

AN OPTICAL STUDY ON THE AGEING OF SILVER IODIDE COLLOIDAL SOLUTION

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The author has studied, by analyzing the spectral transmittance curves obtained by Beckman type photometer, on the difference between the turbidity of AgI sol owing to ageing and the turbidity owing to the increase of concentration. Measurement in this study has mainly been carried out by colorimetric method.

In the next place, the experimental formula concerning the velocity of ageing and that of $1/\tau\lambda_0^2 = a\lambda_0 - b$ (τ : turbidity, λ_0 : wavelength in water, a , b : constants.) have been obtained with satisfactory accuracy, where radii $R(\text{nm})$ of the particles have been calculated from a or b of the above formula in the range of 26~70 (nm), and the R agree with the results from Rayleigh's formula in case of less than 40 nm.

Introduction

Ageing of sol

The inorganic lyophobic sol, such as the colloidal solution of metal, increases the turbidity slowly owing to the spontaneous growth of particle and precipitates finally.

A technical term "ageing" is used in this case against "coagulation" which is specially used in case of adding a small amount of electrolyte.

As to the cause of ageing, the following are considered. (1) Connection of particles by their brownian motion. In this case the rising of temperature accelerates the ageing. (2) In case of having high solubility, the (primary) particles once dissolved in the solvent deposit again on the surface of other particles and make them larger step by step. For example, as to the silver halide sol, the velocity of ageing is in accordance with the order of AgCl, AgBr and AgI, and this order also agrees with the order of their solubility. (3) A small quantity of impurities of electrolyte in the sol accelerates the ageing. This is because the colloid particles in the solution are generally charged with the same sign, so they are prevented from connecting each other by electro-static repulsive force keeping the sol in a stable state.

In case of adding electrolyte, the coagulation is caused by the neutralization of charge of the particles adsorbing ions which are preferentially charged with opposite sign and each particle joining together grows to be the larger secondary

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particle by the brownian motion.

Purpose of this study

Concerning the phenomena of ageing or coagulation of sol, there remain many complicated problems unsolved.

The author intends to study them applying the optical method, especially colorimetrics. Aqueous solution of silver iodide colloid was selected as a material for its good stability due to a low solubility.

Transmittance of AgI sol

Preparation of AgI sol

160 ml of 0.01 M/l silver nitrate solution is added to 200 ml of 0.01 M/l potassium iodide solution, and the mixing is 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

The percentage transmittance of the purified AgI sol and its dilutions, measured with a spectrophotometer 3 hours after it was prepared, is shown in Table 1. (In the following these are named fresh AgI sol.) There exists a good linearity between concentration C (mM/l) and the logarithm of transmittance $T(\%)$, and this linearity proves the law of Lambert-Beer.

$$\log_{10} T = 2 - KCl = 2 - D. \quad (1)$$

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

The corrected values calculated by applying the above law are listed in parentheses in the Table and the average error between the values measured and calculated is 0.15 % only. K 's of the corrected values are calculated from the equation $K = (6 - \sum \log_{10} T_i) / \sum C_i = (6 - \sum \log_{10} T_i) / 7.778$, and are listed in the same Table.

Concentration line of chromaticity

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

These results are considered to represent the values of fresh AgI sol and are also shown in Fig. 1, where the curve of chromaticity is drawn with a thick solid line, and the author wishes to denominate this line "concentration line of chromaticity" henceforce.

As a matter of fact, it is presumed to deviate from Lambert-Beer's law¹⁾ as the concentration of sol increases and the scattered light multiplies, but the exact

Table 1 Transmittance of AgI sol (λ :Wavelength)

