A STUDY ON THE SPECTRAL TRANSMITTANCE OF AgI COLLOIDAL SOLUTION COAGULATED BY SURFACE ACTIVE AGENT

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§ 1 Introduction

Coagulation of sol

The inorganic lyophobic sol, such as the colloidal solution of metal, increases its turbidity gradually and spontaneously till the precipitation is finished.

In case of adding electrolyte, various degrees of turbidity also take place immediately, according to the concentration of electrolyte.

The former is called "ageing" and the latter "coagulation".

Colloid particles in the solution are charged with the same sign, and so they are prevented from connecting each other by electrostatic repulsive force which keeps the sol in a stable state.

The coagulation is caused mainly by the neutralization of charge of the particle adsorbing ions which are preferentially charged with opposite sign, and each particle joining together grows to be the secondary large particle by the brownian motion.

The least concentration of electrolyte required to easily coagulate and precipitate the sol is called "coagulation value" and its reciprocal is "coagulation power". Generally speaking, the coagulation power is determined in proportion to the ionic valence and adsorption power of electrolyte.

In case the concentration of electrolyte increases to some extent beyond its coagulation value, colloid particles, once precipitated, often return to the state of sol again, dispersing in the solution.

This phenomenon is called "peptization". Peptization is caused because the charge of particle which reverses its sign by excessive adsorption of electrolyte ions.

When the concentration of electrolyte increases more, the second coagulation of particle often appears again with conspicuous turbidity.

Purpose of this study

Concerning the phenomena of coagulation and peptization of sol by electrolyte, there remain many complicated problems unsolved.

The author published in 1973,[9] an optical study on the ageing of aqueous solution of silver iodide colloid. AgI sol, the particle of which is charged negatively, was selected

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as a material for its good stability that is due to a low solubility.

Now, the author intends to study, in the present paper, on the coagulation of AgI sol by Laurylpyridinium-bromide (L. P. B.), a cationic surfacant, analyzing the spectral transmittance curves obtained by spectro-photometer and applying the method of colorimetrics.

Fig. 1 indicates the percentage transmittance of AgI sol of 2. 2 mM/*l*, obtained 10 minutes after L. P. B. of varied concentrations was added by applying a light of wavelength of 600 nm. The coagulation value and peptization value of L. P. B. are about 0. 01 mM/*l* and 0. 05 mM/*l* respectively.

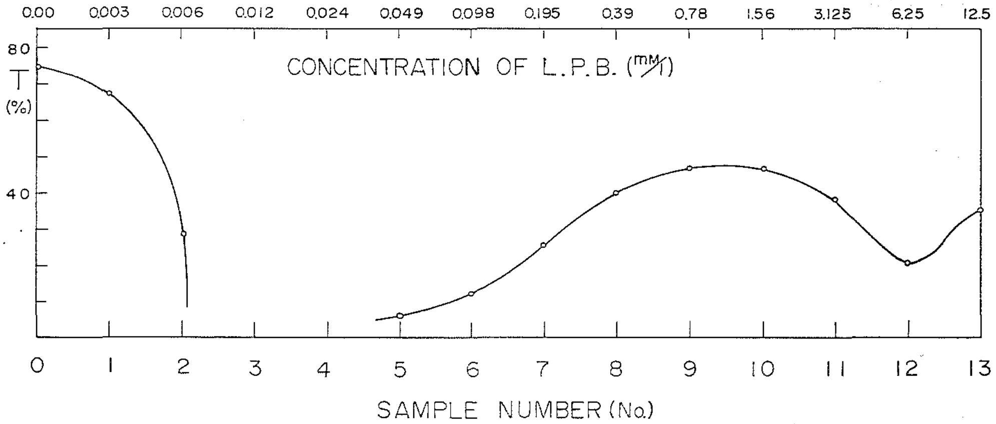

Fig. 1 Transmittance T % of AgI sol of 2. 2 mM/*l* obtained 10 minutes after L. P. B. of varied concentrations was added. Wavelength of photometer is 600 nm and the coagulation value is 0. 01 mM/*l*.

§ 2 Transmittance of AgI sol

Preparation of AgI sol

One hundred and sixty m*l* of 0. 01 M/*l* silver nitrate solution is added to 200 m*l* of 0. 01 M/*l* potassium iodide solution, the mixing must be carried out quickly and thoroughly. The silver iodide sol thus prepared has the concentration of 4. 44 mM/*l* 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.

Law of Lambert-Beer (L-B law)

The percentage transmittance of the purified AgI sol of 2. 22 mM/*l* (=$2C_0$), measured with a spectro-photometer (Shimadzu double beam UV-200 and recorder U-125 MU) 5 hours after prepared, is shown in Table 1 and in Fig. 2. (In the following this is named fresh AgI sol.)

In the former report of 1974, the author verified a fact that there exists a good linearity with average error of 0.15% between the concentration C (mM/l) and the logarithm of transmittance T (%), which proves the law of Lambert-Beer.

$$log_{10}T = 2 - KCl = 2 - D. \tag{1}$$

In the above formula, K is the extinction coefficient (wavelength constant), l is the layer thickness ($l = 1$ cm in this study), and D is the optical density or the extinction.

Concentration line of chromaticity

Table 1 Transmittance of AgI sol of 2.22 mM/l

λ (nm)	T (%)	$K \times 10^5$ (l/mM·cm)
430	0.6	100083
440	17.6	33986
460	33.9	21162
480	43.8	16150
500	51.7	12906
520	58.2	10589
540	63.9	8761
560	68.3	7459
580	72.3	6345
600	75.5	5498
620	78.4	4760
640	80.8	4171
660	82.7	3716
680	84.2	3364
700	85.7	3019

(λ : Wavelength)

The spectral transmittance curves of varied concentrations of AgI sol can be calculated from the values in Table 1 by applying the L-B law, and then the colorimetrical factors of CIE are also obtained in the range from 0.555 mM/l (= 0.5C_0) to 24.44 mM/l (= 22C_0) and are listed in Table 2.

