

Influence of Potential Determining Ions on the Stability of Silver Iodide Colloidal System

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The influence of concentration of I⁻ ions on the stability of the AgI/I⁻ colloidal system has been investigated. The rate constant of coagulation is determined using tyndallometry. The applicability of the method is discussed. The rate constants of coagulation do not change significantly in the range of iodide ion conc. from 0.04 mol/m³ to 2 mol/m³ at 1 < W < 10,000.

THE colloidal stability¹ of lyophobic colloids is due to electrical repulsion between charged particles^{2,3}. The presence of counter ions near the particle surface decreases the effect of charge, thereby reducing the stability of such systems. Although many experiments have been reported³⁻¹⁰ describing either the dependence of coagulation rate on the activity of counter ions for a certain activity of potential determining ions, or the dependence of the c.c.c. of counter ions on the activity of potential determining ions, no systematic investigation of the coagulation rate on both the activity of potential determining and that of counter ions has yet been made.

We, therefore, decided to study the stability of the negatively charged silver iodide colloid as a function of the potential determining iodide ion and Mg²⁺ ion concentrations. The silver iodide has been chosen because it is already a well investigated model system and also because it is suitable for using tyndallometry for the evaluation of the coagulation rate constant. Magnesium ions have been chosen since they do not form any associates with other ions in the systems.

Calculations

The rate constant (*k*) of coagulation is defined by the following equation¹¹:

$$dc/dt = -kc^2 \quad \dots(1)$$

where *c* is the (total) concentration of colloidal particles. It was determined by measuring the change of the intensity of scattered light with time. After Oster¹¹ the following equation was used as the basis of the method:

$$I_{rel} = Af(V_i/V_s)^2 kt \quad \dots(2)$$

where *I_{rel}* is the relative intensity of scattered light at an angle π/4 to the transmitted beam, *A* the proportionality constant of the Rayleigh equation, *V_s* the volume of the colloidal system, and *V_i* is the total volume of all particles. For polydisperse system *A* should be corrected for the effect of polydispersity on light scattering by a factor *f*, which is equal to the intensity ratio of the light scattered

by the polydisperse system to that by the monodisperse system of same total volume and concentration of colloidal particles. The total volume of colloidal particles is equal to:

$$V_i = \frac{n_E M_E}{\rho} \frac{1}{1-\phi} \quad \dots(3)$$

where *n_E* is the amount of entities (in the present case AgI) comprising the aggregate, *M_E* the molar mass of this entity, ρ the density of primary particles and φ the volume fraction of the intermicellar liquid in the aggregate. Since AgI/I⁻ was prepared by mixing of the precipitation components the initial amount of KI was greater than that of AgNO₃, the total volume of colloidal particles is proportional to the initial amount of AgNO₃. By using equations (2) and (3) the relative rate constant of coagulation (*k_{rel}*) can be obtained as follows:

$$k_{rel} = kAf \left(\frac{M(\text{AgI})}{\rho} \frac{1}{1-\phi} \right)^2 s \text{ mol}^2 \text{ m}^{-6} \\ = \frac{dI_{rel}}{d(t/s)} \left(\frac{c_{in}(\text{AgNO}_3)}{\text{mol m}^{-3}} \right) \quad \dots(4)$$

where *c_{in}*(AgNO₃) stands for the initial concn. of AgNO₃. Eq. (4) was used to determine the *k_{rel}* under the assumption that *A*, φ and *f* do not change significantly during the coagulation process. This was used to calculate the stability coefficient by:

$$W = k_{rel, diff} / k_{rel} \quad \dots(5)$$

where the relative rate constant of coagulation controlled by diffusion *k_{rel, diff}* is assumed to be maximum value of *k_{rel}* obtained by the addition of electrolyte. This applies for systems where

$$dk_{rel}/dc_{counterion} = 0$$

Materials and Methods

All the chemicals used were analytically pure; AgNO₃ and KI were from Merck, and Mg(NO₃)₂ from Kemika, Zagreb.

The solutions in water were prepared by dissolving the salts in redistilled water. The solutions were standardized by potentiometric titration. The colloidal systems were prepared by direct mixing

of equal volumes of silver nitrate and potassium iodide solutions. One minute after the preparation of colloid, the system was poured into magnesium nitrate solution. This time was taken as the zero time of coagulation. The components and the colloidal system were kept at 293K. The relative intensity of scattered light at the angle of $\pi/4$ to the transmitted beam was measured on a Zeiss tyndallometer. The $I_{rel.}$ values were plotted against time. Using Eq. (4) the relative rate constants of coagulation were determined from slopes of the linear plots. The wavelength of light was 527 nm.

