

STUDIES ON ORGANOGELS (I)

The Gel* from Cadmium Oleate Oleic Acid Solution

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Introduction.

Some years ago the methods of dispersing various kinds of metals or salts in oils and fats were discovered by M. Odagiri, H. Baba, Y. Miyazaki, T. Kiyota and T. Maekita under Professor S. Horiba's guidance¹⁾⁻⁹⁾ and the methods have already been applied to the preparation of colloidal medicines and bottom paints. One of these methods is a mechanical dispersion by a colloid mill. When cadmium amalgam is mechanically dispersed by this method in the mixture of olive oil and oleic acid, a gel is obtained.⁵⁾ In this case both metallic cadmium and oleic acid are indispensable for the formation of the gel. It is, therefore, considered that oleic acid reacts upon metallic cadmium and the oleate formed is gelatinized in the dispersion medium.

It has been reported⁶⁾⁻⁹⁾ that various kinds of metallic soaps are dissolved in nonpolar, or barely polar, organic solvents, such as benzene, toluene, carbon tetrachloride, chloroform, and liquid paraffin, and that from the solutions thus made a gel is obtained. But there is yet no report that a gel is obtained from either oleic acid or the mixture of oleic acid and olive oil in which a metallic soap is dissolved. The present author dissolved oleates of various metals in oleic acid or in the mixture of oleic acid and olive oil, and could obtain gels from oleates of zinc, mercury, silver, as well as cadmium, of which mercury and silver salts were remarkably unstable and apt to be reduced to pure metals.

In the present report the process of gelation, the properties, and the structure of the gel, and the mechanism of gelation will be discussed concerning the cadmium

* M. E. Laing and J. W. McBain discovered that sodium oleate water solution is unique among the gelling systems, in the fact that the gel can exist in two forms, the clear jelly and the opaque curd. (*J. Chem. Soc.*, 115, 1279 (1919); 117, 1506 (1920)). The gel from cadmium oleate oleic acid solution may belong to the opaque curd in its optical properties.

1) M. Odagiri, Japanese Patent No. 90132.

2) S. Horiba, M. Odagiri and T. Kiyota, Japanese Patent No. 97336, 97513, 98481, 100366, 101948, 105102, 109624.

3) S. Horiba, M. Odagiri, Y. Miyazaki and H. Baba, Japanese Patent No. 105655.

4) S. Horiba and T. Maekita, Japanese Patent No. 121701.

5) S. Horiba "Collections of Lectures of the Institute for Chemical Research" 9, 139 (1939).

6) A. E. König, *J. Am. Chem. Soc.*, 36, 951 (1914).

7) McBain and McClatchie, *J. Phys. Chem.*, 36, 2567 (1932).

8) C. J. Bower, *J. Ind. Eng. Chem.*, 29, 58 (1937).

9) A. S. C. Lawrence, *Trans. Farad. Soc.*, 34, 600 (1938).

oleate—oleic acid system, which requires many hours for gelatinization and is remarkably stable in the form of the gel (olive oil was not added in order to simplify the composition of the dispersion medium).

Experimental

A. Formation of Gel

Oleic acid used as the dispersion medium was obtained by collecting the fraction of E. Merck's purest oleic acid flowing out under vacuum distillation at 15 m.m. and 231—233°C. Its specific gravity was 0.89934 (11.5°C.) and its solidifying point 6—7°C.

Cadmium oleate** was prepared in oleic acid by the following procedure. Kahlbaum's cadmium nitrate was decomposed by heating into cadmium oxide, from which, after further heating in a pyrex tube under vacuum, the impurities, that were probably adsorbed, were removed as much as possible. Cadmium oxide thus obtained was added to oleic acid and heated under gradual rise of temperature. At 120—130°C. it foamed actively and after 10 minutes or so dark-brown cadmium oxide disappeared, and it became difficult to distinguish it from the pure dispersion medium even ultramicroscopically as well as with the naked eye. As the material seven kinds of solutions were used in the concentration range of 0—7.11%. The solutions which were greater than 4.42% in concentration became a gel at 11°C. or so in several days.

