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ORIGINAL CONTRIBUTION

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An experimental trial for the determination of the critical coagulation concentration using the sedimentation method

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Abstract A method for determining the critical coagulation concentration (C_c) from the change in the transmittance of the sol with stand time after adding a coagulating agent is discussed. Potassium nitrate was used as the coagulating agent because the specific adsorption of electrolyte ions on the particle and the hydrolysis of electrolyte ions are negligible. Apparent critical coagulation concentrations, C_c^a, of iron (III) hydroxide and silver iodide sols were obtained from the transmittance vs. potassium nitrate concentration curves for various stand times. The values of C_c^a decreased with increasing stand time. The C_c^a value obtained for the shortest stand time was closer to C_c obtained from the initial turbidity change of the sol by applying Rayleigh's law. The Hamaker constant for the particle in water was calculated from the C_c^a value obtained at the shortest time and the experimentally determined outer Helmholtz plane potential. The calculated Hamaker constants were comparable to the theoretical values for iron (III) hydroxide and silver iodide.

Key words Critical coagulation concentration – iron (III) hydroxide sol – silver iodide sol – sedimentation – Hamaker constant

Introduction

The stability of colloidal dispersions is related to various phenomena in many industrial processes, and hence, the stability measurements are important in practical use as well as in fundamental investigations of the interaction between two bodies. The critical coagulation concentration, C_c, is usually spectrophotometrically determined from the change in turbidity of the dispersion after adding a coagulating electrolyte (the turbidity method) [1–6]. The turbidity method is not applicable for larger particles to which Rayleigh's law cannot be applied. In this case, transmittance of the suspension after standing for a certain period is measured for experimental convenience (the sedimentation method) [1, 7–9]. There is not enough of the necessary basic data about adequate stand times for determining C_c using the sedimentation method.

In the evaluation of the Hamaker constant from coagulation experiments of colloidal dispersions on the basis of the DLVO theory [10, 11], the experimental electrokinetic potential at the critical coagulation concentration is approximated as the outer Helmholtz plane (OHP) potential [1]. This approximation is not suitable because the ionic strength is sufficiently large at the critical coagulation concentration and the electrokinetic potential is much less than the OHP potential in the absolute value [12]. In fact, the experimentally derived Hamaker constants substantially deviate from the theoretically calculated ones in a large number of cases [13].

As stated above, some questions remain for the determination of the C_c value and that of the OHP potential when the Hamaker constant is experimentally estimated from the colloid stability measurements. In the present study, the coagulation experiments were carried out using the turbidity and sedimentation methods with aqueous iron (III) hydroxide and silver iodide sols whose stabilities can be evaluated on the basis of Rayleigh's law. Potassium nitrate was used as the coagulating electrolyte because the specific adsorption of electrolyte ions on the particle and the hydrolysis of electrolyte ions are negligible. In the sedimentation method, the apparent values of C_c were obtained as a function of stand time from transmittance recordings of the sols after adding the electrolyte solution, and were compared with the C_c value obtained using the turbidity method.

The Hamaker constant for the particle in water was calculated from the C_c value and the OHP potential which was estimated by the analysis of the experimental electrokinetic potential vs. the potassium nitrate concentration curve.

Experimental

Materials

The iron (III) hydroxide sol was prepared by pouring 1×10^{-2} dm^3 of an aqueous iron (III) chloride solution (1 mol/dm^3) into 1 dm^3 of boiling water, and then aged for 24 h. The sol was dialyzed against distilled water. The final pH of the sol was 4.5. The iso-electric point of the iron (III) hydroxide particle was determined to be pH 7.5 by microelectrophoresis [4, 5]. The particle diameter determined using an electron microscopy was 20 nm [5, 6].

The silver iodide sol was prepared by adding an aqueous silver nitrate solution of 3×10^{-4} mol/dm^3 to an aqueous potassium iodide solution of 5×10^{-4} mol/dm^3 in the same volume under rigorous stirring, followed by aging for 4 h at 80 °C. The silver iodide particle was found to be negatively charged based on microelectrophoresis. The diameter of the particle thus prepared is considered to be on the order of 10 nm [14–18].

Extra pure grade reagents were used without further purification. Deionized water was doubly distilled using a borosilicate glass apparatus.

Glassware was soaked in a dichromate-sulfuric acid solution, rinsed with water, and cleaned using steam.

