

Influence of Temperature on the Stability of Negative Silver Iodide Colloid

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The influence of temperature on the coagulation rate of a negative silver iodide colloid has been examined. The results have been satisfactorily explained on the basis of activation energy concept. The activation energy has been evaluated by measuring the rate constant of coagulation from its temperature dependency and relating it to the rate constant of rapid coagulation.

THE energy barrier generated as a result of repulsive forces among particles prevents the colloidal particle collision and is responsible for the stability of lyophobic colloids. In theoretical studies the energy barrier influence on stability is presented by colloid particle interaction energy depending upon the distance between particles^{1,2}.

The interpretation of experiments giving data about the colloid system stability gives an experimental parameter and that parameter is the activation energy of aggregation³. The aim of this study is the experimental examination of the activation energy for aggregation of negatively charged silver iodide colloid in a neutral electrolyte medium.

Theoretical

The total activation energy (E_{total}) of coagulation process is defined by relation (1)

$$k = k_d \exp(-E_{total}/RT) \quad \dots(1)$$

where k is the rate constant of coagulation, k_d is rate constant of coagulation controlled by diffusion, R is gas constant and T is thermodynamic temperature.

The rate constant k_d for monodispersed and spherical particles according to von Smoluchowski⁴ is given in Eq. (2).

$$k_d = 4RT/3\eta \quad \dots(2)$$

where η is medium viscosity; and the rate constant of coagulation k is defined by Eq. (3)

$$dc/dt = -kc^2 \quad \dots(3)$$

c is colloid particle concentration and t is the time. As the medium viscosity also depends upon temperature as seen from Eq. (4)

$$\eta = A \exp(E_v/RT) \quad \dots(4)$$

where A and E_v are constants (independent of the temperature) characterizing the medium, we get:

$$k = [4RT/3A] \exp[-(E_{total} + E_v)/RT] \quad \dots(5)$$

The total activation energy of a certain process with the rate constant k can be determined by measuring the dependence of k upon temperature according to the Eq. (5). The procedure is based on the assumption that activation energy does not depend upon temperature and includes knowing the E_v value.

For an aqueous medium neglecting the electrolyte influence on viscosity, according to Eq. (4), we get⁵:

$$E_v = 17,8 \text{ kJ/mol} \quad \dots(6)$$

The activation energy of coagulation can be divided into attraction part (E_a) and the electric part (E_e) (Eq. 7).

$$E_{total} = E_a + E_e \quad \dots(7)$$

By adding the electrolytes to a stable lyophobic colloid system the rate constant of coagulation increases reaching its maximum value. This maximum value of the rate constant corresponds to rapid coagulation which should be distinguished from the diffusion-controlled process. The ratio of the rate constant of the relatively stable system (k) to that of the rapid coagulation (k_0) gives the relation:

$$RT \ln (k_0/k) = E_e + E_a - E_{e,0} - E_{a,0} \\ = E_{total} - E_{total,0} \quad \dots(8)$$

where quantities marked by subscript 0 correspond to the rapid coagulation.

Assuming $E_{e,0} \approx 0$ or $E_e \gg E_{e,0}$ for stable systems and small value of $E - E_{a,0}$, i.e. no significant change in attraction part of activation energy one can estimate E_e value from Eq. (9).

$$E_e \approx RT \ln (k_0/k) \quad \dots(9)$$

Materials and Methods

The colloidal systems of negative silver iodide were prepared by mixing aqueous solutions of KI and AgNO_3 . Thirty seconds after mixing the precipitating components a neutral electrolyte, aq. $\text{Mg}(\text{NO}_3)_2$ solution was added. All the systems were prepared so that after precipitation of the colloid system free I^- ion concentration was 10^{-3} mol/dm³. The inorganic salts which were used were of E. Merck grade.

The relative value of the coagulation rate constant was determined by the tyndallometric method according to the following equation:

$$k_{rel} = \frac{dI_{rel}}{dt/s} \left(\frac{[\text{AgI}(s)]}{\text{mol m}^{-3}} \right)^{-2} \quad \dots(10)$$

where I_{rel} is the relative intensity of scattered light at 45° to the transmitted beam. The light of wave length $\lambda = 527$ nm was used.

It is supposed that relative values of the rate constant of coagulation are proportional to the rate constant of coagulation with proportionality factor independent of the temperature and electrolyte addition.

Results and Discussion

In Figs. 1 and 2 the light scattering intensity against time has been plotted. Fig. 1 corresponds to rapid coagulation. It was found that $E_{total,0} = E_{e,0} + E_{a,0} = (0,8 \pm 2) \text{ kJ/mol}$.

Fig. 2 corresponds to slow coagulation. An increase in the coagulation rate with increase in temperature is noted. Fig. 3 shows the Arrhenius plot the slope of which gives the total activation energy. The linear plot in Fig. 3 indicates that activation energy does not change much in the temperature range of the present study. In the present case the stability was observed in slightly larger temperature region.