λ (nm)	1.11 (mM/l)	2.22 (mM/l)	4.44 (mM/l)	K (l/mM•cm)
410	3.3(3.3)%	0.1(0.2)%	0.0(0.0)%	
420	2.0(2.0)	0.0(0.0)	0.0(0.0)	
430	17.9(17.9)	3.3(3.2)	0.1(0.1)	0.6723
440	56.0(55.7)	31.1(31.1)	9.6(9.7)	0.2285
460	68.3(68.0)	46.3(46.2)	21.2(21.4)	0.1509
480	74.7(74.5)	55.8(55.5)	30.6(30.8)	0.1150
500	79.0(78.9)	62.5(62.2)	38.5(38.7)	0.0927
520	82.6(82.5)	68.2(68.0)	46.1(46.3)	0.0753
540	85.4(85.3)	73.2(72.8)	52.6(53.0)	0.0621
560	87.5(87.5)	76.8(76.6)	58.3(58.6)	0.0523
580	89.3(89.3)	80.0(79.7)	63.2(63.5)	0.0444
600	90.8(90.8)	82.7(82.5)	68.0(68.1)	0.0375
620	92.1(92.1)	84.8(84.9)	72.1(72.0)	0.0321
640	93.0(93.0)	86.5(86.6)	75.1(75.0)	0.0281
660	93.8(93.9)	88.0(88.2)	78.0(77.8)	0.0246
680	94.5(94.6)	89.2(89.4)	80.2(80.0)	0.0219
700	95.0(95.1)	90.3(90.5)	82.2(81.9)	0.0195
720	95.4()	91.4()	84.0()	
740	95.8()	92.2()	85.5()	
760	95.9()	92.8()	86.7()	

Table 2 Colorimetical factors of fresh AgI sol

Conc.	C_0	$2C_0$	$4C_0$	$6C_0$	$8C_0$	$10C_0$
$Y(\%)$	85.97	74.30	56.10	42.35	32.92	25.58
x	0.3456	0.3719	0.4157	0.4513	0.4766	0.4997
y	0.3682	0.3956	0.4288	0.4434	0.4500	0.4501
λ_d (nm)	572.5	574.2	576.8	579.0	580.6	582.3
P	0.236	0.379	0.589	0.721	0.804	0.869
Conc.	$12C_0$	$14C_0$	$16C_0$	$18C_0$	$20C_0$	$22C_0$
$Y(\%)$	20.09	15.82	12.50	10.02	7.87	6.28
x	0.5200	0.5359	0.5500	0.5611	0.5753	0.5859
y	0.4477	0.4421	0.4340	0.4282	0.4173	0.4093
λ_d (nm)	584.1	585.7	587.5	588.8	590.8	592.5
P	0.917	0.947	0.960	0.973	0.985	0.990

$C_0=1.11(\text{mM/l})$, Y : Luminance factor, x, y : Chromaticity coordinate, λ_d : Dominant wavelength, P : Excitation purity

