*The Mechanism of the Gelation of a Lead Aldose-cysteinate Solution**

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Previous papers have described studies of the properties of the gel and the structure of lead aldose-cysteinate[1]. On measuring the rigidity of the gel, the pH value of a lead glucose-cysteinate solution was found to vary with the lapse of time, as is shown in Table I. From this fact, it was suggested that the internal structure of a lead glucose-cysteinate solution, which appeared to be transparent initially, might also change with the lapse of time.

In this paper, the study of the mechanism of gelation deals with the measurement of such various developments as the pH value, the conductivity, the optical density, and the gelation time.

Experimental

Materials.—All materials used are the same as have been described in the previous papers[1].

Apparatus.—The measurements of the pH value, the conductivity, and the optical density were carried out with a portable pH meter, a Yanagimoto conductometer, model MY-6, and an Erma Lippich Polarimeter respectively. The measurements of volume change were carried out with a 25 ml. pycnometer with an attached, graduated glass tube (0.0~0.1 ml.) shown in Fig. 1.

Procedure.—All the measurements were carried out from the time when a solution of lead salt was mixed with a solution of HSC at a constant temperature in the thermostats. The different pH value of the solution was adjusted by the addition of an appropriate amount of nitric acid or sodium hydroxide. Re-distilled water ($2.0\times10^5\ \Omega\cdot$cm.) was used for conductivity water measurements.

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* Gelation of Lead Aldose-cysteinate: Part III.

[1] F. Takahashi and J. Mizuguchi, This Bulletin 35, 1823 (1962).

TABLE I. pH CHANGE

0.06 M NaGC, 0.03 M $Pb(CH_3COO)_2$ or $Pb(NO_3)_2$, appropriate amount of HNO_3 or NaOH. 25°C. Rigidity was measured after 3 hr. from the gelation time.

pH		The gelation time	Rigidity
Initial	Final (after gelation)	min.	g./cm²
3.6	3.3	Not form gel	—
4.2	3.3	5.5	65
4.8	3.5	4	140
5.2	3.7	5	200
5.5	4.4	8	260
6.0	5.3	9	300
6.8	6.6	8.5	150
7.6	7.5	10	75
8.0	8.5	5	70
8.4	8.7	3	125
9.2	9.9	4	155
10.0	10.3	10	125
10.7	10.6	1 day	55

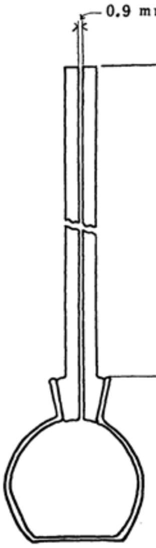


Fig. 1

All the measurements of the gelation time were carried out with test tubes in which a solution containing 0.15 to 2.5 ml. of 0.2 M NaGC** or 0.05 M NaGaC** and 0.15 to 2.5 ml. of 0.1 or 0.2 M lead acetate or nitrate was diluted to 5.0 ml. with distilled water. The mixtures were allowed to stand for a while. The time when a mixture lost fluidity was adopted as the gelation time.

Precipitates obtained in the pH Range between 8 and 10. — White precipitates were obtained when 10 ml. of 0.2 M lead acetate was added to a mixture of 10 ml. of 0.2 M NaGC and 30 ml. of 0.1 M sodium hydroxide. The precipitates were filtered and washed with a little amount of water and then with methanol as fast as possible for fear that precipitates might redissolved; yield, 0.40 g.

Found: C, 13.1; H, 2.1; N, 1.6; ash, 71.2%.

Results

pH Value. — In the pH range below 8, the lower the initial pH value, the more this pH

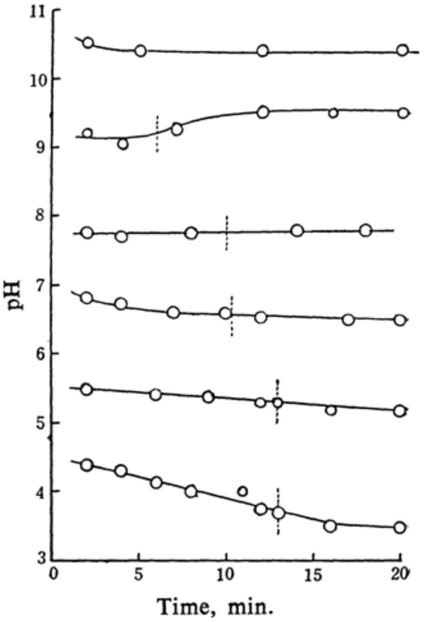


Fig. 2. pH change.
0.04 M NaGC, 0.04 M lead salt
The sign ⋮ denotes the gelation time.

