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**Methorics of Coagulation Processes. XIII.**  
**Systematic Comparison of Coagulation Values for Various Cations**  
**on Negative Silver Halogenide Sols\***

*E. Matijević, K. F. Schulz and B. Težak*

*Laboratory of Physical Chemistry, Faculty of Science, University,  
Zagreb, Croatia, Yugoslavia*

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The results on coagulating effects of the following electrolytes are reported: on negative silver bromide sol:  $\text{HNO}_3$ ,  $\text{LiNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{Li}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Mn}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{MgSO}_4$ ,  $\text{MnSO}_4$ ,  $\text{CaSO}_4$ ,  $\text{Al}(\text{NO}_3)_3$ ,  $\text{Ce}(\text{NO}_3)_3$ , and  $\text{La}(\text{NO}_3)_3$ ; on negative silver iodide sol:  $\text{LiNO}_3$ ,  $\text{NaNO}_3$ ,  $\text{KNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{Li}_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Mn}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{MgSO}_4$ ,  $\text{MnSO}_4$ ,  $\text{CaSO}_4$ ,  $\text{Al}(\text{NO}_3)_3$ ,  $\text{La}(\text{NO}_3)_3$ , and  $\text{Al}_2(\text{SO}_4)_3$ ; on negative silver chloride sol:  $\text{KNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{MgSO}_4$ ,  $\text{CaSO}_4$ ,  $\text{Al}(\text{NO}_3)_3$ , and  $\text{La}(\text{NO}_3)_3$ .

As shown earlier<sup>9</sup> a linear relationship exists between the crystallographic radii of the counterions of the same valency and the logarithms of the corresponding coagulation values; the characteristic coagulation values obtained when extrapolating the straight lines of the preceding plots to the zero radius were used for testing the validity of expression for quantitative interpretation of the Schulze-Hardy rule. The equations which follow from the theories of Freundlich and Verwey and Overbeek did not fit the experimental observations, while the equations of Whetham and Težak showed quite a good agreement.

#### INTRODUCTION

It is well known that the interpretation of the phenomena of electrolytic coagulation of lyophobic sols represents a problem which has not yet been completely solved. Therefore it is necessary to collect a very extensive experimental material, on well defined sols under controlled conditions.

When investigating the electrolytic coagulation effects we also performed systematic determinations of coagulation values of various cations of different valencies for negative silver bromide, silver iodide, and silver chloride sols *in statu nascendi*. The advantages of these sols as well as of the method *in statu nascendi* used in our experiments have already been described elsewhere<sup>1,2,3</sup>.

A part of our experimental data are disseminated in various papers dealing with the methorics of coagulation processes.<sup>4-9</sup> In this communication we intend to give a rather complete presentation of our results. As the experiments were

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performed with three related sols of different but known specific properties and all the important variables were taken into account (e. g. sol concentration, concentration of the stabilizing ions etc.), the coagulation values obtained on the basis of a kinetic treatment may be considered as correct and objective. These values offer therefore the possibility for a quantitative or at least a semiquantitative proof of various coagulation theories. To our knowledge, there is no comprehensive collection of coagulation data in the literature determined in the same way.

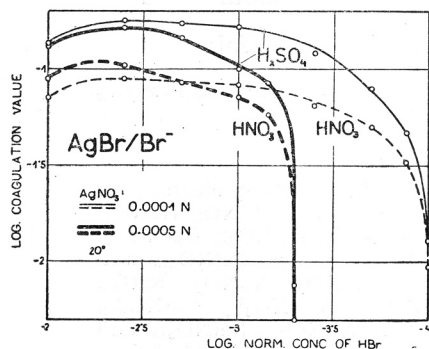


Fig. 1.

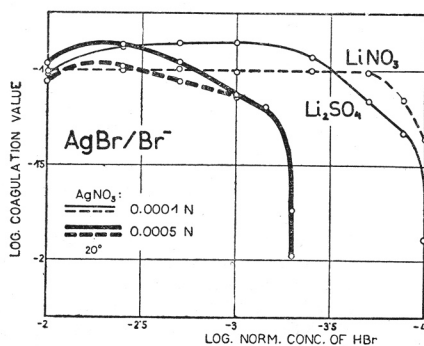


Fig. 2.

Fig. 1. Coagulation values of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  for silver bromide sol *in statu nascendi* in presence of various concentrations of the stabilizing ion ( $\text{Br}^-$ ) and two different Li sol concentrations (0.0001 M and 0.0005 M).

