An Optical Study on the Coagulation and Peptization of Silver Iodide Colloidal Solutions by Surface Active Agent

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Introduction

The study on the phenomena of coagulation and peptization of colloidal or macromolecular solutions by surface active agents initiated by Tamamushi(1) in 1947 has been developed by a number of investigators in this country. (2)(3)(4)

The author has studied, under the guidance of Prof. B. Tamamushi, the effect of a cationic surface active agent, dodecylamine hydrochloride, * on the coagulation and peptization of the colloidal solution of silver iodide, the particle of which was negatively charged. When a small amount of D. A. H. is added to the solution, it becomes turbid due to the coagulation of the colloid particles, and the turbidity increases with the concentration of D. A. H. added. But at a certain concentration of D. A. H., the effect of the agent reverses from coagulation to peptization and the turbidity begins to decrease with the rise of the concentration of D. A. H., the peptized AgI sol being charged positively. The change of the percentage transmittance of the mixed solution with the concentration of D. A. H. is shown in Fig. 1.

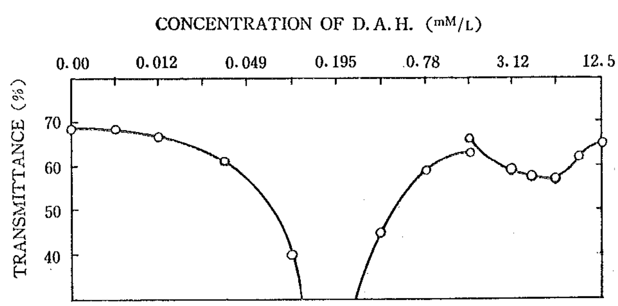


Fig. 1. Percentage transmittance of AgI sol of 2.2 mM/L obtained 20 minutes after D. A. H. of varied concentrations was added. Wavelength of photometer is 650 mμ. Coagulation value is 0.08 mM/L.

* Henceforce to be abbreviated as D. A. H.

The main object of this study is to examine the change of the state of the colloidal solution in the course of coagulation and peptization processes, especially to detect the difference of state of sols just before coagulation and after peptization by applying the optical methods, namely, the transmittance measurement on one hand and the particle size measurement on the other.

Experimental

160 cc of 0.01 M/L silver nitrate solution is added to 200 cc of 0.01 M/L potassium iodide solution, the mixing being carried out quickly and thoroughly. The silver iodide sol thus prepared has the concentration of 4.4 mM/L (as AgI) and is charged negatively.

The sol is then purified by electrodialysis. As the sol is sensitive to light, it should be kept from light during this procedure. The percentage of transmittance obtained with the purified sol and its dilutions is shown in Table 1. A good linearity holds between the concentration and the logarithm of transmittance, which proves the Rule of Lambert–Beer.

Table 1. Percentage transmittance of AgI sol of various concentrations.

λ_0(mμ) \ CONC.	4.4 (mM/L)	2.2 〃	1.1 〃
450	2.2%	13.2%	36.2%
500	13.0	36.0	59.6
550	29.0	53.1	72.6
600	43.1	65.1	80.2
650	56.0	74.2	86.0
700	66.1	81.0	90.0
750	73.4	85.2	92.0
800	79.0	88.8	94.0
850	83.1	91.0	95.0
900	86.9	93.0	96.2
950	89.1	94.0	97.0
1000	91.1	95.2	97.1
1040	92.5	96.1	97.8
1080	93.2	96.5	98.0
1100	93.5	96.8	98.0
1120	93.5	96.5	98.0
1160	93.0	96.2	98.0
1200	92.0	95.8	97.4

(λ_0 : wavelength in air)

Table 2 and Figures 2~3 show the transmittance percentage of the mixed solutions of the silver iodide sol and D. A. H. solution of the same volume but various concentrations, where "t" denotes the time between the mixing and the observation and λ_0 the wavelength of light in air.

When the concentration of D. A. H. is below 0.035 mM/L, the transmittance percentage immediately after the mixing is the same with that of the original sol of 2.2 mM/L concentration. But when the sol is mixed with D. A. H. whose concentrations are greater than 0.39 mM/L in the mixed solutions, some increase of turbidity can be observed at once. Such increase of turbidity is most remarkable when the D. A. H. concentration is 0.39 mM/L as shown in Table 2 and Fig. 2.