Determination of critical coagulation concentrations

The coagulation experiments were performed using a spectrophotometer (Shimazu Spectronic 20). To 3×10^{-3} dm^3 of the sol in the spectrophotometer cell (optical path length: $L = 1$ cm), a small amount of an aqueous potassium nitrate solution was added with a plunger with three tiny holes at the bottom [4–6]. After mixing, the change in transmittance with time was recorded (the turbidity method). The final particle concentration and final volume of each sol were adjusted to be constant in all experiments. The center position of the beam of incident light was 2 cm from the bottom of the cell.

When the sol is standing after adding the coagulating agent, the transmittance of the sol may increase because of sedimentation of the aggregates. Since larger aggregates exhibit larger sedimentation rates, the transmittance after standing for a certain period can be regarded as a measure of the stability of the sol. In this case, an adequate stand time should be determined. Therefore, the transmittance was recorded for 72 h (the sedimentation method).

In both the turbidity and sedimentation methods, the transmittance was measured at the wavelength of 615 nm, at which consumptive light absorption was negligible.

Electrophoretic mobility measurements

Electrophoretic mobilities of the particles in aqueous potassium nitrate solutions were measured using the Rank Brothers Mark II microelectrophoresis apparatus. Zeta potentials of the particles were calculated from electrophoretic mobilities using the equation of Wiersema et al. [19, 20] in which the electrophoretic retardation and relaxation effects are taken into consideration.

All the experiments were carried out in a room maintained at 20 °C ± 1 °C.

Results and discussion

Critical coagulation concentrations using the turbidity method

According to Rayleigh's law concerning light scattering, the turbidity of the sol, τ, is related to the number of particles per cm^3, N, and the individual particle volume, v, when the particle radius is less than 0.05λ (λ: wavelength) and the consumptive light absorption is absent:

$$\tau = YNv^2 \, , \tag{1}$$

where Y is the optical constant. Since Nv is the volume fraction of the particles in the sol and is constant during the coagulation process, the turbidity can be used as a measure of the size of the secondary particle in the coagulation process and hence of the stability of the sol.

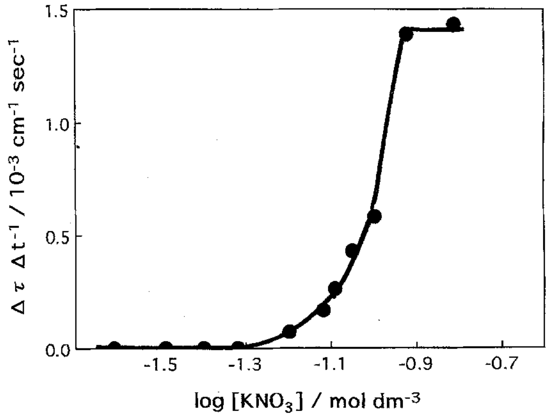

Fig. 1 Coagulation rate of silver iodide sol as a function of potassium nitrate concentration $\Delta\tau/\Delta t$ was obtained from the slope of turbidity (τ) vs. time (t) curve

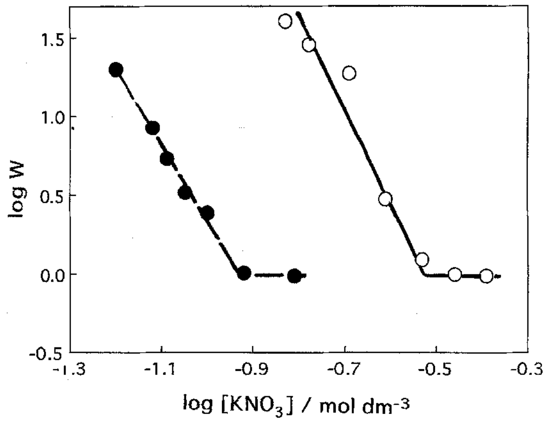

Fig. 2 Plots of stability ratio against potassium nitrate concentration for iron (III) hydroxide sol (○) and silver iodide sol (●)

The turbidity of the sol was obtained using the following equation:

$$\tau = -\ln T/L\ , \tag{2}$$

where T is the transmittance of the sol, and L is the optical path length.

The turbidity for the silver iodide sol increased almost linearly with time in the early stage, and became constant after 1–2 min. In the case of the iron (III) hydroxide sol, the turbidity rapidly increased immediately after mixing and became constant after 1–2 s. Therefore, the slope of the turbidity vs. time curve for the silver iodide sol and the change in turbidity after 2 s for the iron (III) hydroxide sol were adopted as measures of the coagulation rate (the turbidity method). The difference in time dependence of turbidity between the silver iodide and iron (III) hydroxide sols was probably caused by the difference in the number of particles per unit volume because the half-value period of coagulation is inversely proportional to the initial number of particles. In fact, the number of iron (III) hydroxide particles was estimated to be greater than that of the silver iodide particles by a factor of 100.