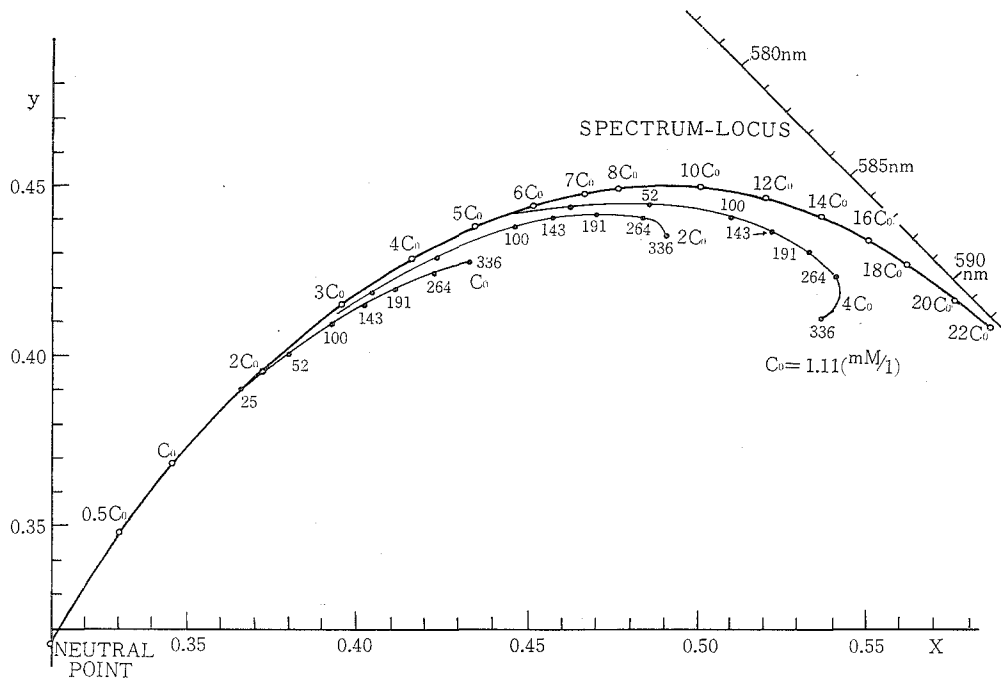


Fig. 1 Chromaticity diagrams of concentration line (thick line) and ageing lines (thin lines). Figures on ageing lines indicate ageing time t (hr).

chromaticity point can not be measured because of its unstableness at the state of high concentration, so this line is an ideal standard model, and satisfies the law at any concentration, imagined to compare the difference between the turbidity of sol caused by ageing and that of sol caused by the increase of concentration.

The luminance factor (luminous transmittance) Y decreases from 85.97 % to 6.28% and the dominant wavelength shifts from 572.5 nm to 592.5 nm in the same range of concentration.

Ageing line of chromaticity

The author has measured the spectral transmittance of AgI sol of various concentrations for various time intervals in the range from 3 to 336 hrs. A Beckman type spectrophotometer has been used, where the interval of the wavelength applied is 20 nm.

The colorimetric 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 preparation and the observation. In Fig. 1, three thin solid lines, representing the concentration of 1.11, 2.22 and 4.44 mM/l respectively, indicate the change of chromaticity with time.

The initial points of these curves are nearly on the concentration line of

Table 3 Colorimetric factors of aged AgI sol

Conc. t (hr)		3	25	52	100	143	191	264	336
C_0	$Y(\%)$	85.97	76.95	70.62	64.52	59.32	54.40	45.78	39.37
	x	0.3456	0.3655	0.3790	0.3918	0.4012	0.4098	0.4215	0.4292
	y	0.3682	0.3899	0.4014	0.4107	0.4172	0.4204	0.4271	0.4274
$2C_0$	$Y(\%)$	74.30	59.67	51.15	42.02	36.43	31.13	22.72	17.58
	x	0.3719	0.4046	0.4242	0.4455	0.4570	0.4699	0.4829	0.4889
	y	0.3956	0.4195	0.4314	0.4393	0.4435	0.4428	0.4417	0.4372
$4C_0$	$Y(\%)$	56.10	37.75	28.03	19.92	15.15	11.42	6.77	4.38
	x	0.4157	0.4619	0.4855	0.5106	0.5217	0.5333	0.5390	0.5320
	y	0.4288	0.4465	0.4453	0.4421	0.4389	0.4323	0.4229	0.4124

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

chromaticity, and these concentrations on the line are equivalent to those of the three curves.

The author wishes to denominate these curves "ageing line of chromaticity".

For reference, the average deviations of aged sol from the law of Lambert-Beer with time, in case of the percentage transmittance of 500 and 600 nm, are shown as follows:

0.15% (3 hr), 0.20% (25 hr), 0.22% (52 hr), 0.18% (100 hr), 0.10% (143 hr),
0.27% (191 hr), 0.28% (264 hr), 0.43% (336 hr).

Comparison of the ageing line with the concentration line

The luminance factor Y of the ageing line decreases with time and the turbidity or the purity increases also with time, but the difference against the concentration line, indicating the law of Lambert-Beer, is extended gradually. This is due to the difference between the growth of colloidal particle in the former and the increase of concentration in the latter.

On comparing the two curves of the spectral transmittance of aged sol and those of fresh sol, it is evident that the former is larger at the short wavelength region and that the latter is larger at the long wavelength region, when the degrees of luminance factor are nearly the same. Fig. 2 shows the relation by way of examples.