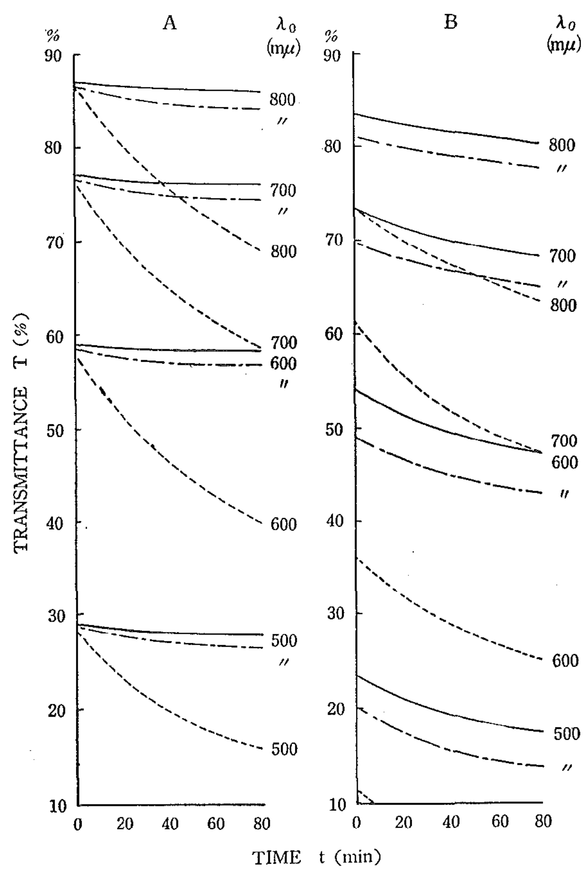


Fig. 2. Change of transmittance after the mixing.

	CONC. of D. A. H. A	B
solid	0.006 mM/L	1.56 mM/L
chain	0.012 mM/L	0.78 mM/L
dotted	0.035 mM/L	0.39 mM/L

Table 2a. Percentage transmittance of the mixed solutions.

D. A. H. CONC. / λ_0 (mμ)	0.006 (mM/L)	0.012 〃	0.035 〃	t (min.)
	%	%	%	
450	8.9	8.7	7.5	5
500	28.9	28.3	25.8	6
550	45.6	45.0	42.0	7
600	59.0	58.2	55.0	8
650	69.2	68.4	64.9	9
700	76.5	75.8	72.0	10
〃 *	76.8	76.0	72.7	11
750	82.5	81.7	78.2	12
800	86.4	85.7	82.3	13
850	89.0	88.2	85.0	14
900	91.2	90.5	87.7	15
950	92.9	92.0	89.2	16
1000	94.2	93.3	91.0	17
1050	95.0	94.5	92.0	18
1080	95.0	94.5	92.0	19
1100	95.2	94.8	92.0	20
1150	95.2	94.7	92.0	21
1200	94.9	94.1	91.4	22
450	8.8	8.5	6.2	23
500	28.5	28.0	22.1	24
550	45.7	44.7	37.6	25
600	58.5	57.2	49.7	26
650	69.0	68.2	59.6	27
700	76.3	75.2	68.0	28
〃 *	76.8	75.3	68.0	29
750	82.0	81.0	73.9	30
800	86.0	84.9	77.8	31
850	88.9	87.5	81.0	32
900	91.0	90.0	83.6	33
950	93.0	92.0	86.0	34
1000	94.0	93.0	88.0	35
1050	95.0	94.6	89.4	36
1080	95.1	94.2	89.2	37
1100	95.0	94.7	89.5	38
1150	95.0	94.5	89.0	39
1200	95.0	94.0	88.5	40
450	8.5	8.0	5.0	41
500	28.0	27.0	18.8	42
550	45.0	43.8	33.0	43
600	58.7	57.0	45.0	44
650	69.0	67.2	55.0	45
700	76.0	74.7	63.2	46
〃 *	76.5	75.0	63.8	47
750	82.0	80.5	69.8	48
800	86.0	84.5	73.8	49
850	88.7	87.2	77.0	50
900	91.0	89.9	80.0	51
950	92.5	91.5	82.5	52
1000	94.0	93.1	85.0	53
1050	95.0	94.0	86.0	54