Fig. 2. Coagulation curves as in Fig. 1 for  $\text{LiNO}_3$  and  $\text{Li}_2\text{SO}_4$ .

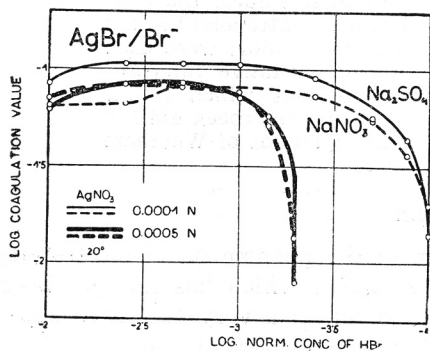


Fig. 3.

Fig. 3. Coagulation curves as in Fig. 1 for  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$ .

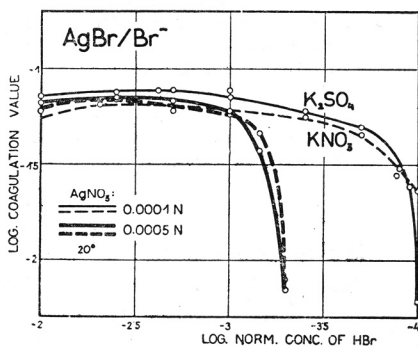


Fig. 4.

Fig. 4. Coagulation curves as in Fig. 1 for  $\text{KNO}_3$  and  $\text{K}_2\text{SO}_4$ .

#### EXPERIMENTAL

The experimental technique used was described in detail previously<sup>10</sup>. We measured the change of the light scattering intensity with time for systems consisting of precipitation components and the added neutral electrolyte. A series of test tubes contained the solution of one precipitation component (the silver nitrate) at a fixed concentration whereas a second series of test tubes was filled with a solution consisting of the other precipitation component (the hydrogen halides) again at the same concentration, mixed with the neutral electrolyte of varying concentrations. As the intention was to investigate the influence of the cations, the concentration of the halide component was always higher than the concentration of silver

nitrate. The volume of the solutions in each test tube was adjusted to 5 ml. Thus after mixing both precipitation components the volume amounted 10 ml. All the concentrations are given in normalities calculated to this volume. The changes in the tyndallometric values were followed kinetically by means of a Zeiss nephelometer in combination with a Pulfrich photometer.

The coagulation values were evaluated graphically from concentration-tyndallograms as shown in another paper<sup>10</sup>.

The chemicals used were always of analytical grade. Only if it was not possible to get the chemicals of the highest purity, we used the *purissimum* grade. This is a very important fact since the contaminations of the chemicals may very much influence the coagulation effects and consequently the coagulation

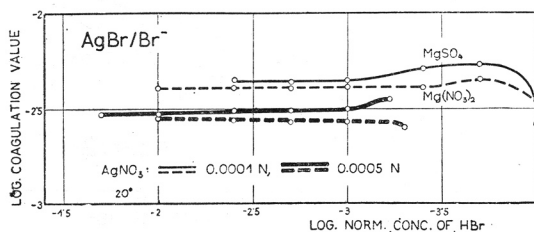


Fig. 5. Coagulation curves as in Fig. 1 for  $\text{Mg}(\text{NO}_3)_2$  and  $\text{MgSO}_4$ .

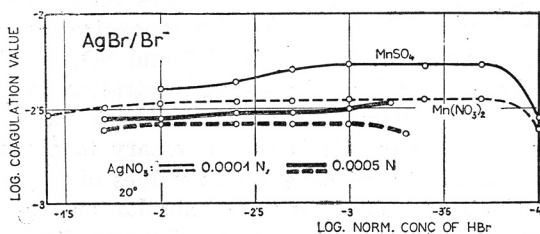


Fig. 6. Coagulation curves as in Fig. 1 for  $\text{Mn}(\text{NO}_3)_2$  and  $\text{MnSO}_4$ .