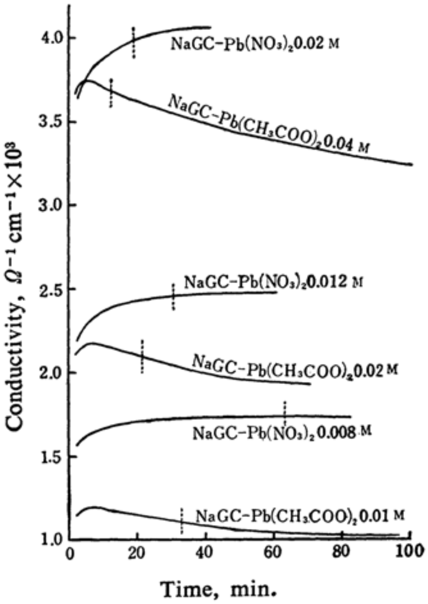


Fig. 3. Conductivity change.
The sign ⋮ denotes the gelation time.
25°C.

** See This Bulletin 35, 1819 (1962).

value gradually decreased with the lapse of time. In the pH range between 8 and 10, white precipitates were obtained. These precipitates were gradually redissolved with the rise of the pH value. The results are shown in Fig. 2.

From the analytical results, the precipitates were found to be neither pure lead glucose-cysteinates, the lead content of which is less than 41%, nor pure lead hydroxide. It is seen that the precipitates presumably consist of lead hydroxide and lead glucose-cysteinate coprecipitated.

Conductivity and Optical Density.—The conductivity of the mixture of NaGC and lead acetate gradually. In the mixture of NaGC and lead nitrate, the conductivity increased initially and then stayed constant (Fig. 3).

The mutarotation toward dextrorotary occurred in every case. Optical rotation could not determined after gelation (Fig. 4).

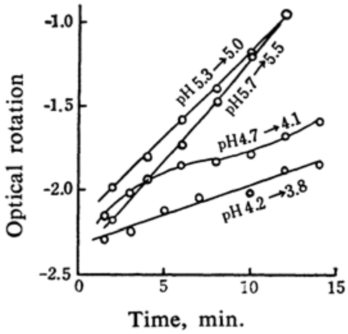


Fig. 4. Optical rotation change. 0.04 M NaGC, 0.04 M lead salt. 4 dm. tube, 20～24°C.

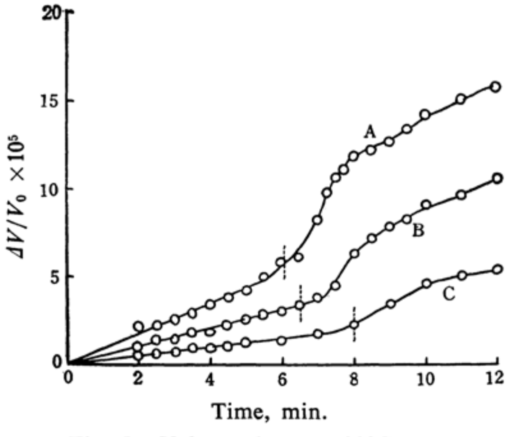


Fig. 5. Volume change. 20°C

The sign ⁝ denotes the gelation time.

	NaGC	Pb(CH$_3$COO)$_2$
A	0.50 M	0.50 M
B	0.33 M	0.33 M
C	0.20 M	0.20 M

Volume Change.—In the case of the mixture of NaGC and lead acetate, the volume of the mixture increased proportionally with the lapse of time before gelation. The rate of increase of the volume rose remarkably after gelation. After about an hour, however, the rate of increase slowed down. The results are shown in Fig. 5.

In the case of the mixture of NaGC and lead nitrate, the increase also occurs, but it was not proportional to the lapse of time.