D. A. H. CONC. / λ_0 (mμ)	0.39 (mM/L)	0.78 〃	1.56 〃	t (min.)
	%	%	%	
450	1.4	4.0	5.0	11
500	9.0	18.2	22.0	12
550	20.2	34.0	38.4	13
600	33.0	47.5	52.0	14
650	45.1	59.3	63.2	15
700	55.2	68.2	71.8	16
〃 *	55.3	68.6	71.8	18
750	64.6	75.0	78.0	19
800	70.0	80.0	82.5	20
850	75.0	83.9	86.0	21
900	79.0	87.0	88.9	22
950	82.7	89.3	91.0	23
1000	86.0	91.6	92.9	25
1050	88.0	92.8	94.0	26
1080	88.5	93.1	94.1	27
1100	88.3	93.0	94.0	28
1150	88.0	92.8	93.9	29
1200	87.0	92.1	93.1	30
450	1.0	3.2	4.8	32
500	6.8	16.2	20.0	33
550	17.0	31.8	36.1	34
600	29.1	45.5	50.0	35
650	41.1	57.5	61.5	36
700	51.3	66.8	70.0	38
〃 *	52.2	67.2	70.5	40
750	60.3	73.9	76.9	41
800	67.5	79.2	81.6	42
850	73.0	83.2	85.2	43
900	77.1	86.5	88.2	44
950	78.0	88.8	90.2	45
1000	83.8	90.8	92.0	46
1050	86.0	92.1	93.3	47
1100	87.2	92.9	94.0	48
1150	86.6	92.1	93.3	49
1200	85.2	91.8	92.9	50
450	0.7	2.5	4.0	52
500	5.0	14.2	18.2	56
550	15.0	30.0	34.8	57
600	26.8	44.0	48.1	59
650	38.8	56.0	60.2	60
700	49.0	65.7	69.1	61
〃 *	49.3	65.7	69.3	62
750	58.5	73.0	76.0	63
800	65.2	78.2	80.8	64
850	70.7	82.2	84.5	65
900	75.0	85.5	87.2	66
950	79.2	88.5	90.0	67
1000	82.7	90.8	92.0	68
1050	85.0	92.0	93.0	69
1080	85.7	92.2	93.2	70

1100	95.3	94.2	87.0	56
1150	95.1	94.1	86.5	57
1200	94.9	93.8	86.0	58
450	8.3	8.0	4.2	59
500	28.0	27.0	17.2	60
550	45.0	43.6	30.8	61
600	58.5	56.5	42.0	62
650	69.0	67.0	52.0	63
700	76.0	74.0	60.0	64
〃 *	76.2	74.5	60.7	65
750	82.0	80.1	67.0	66
800	86.0	84.2	71.0	67
850	88.8	87.0	74.5	68
900	90.6	89.3	77.3	69
950	92.7	91.3	80.2	70
1000	94.0	92.8	82.6	71
1050	95.0	94.0	84.1	72
1100	95.3	94.2	84.9	74
1150	94.9	93 6	84.0	75
1200	94.9	93.5	84.0	76

Table 2b. Percentage transmittance of the mixed solutions

D. A. H. CONC. / λ_0 (mμ)	1.56**(mM/L)	6.25 〃	12.5 〃	t (min.)
	%	%	%	
450	7.2	3.5	7.0	23
500	25.8	16.9	24.5	24
550	42.2	32.0	41.0	25
600	55.8	45.6	54.2	26
650	66.3	57.1	65.1	27
700	73.8	66.2	73.0	28
〃 *	74.3	67.0	73.5	29
750	79.9	73.3	79.2	30
800	84.0	78.8	83.7	31
850	87.0	82.5	86.9	32
900	89.7	86.0	89.2	33
950	91.3	88.2	91.2	34
1000	93.0	90.1	92.7	35
1050	94.0	91.7	93.9	36
1100	94.2	92.0	94.0	37
1150	94.2	92.0	94.0	38
1200	94.0	91.9	93.9	39
450	6.9	3.2	6.7	40
500	24.7	15.8	23.5	41
550	41.3	31.0	40.2	42
600	54.5	44.2	53.5	43
650	65.7	56.3	64.9	44
700	73.0	65.5	72.6	45
750	79.5	73.0	79.2	47
800	83.7	78.0	83.3	48
850	87.0	82.2	86.9	49
900	89.2	85.7	89.2	50
950	91.8	88.6	91.8	51
1000	92.3	90.0	92.5	52
1050	93.9	91.5	93.9	53

1100	85.8	92.2	93.1	71
1150	85.7	92.1	93.1	72
1200	84.3	91.5	92.5	73
450	1.2	2.7	4.0	75
500	5.0	14.0	17.5	76
550	14.0	29.0	33.2	77
600	25.0	42.5	47.0	78
650	36.4	54.8	59.0	79
700	47.0	64.7	68.0	80
〃 *	47.2	65.0	68.5	81
750	56.0	72.3	75.2	82
800	63.0	77.5	80.0	83
850	69.2	82.2	84.2	84
900	73.6	85.2	87.0	85
950	78.0	88.3	90.0	86
1000	81.0	90.0	91.3	87
1050	83.8	91.9	92.8	88
1100	85.0	92.0	93.1	90
1150	84.0	92.0	93.0	91
1200	83.3	91.2	92.2	92

Table 2b (continued)