B. Characters of Gel

Though the gel of low concentration just formed is almost transparent to the naked eye, white turbidity increases with the lapse of time and with the increase of concentration.

When the gel is put in a thermostat and the temperature raised at the rate of about 2°C. per hour, it fuses at the temperatures shown in Table I.

Table I.

Concentration (wt. %)	Melting Point (°C)
4.42	30.0—31.8
5.10	31.5—33.5
7.11	33.5—35.3

Even if left for some months the gel can not be separated from the dispersion medium at the temperatures below the melting points, and the phenomenon of syneresis is hardly recognized. It is in this respect that the gel in question is different from the gels which have hitherto been

obtained from metallic soaps in organic solvents.

** Using cadmium oleate prepared by double decomposition of potassium oleate and cadmium acetate, the same results are obtained as in the case where cadmium oleate is formed by the reaction between oleic acid and cadmium oxide.

The specific gravity of the solution was measured by means of a pycnometer whose capacity was about 25 c.c. Variation in specific gravity was hardly recognized before and after the formation of the gel. The relation between specific gravity and concentration is given in Table II.

Table II

Concentration (wt. %)	0	0.82	2.05	3.28	4.42	5.1	7.11
Specific Gravity	0.8993	0.9006	0.9024	0.9043	0.9060	0.9070	0.9100

C. Structure of Gel

Fig. 1 is the micro-photograph of the gel of 4.42% in concentration taken by means of an ultramicroscope with a cardioid condenser. The distribution of the fibrous construction, which looks white in the figure, is fairly uneven.

D. Variation in Polarisation of the System during Gelation¹⁰⁾⁻¹³⁾.

When cadmium oleate oleic acid solution with a concentration just suitable to form a gel lost liquidity and was solidified by being left alone, it was examined as to the question whether the rate, at which the orientation polarisation was affected by the dipoles of polar molecules composing the system (the dipole moments of oleic acid and cadmium oleate molecules are $1.009 \cdot 10^{-18}$ e.s.u.¹⁴⁾ and $4.37 \cdot 10^{-19}$ e.s.u.¹⁵⁾ respectively), varied or not. To know whether there is any variation in polarisation during gelation, the measurement of dielectric constant is necessary.



Fig. 1. Microphotograph of Cd Oleate Oleic Acid Gel

Although there are many methods^{16),17)} for measuring the dielectric constant, the resonance method is most desirable, because it is said to give fairly precise values, and to be applicable even to somewhat conductive solution. Fig. 2 shows the electric circuits of the apparatus used to measure the dielectric constant by the resonance method. I is the oscillator, whose wave length was controlled by

10) H. Kallmann and W. Kreidle, *Z. physik. Chem.*, A, 159, 322 (1932).

11) G. S. Kistler, *J. Phys. Chem.*, 35, 815 (1931).

12) P. J. Deneke and H. R. Krut, *Kolloid-Z.*, 81, 62 (1937).

13) S. Lee and I. Sakurada, *J. Soc. Chem. Ind. Japan*, 38, 36 (1935).

14) G. R. Paranjpe and D. J. Daver, *Indian J. Phys.*, 12, 283 (1938).

15) W. Ostwald and R. Riedel, *Kolloid-Z.*, 69, 191 (1934).

16) N. Isegai, *This Journal*, 3, (Reviews) 111 (1929).