The Gelation Time.—In every case, the gelation time was proportional to the reciprocal

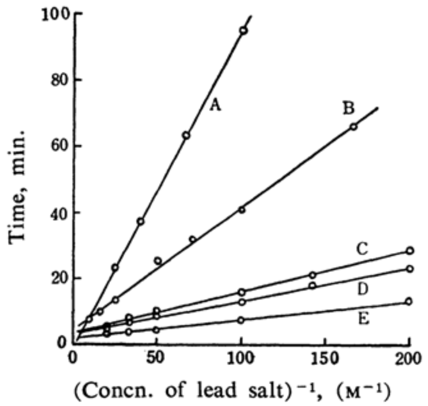


Fig. 6. Effect of concentration on the gelation time.

A NaG$_a$C : Pb(CH$_3$COO)$_2$=1 : 1, 25°C
B NaGC : Pb(CH$_3$COO)$_2$=1 : 1, 25°C
C NaGC : Pb(CH$_3$COO)$_2$=2 : 1, 25°C
D NaGC : Pb(NO$_3$)$_2$=2 : 1, 25°C
E NaGC : Pb(CH$_3$COO)$_2$=2 : 1, 35°C

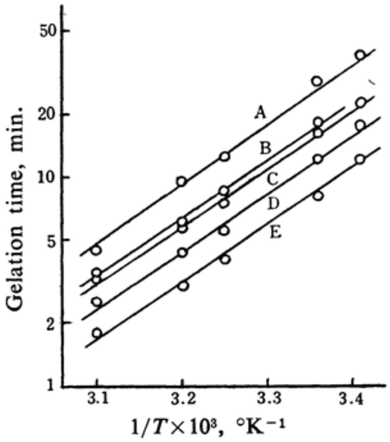
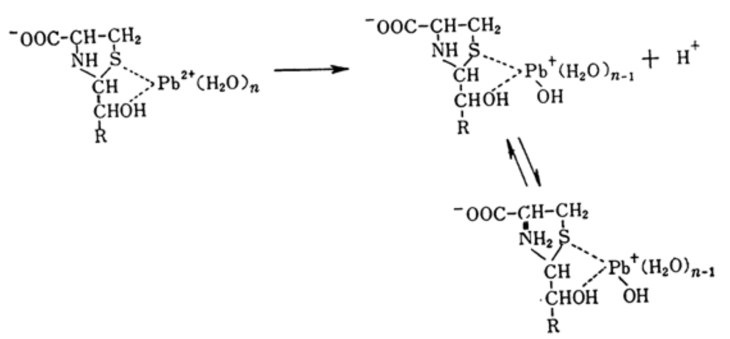


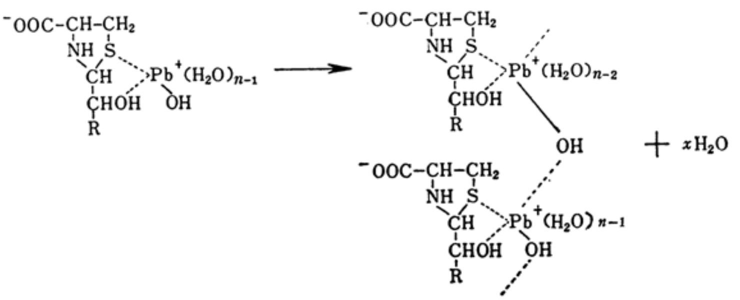
Fig. 7. Effect of temperature on the gelation time.

	NaGC	Pb(CH$_3$COO)$_2$
A	0.03 M	0.06 M
B	0.03 M	0.03 M
C	0.02 M	0.01 M
D	0.03 M	0.01 M
E	0.06 M	0.03 M



(1)

R: -(CHOH)$_3$-CH$_2$OH



(2)

of the concentration of lead salt (Fig. 6). Regarding temperatures between 20 to 50°C, straight lines are given in Fig. 7.

Discussion

In the previous paper(1), Eq. 1 was assumed from the fact that lead glucose-cysteinate hydroxide was isolated from the solution of NaGC and lead acetate.

The "ol" structure has been proposed by Hall and Eyring(2), who have studied the conductance of chromic salts in solution. It can be assumed that the "olation" of lead glucose-cysteinate occurs by the same mechanism as that of the hexaaquo chromic ion. Accordingly, the complex ion of hydrated lead glucose-cysteinate may be transformed into an "ol" structure with dehydration (Eq. 2). Perhaps the gelation occurs when an infinite three-dimensional structure is formed by olation.