According to this fact, the aged sol has a large Z but a similar ratio of chromaticity coordinate $x:y$ against the fresh sol.

Therefore, the chromaticity point of the aged sol shifts to the left and lower side of the concentration line representing the chromaticity of fresh sol.

Velocity of ageing

Between the luminance factor $Y(\%)$ of AgI sol and the time t (hr) shown in

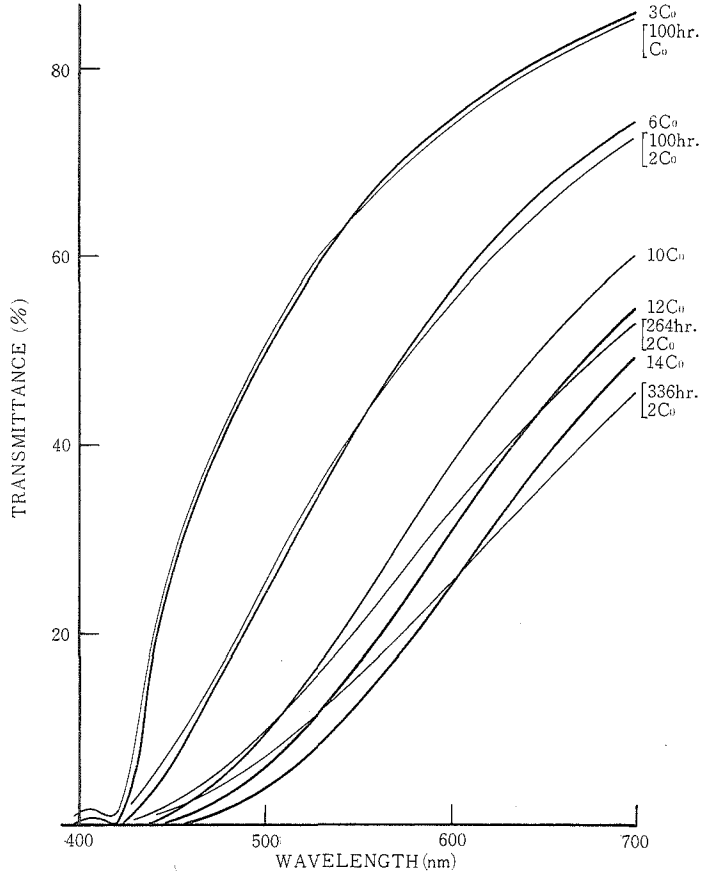


Fig. 2 Transmittance curves of fresh sol (thick line) and aged sol (thin line).
 $C_0 = 1.11 (mM/l)$.

Table 3, the following empirical formula is obtained with satisfactory accuracy from Fig. 3.

$$Y = A \cdot 10^{-bt} \quad (2)$$

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

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

The rate of diminution of luminance factor $-\frac{dY}{dt}$, or the velocity of ageing, is then calculated as follows:

$$Y = A \cdot e^{-bt/M} \quad (M = 0.4343) \quad (4)$$

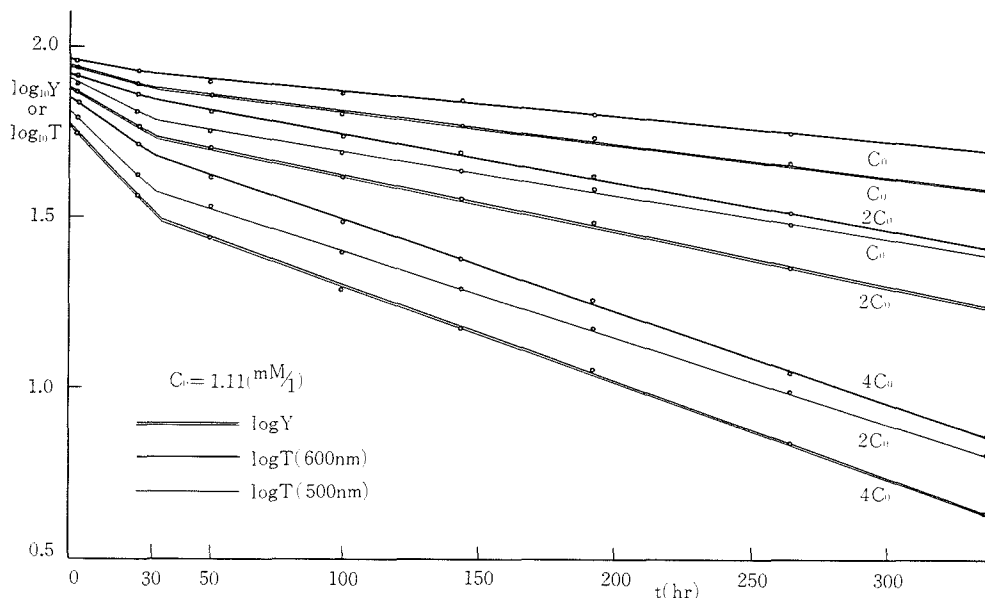


Fig. 3 Relation between $\log_{10} Y$ (Y : luminance factor) or $\log_{10} T$ (T : percentage transmittance) and ageing time t (hr), indicating the formula Y (or T) = $A \cdot 10^{-bt}$.

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

Conc. (mM/l)	λ (nm)	$0 < t < 30$ (hr)		$30 < t < 336$ (hr)		
		A	$b \times 10^3$	A	$b \times 10^3$	H (hr)
1.11	500			66.3	1.265	238
	555	88.5	2.27	81.1	0.924	326
	(Y)	87.3	2.19	80.0	0.925	325
	600			89.2	0.735	409
2.22	500			44.4	2.48	121
	555	77.8	4.35	63.2	1.70	177
	(Y)	76.6	4.33	62.0	1.63	185
	600			76.9	1.41	214
4.44	500			21.4	4.90	61
	555	60.6	8.26	38.1	3.04	99
	(Y)	59.2	7.82	39.4	2.85	106
	600			57.3	2.65	114

$$-\frac{dY}{dt} = bY/M = \frac{b}{M} A \cdot e^{-bt/M} \quad (5)$$

At the initial period, the growth of the primary colloid particles, multiplying the turbidity, accelerates the velocity of ageing. Therefore, the constant b , in proportion to the velocity, takes the larger values 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), the percentage transmittance $T(\%)$ by the respective monochromatic light also satisfies the formulae (2)~(5), instead of Y , with a similar accuracy.

Constant A and b , by applying the monochromatic lights of 500, 555, and 600 nm, are listed in the same table by way of examples.

Radius of the particle

Radius of the particle observed by electron microscope

The author has measured the radius of the AgI colloid particle by electron microscope 3 hours after it was prepared. The results are shown in Fig. 4 and Fig. 5, and the average radius calculated from them is 13.2 nm.

Only the separate particles of clear roundness are picked up as the objects of calculation, and those having lost their round forms due to aggregation are excluded from calculation, because it is rather difficult to determine whether they have lost their round forms in the solution or have overlapped themselves while they were dried on the collodion membrane.

With reference to the most probable value of the radius of AgI colloid particle, prepared by the same method as the author does, 14.0 nm (fresh sol) and 15.0 nm (aged sol) were obtained by Overbeck et al. in 1953.²⁾

Analysis of the spectral transmittance of aged sol

From the 24 spectral transmittance curves of AgI sol of various concentrations (1.11, 2.22 and 4.44 mM/l) for various time intervals between the preparation

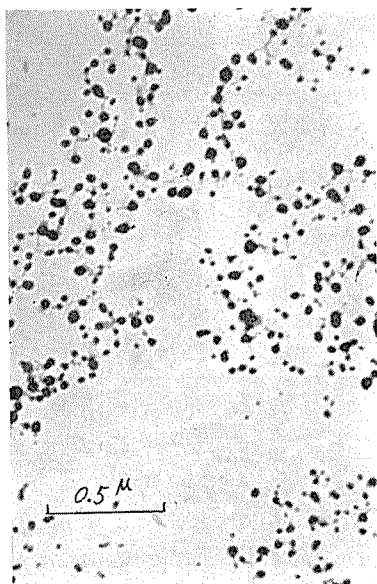


Fig. 4 Electron micrograph of fresh AgI colloid particles.

