STUDIES IN INORGANO-ORGANIC GELS IN PINENE

Part IV. The Kinetics of Syneresis of Sodium Oleate Gels in Pinene

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GRAHAM[1] observed that when a freshly prepared gel of silicic acid is allowed to stand, it exudes liquid spontaneously. Later on, many gels of widely different properties were found to exhibit this extraordinary phenomenon called " syneresis ".

Holmes, Kaufmann and Nicholas[2] were the first to investigate the syneresis of silicic acid gels systematically. They found that it increases with an increase in the concentration of silicic acid and mineral acids, but decreases in the presence of excess of organic acids. Maximum syneresis was observed with moderately basic gels, the liquid exuded being, in some instances, as much as 90% of the total volume of the gel. Later, Fergusson and Appleby[3] studied the kinetics of the syneretic process of the silicic acid gel by a new type of apparatus. They found that the volume of the liquid exuded is independent of the shape and free external surface of the gel and is exactly equal to the contraction suffered by the gel. Further they found that the more rapid is the setting of the gel, the greater is the initial velocity of syneresis and shorter is the period which the gels take to start synerising which follows an autocatalytic course. The influence of temperature on syneresis is very marked, the velocity of syneresis being approximately doubled for each 10° rise in temperature.

In two recent communications Bonnel[4] has described a synerometer by which the velocity of syneresis and the final equilibrium can be quantitatively determined. He finds that, within certain limits, the initial velocity of syneresis and the final volume of liquid exuded increase with increasing silica content.

The syneresis of a number of inorganic jellies has been studied by Prakash and Dhar[5] who find that it increases with time until it reaches a maximum value and is enhanced with the addition of increasing amounts of electrolytes and with rise of temperature.

The velocity of syneresis and the total amount of liquid exuded have also been measured in the case of organic gels. Lipatov[6] carried out a series of systematic investigations on the syneresis of geranin gels and found that the velocity of syneresis increases with (1) rise in temperature and (2) increase in the concentration of the gel; with more concentrated gels syneresis starts earlier but the total amount of liquid exuded is less. He also found that the addition of alcohol accelerates the process of syneresis, the degree of acceleration increasing with the increasing amount of alcohol in the gel. On examining the constitution of the synereticum exuded by the geranin gels he found it to consist of small quantities of single and double molecules of the dyestuff.

The syneresis of viscose gels has been studied by Mukoyama[7] and Lipatov[8]; both of them observed that syneresis appears earlier with dilute gels and at higher temperatures.

It was observed by Prasad and Mathur[9] that gels of sodium oleate in pinene exhibit the phenomenon of syneresis to a marked extent. In the present investigation, the velocity of syneresis of these gels has been systematically studied, and the effects of several factors, such as concentration, temperature, area of exposed surface, and others, on the velocity of syneresis have also been determined, and the nature of the syneretic liquid has been examined.

EXPERIMENTAL TECHNIQUE

The syneresis of the sodium oleate gels in pinene is peculiarly different from those of the gels mentioned before. These gels leave the sides of the tube soon after setting and the syneresis, which starts immediately, is spontaneous. Hence, the method of pouring out the liquid adopted by several previous workers for the measurement of the velocity of syneresis could not be used in the present case because the synereticum which surrounds the gel could not be taken out to the last drop without allowing the gels to fall out of the tube.

In Bonnel's method, the gel is allowed to set in a cone coated with a thin layer of vaseline to prevent adhesion and is then transferred to another cone, which is previously saturated with the syneretic liquid of a similar gel, and weighed. The cone containing the gel is placed inside the synerometer wherein it could be conveniently weighed and the amount of syneresis determined. Since sodium oleate gels in pinene are very soft, particularly the less concentrated ones, they do not keep their stiff form on being transferred from one container to the other, and a little squeezing in the process of transference increases the amount of synereticum to a large extent. Hence Bonnel's method was also found unsuitable in the case of these gels.