Figure 1 gives the coagulation rate of the silver iodide sol as a function of the final potassium nitrate concentration after mixing. The coagulation rate increased with increasing concentration, and reached almost a constant value, which corresponded to the rate of rapid coagulation. Considering slow coagulation as a diffusion process in the potential field, the stability ratio, W, can be defined as the ratio of the rapid coagulation rate to the slow coagulation rate [8]. The results obtained for the iron (III) hydroxide and the silver iodide sols are presented in the form of the logarithm of the stability ratio against the logarithm of electrolyte concentration (Fig. 2). The curves are linear in the slow-coagulation range and become parallel to the abscissa in the rapid-coagulation range. The critical coagulation concentration, C_c, was obtained from the intersection of these two sections of the curve, i.e., C_c corresponds to the minimum electrolyte concentration for $W = 0$. The C_c values thus obtained are presented in Table 1.

Table 1 Comparison between critical coagulation concentration, C_c, obtained using the turbidity method and apparent critical coagulation concentration, C_c^a, obtained using the sedimentation method for various stand times

Particles	Methods	Stand time/h	C_c/mol dm^{-3}	C_c^a/mol dm^{-3}
iron (III) hydroxide	Turbidity	0	2.92×10^{-1}	
	sedimentation	0.333		2.40×10^{-1}
		0.5		1.70×10^{-1}
		1		1.57×10^{-1}
		24		1.12×10^{-1}
		72		9.70×10^{-2}
silver iodide	turbidity	0	1.22×10^{-1}	
	sedimentation	4		1.05×10^{-1}
		5		1.00×10^{-1}
		6		9.60×10^{-2}
		24		9.10×10^{-2}
		72		8.30×10^{-2}

Critical coagulation concentrations by the sedimentation method

Changes in the transmittance of the iron (III) hydroxide sol with time after adding the potassium nitrate solution are shown in Fig. 3. At a low concentration of potassium nitrate (the curve shown by the open circles in Fig. 3), the transmittance did not change within 1 h and then decreased. The decrease in transmittance at 24 h means an increase in the turbidity due to particle aggregation. After 72 h, the transmittance increased, and this increase suggests the sedimentation of the aggregates. A similar tendency was observed for the other cases with different electrolyte concentrations (the curves denoted by open triangles and open squares in Fig. 3).

The relations between the transmittance and potassium nitrate concentration for various stand times are given in Figs. 4 and 5. The transmittance decreased with increasing electrolyte concentration for stand times of 5–10 min and 1–3 h in the cases of iron (III) hydroxide and silver iodide, respectively. After standing for more than 20 min for the iron (III) hydroxide sol and 4 h for the silver iodide sol, the transmittance decreased, then increased, and reached saturation with increasing electrolyte concentration. In the plateau region, rapid coagulation occurs. Since the critical coagulation concentration is defined as the minimum concentration of the electrolyte necessary to initiate the rapid coagulation, the apparent critical coagulation concentration was determined from the break in each curve (indicated by arrows in Figs. 4 and 5).

The apparent critical coagulation concentration, C_c^a, obtained at different stand times is given in Table 1. For both the iron (III) hydroxide and silver iodide sols, C_c^a decreased with increasing stand time. The C_c^a value obtained at 20 min for the iron (III) hydroxide sol and that obtained at 4 h for the silver iodide sol were closer to the corresponding C_c values determined by the turbidity method. This suggests that the C_c value in the sedimentation method should be determined for the shortest stand time. The transmittance of the supernatant after a long stand time cannot be used as a measure of the colloid stability because aggregates in the slow coagulation process as well as in the rapid coagulation process sufficiently settle down.

The Hamaker constant for the particle in water from the experimental value of C_c was estimated. Since C_c is defined as the minimum concentration of electrolyte necessary to initiate the rapid coagulation as mentioned above, the potential energy barrier to particle aggregation disappears at C_c. From the calculation of the potential energy of interaction between particles on the basis of the DLVO theory [10], the experimentally determined zeta potential at C_c is often approximated as the OHP potential [1]. In