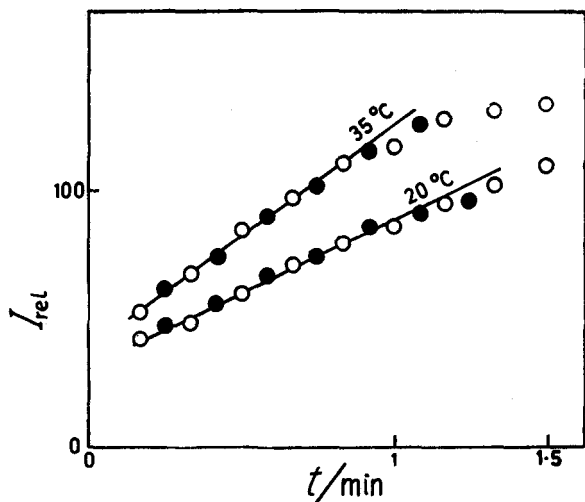


Fig. 1 — Temperature influence on the rate of rapid coagulation of AgI/I⁻ colloid at [I⁻]=10⁻³M and [AgI(s)]=4 × 10⁻⁴M [(○) [Mg²⁺]=2 × 10⁻²M; and (●) [Mg²⁺]=6.7 × 10⁻²M]

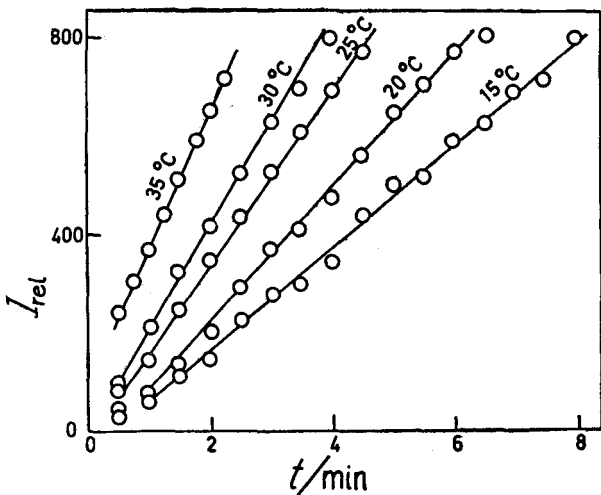


Fig. 2 — Temperature influence on AgI/I⁻ colloid coagulation at [I⁻]=10⁻³M, [Mg²⁺]=1.5 × 10⁻³M and [AgI(s)]=4 × 10⁻⁴M

In Fig. 4 the influence of counter ion concentration [Mg²⁺] on the activation energy of coagulation of AgI/I⁻ colloid is presented. The results on E_{total} obtained by modified Arrhenius plot are in agreement with those obtained from the relation $E_{total} - E_{total,0} \approx E_e$ at constant temperature by relating the corresponding rate constant to the rate constant of rapid coagulation. It should be pointed out that the agreement in these values was obtained for relatively unstable colloids as well as for rapid coagulation. At lower [Mg²⁺] i.e. for more stable systems the values obtained for total activation energy are higher than those obtained from k_0/k ratio. This may be due to the possibility that the particle growth is directed not only by the aggregation mechanism but also by crystallization (unpublished results).

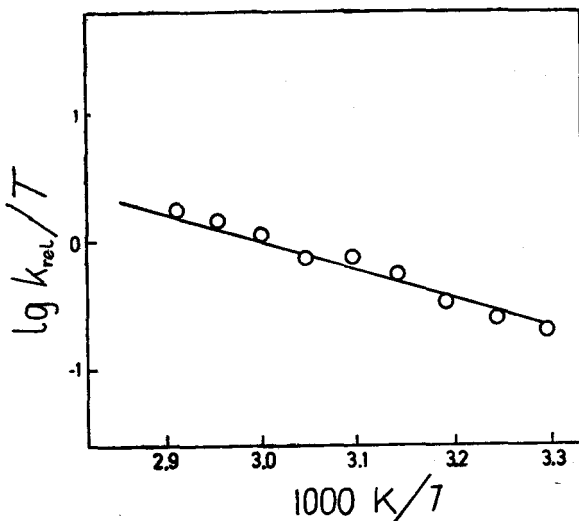


Fig. 3 — Total activation energy determination of AgI/I⁻ coagulation at [I⁻]=10⁻³M and [Mg²⁺]=10⁻³M [The log of the ratio of relative rate constant to thermodynamic temperature is plotted against reciprocal thermodynamic temperature]

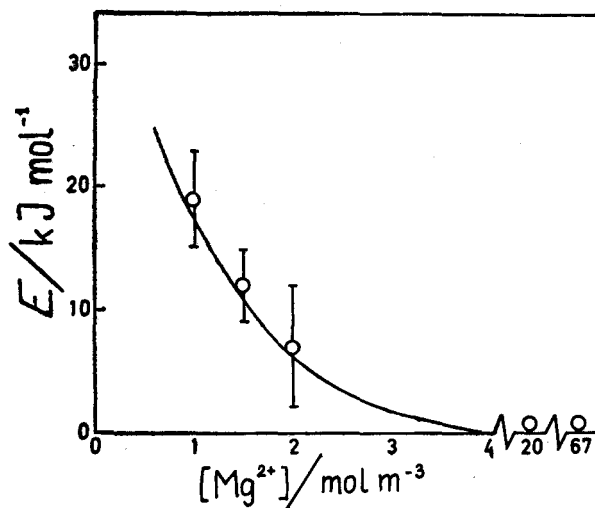


Fig. 4 — Influence of varying [Mg²⁺] concentration on the activation energy for coagulation of AgI/I⁻ colloid at [I⁻]=10⁻³M and T=293 K [Points on diagram show total activation energy obtained from temperature dependency measurements. The curve corresponds to $E_{total} - E_{total,0}$ value which is approximately equal to E_e]

The influence of temperature on the coagulation rate can be attributed the change in collision number (k_d) and to the activation energy influence. Temperature dependency on activation energy, which is negligible, can be considered on the basis of other parameters playing an important role in colloidal stability and influenced by temperature.

The influence of electrolytes on the stability of lyophobic colloids can be explained on the basis of decrease in electric part (E_e) of the activation energy. This decrease is related to compensation of electrical forces between charged particles caused by the

presence of counter ions in the double layer at the particle surface.

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