1100	94.1	92.0	94.1	54
1150	94.1	92.0	94.1	55
1200	93.9	91.6	93.9	56
450	6.2	3.0	6.1	57
500	23.5	15.0	22.9	58
550	40.0	30.0	39.6	59
600	54.0	43.6	53.0	60
650	64.5	55.2	64.0	61
700	73.2	65.5	73.0	62
750	78.9	72.0	78.7	63
800	83.1	77.1	83.0	64
850	86.6	82.0	86.7	65
900	89.0	85.0	89.1	66
950	91.0	88.0	91.0	67
1000	92.5	90.0	92.9	68
1050	93.3	91.0	93.5	69
1100	94.0	92.0	94.0	70
1150	93.9	91.8	93.9	71
1200	93.7	91.2	93.7	72
450	6.0	2.7	5.9	73
500	22.8	14.4	22.0	74
550	39.5	29.0	39.0	75
600	53.0	42.9	52.4	76
650	64.0	54.8	63.7	77
700	72.8	65.0	72.5	78
750	78.6	72.0	78.6	79
800	82.9	77.1	82.9	80
850	86.2	81.7	86.5	81
900	89.0	85.0	89.0	82
950	91.0	87.9	91.0	83

Measurement has been done with use of a Beckman type spectrophotometer, where the length of absorbing layer of solution is 1 cm.

* Exchange of photo-multiplier for Cs photo-tube.

** A different source of the sol has been used.

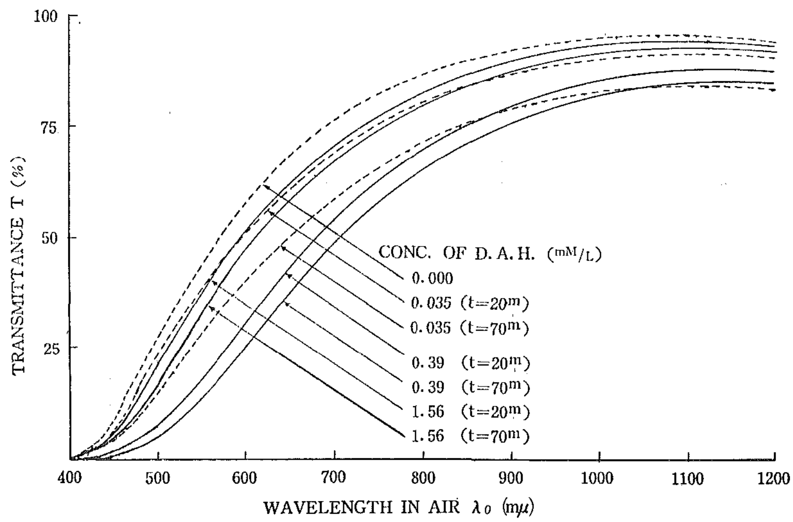


Fig. 3. Absorption curves of the mixed solutions.

This may be due to the adsorption of D. A. H. molecules by the colloid particles. Figure 3 shows the absorption curves of the mixed solutions at the certain time t elapsed after the mixing. The curves at the intersecting point are always steeper when the D. A. H. concentration is high than when it is low.

Absorption at the wavelength 422 mμ.

As shown in Fig. 4, an absorption band of AgI appears at the wavelength 422 mμ, and the minimum point of the transmittance shifts from 422 mμ to 428 mμ according to the increase of turbidity.

Such relation can be observed when the sol is diluted down to the concentration of 0.44 $^{mM}/_{L}$, whose coagulation and peptization values being found 0.08 $^{mM}/_{L}$ and 0.35 $^{mM}/_{L}$, respectively.

Variation of the maximum transmittance.

The maximum point of the transmittance appears in the neighbourhood of wavelength 1100 mμ. The curves are less steep at this point and therefore the exact position of the maximum point is difficult to find.

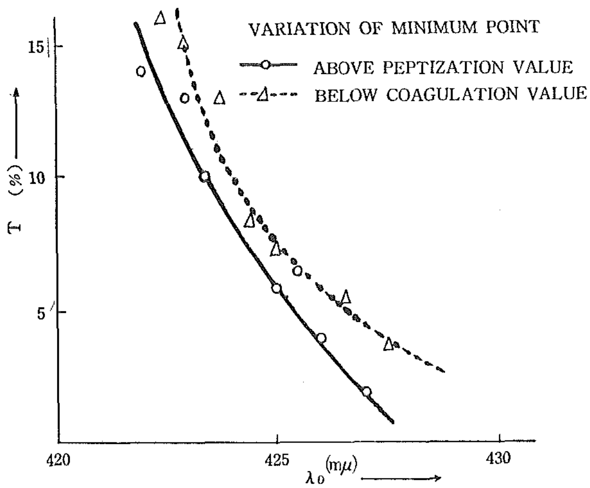
Analysis of the transmission.

