for silver bromide sols in a medium of different pH

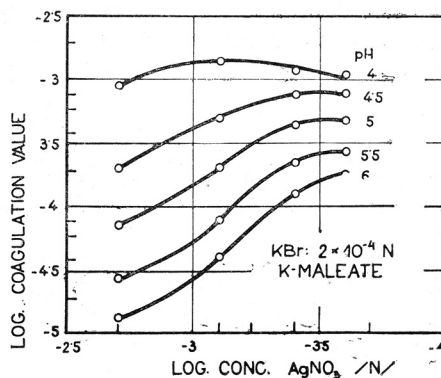


Fig. 5. Coagulation values of potassium maleate for silver bromide sols in medium of different pH

The effect of concentration of hydrogen ions on the coagulation capacity of these anions is pronounced. From Fig. 2 and 3 it appears that coagulation values of potassium succinate and potassium maleate are dependent not only on the concentration of the stabilizing ion, but also on the concentration of hydrogen ion. This is more evident from Fig. 4 and 5, obtained by cutting the diagrams (Fig. 2 and 3) at the equivalent pH values parallel with the abscissa. The coagulation values of potassium succinate and potassium maleate corresponding to the intersecting lines are then plotted logarithmically against the corresponding concentrations of silver nitrate. The reason for such behaviour of the aforesaid electrolytes is to be found in the shifting of ionic equilibrium,



of fumaric respectively maleic acid with change of concentration of hydrogen ions. With the increase of concentration of these ions, the equilibrium shifts to the left, i. e. bivalent anions decrease, and monovalent anions and non-dissociated molecules increase in number. Since the coagulation value is

greater, when the valency is smaller, it is understandable why with increasing concentration of hydrogen ions the coagulation values of fumarate- and maleate-ions shift towards greater values.

The form of the curves in Fig. 4 and 5 at greater pH values is similar to the form of curves given in Fig. 1.

Since the solubility of the compound »stabilizing ion —counter ion« is small it is very probable that at greater concentrations of the stabilizing ion the solid phase consists not only of pure silver bromide but also of silver fumarate and silver maleate, respectively. That must be inevitably reflected in coagulation values.

With smaller pH values ($\text{pH} < 4$) there is a decrease in coagulation values only at larger concentrations of the stabilizing ion ($10^{-3}N$). It is probable that the reason lies in the effect not only of the coagulation ion (fumarate, maleate), but also of nitrate ion, the concentration of which attained a high value on account of the relatively great concentration of silver nitrate and nitric acid, added in order to achieve a definite pH-value.

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IZVOD

Metorika koagulacionih procesa. XI.

Koagulacioni utjecaj kalijeva sukcinata, kalijeva fumarata i kalijeva maleata na pozitivni sol srebrnog bromida

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Ovisnost koagulacione vrijednosti dvovalentnih sukcinat-, fumarat- i maleat-iona za sistem srebrnoga bromida *in statu nascendi* o koncentraciji stabilizacionog iona analogna je takvoj ovisnosti dvovalentnih SO_4 iona¹. Iako su spomenuti ioni jednakovalentni, koagulacione su im vrijednosti različite kod jednake koncentracije stabilizacionog iona; uzrok tome treba tražiti u različitoj topljivosti spoja »stabilizacioni ion — protuion«. Utjecaj koncentracije vodikovih iona na koagulacionu vrijednost rezultira iz pomicanja ravnoteže »asocijacija \rightleftharpoons disocijacija«, o čemu se diskutiralo ne samo u ovom radu, nego i u jednom od prethodnih radova¹.

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