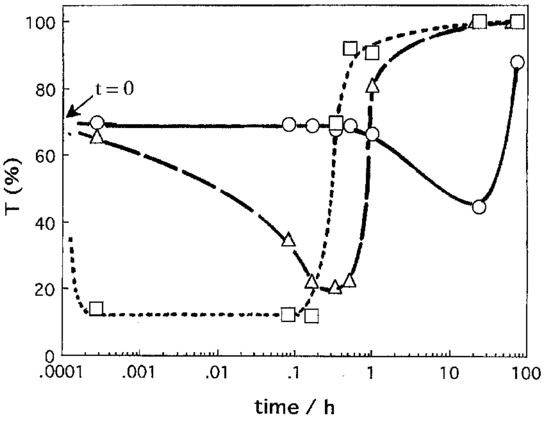

Fig. 3 Change in transmittance of iron (III) hydroxide sol with time at potassium nitrate concentrations of 0.074 mol/dm^3 (○), 0.148 mol/dm^3 (△), and 0.331 mol/dm^3 (□)

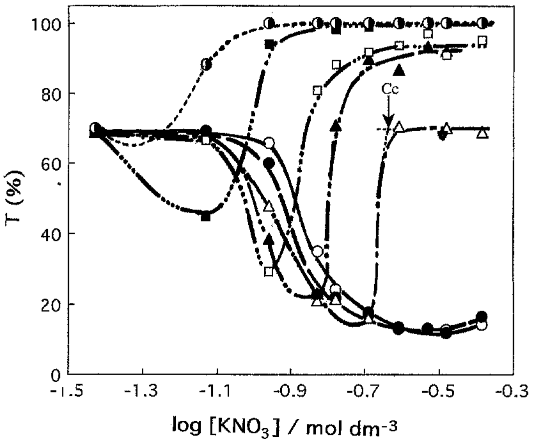

Fig. 4 Transmittance of iron (III) hydroxide sol as a function of potassium nitrate concentration. ○: 5 min, ●: 10 min, △: 20 min, ▲: 30 min, □: 1 h, ■: 24 h, ◑: 72h

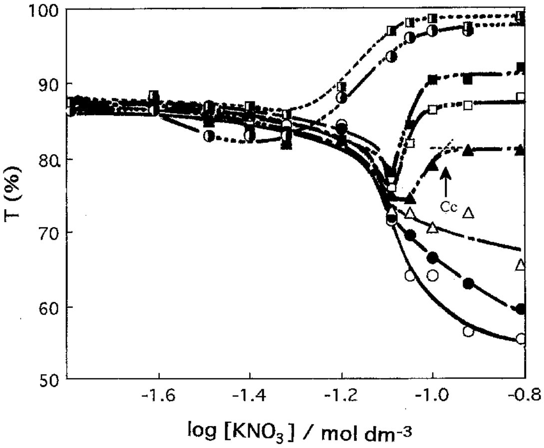

Fig. 5 Transmittance of silver iodide sol as a function of potassium nitrate concentration. ○: 1 h, ●: 2 h, △: 3 h, ▲: 4 h, □: 5 h, ■: 6 h, ◑: 24h, ◨: 72 h

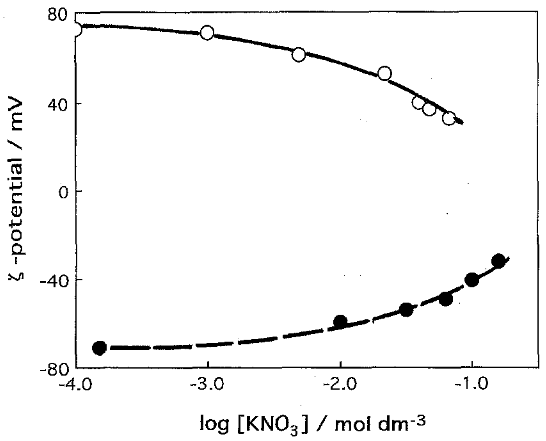

Fig. 6 Zeta potentials of iron (III) hydroxide particles (○) and silver iodide particles (●) as a function of potassium nitrate concentration

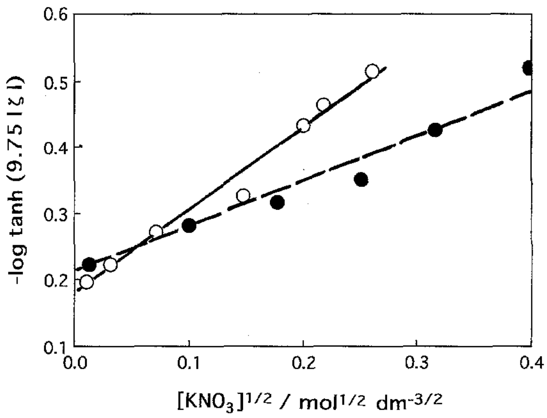

Fig. 7 Relation between $-\log\tanh(9.75\,|\zeta|)$ and $[\mathrm{KNO_3}]^{1/2}$ for iron (III) hydroxide particles (○) and silver iodide particles (●)

this case, the magnitude of this approximated OHP potential may be underestimated because the electric potential rapidly decreases with increasing distance from the particle surface in the double layer for the high ionic strength at C_c [12]. Therefore, we will determine the OHP potential from the electrokinetic data in aqueous potassium nitrate solutions given in Fig. 6.