17) Y. Hoshino, *J. Electrochemical Assoc. Japan*, 7, 26, 67 (1939).

the coil L and the variable condenser C , using the Hartley circuit. The plate power supply was obtained by converting 100 a.c. voltage to 180 d.c. voltage through the rectifier K . II is the detector, whose sensitivity was increased by the regenerative method, and amplified in two stages with audiofrequency transformers (T_1 and T_2). The coil L of the oscillator was loosely coupled to the coil L_1 of the detector. By regulating a large variable condenser C_1 and a precise variable condenser C_2 which were connected in parallel with the tuned circuit, the turning spot was found at the point where a milli ammeter G indicated maximum deflection. The condenser C in which the material was to be put consisted of two cylinders of stainless steel arranged homocentrically and fixed together at the distance of about 1 m.m. with pieces of glass, and was kept in a glass vessel. In order to keep the temperature of the material constant during measurement, the measurement box was put in a far larger iron container which was immersed in a thermostat and earthed. The condenser was calibrated by air and purified benzene used as the standard. As the dielectric constant of air and purified benzene at the measuring temperature 11.5°C ., 1 and 2.298 were taken respectively. The material was, after the preparation, left to stand at room temperature for 30 minutes and then put in the thermostat kept at 11.5°C .; the measurement was begun 30 minutes later. The wave-length used was 173 meters.

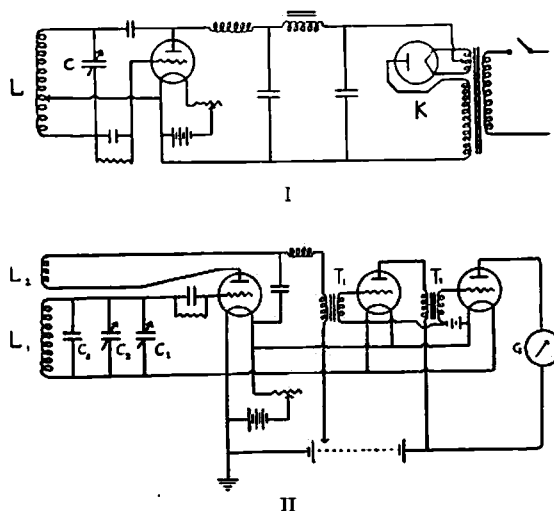


Fig. 2. Electric Circuits of the Apparatus for measuring Dielectric Constant,

- I. Oscillator
II. Detector

Table III gives the results obtained by measuring the variation of the dielectric

constant with time of cadmium oleate oleic acid solution at 11.5°C. in various concentrations.

Table II is visualized in Fig. 3 in order to elucidate the tendency of the change of the dielectric constants with time. The dielectric constant of the solution which is too dilute to form a gel hardly varies with time, but that of the solution of a concentration sufficient to form a gel shows a fairly remarkable decrease. It is clear from Fig. 3 that when concentration is sufficient for forming a gel the decrease of dielectric constant tends to set in at an almost fixed point.

Table III

0%		0.82%		2.05%		3.28%		4.42%		5.1%		7.11%	
Time (hour)	ϵ_{12}	Time (hour)	ϵ_{12}	Time (hour)	ϵ_{12}	Time (hour)	ϵ_{12}	Time (hour)	ϵ_{12}	Time (hour)	ϵ_{12}	Time (hour)	ϵ_{12}
0	2.442	0	2.456	0	2.477	0	2.505	0	2.532	0	2.546	0	2.578
1.5	2.443	1.5	2.457	1.5	2.478	3	2.506	3	2.533	3	2.546	2.5	2.579
7.5	2.443	7.5	2.455	5	2.479	4.5	2.507	7.5	2.534	5	2.548	4.5	2.579
15	2.442	15	2.455	8	2.479	5.5	2.507	11	2.534	8	2.546	6.5	2.578
32	2.442	32	2.455	12	2.479	10.5	2.508	21.5	2.533	17.5	2.544	10.5	2.576
68	2.443	60	2.454	23	2.479	27	2.505	26	2.532	23	2.544	21	2.566
90	2.442	96	2.455	31	2.478	36	2.503	32	2.532	27.5	2.542	25.5	2.558
				48	2.479	58	2.504	45	2.529	32.5	2.540	28.5	2.554
				72	2.478	72	2.504	58.5	2.527	45.5	2.536	33	2.551
				96	2.478	96	2.504	69	2.526	66	2.531	52	2.541
								84	2.526	71	2.530	57.5	2.539
								96	2.525	81.5	2.528	61.5	2.538
										90	2.530	95	2.534
										100	2.528	105	2.532
												117	2.530