From the results obtained in Table 2, the turbidity τ can be determined, applying the following empirical formula.[6]

$$\tau = \frac{KR^{n-1}}{\lambda^n}, \tag{1}$$

where, R: radius of the particle.

λ: wavelength in solvent, namely, in water in this experiment.



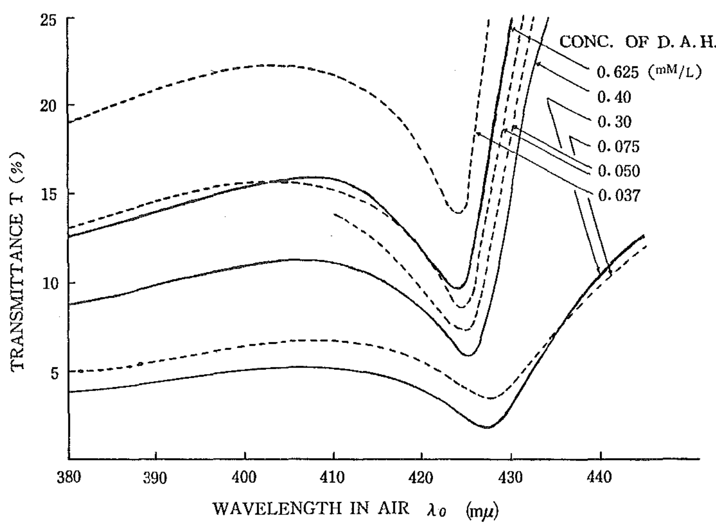


Fig. 4. Absorption at the wavelength 422~428 mμ.

K: proportional constant unrelated with R and λ.

From the graph of $\log\tau \sim \log\lambda$ or $\log\tau \sim \log\lambda_0$ (λ_0 represents the wavelength in air) the index of λ can be obtained as follows:

$$n = -\frac{\Delta\log\tau}{\Delta\log\lambda} = -\frac{\Delta\log\tau}{\Delta\log\lambda_0} \quad . \tag{2}$$

As shown in Fig. 5 and Table 3 the value of n varies from 4.0 to 2.7. When n is 4.0, the well-known formula of Rayleigh is applicable.[5]

$$\tau = \frac{24\pi^3 N V^2}{\lambda^4}\left(\frac{m^2-1}{m^2+2}\right)^2 \quad , \tag{3}$$

where, N: number of the particles in unit volume.

$m=n/n_0$, n : refractive index of the particle. n_0 : that of solvent.

In this case the radius R of the particle is smaller than 0.05λ. When R grows greater than 0.05λ, n becomes smaller than 4.0. These relations between n and R have been already reported by some researchers.[6][7]

Table 3. Values of $\log\tau$ $[\tau]=[cm^{-1}]$

D. A. H. CONC. (mM/L)		0.000		0.012		0.035	
		t=0m n=4.0		t=80m n=3.75		t=70m n=2.7	
λ_0	λ	T (%)	$\log\tau$	T (%)	$\log\tau$	T (%)	$\log\tau$
mμ	mμ						
650	489	69.4	$\bar{1}$.5625	66.7	$\bar{1}$.6074	51.1	$\bar{1}$.8270
700	526	77.3	.4107	74.1	.4768	59.4	.7167
750	565	82.7	.2786	80.0	.3486	66.3	.6138
800	603	86.8	.1510	84.1	.2384	70.5	.5438
850	641	89.5	.0451	86.8	.1509	74.1	.4768
900	678	91.6	$\bar{2}$.9431	89.2	.0580	77.3	.4107
950	714	93.2	.8477	91.3	$\bar{2}$.9592	80.2	.3437
1000	751	94.5	.7526	92.7	.8797	82.8	.2759

D. A. H. CONC. (mM/L)		0.39				0.78	
		t=0m n=4.0		t=80m n=3.6		t=0m n=4.0	
λ_0	λ	T (%)	$\log\tau$	T (%)	$\log\tau$	T (%)	$\log\tau$
mμ	mμ						
650	489	48.0	$\bar{1}$.8657	36.3	0.0058	60.6	$\bar{1}$.6997
700	526	58.2	.7375	47.0	$\bar{1}$.8780	69.6	.5592
750	565	67.8	.5896	56.3	.7593	76.0	.4385
800	603	72.9	.4999	63.4	.6587	81.1	.3212
850	641	77.8	.3997	69.6	.5592	85.0	.2109
900	678	81.8	.3030	74.0	.4787	88.0	.1067
950	714	85.4	.1982	78.3	.3885	90.4	.0040
1000	751	89.0	.0665	81.5	.3108	92.5	$\bar{2}$.8919