These results are considered to represent the values of fresh AgI sol in which no aged or no coagulated particle grows after the measurement of transmittance, and these are also shown in Fig. 3, where the curve of chromaticity is drawn with a thick solid line, and the author wishes to denominate this line "concentration line of chromaticity" henceforth.

As a matter of fact, it is generally assumed that transmittance deviates from Lambert-Beer's law as the concentration of sol increases and the scattered light multiplies,[2] so that this line is an ideal standard model of fresh AgI sol, and satisfies the L-B law at any concentration, and this is imagined to compare the difference between the turbidity of sol caused by ageing or coagulation and that of sol caused by the increase of concentration.

The luminance factor (luminous transmittance) Y decreases from 89.97 % to 2.27 % and the dominant wavelength shifts from 571.2 nm to 597 nm in the same range of concentration. As Fig. 2 and Fig. 3 show, stimulus value Z and chromaticity coordinate z decreases rapidly and the chromaticity point approaches the spectrum locus according as the concentration increases. (z indicates the horizontal distance from the chromaticity point to the spectrum locus.)

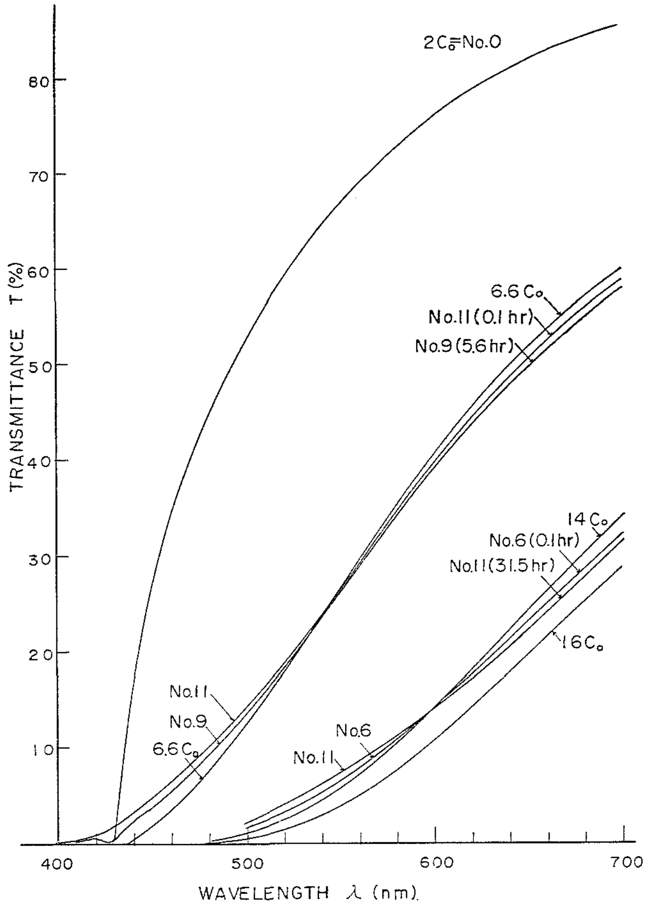

Fig. 2 Transmittance curves of fresh AgI sol (nC_0) and coagulated AgI sol (No. n). Figures in parentheses indicate the time between the mixing with L.P.B. and the observation. $C_0 = 1.11$ mM/l.

Table 2 Colorimetrical factors of fresh AgI sol

Conc.	$0.5C_0$	C_0	$2C_0$	$3C_0$	$4C_0$	$5C_0$	$6C_0$
Y(%)	89.97	81.05	66.10	54.26	44.71	36.98	30.65
x	0.3376	0.3569	0.3903	0.4188	0.4434	0.4636	0.4824
y	0.3599	0.3820	0.4121	0.4330	0.4443	0.4497	0.4521
Conc.	$8C_0$	$10C_0$	$12C_0$	$14C_0$	$16C_0$	$18C_0$	$22C_0$
Y(%)	21.32	15.20	10.91	7.85	5.75	4.17	2.27
x	0.5118	0.5315	0.5498	0.5653	0.5784	0.5909	0.6133
y	0.4477	0.4440	0.4343	0.4234	0.4137	0.4046	0.3857