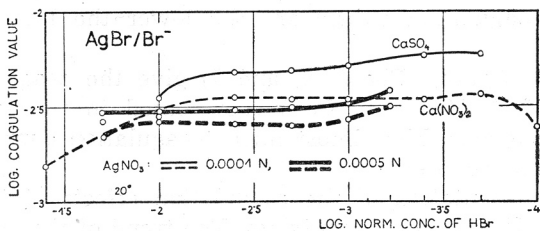


Fig. 7. Coagulation curves as in Fig. 1 for  $\text{Ca}(\text{NO}_3)_2$  and  $\text{CaSO}_4$ .

values. It seems that especially the presence of very minute amounts of one halide component in another halide system considerably influences the coagulation values<sup>11,12</sup>. The reproducibility depends also on the nature of the sol. As it will be shown later the reproducibility of the results with the silver chloride sol is much worse than with other silver halides.

In some cases we succeeded in establishing the reason for bad reproducibility but there were systems where all attempts in discovering them failed.

Generally, the coagulation of silver halide sols *in statu nascendi* gives satisfactory results if performed in a systematic sequence and with very pure chemicals. In such case the reproducibility may be excellent, much better than it is usual in colloid chemistry<sup>9</sup>.

## RESULTS

First, we shall present the results obtained with silver bromide sol since they are most complete and the reproducibility is satisfactory. In Figures 1 to 4 the coagulation values of four univalent counterions ( $H^+$ ,  $Li^+$ ,  $N^+$ ,  $K^+$ ) are plotted against the concentration of the stabilizing ion ( $Br^-$ ), the concentration

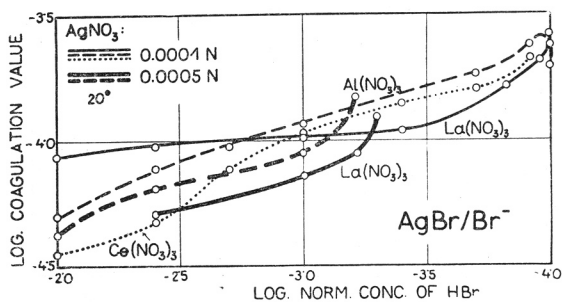


Fig. 8. Coagulation curves as in Fig. 1 for  $Al(NO_3)_3$ ,  $Ce(NO_3)_3$ , and  $La(NO_3)_3$ .

of  $AgNO_3$  being constant. The coagulation values of each cation are given for two sol concentrations (determined by the concentration of silver nitrate) and for two different accompanying ions ( $NO_3^-$  and  $SO_4^{2-}$ ). The trends of the curves as well as the influence of the sol concentration in these and in the following diagrams are in complete accordance with our results published and discussed earlier<sup>7</sup>. Therefore, it is not necessary to explain these effects again. For a better comparison of coagulation values of a series of cations of the same valency which are obtained under similar experimental conditions the corresponding curves are drawn in a single diagram. Such review diagrams for univalent counterions together with the coagulation curves of rubidium and caesium have already been shown (Fig. 7 and 8 in paper ref. 8). It is evident that the coagulation values are the lower the larger is the radius of the counterion.

The next three figures (Fig. 5, 6, and 7) give the coagulation values of divalent cations ( $Mg^{++}$ ,  $Mn^{++}$ , and  $Ca^{++}$ ) represented in the same manner as in the foregoing diagrams. The almost linear coagulation curves are characteristic for all divalent counterions.

Fig. 8 is the presentation of the coagulation effects of trivalent cations ( $Al^{+++}$ ,  $Ce^{+++}$ , and  $La^{+++}$ ) added as nitrates. The trend of the curves is opposite to that of the univalent counterions.

Figs. 9 and 10 give the coagulation curves of univalent counterions for a negative silver iodide sol when alkaline nitrates and sulfates were used as coagulating electrolytes. The coagulation values obtained are markedly higher than the corresponding values for silver bromide sol.

The coagulation curves of divalent nitrates ( $Mg$ ,  $Mn$ ,  $Ca$ ,  $Sr$ , and  $Ba$ ) and sulfates ( $Mg$ ,  $Mn$ , and  $Ca$ ) for a silver iodide sol are given in Figs. 11 and 12. Although the linearity of these curves is not so marked as in the case of silver bromide sol, the coagulation values are in both cases very close.

The last figure of this series (Fig. 13) shows the coagulation curves of lanthanum- and aluminium nitrate and aluminium sulfate for a silver iodide

sol. In the case of trivalent counterions the coagulation values for a silver iodide sol are lower than the corresponding values for a silver bromide sol. Another difference may be noted in the trend of the curves in the region of high concentrations of the stabilizing ion ( $I^-$ ).