D. A. H. CONC. (mM/L)		0.78		1.56			
		t=80m n=4.0		t=0m n=4.0		t=80m n=4.0	
λ_0	λ	T (%)	$\log\tau$	T (%)	$\log\tau$	T (%)	$\log\tau$
mμ	mμ						
650	489	54.8	$\bar{1}$.7792	64.6	$\bar{1}$.6405	58.9	$\bar{1}$.7237
700	526	64.8	.6373	73.1	.4960	68.2	.5829
750	565	72.4	.5092	79.2	.3677	75.3	.4529
800	603	77.6	.4042	83.7	.2502	80.2	.3437
850	641	81.9	.3003	87.0	.1438	84.2	.2355
900	678	85.2	.2046	90.0	.0227	87.0	.1438
950	714	88.2	.0989	92.0	$\bar{2}$.9211	89.6	.0407
1000	751	90.3	.0087	94.0	.7915	91.5	$\bar{2}$.9486

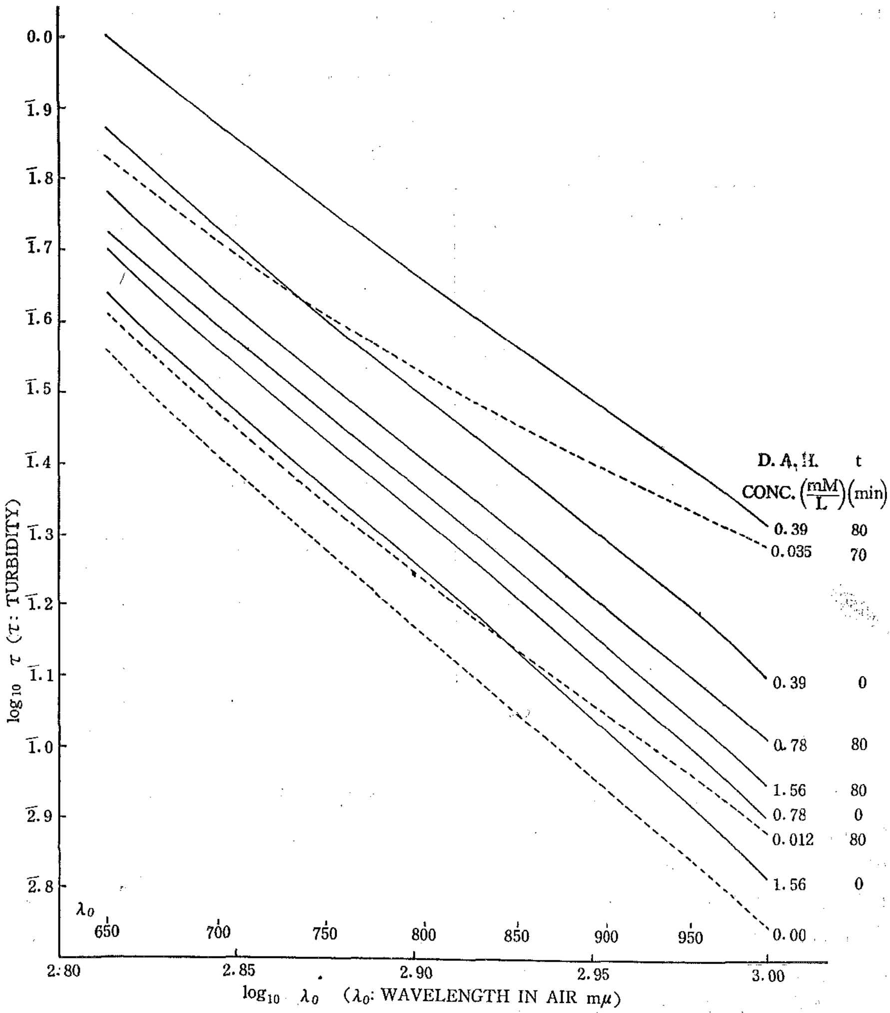


Fig. 5. Curves representing log τ plotted against log λ_0

Ratio of refractive index and radius of particle.

It is assumed that the increase of turbidity which takes place immediately after the mixing corresponds to the increase of m, the ratio of refractive index of the sol and its solvent, while the successive increase is due to the aggregation of particles.

In case of $n=4.0$, the radius of particle R and the ratio m can be obtained from Rayleigh's formula (3) as shown in Table 4, where, m, the ratio of refractive index of AgI in solvent (water), is equal to 1.7 and NV, the volume fraction of $2.2\ ^{mM}/_{L}$ AgI sol, is 9.1×10^{-5}. In the calculation of

R and m, the wavelength in water has been controlled to take a value between 603 mμ and 641 mμ, where n is 4.00 in the original sol.

Table 4. Values of m, n and R.