$C_0 = 1.11$ (mM/l) Y: Luminance factor, x, y: Chromaticity coordinate

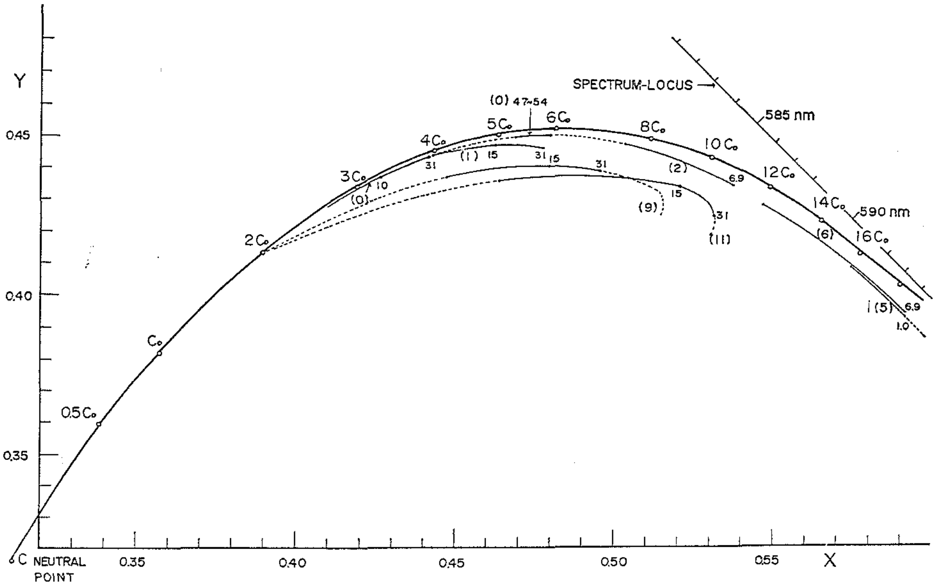

Fig. 3 Chromaticity diagrams of concentration line (thick line) and coagulation lines (thin lines). Figures on coagulation line and in ( ) indicate coagulation time (hr) and sample number respectively. Dotted lines are estimated changes. $C_0=1.11$ mM/l of AgI sol.

§ 3 Coagulation line of chromaticity

Coagulation line of chromaticity

The author has measured the spectral transmittance of AgI sol of 2.22 mM/l added by L. P. B. of various concentrations which are divided into two groups: G. 1 and G. 2. In Fig. 1, sample number No. 0, No. 1, No. 9 and No. 11 belong to G. 1 and the coagulation increases slowly, while No. 2, No. 5 and No. 6 belong to G. 2 and the coagulation increases rapidly.

For the convenience of measurement, the time intervals between the preparation of AgI sol and the mixing with L. P. B. are 5 hrs. in G. 1 and 52 hrs. in G. 2 respectively. The colorimetrical factors calculated through 30 selected ordinate method by C standard illuminant from these transmittance curves are shown in Table 3, where "t" denotes the time between the mixing and the observation, and in Fig. 3, where seven thin solid lines, representing the above-mentioned samples, indicate the change of chromaticity with time. The author wishes to denominate these curves "coagulation line of chromaticity". In case of No. 0, it may well be called "ageing line of chromaticity".

Comparison of the coagulation line with the concentration line

Each coagulation line is always under the concentration line and chromaticity point has a large z compared with that of the concentration line when the degrees of luminance factor Y are nearly the same. Therefore, the two curves of the spectral transmittance of coagulated sol and those of fresh sol being compared, it is evident that the former is larger at the short wavelength region less than 560 nm and that the latter is larger at the long wavelength region. Fig. 2 shows the relation by way of examples. Moreover, the coagulation lines of No. 9 and No. 11 are situated at the center of Fig. 3. This fact denotes that z of them is much larger than the others.

Fig. 4 explains the above reason. The original AgI sol absorbs the mono-chromatic light of 425 nm conspicuously, but the particle of sol covered by the molecules of L. P. B. diminishes the power gradually, and then the absorbance at 425 nm decreases as the concentration of L. P. B. increases.

In the cases of No. 0, No. 8 and No. 12, T_{425}: T_{500} are 0.029, 0.095 and 0.301 respectively, where T_{425} and T_{500} are percentage transmittance at the wavelength of 425 nm and 500 nm. (Concentration of AgI sol is 0.9 mM/l in Fig. 4.)

The scattering light increases the white color sensation remarkably in case of more than No. 10.

Table 3 Colorimetrical factors of coagulated AgI sol

G.1 No. \ t (hr)		0.1	15.5	31.5	G.2 No. \ t (hr)		0.1	2.65	6.93
No. 0	Y (%)	66.10	50.63	45.88	No. 0	Y (%)	32.88	32.37	31.28
	x	0.3903	0.4277	0.4411		x	0.4713	0.4739	0.4779
(0 mM/l)	y	0.4121	0.4366	0.4426	(0 mM/l)	y	0.4494	0.4498	0.4502
	λ_d (nm)	575.0	577.2	578.1		λ_d (nm)	580.2	580.4	580.6
No. 1	Y (%)	59.72	35.65	30.15	No. 2	Y (%)	20.27	15.67	11.32
	x	0.4034	0.4607	0.4774		x	0.5051	0.5207	0.5380
(0.003 mM/l)	y	0.4219	0.4466	0.4467	(0.006 mM/l)	y	0.4463	0.4418	0.4347
	λ_d (nm)	575.8	579.5	581.0		λ_d (nm)	583.2	584.7	586.6
No. 9	Y (%)	36.83	23.74	20.10	No. 6	Y (%)	8.31	2.56	1.62
	x	0.4493	0.4809	0.4918		x	0.5469	0.5811	0.5917
(0.78 mM/l)	y	0.4353	0.4400	0.4388	(0.098 mM/l)	y	0.4279	0.4032	0.3961
	λ_d (nm)	579.7	582.0	583.1		λ_d (nm)	588.1	593.2	594.6
No. 11	Y (%)	28.46	11.30	8.74	No. 5	Y (%)	4.01	0.69	0.45
	x	0.4647	0.5238	0.5329		x	0.5759		
(3.125 mM/l)	y	0.4356	0.4339	0.4261	(0.049 mM/l)	y	0.4101		
	λ_d (nm)	581.1	585.8	587.5		λ_d (nm)	591.9		

λ_d : Dominant wavelength, ( ): Concentration of L.P.B.