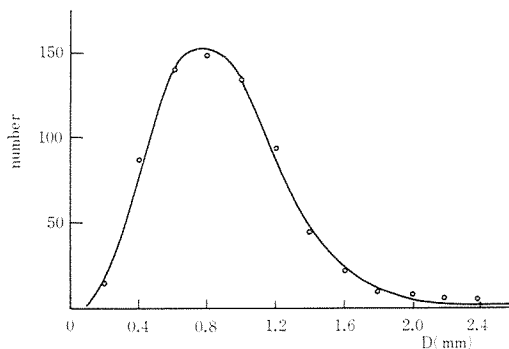


Fig. 5 Distribution of diameter D of fresh AgI colloid particle.

and the observation (3, 25, 52, 100, 143, 191, 264, 336 hr), the turbidity τ (1/cm) can be determined by the definition.

$$\tau = \frac{1}{0.4343 l} (2 - \log_{10} T). \quad (6)$$

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

$$\tau = kR^{n-1}/\lambda_o^n, \quad (7)$$

where, l : layer thickness of sol (1 cm in this study),

R : radius of the particle,

λ_o : wavelength in solvent, namely, in water in this study,

k : proportional constant unrelated with λ_o .

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

$$n = -\frac{\Delta \log \tau}{\Delta \log \lambda_o} = -\frac{\Delta \log \tau}{\Delta \log \lambda}. \quad (8)$$

As shown in Fig. 6, each curve is not exact linear owing to the absorptions at the wavelength 422.5 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 680 nm (i. e. $\lambda_o = 510$ nm), where n is 4.00 in the fresh sol. The values of n are listed in Table 5 varying from 4.0 to 3.33.

When n is 4.0, the well-known formula of Rayleigh is applicable.^{3~5)}

$$\tau = \frac{24\pi^3 NV^2}{\lambda_o^4} \left(\frac{m^2 - 1}{m^2 + 2} \right)^2 = \frac{32\pi^4 NV R^3}{\lambda_o^4} \left(\frac{m^2 - 1}{m^2 + 2} \right)^2, \quad (9)$$

where, m : ratio of the refractive index of the particle and that of solvent ($m = 1.72$ in this experiment),

N : number of the particles in unit volume,

V : volume of a particle.

The molecular weight and the density of AgI are 235 and 5.67 (g/cm³), so NV , the volume fractions of 2.22 and 4.44 mM/l of AgI sol are 9.20×10^{-5} (cm³) and 18.40×10^{-5} (cm³) respectively.

When R grows larger, n becomes smaller than 4.0. The relations between n

Table 5 Values of n and R of aged AgI sol

Conc. (mM/l)	t (hr)	3	25	52	100	143	191	264	336
2.22	n	4.0	4.0	4.0	4.0	4.0	3.9	3.7	3.4
	R (nm)	25.7	31.2	33.8	37.3	40.4			
4.44	n	4.0	4.0	4.0	4.0	3.87	3.66	3.5	3.33
	R (nm)	25.7	30.7	34.1	37.5				