D. A. H. CONC. (mM/L)	m	t (min)	n	R (mμ)
0.000	1.7	40 80	4.0 4.0	34 35
0.012	1.7	40 80	3.8 3.7	
0.035	1.7	40 70	3.2 2.7	
0.39	2.3	40 80	3.8 3.6	
0.78	1.9	40 80	4.0 4.0	35 36
1.56	1.8	40 80	4.0 4.0	35 36.5
6.25	2.0	40 80	4.0 4.0	35 36
12.5	1.8	40 80	4.0 4.0	34.5 35

"m" is one of the important factors which indicates the state of the surface of the particles. It takes the maximum value when the concentration of D. A. H. is 0.39 mM/L. On the other hand R is smaller at D. A. H. concentration of 0.78~12.5 mM/L and greater at 0.00~0.39 mM/L, according to the fact that the sol particles aggregate on losing their electric charge by the adsorption of the cationic agent.

Radius of the particle observed by electron microscope.

Fig. 6 shows the colloid particles observed by electron microscope without metallic shadow casting. The approximate values of the radii are shown in Table 5, although they vary slightly according to optical fields.

Table 5. R obtained from the electron micrograph.

D. A. H. CONC. (mM/L)	0.000	0.035	0.78	1.56	12.5
R (mμ)	13	13	16	17	19

Only separate particles of clear roundness are picked up as the objects of

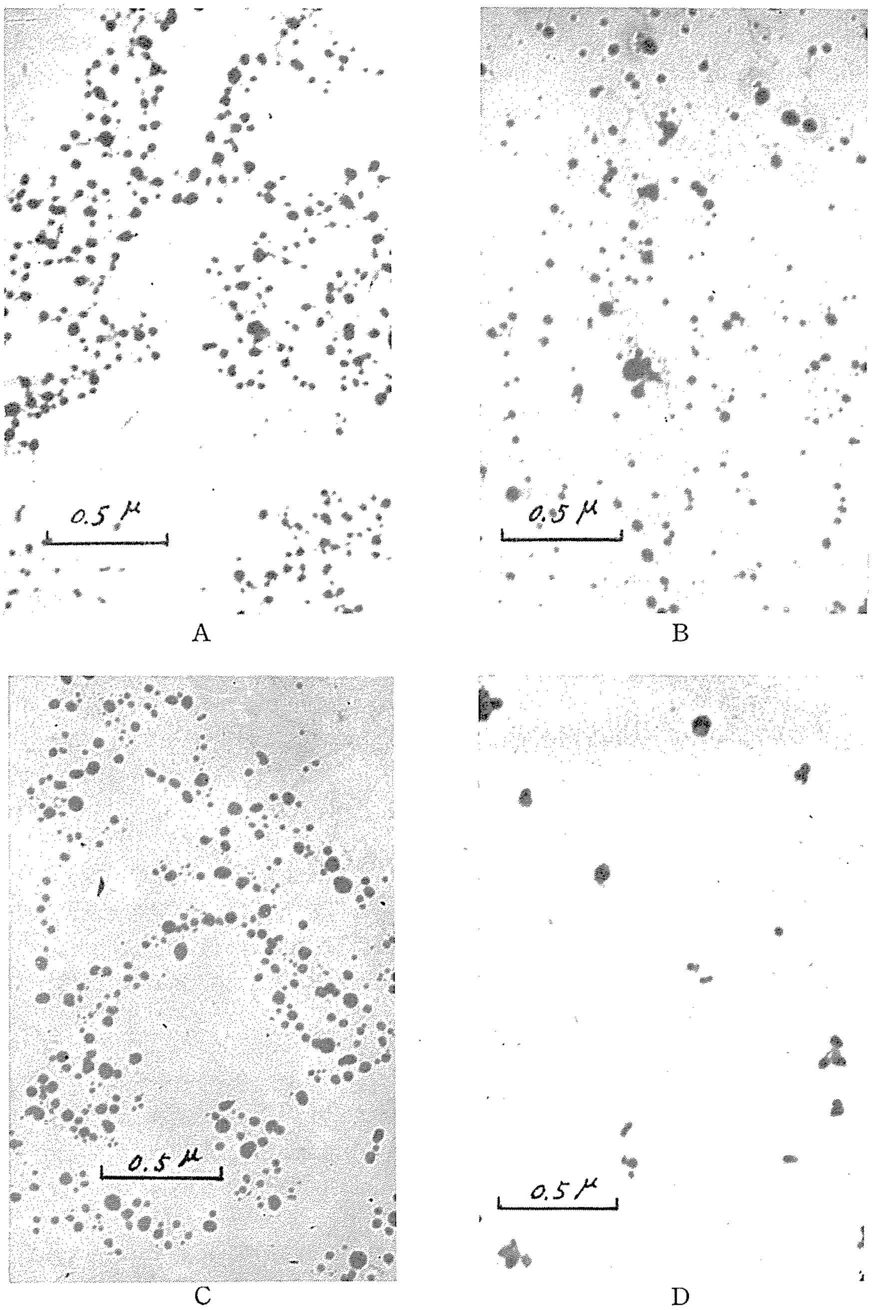


Fig. 6. Electron micrographs of AgI sol mixed by D. A. H. of varied concentrations. (A) 0.00mM/L, (B) 0.78mM/L, (C) 1.56mM/L, (D) 12.5mM/L.