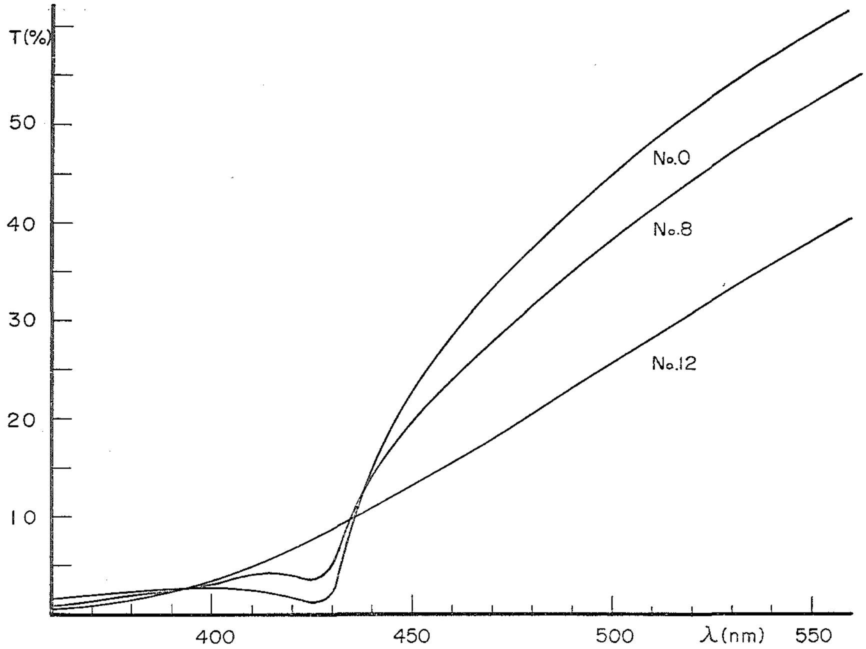

Fig. 4 Absorption at 425 nm in the cases of No. 0, No. 8 and No. 12. (T: Transmittance, λ: Wavelength)

§ 4 Velocity of coagulation

Slow coagulation (*G. 1*)

Between the transmittance $T(\%)$ of coagulated AgI sol which is applied the respective monochromatic light and the time t (hr), the following experimental relation is obtained with satisfactory accuracy from Fig. 5.

$$T = A \cdot 10^{-bt}. \qquad (2)$$

In the above equation, $A\,(\%)$ and $b\,(1/\mathrm{hr})$ are constants classified in two or three groups according to the range of time as listed in Table 4. The average errors of T between the values measured and calculated from (2) are less than 0.5 %. The half-life H(hr) of T is calculated from the equation

$$H = (log_{10}2)/b. \qquad (3)$$

The rate of diminution of transmittance $-\frac{dT}{dt}$, or the velocity of coagulation, is then calculated as follows:

$$T = A \cdot e^{-bt/M}\,. \quad (M = 0.4343) \qquad (4)$$

$$-\frac{dT}{dt} = bT/M = \frac{b}{M}A \cdot e^{-bt/M}\,. \qquad (5)$$

Constant b, in proportion to the velocity, takes larger values at the initial period than those of the later period.

Now that the luminance factor $Y(\%)$ is the collective percentage transmittance within a range of the visible light (its center of wavelength is 555 nm), Y, instead of T, also satisfies the equation (2)~(5) with the similar accuracy.

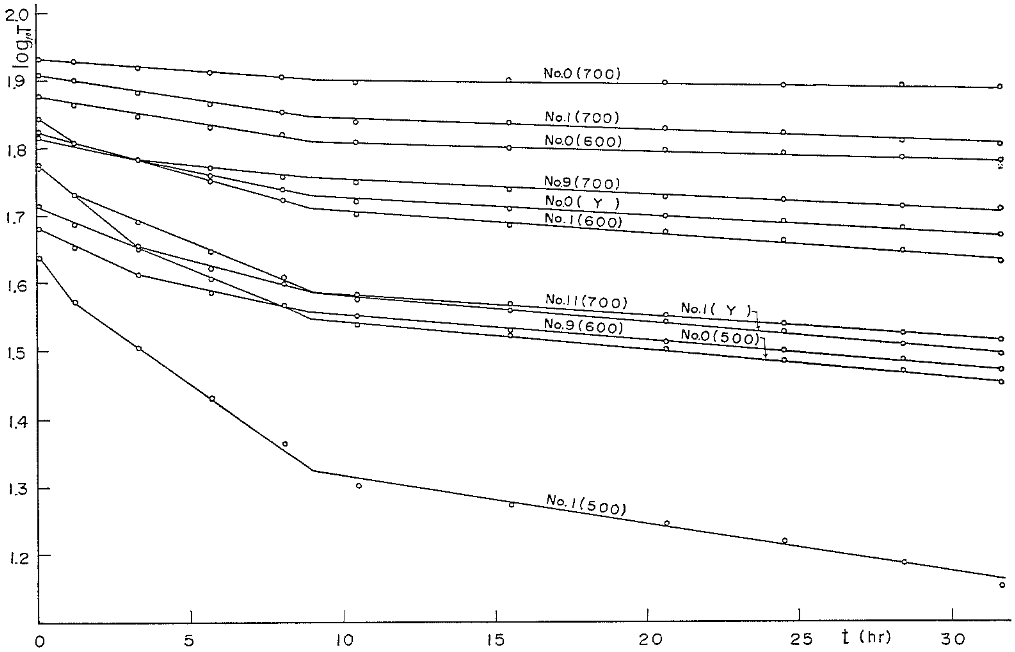

Fig. 5 Relation between $\log_{10}T$ (or $\log_{10}Y$) and t (hr), indicating the equation T(or Y) $= A\cdot 10^{-bt}$. Figures in ( ) are wavelength (nm). (T: percentage transmittance, Y: luminance factor, t: coagulating time)