Results and Discussion

The results are given in Table 1. The application of the light scattering (turbidity) method for the rate of coagulation measurements is familiar in colloid chemistry, but there are a few queries which need to be answered before the results can be taken as valid. These questions involve the applicability of the Rayleigh theory, the constancy of the total volume of particles, and of the polydispersity effect,

i.e. whether the value of A remains constant during the coagulation process. Assuming constant A , ϕ and f the change in k in the coagulation can be investigated by plotting $I_{rel.}$ as a function of time. If a linear relationship is obtained k can be taken as independent of the size of aggregates. The Rayleigh theory is a basis of Eq. (2). For the wavelength of 527 nm the theory is applicable¹² to particles diameter smaller than 50 nm. Initially the AgI/I⁻ system contained particles of diameters^{13,14} in the range from 5 nm to 10 nm. During the experiment $I_{rel.}$ increases to a value 10 times higher than the initial. According to the Rayleigh equation this increase corresponds to a change in the particle diameter from 10 nm to approximately 20 nm. The ratio of the intensities of scattered light at angle $\pi/4$ to that at $3\pi/4$ was determined and it was never found to be greater than 1.2, which also indicates that Rayleigh theory is applicable. After a certain stage of coagulation ϕ and the total volume of particles can be assumed to be constant. At the same number and total volume of particles

TABLE 1 — VALUES OF THE VARIOUS PARAMETERS

Initial concentration (c_{in}) (mol m ⁻³)			c (I ⁻) (mol m ⁻³)	$\frac{dI_{rel.}}{d}$ (t/s)	$k_{rel.}$	log W
(AgNO ₃)	KI	Mg(NO ₃) ₂				
0.10	0.14	0.80	0.04	2.1 10 ⁻⁵	2.1 10 ⁻³	3.05
0.10	0.14	1.30	0.04	3.1 10 ⁻⁵	3.1 10 ⁻³	2.88
0.10	0.14	1.50	0.04	8.0 10 ⁻⁵	8.0 10 ⁻³	2.46
0.10	0.14	2.00	0.04	8.8 10 ⁻⁴	8.8 10 ⁻²	1.43
0.10	0.14	3.00	0.04	8.2 10 ⁻³	8.2 10 ⁻¹	0.46
0.10	0.14	4.00	0.04	1.3 10 ⁻²	1.3	0.27
0.10	0.20	1.00	0.10	3.0 10 ⁻⁵	3.0 10 ⁻³	2.89
0.10	0.20	1.30	0.10	4.0 10 ⁻⁵	4.0 10 ⁻³	2.76
0.10	0.20	2.00	0.10	9.0 10 ⁻⁴	9.0 10 ⁻²	1.41
0.10	0.20	3.00	0.10	1.2 10 ⁻²	1.2	0.29
1.00	1.50	1.00	0.50	1.2 10 ⁻³	1.2 10 ⁻³	3.31
0.40	0.90	1.00	0.50	4.1 10 ⁻⁴	2.6 10 ⁻³	2.96
1.00	1.50	1.30	0.50	8.8 10 ⁻³	8.8 10 ⁻³	2.43
1.00	1.50	1.50	0.50	5.0 10 ⁻²	5.0 10 ⁻²	1.67
0.40	0.90	2.00	0.50	4.1 10 ⁻⁴	2.3 10 ⁻¹	1.00
1.00	2.00	0.60	1.00	1.2 10 ⁻⁴	1.2 10 ⁻⁴	4.29
1.00	2.00	0.80	1.00	4.5 10 ⁻⁴	4.5 10 ⁻⁴	3.71
0.40	1.40	1.00	1.00	2.2 10 ⁻⁴	1.3 10 ⁻³	3.74
0.60	1.60	1.00	1.00	5.1 10 ⁻⁴	1.4 10 ⁻³	3.22
0.80	1.80	1.00	1.00	8.8 10 ⁻⁴	1.4 10 ⁻³	3.22
1.00	2.00	1.00	1.00	1.3 10 ⁻³	1.3 10 ⁻³	3.24
0.15	1.15	1.30	1.00	2.9 10 ⁻⁴	1.2 10 ⁻²	2.26
0.20	1.20	1.30	1.00	5.0 10 ⁻⁴	1.3 10 ⁻²	2.27
0.15	1.15	1.50	1.00	9.3 10 ⁻⁴	4.1 10 ⁻²	1.75
0.20	1.20	1.50	1.00	1.6 10 ⁻³	4.0 10 ⁻²	1.77
0.04	1.04	2.00	1.00	2.6 10 ⁻⁴	1.6 10 ⁻¹	1.17
0.10	1.10	2.00	1.00	1.9 10 ⁻³	1.9 10 ⁻¹	1.09
0.40	1.40	2.00	1.00	2.6 10 ⁻²	1.6 10 ⁻¹	1.16
0.10	1.10	3.00	1.00	1.1 10 ⁻²	1.1	0.33
0.04	1.04	4.00	1.00	3.3 10 ⁻³	2.0	0.06
0.04	1.04	6.00	1.00	3.9 10 ⁻³	2.4	-0.02
0.04	1.04	10.00	1.00	3.7 10 ⁻³	2.3	0.01
0.04	1.04	67.00	1.00	3.7 10 ⁻³	2.3	0.01
0.40	2.40	0.60	2.00	1.0 10 ⁻⁴	6.3 10 ⁻⁴	3.57
0.40	2.40	0.80	2.00	2.1 10 ⁻⁴	1.3 10 ⁻³	3.26
0.40	2.40	1.00	2.00	3.9 10 ⁻⁴	2.4 10 ⁻³	2.98
0.40	2.40	1.30	2.00	2.2 10 ⁻³	1.3 10 ⁻²	2.24
0.40	2.40	2.00	2.00	1.9 10 ⁻²	1.2 10 ⁻¹	1.30
0.40	2.40	4.00	2.00	2.7 10 ⁻¹	1.7	0.15
0.40	2.40	10.00	2.00	3.8 10 ⁻¹	2.4	0.00
0.40	2.40	15.00	2.00	3.7 10 ⁻¹	2.3	0.00