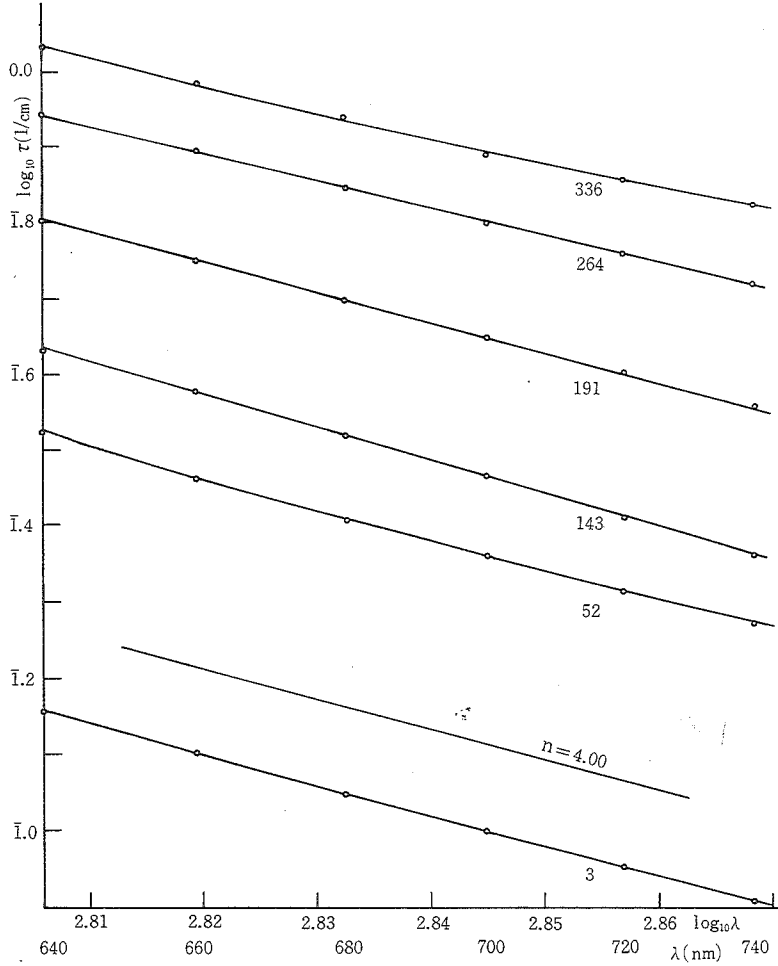


Fig. 6 Relation between $\log_{10} \tau$ (τ : turbidity) and $\log_{10} \lambda$ (λ : wavelength in air) in case of 2.22 mM/l AgI sol. Figures indicate the ageing time t (hr).

and R have already been reported by some researchers with several other substances.⁷⁾

In case of $n=4.0$, the radius of particle R (nm) can be obtained from Rayleigh's formula (9) or from the value of τ (1/cm) as follows:

$$\begin{aligned} 3 \cdot \log_{10} R &= 5.1797 - \log_{10} \tau, \quad (2.22 \text{ mM/l}) \\ 3 \cdot \log_{10} R &= 4.8786 - \log_{10} \tau, \quad (4.44 \text{ mM/l}) \end{aligned} \quad (10)$$

and the results are listed in Table 5. The radius of the particle of fresh sol is 25.7 nm and is twice of that obtained from the electron microscope. This is due to the exception of the massive particles from the calculation of radius in the latter.

Radius of the large particles

When R , radius of the particle of sol, regarding indefinite massive forms as spheres, is larger than 40 nm, Rayleigh's formulae (9)~(10) are not applicable and n , index of λ_0 , takes smaller values than 4.0. In the present experiment of the author's, R can not be obtained from the empirical formula (7). But the author's formula

$$1/\tau\lambda_0^2 = a\lambda_0 - b \quad (11)$$

can satisfactorily be applied as shown in Fig. 7. The average errors between the left side and the right side of (11) are 5% approximately within the range of λ 620~760(nm). The author, moreover, educes that the radius R will be decided from the constant a or b which decreases it's value monotonously with time.

Therefore the relation $a=k/R^2$ is at first considered supposing k is dimensionless, but the values of R from this relation do not agree well with the results from Rayleigh's formula in the range of $n=4.0$. A satisfactory agreement of R can be obtained between the relation of $a=k/R^2$, where constant k has the dimension of [L], and the results from (10).

Similar results are obtained in case of b as listed in Table 6.