Table 4 Values of A and b (H: Half-life of T and Y) (G.1)

	t (hr)	0.1~9		9~31.5		
	λ (nm)	A	$b\times 10^3$	A	$b\times 10^3$	H (hr)
No. 0	700	85.4	3.50	81.5	1.10	274
	600	75.4	7.37	67.0	1.80	167
	(Y)	66.2	10.5	56.1	2.70	111
	500	51.3	17.7	39.0	4.50	67

	t (hr)	0.1 ~ 1.25		1.25 ~ 9		9 ~ 31.5		
	λ (nm)	A	$b\times 10^3$	A	$b\times 10^3$	A	$b\times 10^3$	H (hr)
No. 1	700	82.2	11.7	79.6	6.84	73.2	1.95	154
	600	70.4	25.1	65.5	13.7	55.1	3.60	84
	(Y)	60.0	32.5	57.5	18.3	41.4	4.00	75
	500	44.1	56.6	40.6	29.5	23.9	7.25	42

	t(hr)	0.1 ～ 3.33		3.33 ～ 9		9 ～ 31.5		
	λ(nm)	A	$b\times10^3$	A	$b\times10^3$	A	$b\times10^3$	H(hr)
No. 9	700	66.7	12.0	63.7	5.70	59.4	2.35	128
	600	48.2	21.0	44.5	10.0	39.2	4.00	75
	500	20.6	36.7	17.8	18.6	13.7	7.50	40
No. 11	700	60.0	32.5	49.8	13.0	41.3	3.45	87
	600	39.7	59.5	27.8	17.0	21.1	5.55	54
	500	14.7	117	7.85	35.0	4.17	9.00	33

Rapid coagulation (*G.* 2)

In the cases of No. 6 and No. 5, the coagulation proceeds rapidly because their concentrations of L. P. B. are near the coagulation value and the measurement gets into difficulties 7 hrs. after the mixing.

At the later period in the range from 0. 1(hr) to 7(hr), equations (2)～(5) are applied in the same manner as G. 1, but these relations should be replaced by the different equation (6) or (7) at the initial period.

$$T = B\cdot t^{-c}. \tag{6}$$

$$-\frac{dT}{dt} = B\cdot c/t^{(c+1)}. \tag{7}$$

As shown in Fig. 6, Eq. (6) can be corrected as Eq. (8), which is applied to cover all the range of time with the same accuracy.

$$(T+k) = C\cdot t^{-d}, \tag{8}$$

$$-\frac{dT}{dt} = C\cdot d/t^{(d+1)}. \tag{9}$$

In case of No. 2, the velocity of coagulation is the slowest in G. 2 and the relation between T and t is indicated by Eq. (2). These constants are listed in Table 5.

Table 5 Constants referring to the coagulation velocity (G. 2)

	t(hr)	0.1 ～ 0.56			0.56 ～ 7		
	λ(nm)	A	$b\times10^3$	H(hr)	A	$b\times10^3$	H(hr)
No. 2	700	52.1	16.4	18.4	52.1	16.4	18.4
	600	30.0	31.0	9.71	30.0	31.0	9.71
	500	7.40	124	2.43	6.86	62.0	4.86
	t(hr)	0.1 ～ 2.65			2.65 ～ 7		
	λ(nm)	B	$c\times10^3$	Bc	A	$b\times10^3$	H(hr)
No. 6	700	21.0	211	4.43	19.2	27.3	11.0
	600	6.58	332	2.19	6.0	46.0	6.54
No. 5	700	10.2	354	3.61	8.02	32.0	9.41

t(hr)		0.1 ~ 7			
	λ(nm)	k	C	$d\times10^3$	Cd
No. 6	700	3.5	23.8	195	4.64
	600	2.3	8.87	262	2.32
No. 5	700	2.3	12.6	302	3.81

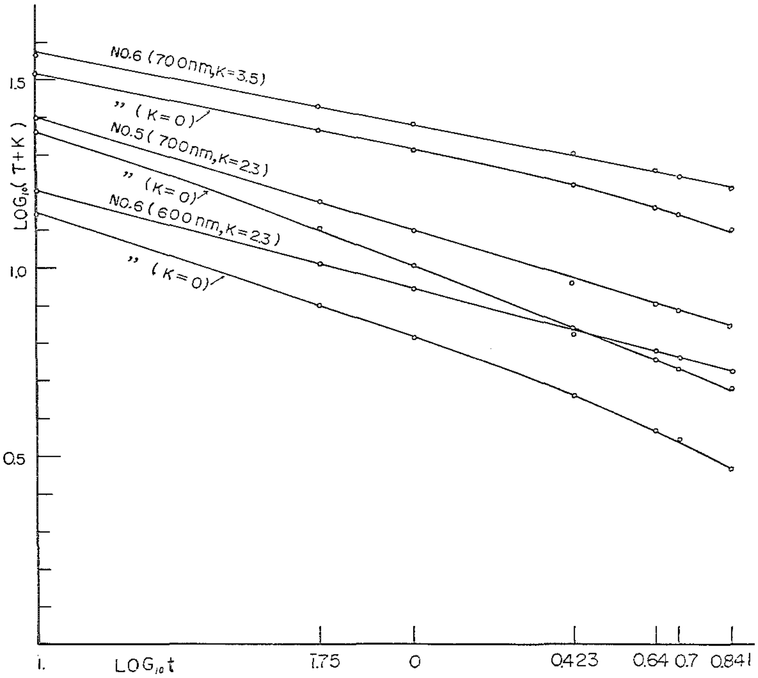

Fig. 6 Relation between Eq. (6) and Eq. (8) in the cases of No. 6 and No. 5.