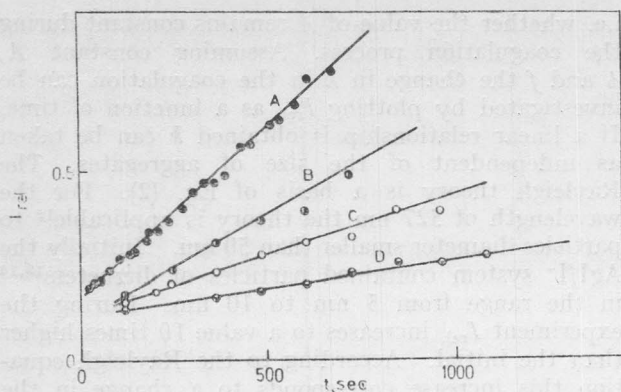


Fig. 1—Influence of the initial concentration of AgNO_3 on the rate of coagulation of AgI/I^- at $c(\text{I}^-) = 1 \text{ mole/m}^3$ and $c(\text{Mg}^{2+}) = 1 \text{ mol/m}^3$ [$c_{\text{in}}(\text{AgNO}_3)/\text{mol m}^{-3}$: (A) 1, (B) 0.8, (C) 0.6, (D) 0.4]

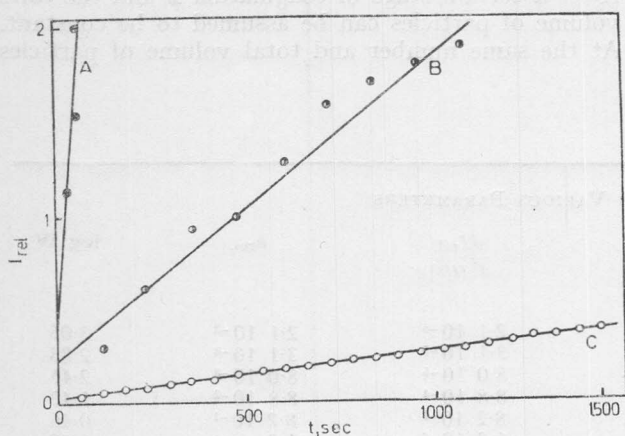


Fig. 2—Influence of the initial concentration of AgNO_3 on the rate of coagulation of AgI/I^- at $c(\text{I}^-) = 1 \text{ mole/m}^3$ and $c(\text{Mg}^{2+}) = 2 \text{ mol/m}^3$ [$c_{\text{in}}(\text{AgNO}_3)/\text{mol m}^{-3}$: (A) 0.4, (B) 0.1, (C) 0.04]