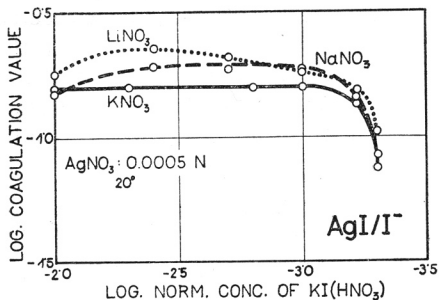


Fig. 9.

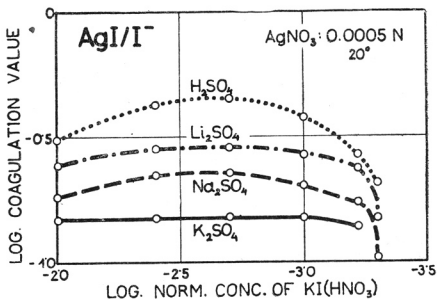


Fig. 10.

Fig. 9. Coagulation values of  $LiNO_3$ ,  $NaNO_3$ , and  $KNO_3$  for silver iodide sol *in statu nascendi* in presence of various concentrations of stabilizing ion ( $I^-$ ). Sol concentration 0.0005 M.

Fig. 10. Coagulation curves as in Fig. 9 of  $H_2SO_4$ ,  $Li_2SO_4$ ,  $Na_2SO_4$ , and  $K_2SO_4$ .

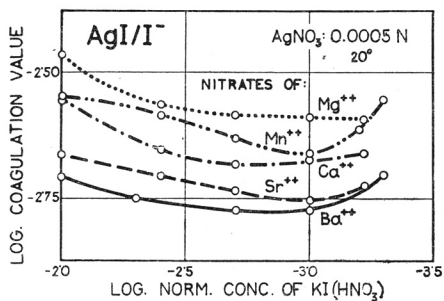


Fig. 11.

Fig. 11. Coagulation curves as in Fig. 9 of  $Mg(NO_3)_2$ ,  $Mn(NO_3)_2$ ,  $Ca(NO_3)_2$ ,  $Sr(NO_3)_2$ , and  $Ba(NO_3)_2$ .

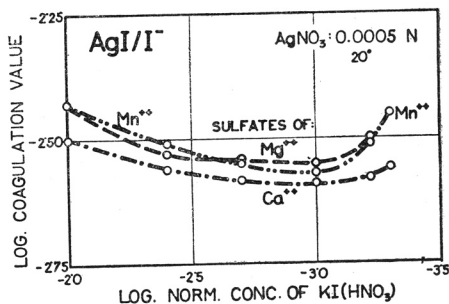


Fig. 12.

Fig. 12. Coagulation curves as in Fig. 9 of  $MgSO_4$ ,  $MnSO_4$ , and  $CaSO_4$ .

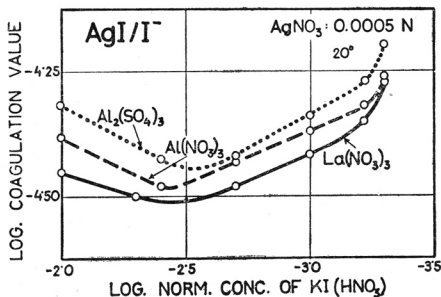


Fig. 13. Coagulation curves as in Fig. 9 of  $Al(NO_3)_3$ ,  $La(NO_3)_3$ , and  $Al_2(SO_4)_3$ .

Figures 14, 15, and 16 give the results for a silver chloride sol. In the first one the coagulation values of potassium nitrate are inserted. It was not possible in this case to reproduce the results and to establish an exact coagulation

value. All the points marked within the hatched region have been obtained irrespective of the fact that the experiments were carried out in exactly the same manner. The reason for this behaviour of silver chloride is probably due to the low density of the surface charge on the primary particles and to the mixed crystallisation and coagulation effects which may be expected when the precipitation of silver chloride occurs. It is noteworthy that the coagulation values of various other univalent counterions (added as nitrates or sulfates) fall within the same limits. When the coagulation experiments were performed by mixing silver nitrate with metal chlorides better results have been obtained<sup>4</sup>.

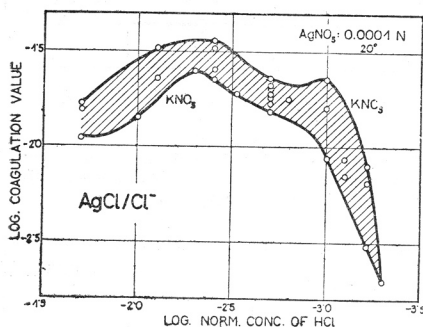


Fig. 14.

