

CCA-755

541.18.046

Conference Discussion

## The Role of Ionic Interactions in the Coagulation Process\*

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Received January 25, 1973

The influence of different combinations of electrolytes on negatively charged silver iodide sols was studied. Wo. Ostwald<sup>1</sup>, Težak<sup>2</sup>, Overbeek<sup>3</sup>, Matijević<sup>4</sup>, Levine<sup>5</sup> and other authors have offered different explanations for these electrolyte effects.

### EXPERIMENTAL

The rate coefficients of coagulation were measured by a light scattering procedure. According to Oster<sup>6</sup> and von Smoluchowski, coagulation is a second order rate process. The rate coefficient of coagulation is proportional to a change in the intensity of scattered light with relationship to time. It will be assumed that the change in the relative intensity ratio at 10 minutes of 0.12 corresponds to the same value of the rate coefficient. The experimental procedure *in statu nascendi* described by Težak *et al.*<sup>7</sup> was used.

### RESULTS

In Tables I and II the concentrations of ions which produced the constant value of the rate coefficient of AgI/I<sup>-</sup> sol coagulation are presented. It is assumed that ion-pairing<sup>8</sup> and adsorption<sup>9</sup> of the ions on the sol surface could be neglected in the calculations of the bulk solution compositions.

The concentration of I<sup>-</sup> ions in bulk solution was calculated as a difference between the initial concentrations of KI and AgNO<sub>3</sub> solutions. Because the solubility product<sup>8</sup> of AgI is 10<sup>-16</sup> mol<sup>2</sup> dm<sup>-6</sup> almost all the silver was assumed to be in a form of AgI sol. The concentration of Mg<sup>2+</sup> ions is equal to the total concentration of Mg(NO<sub>3</sub>)<sub>2</sub> solution. Ionic strengths were calculated by using the concentrations of the ions presented in Tables. The activity coefficients of Mg<sup>2+</sup> ions were calculated by the

TABLE I

The Composition of Solutions of AgNO<sub>3</sub>, KI, Mg(NO<sub>3</sub>)<sub>2</sub> and KNO<sub>3</sub> at Constant Value of Rate Coefficient of AgI/I<sup>-</sup> Sol Coagulation at 20 °C

Concentration of Ions 10 <sup>-3</sup> mol dm <sup>-3</sup>				Ionic Strength 10 <sup>-3</sup> mol dm <sup>-3</sup>	Activity Coefficient of Mg <sup>2+</sup> ions	Activity of Mg <sup>2+</sup> ions 10 <sup>-3</sup> mol dm <sup>-3</sup>
Mg <sup>2+</sup>	K <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	I <sup>-</sup>			
1.50	2.00	3.40	1.60	6.50	0.709	1.06
1.52	3.00	4.44	„	7.56	0.692	1.05
1.60	4.00	5.60	„	8.80	0.674	1.08
1.80	7.00	9.00	„	12.4	0.630	1.13
2.00	12.0	1.44	„	18.0	0.579	1.16
2.25	22.0	2.49	„	28.8	0.513	1.15
2.60	42.0	4.56	„	49.6	0.432	1.12

Initial concentration of AgNO<sub>3</sub> : 4.00 × 10<sup>-4</sup> mol dm<sup>-3</sup>; Initial concentration of KI : 2.00 × 10<sup>-3</sup> mol dm<sup>-3</sup>.

\* Based on a discussion contribution presented at the III International Summer School on the Chemistry of Solid/Liquid Interfaces, Rovinj, Yugoslavia, July 1—5, 1972.

TABLE II

The Composition of Solutions of  $\text{AgNO}_3$ ,  $\text{KI}$ ,  $\text{Mg}(\text{NO}_3)_2$  and  $\text{HNO}_3$  at Constant Value of Rate Coefficient of  $\text{AgI/I}^-$  Sol Coagulation at 20 °C

Concentration of Ions $10^{-3} \text{ mol dm}^{-3}$					Ionic Strength $10^{-3} \text{ mol dm}^{-3}$	Activity Coefficients of $\text{Mg}^{2+}$ ions	Activity of $\text{Mg}^{2+}$ ions $10^{-3} \text{ mol dm}^{-3}$
$\text{Mg}^{2+}$	$\text{H}^+$	$\text{K}^+$	$\text{NO}_3^-$	$\text{I}^-$			
1.50	0.00	2.00	3.40	1.60	6.50	0.709	1.06
1.52	1.00	„	4.44	„	7.56	0.692	1.05
1.65	2.00	„	5.70	„	8.95	0.672	1.11
1.90	10.0	„	14.2	„	17.7	0.582	1.11
2.30	20.0	„	25.0	„	28.9	0.512	1.18
2.65	40.0	„	45.7	„	50.0	0.431	1.14

Initial concentration of  $\text{AgNO}_3$  :  $4.00 \times 10^{-4} \text{ mol dm}^{-3}$ ; Initial concentration of  $\text{KI}$  :  $2.00 \times 10^{-3} \text{ mol dm}^{-3}$ .

formula quoted below which can be used for solutions with ionic strengths up to  $0.1 \text{ mol dm}^{-3}$ . In the case of  $\text{Mg}^{2+}$  ions the equation is<sup>10</sup>

$$-\log f_{\text{Mg}^{2+}} = \frac{2\sqrt{\mu}}{1 + \sqrt{\mu}}$$

where  $\mu$  is the ionic strength. The activities of  $\text{Mg}^{2+}$  ions were calculated as products of the single ion activity coefficients and concentrations of  $\text{Mg}^{2+}$  ions.