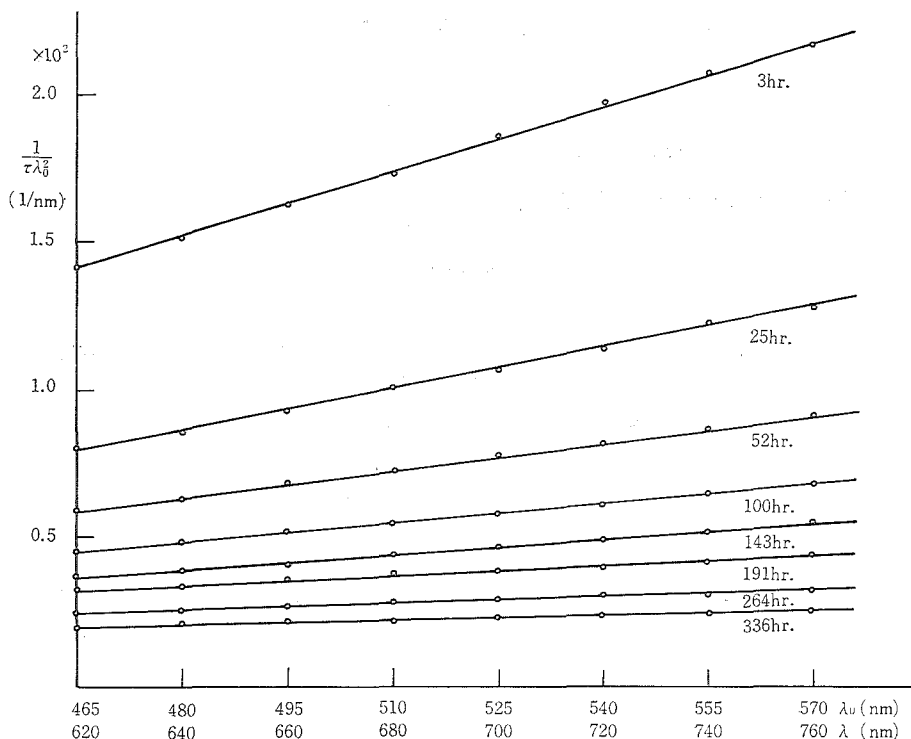


Fig. 7 $1/\tau\lambda_0^2 = a\lambda_0 - b$ (4.44 mM/l)

Table 6 Values of a , b and R of aged AgI sol

Conc. (mM/l)	t (hr)	3	25	52	100	143	191	264	336
2, 22 ($k=2.249 \times 10^4$ (nm) $k'=565.3 \times 10^4$ (nm ²))	a (nm ⁻²)	1,325	0.719	0.612	0.475	0.405	0.302	0.177	0.125
	b (nm ⁻¹)	333	172	164	131	114	77.7	35.9	20.0
	$R=(k/a)^{1/3}$ (nm)	25.7	31.6	33.3	36.2	38.2	42.1	50.2	56.5
	$R=(k'/b)^{1/3}$ (nm)	25.7	32.0	32.6	35.1	36.7	41.7	54.0	65.6
4, 44 ($k=1.231 \times 10^4$ (nm) $k'=332.7 \times 10^4$ (nm ²))	a (nm ⁻²)	0.725	0.479	0.310	0.238	0.179	0.125	0.085	0.063
	b (nm ⁻¹)	196	143	85.6	66.2	46.2	26.0	15.6	10.0
	$R=(k/a)^{1/3}$ (nm)	25.7	29.5	34.1	37.3	41.0	46.2	52.5	58.0
	$R=(k'/b)^{1/3}$ (nm)	25.7	28.6	33.9	36.9	41.6	50.4	59.7	69.3

Therefore, the author determines the following formula as more concrete than (11),

$$1/\tau\lambda_o^2 = k\lambda_o/R^3 - k'/R^3, \quad (12)$$

where k and k' are proportional constants unrelated with R and λ_o .

As shown in Fig. 7 and Table 6, the value of k/R^3 decreases according to the time elapsed, and during this time the particles grow larger, and the first term of the right side is turned out to be neglected at last, then b turns into negative and the turbidity τ and R^3/λ_o^2 are in proportion.

With reference to the coagulation of AgI sol added by a cationic surfacant, the author published the following formula in 1957,

$$1/\tau\lambda_o^2 = k\lambda_o/R^2 + k'/R^4, \quad (13)$$

where k/R^2 decreases also with time.⁸⁾

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Summary

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