Fig. 14. Coagulation values of  $\text{KNO}_3$  for silver chloride sol *in statu nascendi* in presence of various concentrations of the stabilizing ion ( $\text{Cl}^-$ ). Sol concentration 0.0001 M. The low reproducibility of the coagulation values is marked with hatching.

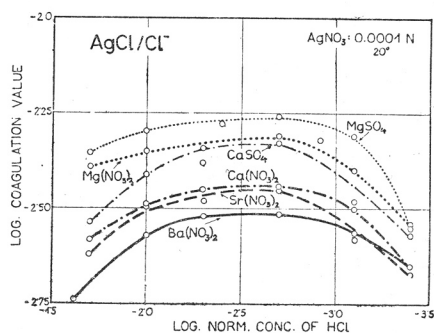


Fig. 15.

Fig. 15. Coagulation curves of  $\text{Mg}(\text{NO}_3)_2$ ,  $\text{Ca}(\text{NO}_3)_2$ ,  $\text{Sr}(\text{NO}_3)_2$ , and  $\text{Ba}(\text{NO}_3)_2$  for silver chloride sol *in statu nascendi*.

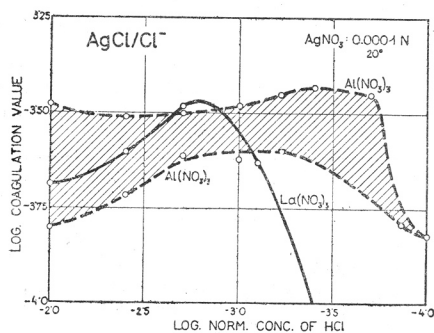


Fig. 16. Coagulation values of  $\text{Al}(\text{NO}_3)_3$  and  $\text{La}(\text{NO}_3)_3$  for silver chloride sol *in statu nascendi*. The low reproducibility of the determined values of  $\text{Al}(\text{NO}_3)_3$  is marked with hatching.

In Fig. 15 the coagulation curves of various divalent nitrates ( $\text{Mg}$ ,  $\text{Ca}$ ,  $\text{Sr}$ ,  $\text{Ba}$ ) and sulfates ( $\text{Mg}$ ,  $\text{Ca}$ ) are drawn, whereas in Fig. 16 the coagulation curves of  $\text{Al}(\text{NO}_3)_3$  and  $\text{La}(\text{NO}_3)_3$  are given. Again the values for  $\text{Al}$ -ions are dispersed within a large concentration region. The reason for this variability of the results lies, apart from the factors mentioned in the case of potassium nitrate, also in the hydrolysis of aluminium salts<sup>13</sup>.

Generally the coagulation values of univalent ions for the silver chloride sol are lower and those of trivalent ions higher than the corresponding values for the silver bromide sol.

## DISCUSSION

The coagulation values of cations of different valencies clearly show that the Schulze-Hardy rule is valid for silver halide sols. However, within a valency group there are differences in the coagulation values obtained under the same conditions. This effect should be attributed to the various sizes of counterions. We have shown that there is a linear relationship between the crystallographic radii and the logarithms of coagulation values<sup>9</sup>. Fig. 17 gives further examples of this rule for a silver bromide sol, where the ionic diameters of the counterions are plotted against the logarithmus of coagulation values; a very good straight line results.

Hence, when comparing and interpreting the coagulation values of various cations two quantities should be taken into account: the valency and the size

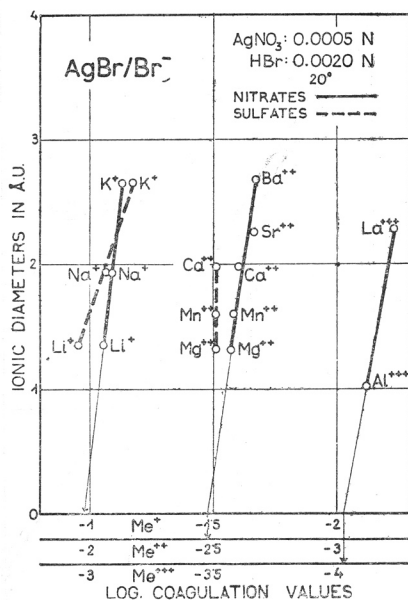


Fig. 17. The linear relationship between the crystallographic radii of the coagulating cations and their coagulation values for negative silver bromide sol *in statu nascendi*. Sol concentration 0.0005 M; concentration of the stabilizing ion 0.0020 N.

of the counterions. One of the main aims of all coagulation theories has been the quantitative interpretation of the Schulze-Hardy rule. However, most of them disregarded the influence of the ionic size of the counterions.