Eversole and Boardman [21] derived the relation between the zeta potential, ζ, and electrolyte concentration, C, according to the theory of the diffuse double layer;

$$-\log\tanh(9.75z\,|\zeta\,|) = -\log\tanh(9.75z\,|\,\psi_\delta\,|) + 0.142\,tzC^{1/2}\,, \qquad (3)$$

where z is the counterion valency, ψ_δ the OHP potential and t the distance between the particle surface and the slipping plane. Figure 7 illustrates the plots of $-\log\tanh(9.75\,|\zeta|)$ versus $[\mathrm{KNO_3}]^{1/2}$ from the electrokinetic data of the iron (III) hydroxide and the silver iodide particles shown in Fig. 6. The linear relations suggest that the decrease in the magnitude of the zeta potential by addition of potassium nitrate is caused only by the decrease in thickness of the electrical double layer, and hence no existence of specific adsorption of ions on the particle surfaces. In such a case, ψ_δ can be evaluated from the intercept of the plot of $-\log\tanh(9.75z\,|\zeta|)$ versus $[\mathrm{KNO_3}]^{1/2}$. The obtained values of ψ_δ were 80.3 mV and −76.2 mV for the iron (III) hydroxide and the silver iodide particles, respectively. Zeta potentials at C_c estimated from the plot in Fig. 7 were 14.6 mV and −37.7 mV for the iron (III) hydroxide and the silver iodide particles, respectively, which were significantly small compared with the corresponding ψ_δ values. The values of t were calculated from the slope of the plots in Fig. 7 to be 0.9 nm and 0.5 nm for the iron (III) hydroxide and the silver iodide particles, respectively.

The calculated Hamaker constants are listed in Table 2 with the values of C_c and ψ_δ. The Hamaker constant obtained for the iron (III) hydroxide particle was on the same order as the constants for oxides calculated on the basis of the Lifshitz theory (1.76–4.17×10^{-20} J) and the constant for iron (III) oxide determined from the dispersive component of surface free energy (3.4×10^{-20} J) [16]. In the case of the silver iodide particle, the experimentally determined Hamaker constant in the present study is in close agreement with the theoretical value calculated using the microscopic procedure with the London constant by the Moelwyn-Hughes equation (9×10^{-20} J) [16].

Table 2 The Hamaker constant of the particle in water, A_{121}, estimated from the critical coagulation concentration, C_c, and the outer Helmholtz Plane (OHP) potential of the particle, ψ_δ

Particles	Methods	Stand time/h	C_c/mol dm^{-3}	ψ_δ*/mV	A_{121}/J
iron (III) hydroxide	turbidity		2.92×10^{-1}	80.3	7.09×10^{-20}
	sedimentation	0.33	2.40×10^{-1}	80.3	8.08×10^{-20}
silver iodide	turbidity		1.22×10^{-1}	−76.2	9.50×10^{-20}
	sedimentation	4	1.05×10^{-1}	−76.2	1.05×10^{-19}

* the OHP potential obtained from the intercept of the plot in Fig. 7

Conclusions

An experimental trial of the critical coagulation concentrations, C_c, of the iron (III) hydroxide and the silver iodide sols by potassium nitrate was carried out by the sedimentation method. The apparent critical coagulation concentrations, C_c^a, were obtained from the breaks in the transmittance vs. electrolyte concentration curves at various stand times. The C_c^a values decreased with increasing stand time. The decrease in C_c^a was considered to be caused by the sedimentation of aggregates during the slow coagulation process. Within the stand time of 10 min for the iron (III) hydroxide sol and 3 h for the silver iodide sol, the C_c^a values were not obtained because of the absence of breaks due to the increase in transmittance because of the sedimentation of aggregates at high electrolyte concentrations. The C_c^a value obtained at 20 min for the iron (III) hydroxide sol and that obtained at 4 h for the silver iodide sol were closer to the corresponding C_c values determied by the turbidity method. The Hamaker constants calculated from the values of C_c obtained at the shortest stand time and the experimentally determined OHP potentials were comparable to the theoretical values for both cases of the iron (III) hydroxide and the silver iodide sols. Conclusively, in the sedimentation method, the C_c value should be determined for the shortest stand time. This study gives useful information on the determination of the critical coagulation concentration of the dispersion consisting of the larger particles to which Rayleigh's law cannot be applied.

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