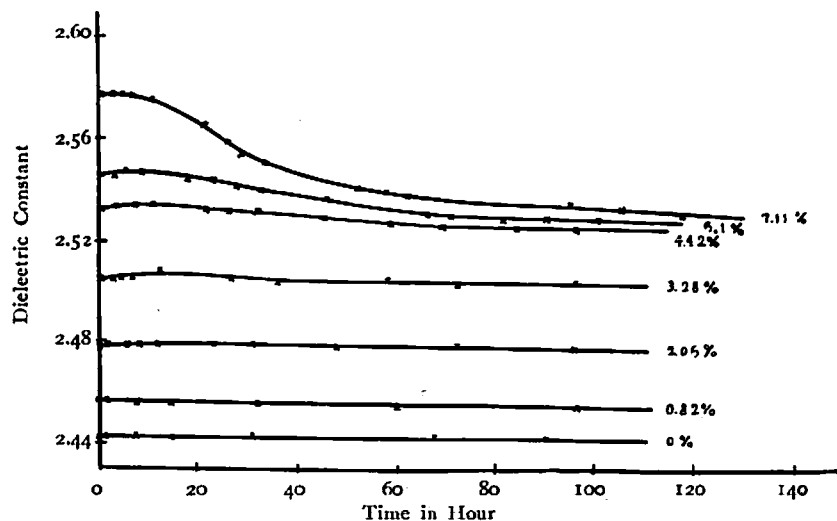


Fig. 3. Variation of Dielectric Constant with Time.

Consideration of the Result of the Experiments

This gel shows a fibrous structure as is clear from Fig. 1. Let us consider how such a structure is formed in the solution.

By examining the benzene solution of aluminium salts of homologous fatty acids, Wo. Ostwald and R. Riedel¹⁰⁾ found out the fact that the dipole moment of a highly viscid metallic soap in solution is, if measured in the benzene solution, smaller than the value given by Debye's theoretical formula which requires that the dipole moment of a molecule is proportional to the square root of its molecular weight. They attributed it to the cause that the high viscosity prevents the dipole of the metallic soap from contributing to the orientation polarisation. Although in the present case it is hard to know clearly in what state the polar molecules of cadmium oleate exist in oleic acid, a polar solvent, the fact that the dielectric constant decreases as shown in Table III and Fig. 3 according as the solution loses liquidity and is solidified may lead to the presumption that the progress of gelation is in parallel relation to the decrease of dielectric constant. If so, by investigating how the dielectric constant varies with time, it would not be impossible to discuss the mechanism of gelation from the view-point of its velocity.

Taking account of the tendency of the change of the dielectric constant shown in Fig. 3, the extrapolation was made. Let ${}_{\infty}\epsilon_{12}$ represent the value of ϵ_{12} , dielectric constant of the solution, in a sufficient lapse of time and let ${}_0\epsilon_{12}$ represent the value of ϵ_{12} at the beginning and P_1 , the difference between them is expressed as follows:

$$P_1 = {}_0\epsilon_{12} - {}_{\infty}\epsilon_{12} \quad (1)$$

The relation between P_1 and K , the concentration, is given in Table IV.

Table IV

K (wt. %)	0	0.82	2.05	3.28	4.42	5.1	7.11
P_1	0	-0.01	+0.01	-0.01	-0.07	-0.18	-0.48

Table IV shows that the value of P_1 is extremely small for the solution which is too dilute to form a gel, but that, for the solution sufficiently concentrated to form a gel, it is not only considerably large but increases according to the increase of K .