The procedure described below was found to give satisfactory results. Sodium oleate and pinene used in this investigation were products of Messrs. E. Merck and Eastman Kodak & Co., respectively. Gel-forming solutions of sodium oleate in 8·6 g. of pinene were prepared in test-tubes of the same diameter ($2r = 1 \cdot 45$ cm.) as described in a previous communication[10]; the tubes were tightly corked and then kept in a water-thermostat maintained at a constant temperature. After a known interval of time the tube was removed from the thermostat, wiped till the outside was completely dry, then allowed to cool down to room-temperature, and finally weighed accurately. Then the synereticum at the top of the gels was removed by absorption with filter-paper, small sheets of which were rolled up in the form of cylinders and were lowered down vertically in the test-tube till they just approached the surface of the liquid. The filter-papers were changed from time to time as they become saturated with the exuded liquid. Precautions were taken that the filter-papers did not touch the surface of the gel. When as much of the exuded liquid as possible was absorbed the tube was weighed again, and the loss in weight due to the removal of the exuded liquid was determined. Fresh samples of gels were taken for each reading.

On using rolls of filter-papers of different ash content (0·00083 g., 0·000076 g., and 0·000089 g.) for absorbing the syneretic liquid, it was found that the accuracy of the results was not vitiated in any way. Filter-paper of 0·00083 g. ash content was used throughout the investigation.

The validity of the technique adopted for measuring the velocity of syneresis was confirmed by repeating an experiment several times under identical conditions. The technique may appear crude at first sight, but the probable error in the reproducibility of results was found to be fairly low, being of the order of ±5%.

A study of the effect of the cross-section of the tube which contained the gel-forming mixture showed that for any given concentration of the soap and at any given interval of time after syneresis has started, the amount of synereticum is slightly greater, larger is the cross-section of the test-tube. These observations are in agreement with those of Kuhn.[11]

The refractive index of the synereticum exuded by gels of different concentrations of soaps at different intervals of time and at several temperatures was measured by means of a very sensitive refractometer (Adam Hilger & Co.). It was found that (i) the concentration of the soap in the gel, (ii) the temperature at which the gel is allowed to synerise, and (iii) the intervals of time at which the amount of syneresis is measured, have no effect on the refractive index of the synerised liquid. The values differ only in the fourth place of decimals and the mean value is 1·4669. The refractive index of the pinene used was 1·4658, and that of pinene, saturated with sodium oleate at 30°, 1·4668, a value which agrees exceedingly well with the value of refractive index of the synereticum. This shows that the synerised liquid is only a saturated solution of sodium oleate in pinene, the saturation being with respect to 30°.

Some of the results obtained are given in Tables I to IV.

TABLE I

Velocity of syneresis of sodium oleate gels at 30° *C.*

Time (hrs.)	0·05 g.	0·08 g.	0·09 g.	0·10 g.	0·125 g.	0·15 g.
	g.	g.	g.	g.	g.	g.
½	2·999	2·523	2·203	1·875	1·585	1·413
¾	3·252	2·756	2·371	2·065	1·845	1·622
1	3·451	2·898	2·556	2·239	2·004	1·758
2	3·862	3·428	3·090	2·723	2·360	2·239
3	4·127	3·631	3·428	3·055	2·675	2·512
5	4·698	4·174	3·936	3·540	3·199	2·951
7	4·955	4·519	4·421	3·890	3·548	3·311

TABLE II

Velocity of syneresis of sodium oleate gels at 70° C.

Time (hrs.)	0·05 g.	0·08 g.	0·09 g.	0·10 g.	0·125 g.	0·15 g.
	g.	g.	g.	g.	g.	g.
½	2·452	1·970	1·759	1·550	1·304	1·148
¾	2·691	2·165	1·948	1·742	1·480	1·300
1	2·854	2·319	2·090	1·863	1·624	1·398
2	3·273	2·726	2·480	2·240	1·979	1·777
3	3·551	3·020	2·787	2·515	2·265	2·020
5	3·887	3·389	3·164	2·887	2·662	2·372
7	4·164	3·677	3·470	3·196	2·949	2·658

TABLE III

Syneresis of gels containing 0·08 g. *of sodium oleate*

Time (hrs.)	−10°	30°	40°	50°	60°	70°
	g.	g.	g.	g.	g.	g.
½	3·236	2·523	2·216	2·113	1·996	1·970
¾	3·548	2·756	2·528	2·320	2·238	2·165
1	3·846	2·898	2·657	2·486	2·425	2·319
2	4·571	3·428	3·012	2·952	2·957	2·726
3	5·070	3·631	3·361	3·234	3·311	3·020
5	5·754	4·174	3·820	3·674	3·951	3·389
7	6·310	4·519	4·338	3·940	3·847	3·677