The concentrations of ions, ionic strengths, activity coefficients and activities in Table II were calculated in the same way as in Table I.

#### DISCUSSION

The results show that the rate of coagulation is a function of the activity of counter-ions. This function includes the ionic strength and the concentration of counter-ions. In Fig. 1 it is demonstrated that the activity of  $\text{Mg}^{2+}$  ions is constant at the same value of rate coefficient of coagulation with increasing ionic strength, but that the concentration of  $\text{Mg}^{2+}$  ions is not constant. The influence of  $\text{KNO}_3$  and  $\text{HNO}_3$  solutions on the activities of the magnesium ions are the same within experimental error. This result is in agreement with the assumption that ion-pairing could be neglected. In the region of activities of  $\text{I}^-$  ions from  $10^{-2}$  until  $10^{-9} \text{ mol dm}^{-3}$

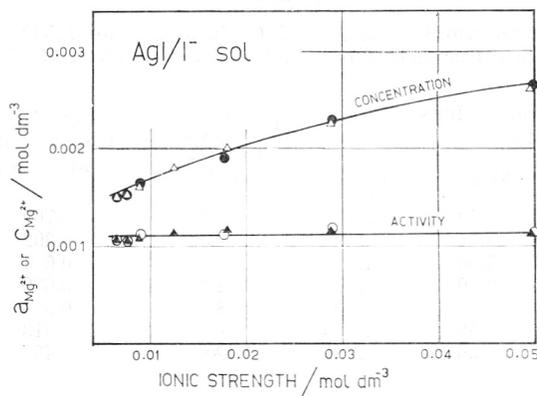


Fig. 1. The influence of ionic strength on the activity of  $\text{Mg}^{2+}$  ions ( $a_{\text{Mg}^{2+}}$ ) and concentration of  $\text{Mg}^{2+}$  ions ( $C_{\text{Mg}^{2+}}$ ) at constant value of rate coefficient of  $\text{AgI/I}^-$  sol coagulation at 20 °C.

Concentration of  $\text{Mg}^{2+}$  ions in the solution which contained: ●  $\text{HNO}_3$ , ▲  $\text{KNO}_3$   
Activity of  $\text{Mg}^{2+}$  ions in the solution which contained: ○  $\text{HNO}_3$ , ▲  $\text{KNO}_3$

no influence on the rate of coagulation of  $\text{AgI/I}^-$  sol was found<sup>11</sup>. The change of ionic strength from  $6 \times 10^{-3}$  to  $6 \times 10^{-2}$  mol  $\text{dm}^{-3}$  produces a change in activity of  $\text{I}^-$  ions approximately from  $1.5$  to  $1.3 \times 10^{-3}$  mol  $\text{dm}^{-3}$  at the concentration of  $\text{I}^-$  ions of  $1.6 \times 10^{-3}$  mol  $\text{dm}^{-3}$ . Therefore the activity range covered in this study was well within the range of  $\text{I}^-$  ion activities which produced no change in the rate of coagulation. Because of the above reasons the influence of the change in activity of  $\text{I}^-$  ions on the rate of coagulation is neglected. The influence of  $\text{H}^+$  and  $\text{K}^+$  as counter-ions on the coagulation rate was negligible up to the concentration of  $0.04$  mol  $\text{dm}^{-3}$  for  $\text{H}^+$  or  $\text{K}^+$  ions. This is in agreement with data<sup>9</sup> on the adsorption of counter-ions on silver iodide sols.

The results from Table III show that the activities of  $\text{H}^+$  ions as counter-ions are practically constant at the same rate coefficient of coagulation for different acids. The small differences in results could be explained by differences in viscosities of acids as a consequence of which the diffusion coefficients of colloidal particles are not constant<sup>6</sup>.

TABLE III

*The Concentrations of Acids, pH and Activities of  $\text{H}^+$  Ions at Constant Value of Rate Coefficient of  $\text{AgI/I}^-$  Sol Coagulation*

Acid	Concentration of acid mol $\text{dm}^{-3}$	pH	Activity of $\text{H}^+$ ion mol $\text{dm}^{-3}$
$\text{HNO}_3$	0.141	0.86	0.138
$\text{H}_2\text{SO}_4$	0.219	0.85	0.141
$\text{H}_3\text{PO}_4$	2.76	0.84	0.145
$\text{CH}_3\text{COOH}$	5.62	0.65	0.224

Initial concentration of  $\text{AgNO}_3$  :  $4.00 \times 10^{-4}$  mol  $\text{dm}^{-3}$ ; Initial concentration of  $\text{KI}$  :  $2.00 \times 10^{-3}$  mol  $\text{dm}^{-3}$   
The activities of hydrogen ions were determined by pH measurements.