§ 5 La Mer's formula and Rayleigh's law

La Mer's formula

From the spectral transmittance curves of coagulated AgI sol added by L. P. B. of various concentrations for various time intervals t(hr) between the mixing and the observation, the turbidity τ (1/cm) can be determined by the following definition.

$$\tau = \frac{1}{0.4343\,l}(2 - log_{10}T) \qquad (10)$$

The above equation can be applied to La Mer's following experimental formula:6)

$$\tau = k\cdot R^{(n-1)}/\lambda_0{}^n, \qquad (11)$$

where, l: layer thickness of sol (1 cm in this study),
R: radius of the particle,

λ_0: wavelength in solvent, namely, in water in this study,
k: proportional constant unrelated with λ_0 and related with R.

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

$$n = -\frac{\Delta \log\tau}{\Delta \log\lambda_0} = -\frac{\Delta \log\tau}{\Delta \log\lambda} \ . \tag{12}$$

As shown in Fig. 7, each curve is not exact linear owing to the absorptions at the wavelength of 425 nm and in the region of more than 760 nm. In case of the determination of n, λ has been selected to take a value of 660 nm (i. e. $\lambda_0 = 495$ nm) in G. 1 and 680 nm (i. e. $\lambda_0 = 510$ nm) in G. 2 respectively, where n is 4. 00 in the

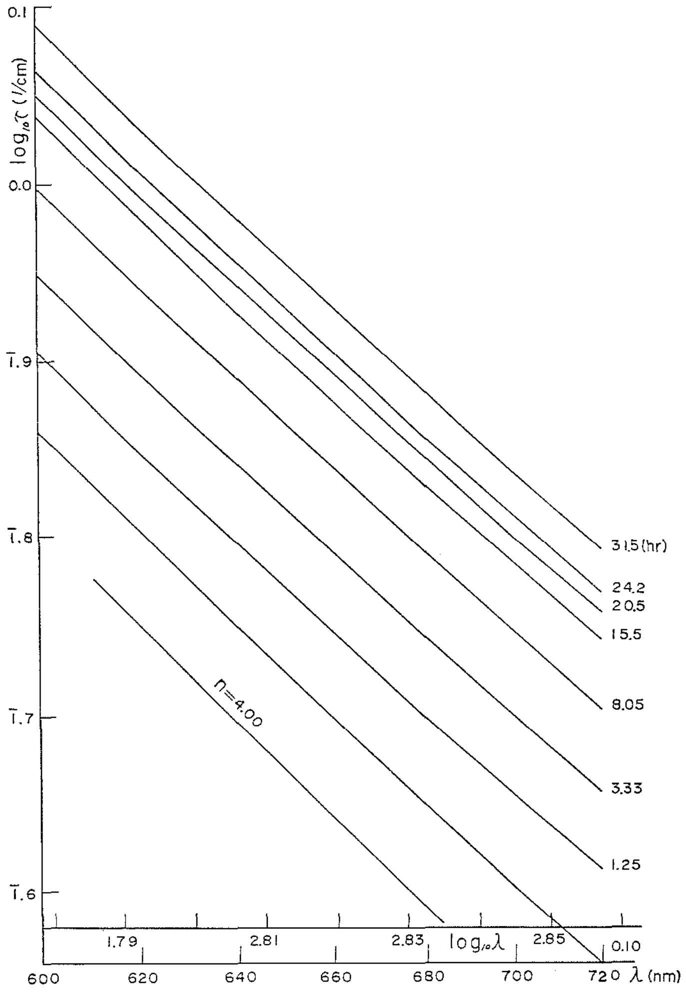

Fig. 7 Determination of n in case of No. 9. Figures indicate the coagulating time t (hr).

original AgI sol (i. e. No. 0). The values of n are listed in Table 6 varying from 4. 0 to 3. 25.

Table 6 Values of n and R of coagulated AgI Sol

No. 0	t (hr)	0. 1 ~ 31. 5 (G. 1)			46. 8 ~ 53. 7 (G. 2)			
	n	4. 0			4. 0			
	R (nm)	23. 4 ~ 36. 3			41. 7 ~ 42. 1			
No. 1	t (hr)	0. 10	1. 25	3. 33	8. 05	15. 5	20. 5	31. 5
	n	4. 0	4. 0	4. 0	4. 0	4. 0	4. 0	4. 0
	R (nm)	32. 0	33. 8	35. 5	38. 5	40. 8	41. 9	42. 8
No. 9	n		3. 75	3. 73	3. 71	3. 70	3,70	3. 67
	R (nm)		47. 6	48. 5	49. 8	51. 0	51. 6	52. 0
No. 11	n	3. 80	3. 75	3. 65	3. 55	3. 50	3. 45	3. 45
No. 2	t (hr)	0. 10	0. 56	1. 00	2. 65	4. 36	5. 00	6. 93
	n	3. 8	3. 8	3. 8	3. 8	3. 8	3. 8	3. 8
	R (nm)	44. 4	44. 9	45. 3	47. 0	48. 2	48. 6	50. 1
No. 6	n	3. 65	3. 55	3. 52	3. 45	3. 40	3. 40	3. 35
No. 5	n	3. 65	3. 55	3. 52	3. 45	3. 40	3. 35	3. 25

Law of Rayleigh

When n is 4. 0, the well-known formula of Rayleigh is applicable.[3~5)]

$$\tau = \frac{24\pi^3 NV^2}{\lambda_0{}^4}\left(\frac{m^2-1}{m^2+2}\right)^2 = \frac{32\pi^4 NVR^3}{\lambda_0{}^4}\left(\frac{m^2-1}{m^2+2}\right)^2 , \qquad (13)$$

where, N: number of the particles in unit volume,
V: volume of a particle,
m: ratio of the refractive index of the particle and that of solvent ($m = 1.72$ in this experiment).