The "olated" lead glucose-cysteinate so formed has to be removed from the system of an equilibrium state. Equation 1 may transfer to the right side in the pH value range between 3.8 and 8, and the concentration of protons may increase. In the pH value range between 8 and 10, the pH value of the solution may rise because of a reaction as is shown in the following equation:

$$\mathrm{Pb(OH)_2 + GC^- \rightarrow PbGCOH + OH^-} \qquad (3)$$

In the solution containing NaGC and lead acetate, the acetate ion shows the buffer action against the proton liberated by the olation:

$$\mathrm{CH_3COO^- + H^+ \rightleftharpoons CH_3COOH} \qquad (4)$$

In the solution containing NaGC and lead nitrate, the nitrate ion does not show any buffer action, so that the pH value of the solution may vary downward because of the liberation of the proton.

It is presumably seen that the optical rotation varies also because the olation occurs.

To verify the above assumptions, the kinetics of gelation was studied by determining the gelation time. The olation of the complex ion of hydrated lead glucose-cysteinate, accompanied with dehydration, was considered to be a process which follows the laws of ordinary chemical reaction. The reaction of the intermolecular combination is of the second order. Therefore, this reaction was expressed as follows:

$$-\mathrm{d}C/\mathrm{d}t = kC^2 \qquad (5)$$

where C is the concentration against the time, t, of the complex ion of lead glucose-cysteinate not "olated"; k is the velocity constant. From 5 and Arrhenius' equation, $k = A\cdot \mathrm{e}^{-\Delta E/RT}$, Eq. 6 was derived:

$$-(1/C_0)\cdot(C_0/C-1) = Kt\cdot \mathrm{e}^{-\Delta E/RT} \qquad (6)$$

where C_0 is the initial concentration of the complex ions of lead glucose-cysteinate and K is constant. This equation has already been

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2) H. T. Hall and H. Eyring, *J. Am. Chem. Soc.*, **72**, 782 (1950).

reported by Hurd and Letteron[3]. They permitted themselves to make an assumption in which C_0/C was constant. Therefore, the following equation was derived:

$$1/C_0=K't\cdot e^{-\Delta E/RT} \tag{7}$$

where K' is constant. The experimental results were found to obey Eq. 7.

It has been known that the volume occupied by a molecule of free water is larger than that occupied by one of bound water[4]. Therefore, it can be suggested that the dehydration makes for a volume increase of the solution and that the rate of olation is parallel to the amount of volume increase. Regarding the gelation time, the concentration of olated lead glucose-cysteinate, C_0-C, is parallel to the ratio of the volume increase to the initial volume; that is,

$$C_0-C=B(\Delta V_t/V_0) \tag{8}$$

where B is constant, ΔV_t is the amount of volume increase at the gelation time, and V_0 is the initial volume. Both sides of Eq. 8 may be divided by C_0. Therefore,

$$1-C/C_0=B(\Delta V_t/V_0)/C_0 \tag{9}$$

The $(\Delta V_t/V_0)/C_0$ calculated from the data of Fig. 5 shows almost constant values (Table II).

TABLE II. VOLUME CHANGE

Concn. of lead aldose-cysteinate C_0, M	$\dfrac{\Delta V_t}{V_0}$	$\dfrac{\Delta V_t}{V_0}\cdot\dfrac{1}{C_0}$
0.50	5.7×10^{-4}	$1.1_4\times10^{-3}$
0.33	3.4×10^{-4}	$1.0_3\times10^{-3}$
0.20	2.1×10^{-4}	$1.0_5\times10^{-3}$

The assumptions concerning the mechanism of gelation seem to have been verified by the determination of the gelation time.

Summary

The mechanism of the gelation of a solution containing aldose-cysteine and lead salt was studied by measuring various developments such as the pH value, the conductivity, the optical density, and the gelation time. From these results, it was suggested that the gelation occurred when the complex ion of hydrated lead glucose-cysteinate was transformed into an "ol" structure with dehydration. The process of this olation was found to follow the laws of ordinary chemical reaction. The reaction was of the second order.

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[3] C. B. Hurd and H. A. Letteron, *J. Phys. Chem.*, **36**, 604 (1932).

[4] T. Yasunaga and T. Sasaki, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zassi*), **70**, 379 (1949).