Two explanations may be found in literature for the connection between the ionic size and the coagulation values (Büchner<sup>14</sup> and Wo. Ostwald<sup>15</sup>). Both of them are only empirical in nature.

We have shown that the following relation may be very successfully applied for interpretation of coagulation results<sup>9</sup>:

$$z \cdot {}_c d + r_i = {}_s d (\log C_{\text{fix}} - \log C_{\text{coag}}) \quad (1)$$

where  $z$  is the valency and  $r_i$  the radius of the coagulating ion whose coagulation concentration is  $C_{\text{coag}}$ ;  $C_{\text{fix}}$  denotes the concentration of uncharged particles which would exert the same coagulating effect;  ${}_s d$  is a distance related to the ionic atmosphere, whereas  ${}_c d$  denotes the critical distance calculated from Bjerrum's equation for uni-univalent ion pair formation

$${}_c d = \frac{e^2}{2 D k T} \quad (2)$$

The above equation (1) follows from the theory developed by one of us (B. T.)<sup>16</sup> and it obviously relates the coagulation value to both valency and the radius of the counterion.

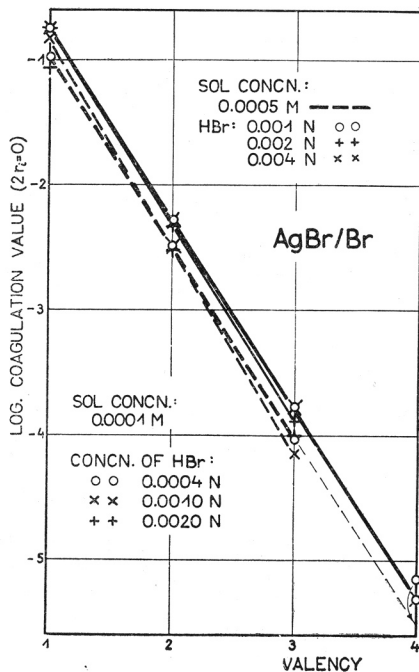


Fig. 18. The relationship between the valency of the coagulating cations and their characteristic coagulation values (for  $2r_i = 0$ ) for silver bromide sol *in statu nascendi* of two different sol concentrations and various concentrations of the stabilizing ion.

The validity of the equation (1) may be tested by inserting the characteristic coagulation concentrations of each valency group. These characteristic values are obtained by extrapolating the straight lines from Fig. 17 to the zero



value of the diameter. In this case the equation takes a much simpler form (since  $r_i = 0$ ) and may be written:

$$\log C_{\text{coag}}(r_i=0) = - \frac{cd}{sd} z + \log C_{\text{fix}} \quad (3)$$

This requirement has been satisfied for silver bromide sol as well as for silver iodide sol (Figure 8 in paper 9). Fig. 18 presents a further evidence for the linear relationship.

In our opinion the *characteristic* coagulation values (for  $2r_i = 0$ ) could be used for checking the validity of other quantitative expressions for interpretation of the Schulze-Hardy rule. The use of these values from which the influence of the ionic size is excluded is justified as none of these expressions takes into account the ionic size.

We shall recall here three such equations developed by Freundlich\*, Verwey and Overbeek<sup>18</sup>, and Whetham<sup>19</sup>:

$$1/C_1 : 1/C_2 : 1/C_3 \dots = 1 : 2^n : 3^n \dots \quad (\text{Freundlich}) \quad (4)$$

$$1/C_1 : 1/C_2 : 1/C_3 \dots = 1 : X : X^2 \dots \quad (\text{Whetham}) \quad (5)$$

where  $C_1$ ,  $C_2$ , and  $C_3$  are the coagulation concentrations of mono-, di-, and trivalent counterions respectively, whereas  $n$  and  $X$  are constants. According to Verwey and Overbeek the coagulation values for monovalent, divalent and trivalent electrolytes should show the following ratios:

$$C_1 : C_2 : C_3 = 1 : (1/2)^6 : (1/3)^6 = 100 : 1.56 : 0.14 \quad (6)$$

We have tried to test the equations (4—6) using our experimental results. For this purpose the characteristic coagulation concentrations of the following systems have been taken as examples:

TABLE I

AgNO <sub>3</sub> : 0.0001 N HBr : 0.0020 N		AgNO <sub>3</sub> : 0.0005 N HBr : 0.0020 N		AgNO <sub>3</sub> : 0.0005 N KI(HNO <sub>3</sub> ) : 0.0020 N	
$C_1$	0.18	0.105		0.28	
$C_2$	0.0053	0.0033		0.004	
$C_3$	0.00011	0.000093		0.000042	
$C_4$	0.000004	—		—	

$C_1$ ,  $C_2$ ,  $C_3$ , and  $C_4$  denote the characteristic concentration of coagulation ( $2r_i = 0$ ) for mono-, di-, tri-, and tetravalent counterions. The values in the second column were calculated from Fig. 17:

\* Freundlich's equation has been developed in this form by Ostwald<sup>17</sup>, who gave in the same paper an extensive review on the role of the valency in the electrolyte coagulation of hydrophobic sols including the above equations (4) and (5).

When inserted in Freundlich's equation (4) the values for a silver bromide sol (first column) give:

$$1 : 34.4 : 1652 : 45500 = 1 : 2^{5.13} : 3^{6.72} : 47.74$$

and for a silver iodide sol:

$$1 : 70.8 : 6700 = 1 : 2^{6.15} : 3^{8.05}$$

Obviously the values of  $n$  are not constant.

The Verwey-Overbeek relation (6) requires theoretically:

$$1 : (1/2)^6 : (1/3)^6 : (1/4)^6 = 100 : 1.56 : 0.14 : 0.0124.$$

With our data for a silver bromide sol the ratios are:

$$C_1 : C_2 : C_3 : C_4 = 100 : 2.88 : 0.61 : 0.0022,$$

and for a silver iodide sol:

$$C_1 : C_2 : C_3 = 100 : 1.4 : 0.014.$$

The results are by no means satisfactory.

Whetham's equation (5) gave the following ratios:  
for silver bromide sol (first column):

$$\begin{array}{l} \text{theor. } 1 : 34.4 : 1180 : 41000 \\ \text{exp. } 1 : 34.4 : 1650 : 45500 \end{array}$$

for silver bromide sol (second column):

$$\begin{array}{l} \text{theor. } 1 : 31.8 : 1130 \\ \text{exp. } 1 : 31.8 : 1020 \end{array}$$

for silver iodide sol (third column):

$$\begin{array}{l} \text{theor. } 1 : 70.8 : 5000 \\ \text{exp. } 1 : 70.8 : 6700. \end{array}$$

It is evident that Whetham's equation agrees much better with experimental results. Whetham attempt to explain the coagulation effects has many common points with ours and the agreement of the theory with experiments in both cases is not unexpected.

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### IZVOD

#### Metorika koagulacionih procesa. XIII.

#### Sistematska usporedba koagulacionih vrijednosti različitih kationa za negativne solove srebrnih halogenida

*E. Matijević, K. F. Schulz i B. Težak*

U nizu dijagrama prikazane su koagulacijske vrijednosti različitih kationa u ovisnosti o koncentraciji stabilizacijskih iona za negativne solove srebrnog bromida, srebrnog jodida i srebrnog klorida *in statu nascendi*. Rezultati pokazuju, da Schulze-Hardyjevo pravilo strogo vrijedi, ali da jasno dolazi do izražaja i utjecaj veličine iona. Ponovno je utvrđeno, da između veličine iona (kristalografski polumjeri) i logaritama koagulacijskih vrijednosti iona iste valencije postoji linearni odnos. Ekstrapolacijom tih pravaca na radius nula dobivaju se karakteristične koagulacijske vrijednosti za svaku grupu iona iste valencije. Te karakteristične koagulacijske vrijednosti poslužile su za ispitivanje valjanosti kvantitativnih izraza za Schulze-Hardyjevo pravilo, koji su izvedeni iz pojedinih teorija elektrolitne koagulacije liofobnih koloida. Pokazalo se da se naši eksperimentalni rezultati ne podudaraju sa zahtjevima izraženim jednadžbama od Freundlicha te Verweya i Overbeeka, a da dobro slijede teoretske izraze, koje su izveli Whetham i Težak.

FIZIČKO-KEMIJSKI INSTITUT  
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