The molecular weight and the density of AgI are 235 and 5. 65 g/cm^3, so NV, the volume fraction of 2. 22 mM/l AgI sol is 9.20×10^{-5} cm^3. The radius of particle R (nm) can be obtained from Eq. (13) or from the value of τ (1/cm) as follows:

$$3\cdot log_{10}R = 5.1278 + log_{10}\tau, \quad (\lambda o = 495 \text{ nm}) \qquad (14)$$

and the results of No. 0 and No. 1 are also listed in Table 6.

Radius of the large particle

When R grows larger, n becomes less than 4. 0. The relation between n and R have already been reported by some researchers with regard to several other substances.[7)]

In the former report[9] and the succeeding studies, the author has also obtained an approximate relation between n and R (nm) of aged AgI sol as listed in Table 7.

In case of $n < 4.0$, R, the radius of the particle regarding indefinite massive forms as sphere, can not be obtained from (13) or (14), but the approximate and relative value of R is calculated from (11) when n or R is about constant.

Table 7 Relation between n and R of aged AgI sol

n	4.0	3.9	3.8	3.7	3.6	3.5	3.4	3.3	3.2
R (nm)	23.4~42.8	43	47	51	54	57	61	64	68

The author, supposing $R = 51.0$ nm when $n = 3.70$ in No. 9 and $R = 47.0$ nm when $n = 3.80$ in No. 2 with reference to the Table 7, calculates the absolute values of R from (11) as listed in Table 6.

In the cases of No. 11, No. 6 and No. 5, R can not be calculated from (11). It is because of the wide variation of n which is related with the proportional constant k in Eq. (11).

§ 6 Another relation between τ and λo

An experimental equation

When R, radius of the particle of AgI sol, grows larger than 43 nm, Rayleigh's formula (13) or (14) is not applicable and n, index of λo, takes smaller values than 4.0.

In case n is less than 4.0 and approximately constant, the relative value of R can be calculated from La Mer's formula (11). Generally speaking, however, n varies widely with time, so R can not be found as stated above.

The author obtained a relation of new pattern between the wavelength λo or λ (nm) and the turbidity τ (1/cm) of coagulated or aged AgI sol, and consequently published in 1957[8] and in 1973[9]. That is the equation of

$$1/\tau\lambda^2_0. = a\lambda o - b \quad . \tag{15}$$

In the present study, Eq. (15) can be applied also with satisfactory accuracy to both cases of G. 1 and G. 2. Fig. 8 shows the relation in case of No. 9, for example, and the constant values of a and b are listed in Table 8, where a, indicating a rising gradient of each straight line, decreases with time.

Relative errors of the equation

Table 9 shows the relative errors between the left side and the right of the equation (15). The average errors at the wavelength in water 435 nm (i. e. 580 nm in air) and 555 (740) nm are larger compared with the errors in the region from 450 (600) nm to 540 (720) nm owing to the absorptions at 319(425) nm and at the long wavelength side more than 570 (760) nm.

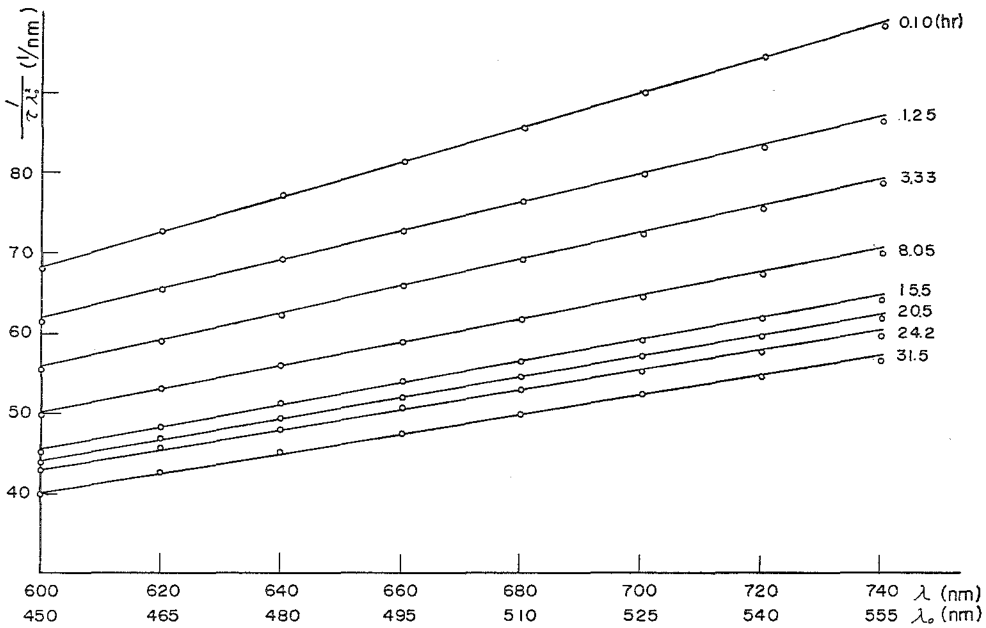

Fig. 8 $1/\tau\lambda_0^2 = a\lambda_o - b$ (No. 9)