the intensity of scattered light increases with increasing polydispersity of the system. It was found¹⁵⁻¹⁷ that coagulation is a "self preserving process" i.e. that polydispersity becomes constant after a certain time and is practically independent of the initial condition so that constant k_{diff} and f can be assumed. Linear relationship between I_{rel} and time are shown in Fig. 1 and 2. Such linear relationships were obtained in all the experiments carried out in this study. There are two possible explanations of these results. The first is, that neither k_{diff} and W nor the A , f , and ϕ values change during the measurements. The second explanation could be that the effects of change in k , A , f , and ϕ values compensate each other in all the examined systems. However, this is rather improbable since the stability coefficient changes by four orders of magnitude. The first assumption is supported by the fact that the slopes in Figs. 1 and 2 are proportional to the square of the initial concentration of AgNO_3 , in agreement with Eq. (4). Hahn and Stumm¹⁸ have found similar linear relationships

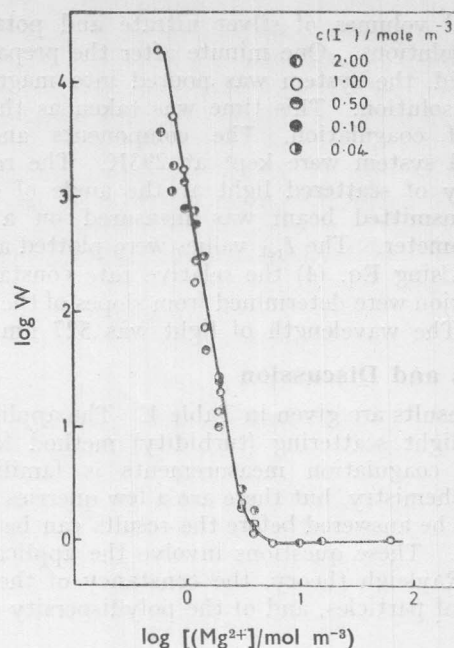


Fig. 3—Influence of the $c(\text{I}^-)$ and $c(\text{Mg}^{2+})$ on the stability of AgI/I^-

for Ludox particles (initial diameter: 15 nm) as well as the slopes proportional to the square of the initial concentration of colloidal particles. The influence of the total volume of colloidal particles is taken into account in Eqs. (2) and (4) and it should be included in the operational definition of the relative rate constant of coagulation.

The effect of potential determining ions on the stability of lyophobic colloids was previously investigated^{9,10} by examining the dependence of the c.c.c. of counterions on the activity of potential determining ions. The c.c.c. was found to be constant in a wide range of activity. Such results were found for the AgBr/Br^- and AgI/I^- systems. This is in agreement with our results shown in Fig. 3. We have found no significant change in the stability coefficient in the iodide ion concentration range from 0.04 mol/m^3 to 2 mol/m^3 at $1 < W < 10000$. According to Reerink and Overbeek⁴ this effect can be explained by the assumption that the potential in the Stern layer remains constant in spite of the change of surface potential which is proportional to the logarithm of the iodide ion activity. The statement that the potential in Stern layer does not depend on the activity of potential determining ions in slow coagulation region should be the subject of theoretical investigations which should lead to further refinement of a modern theory of colloidal stability.

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The observed diffusion potential and the diffusion potential of the electrode are compared with the theoretical values. The experimental values are compared with the theoretical values. The experimental values are compared with the theoretical values.

Results and Discussion

The observed diffusion potential and the diffusion potential of the electrode are compared with the theoretical values. The experimental values are compared with the theoretical values. The experimental values are compared with the theoretical values.

The first and the second part of the paper are devoted to the study of the diffusion potential of the electrode. The experimental values are compared with the theoretical values. The experimental values are compared with the theoretical values.

As reported in our earlier communication, the observed diffusion potential is the sum of the diffusion potential and the diffusion potential of the electrode. The experimental values are compared with the theoretical values. The experimental values are compared with the theoretical values.

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Materials and Methods

The experimental procedure for the measurement of the diffusion potential and the diffusion potential of the electrode is described in detail. The experimental values are compared with the theoretical values. The experimental values are compared with the theoretical values.

TABLE I - POTENTIALS AND SOME CHARACTERISTICS OF ELECTRODES AT 25°C

Electrode	Diffusion potential (mV)	Electrode potential (mV)	Observed potential (mV)	Temperature (°C)	Electrolyte concentration (mol/l)
Ag/AgI	-20	-35	-55	25	0.01
Ag/AgI	-18	-32	-50	25	0.01
Ag/AgI	-16	-30	-46	25	0.01

The values in the table are the mean values of three measurements. The standard deviation is given in parentheses. The values are given in millivolts.