On the other hand, let us express the velocity of gelation by the change of dielectric constant as follows:

$$x = {}_0\epsilon_{12} - {}_t\epsilon_{12} \quad (2)$$

where ${}_t\epsilon_{12}$ is the value of ϵ_{12} after t hours from the beginning. The relation

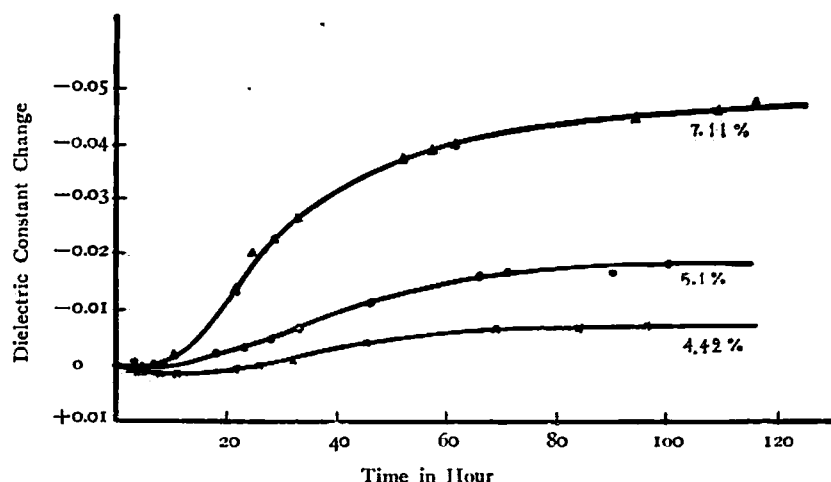


Fig. 4. Dielectric Constant Change during Gelation.

between α and t is shown in Fig. 4. The curves indicating the $\alpha-t$ relation, though different according to concentration, are equally apt to take the shape of letter S. Namely, the gelation velocity viewed from the stand-point of the change of dielectric constant, i.e. polarisation loss, is at first extremely low and then becomes high and finally low again.

If the association of polar molecules should proceed at uniform velocity from the beginning, the reason why the velocity is low in the earlier period of gelation as shown in Fig. 4 must lie in the manner of association, i.e. the so-called coassociation^{18),19)} in which some polar molecules, make their association without decreasing their own polarity. For an instance, if a single molecule whose dipole moment is μ associates with another molecule turned towards the same direction, these associated molecules now come to have about 2μ as the value for dipole moment. Accordingly, the case of such an association is, after all, scarcely different from the case in which two molecules exist separately, from the dielectric point of view.

As a group of associated molecules formed by coassociation still retain their polarity, it might probably grow longer and longer in the shape like a straight chain, unless either there occurs an association that destroys polarity or the association is obstructed by heat motion etc.

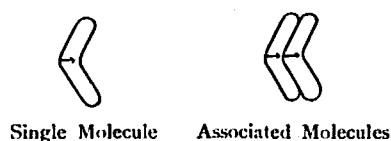


Fig. 5. Molecular Models Showing Coassociation of Cd Oleate

18) J. N. Wilson, *Chem. Rev.*, 25, 377 (1939).19) Mayer and Mark, "*Hochpolymere Chemie*," 99 (1940).

But, when the length of the group exceeds a certain limit, it will become difficult for the group to obey the direction of vibration of alternating electric field. This causes polarisation loss, and consequently the gelation velocity becomes higher from the view-point of the change of polarisation loss. The slender complex thus generated is considered to form, through intertwining, a fibrous structure such as shown in the micro-photograph of Fig. 1.

Summary

1) It has been found out that cadmium oleate forms a gel in oleic acid; and some characters of the gel have been investigated.

2) It has been recognized by means of an ultramicroscope that the gel is of fibrous structure.

3) The velocity of gelation has been examined by seeing how the decrease of the dielectric constant of the system during gelation varies with time, and the mechanism of gelation has been deduced in connection with the ultramicroscopic structure of the gel.

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