Table 8 Values of a, b and R of coagulated AgI sol

	t (hr)	0.10	1.25	3.33	8.05	15.5	20.5	31.5
No. 1 $k = 2157 \times 10$ (nm) $k' = 5199 \times 10^3$ (nm^2)	$a \times 10^3$ (nm^{-2})		521	461	378	306	288	272
	b (nm^{-1})		117	107	91.1	69.7	67.7	64.9
	$R = (k/a)^{1/3}$ (nm)		34.6	36.0	38.5	41.3	42.2	43.0
	$R = (k'/b)^{1/3}$ (nm)		35.4	36.5	38.5	42.1	42.5	43.1
No. 9 $k = 2388 \times 10$ (nm) $k' = 4669 \times 10^3$ (nm^2)	$a \times 10^3$ (nm^{-2})	294	241	225	193	180	173	165
	b (nm^{-1})	64.2	46.6	45.6	36.7	35.2	33.6	32.2
	$R = (k/a)^{1/3}$ (nm)	43.3	46.3	47.4	49.8	51.0	51.7	52.5
	$R = (k'/b)^{1/3}$ (nm)	41.8	46.4	46.8	50.3	51.0	51.8	52.5
No. 11 $k = 1992 \times 10$ (nm) $k' = 3499 \times 10^3$ (nm^2)	$a \times 10^3$ (nm^{-2})	227	186	132	111	101	97.0	92.2
	b (nm^{-1})	49.6	37.0	26.0	19.1	17.0	16.5	16.2
	$R = (k/a)^{1/3}$ (nm)	44.5	47.5	53.2	56.4	58.2	59.0	60.0
	$R = (k'/b)^{1/3}$ (nm)	41.3	45.6	51.3	56.8	59.0	59.5	60.0
	t (hr)	0.10	0.56	1.00	2.65	4.36	5.00	6.93
No. 2 $k = 1672 \times 10$ (nm) $k' = 3893 \times 10^3$ (nm^2)	$a \times 10^3$ (nm^{-2})	183	178	173	161	149	147	136
	b (nm^{-1})	41.0	40.4	38.9	37.5	34.7	34.5	32.1
	$R = (k/a)^{1/3}$ (nm)	45.0	45.5	45.9	47.0	48.2	48.5	49.7
	$R = (k'/b)^{1/3}$ (nm)	45.6	45.9	46.4	47.0	48.2	48.3	49.5

No. 6 $k=1171\times10$(nm) $k'=2107\times10^3$(nm^2)	$a\times10^4$ (nm^{-2})	1000	744	667	556	506	488	467
	b (nm^{-1})	20.0	14.1	12.0	8.9	7.9	7.6	7.2
	$R=(k/a)^{1/3}$(nm)	48.9	54.0	56.0	59.5	61.4	62.2	63.1
	$R=(k'/b)^{1/3}$(nm)	47.2	53.1	56.0	61.9	64.4	65.2	66.4
No. 5 $k=8008$ (nm) $k'=1423\times10^3$(nm^2)	$a\times10^4$ (nm^{-2})	733	511	456	367	333	311	300
	b (nm^{-1})	13.7	9.2	8.1	5.9	4.9	4.1	3.65
	$R=(k/a)^{1/3}$(nm)	47.8	53.9	56.0	60.2	62.2	63.6	64.4
	$R=(k'/b)^{1/3}$(nm)	47.0	53.7	56.0	62.2	66.2	70.3	73.0

Table 9 Relative errors of the equation (15) (%)

λo	435 (nm)			450～540 (nm)			555 (nm)		
t (hr)	1.25	31.5	$\bar{t}$	1.25	31.5	$\bar{t}$	1.25	31.5	$\bar{t}$
No. 0	3.9	0.9	2.4	1.0	0.53	0.76	5.6	3.5	5.0
No. 1	1.8	1.3	1.5	0.58	0.51	0.55	4.4	1.7	3.0
No. 9	0.86	0.20	1.2	0.33	0.33	0.32	2.7	1.7	2.0
No. 11	0.23	0.42	0.50	0.18	0.38	0.31	2.0	2.0	2.0

$\bar{t}$: Average errors of total time

The fact to which special attention should be paid is that these errors decrease and the linearity of Eq. (15) increases in proportion to the sample number and as the concentration of L. P. B. increases.

It is due to the diminution of absorption power by L. P. B. at the wavelength in air 425 nm and at the long wavelength region. The similar tendency is shown in case of the determination of n in Fig. 7.

Determination of the radius of particle

The author, in the former report[9)], obtained the radius of particle R (nm) of aged AgI sol from the relations

$$a = k/R^3 \qquad \text{and} \qquad b = k'/R^3 \ , \qquad (16)$$

where, a or b is the constant, in the equation (15), which decreases it's value monotonously with time and k or k' is proportional constant unrelated with R and λo.

The author, by the same manner in the case of La Mer's formula, supposes that the radii of particle are 51. 0, 60. 0, 47. 0 and 56. 0 nm respectively corresponding to the values of n are 3. 70, 3. 45, 3. 80 and 3. 52. The results thus obtained from Eq. (16) are listed in Table 8. The values of R calculated from a agree well with the results from b. As shown in Fig. 8 and Table 8, the values of k/R^3 or k'/R^3 decreases according as the time passes.

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Summary

The author has studied, analyzing the spectral transmittance curves obtained by a double beam type spectrophotometer and applying the method of colorimetrics, on the coagulation of AgI sol by Laurylpyridinium-bromide, a cationic surfacant. Next, the experimental formula concerning the velocity of coagulation and that of $1/\tau\lambda o^2 = a\lambda o - b$ (τ: turbidity, λo: wavelength in water) have been obtained with satisfactory accuracy, where radii R of the particles are also calculated from constant a or b of the above equation in the range of $34.6 \sim 73.0$ nm,