The activities of ions can be evaluated from the rate coefficient of coagulation measurements. In this evaluation the empirical equation of Paine<sup>12</sup> is used

$$\log k' = K + n \log a$$

where  $k'$  is the value proportional to the rate coefficient of coagulation,  $K$  and  $n$  are constants, and  $a$  is the activity of counter-ion which is used instead of the concentration. Sensitivity of the measurements depends on the constant  $n$ . Constant  $n$  was determined in this study for the system  $\text{AgI/I}^-$ . The  $n$  value for this system is 6.70. This procedure was used for determining the dissociation constants of ion-pairs  $\text{La SO}_4^+$  and  $\text{MgSO}_4$ . The dissociation constants were calculated and will be published separately<sup>13</sup>.

The values of concentration of electrolytes chosen by the rate constant proportional to 0.12 were not the usual critical coagulation concentrations. The values used in this study are between the critical coagulation concentrations defined by Težak<sup>7</sup> and the values defined by Reerink and Overbeek<sup>14</sup>. The reason for choosing these rate coefficients was the sensitivity of the rate of coagulation towards the activities of counter-ions. In this region of coagulation rates the empirical equation from Paine<sup>12</sup> could be used.

When critical coagulation concentrations of electrolyte combinations were used, antagonistic effects were observed<sup>1,2</sup>. This effect was explained in different ways. Overbeek<sup>3</sup> indicated (in the discussion of a paper) that antagonistic effects often disappear if activities of the counter-ions are calculated. This study supports the conclusion that in the examined combinations of electrolytes the behaviour could be explained by the influence of bulk solution composition on the activity of counter-ions.

## REFERENCES

1. Wo. Ostwald, *Kolloid Z.* **88** (1939) 1.
2. B. Težak, *Croat. Chem. Acta* **42** (1970) 81.
3. J. Th. Overbeek, *Discussions Faraday Soc.* **18** (1954) 200.

4. E. Matijević, S. Kratochvil, and J. Stickels, *J. Phys. Chem.* **73** (1969) 564;  
L. J. Stryker and E. Matijević, *J. Phys. Chem.* **73** (1969) 1484.
5. S. Levine and G. M. Bell, *J. Colloid Sci.* **17** (1962) 838;  
S. Levine and G. M. Bell, *J. Colloid Sci.* **20** (1965) 695.
6. G. Oster, *J. Colloid Sci.* **2** (1947) 291.
7. B. Težak, E. Matijević, and K. Schulz, *J. Phys. Chem.* **55** (1951) 1557.
8. L. G. Sillen and A. E. Martell, *Stability Constants*, Special Publication No. 17., London: The Chemical Society, Burlington House, London 1964.
9. M. J. Herak and M. Mirnik, *Kolloid Z.* **179** (1961) 130.
10. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, London, Butterworths, 1955, p. 230.
11. K. F. Schulz and B. Težak, *Arhiv Kem.* **26** (1954) 187;  
M. Mirnik, F. Flajšman, K. F. Schulz, and B. Težak, *J. Phys. Chem.* **60** (1956) 1473.
12. H. H. Paine in H. Reerink and J. Th. Overbeek, *Discussions Faraday Soc.* **18** (1954) 74.
13. N. Kallay, to be published.
14. H. Reerink and J. Th. Overbeek, *Discussions Faraday Soc.* **18** (1954) 74.

### IZVOD

#### Uloga ionskih interakcija kod koagulacionih procesa

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Ispitan je zajednički utjecaj otopina  $Mg(NO_3)_2$  i  $KNO_3$  te  $Mg(NO_3)_2$  i  $HNO_3$  na brzinu koagulacije negativnog sola AgJ. Uz pretpostavku da se prisustvo ionskih parova može zanemariti, izračunati su aktiviteti  $Mg^{2+}$  iona. Ustanovljeno je, da je aktivitet  $Mg^{2+}$  iona konstantan uz konstantnu vrijednost koeficijenta brzine koagulacije unatoč promjeni ionske jakosti u koloidnom sistemu. Mjerenjem pH ustanovljen je približno konstantni aktivitet  $H^+$  iona uz konstantni koeficijent brzine koagulacije za otopine  $HNO_3$ ,  $H_2SO_4$ ,  $H_3PO_4$  i  $CH_3COOH$ . Antagonistički efekt objašnjava se utjecajem sastava elektrolita na aktivitet protuiona.

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Primljeno 25. siječnja 1973.