observation, and those which have lost their round forms due to aggregation are excluded from observation, because it is rather difficult to determine whether they have lost their round forms in the solutions or have overlaped themselves while they were dried on the collodion membrane. The radii of the original sol particles are less than the half of those obtained from the transmittance and the particles grow larger and larger with the increase of the concentration of the agent added.

This is contrary to what was observed in Table 4.

The above fact shows that the individual and separate particles are slightly larger and more stable and less inclined to aggregate when the concentration of D. A. H. is above 0.78 $^{mM}/_{L}$ than those when the concentration is under 0.39 $^{mM}/_{L}$.

Mechanism of the coagulation and peptization.

In their reports [3] [4] on the mechanism of coagulation and peptization of colloid particles by surface active agents, K. Meguro and S. Saito assumed that the particles, once loosing their electric charge due to the adsorption of the agent molecules with opposite charge, become hydrophobic and coagulate, but they gain the electric charge again and become hydrophilic when the surface active agent is added further.

The present author is inclined to think that the particle must be the most hydrophobic when the ratio m is the largest and consequently that the main cause of coagulation, when the concentration of D. A. H. is not greater than its coagulation value 0.08 $^{mM}/_{L}$, should be the neutralization of the electric charge.

Light scattering by large particles.

When the radius of the particle of sol is larger than 0.05λ, Rayleigh's formula (3) is not applicable, and n, index of λ, will take smaller values than 4.0. In the present author's experiment, R, the radius of the particle, can not be obtained from the empirical formula (1). But another formula

$$\frac{1}{\tau\lambda^2}=\frac{K}{R^2}\lambda+\frac{K'}{R^4} \qquad (4)$$

$$(NV=\text{constant})$$

is satisfactorily applied and, moreover, the radius R calculated from this formula agrees with Heller's n–R relation[7] obtained with polystyrene or polyisoprene emulsion. (Fig. 7.)

Table 6 shows the values of R calculated by this formula, when D. A. H. concentration is 0.035 $^{mM}/_{L}$.

Table 6. Relation between n and R.

TIME t (min.)	n	R (mμ)
0	4.0	34
20	3.6	51
40	3.2	68
60	2.8	80
70	2.7	88

There is a tendency of diminishing in the first term of the right side of the equation (4) according to the time elapsed, during which the particles grow larger as shown in Fig. 7.

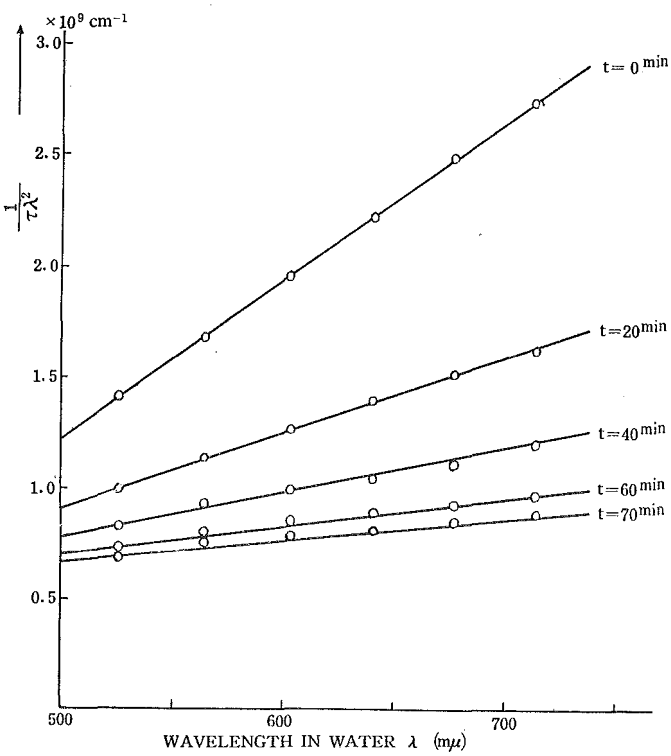


Fig. 7. $1/\tau\lambda^2 \sim \lambda$ (D.A.H. 0.035 mM/L)

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