TABLE IV

Syneresis of gels containing 0·125 g. *of sodium oleate*

Time (hrs.)	−10°	30°	40°	50°	60°	70°
	g.	g.	g.	g.	g.	g.
½	2·399	1·585	1·421	1·418	1·350	1·304
¾	2·692	1·845	1·661	1·584	1·569	1·480
1	2·917	2·004	1·821	1·736	1·737	1·624
2	3·548	2·360	2·212	2·188	2·114	1·979
3	4·027	2·675	2·453	2·450	2·402	2·265
5	4·732	3·199	2·976	2·888	2·820	2·662
7	5·188	3·548	3·460	3·177	3·054	2·949

DISCUSSION OF RESULTS

The curves obtained on plotting the amount of synereticum against time show that the rate of exudation of the syneretic liquid is rapid in the beginning and slows down continuously with time. In no case are the curves S-shaped as was found by Fergusson and Appleby[3] in the case of silicic acid gels. The amount of liquid exuded at any temperature at any given interval of time after syneresis has started is smaller, larger is the soap content of the gel and the total amount of synereticum exuded in 7 hours is greatest from the most dilute gels and least from the most concentrated ones. These results are quite contrary to those obtained with gels of silicic acid.

The effect of temperature on the velocity of syneresis is also marked. The velocity of syneresis is greater, lower is the temperature at which the gel is allowed to synerise. These results are again in contradiction to those obtained with silicic acid gels.

It was observed that the gels of other soaps in pinene are quite firm and do not show the phenomenon of syneresis as remarkably as do the gels of sodium oleate in pinene. Further, gels of sodium oleate and sodium stearate in xylene synerise markedly, probably to an equal or greater extent than those of sodium oleate in pinene, while gels of sodium oleate and sodium stearate in nujol do not synerise at all. Thus it would appear that the phenomenon of syneresis is not related either to the constitution of the gel-forming substance or to the nature of the dispersion medium, but it seems to be a characteristic of the gel-forming system itself. It was further observed that when small amounts of certain addition agents (other soaps, non-aqueous media, etc.) are added to the gel-forming solutions of sodium oleate in pinene, the syneresis is either accelerated or retarded. These effects are being systematically investigated into.

The solution of sodium oleate in pinene is a molecular solution of the soap at a high temperature and as it is gradually cooled, it first becomes saturated, and then super-saturated with the soap, and subsequently the soap goes over to the colloidal state with the saturated solution as the dispersion medium; on further cooling, further super-saturation causes an increase in the size and probably the number of the colloidal particles. All the aforesaid changes take place more rapidly the lower the temperature to which the solution is allowed to cool. An increase in the amount of the soap in the gel-forming mixture as well as cooling to a lower temperature increase the number of micelles in the solution.

The colloidal particles (associated phase of Arsem[12]) in a gel are bound to each other by residual valencies more loosely and irregularly than in a crystal. Further, progressive association and orientation or alteration of the structural units continue during and after the setting of gels. If the initial arrangement of the structural units of a gel is unstable, that is, the force of residual valencies (binding) is weak, the shrinkage of the gel would take place, which would cause the exudation of liquid. Hamaker[13] has shown that the magnitude and direction of the force between the colloidal particles can be determined from the curve characteristic for a particular colloid, obtained by plotting energy against the distance between the particles. Usher[14] argues that if a solid framework of a rigid two-phase system becomes thickened in consequence of an internal packing, the system must itself become physically heterogeneous, which appears to him to be an adequate explanation of syneresis.

Assuming the validity of the theories of syneresis given above, it can be concluded that a solution of sodium oleate in pinene, on cooling, becomes so thickened in consequence of the internal packing that the system becomes physically invisibly heterogeneous and the exudation of the interstitial liquid phase takes place; hence, syneresis is more prominent at a lower temperature than at a higher one. It is not quite easy to explain the effect of concentration of sodium oleate on the velocity of syneresis on this theory, but the observed results show that the linking of the structural units in the dilute gels is not as strong as in the concentrated ones.

Syneresis has been considered to be a phenomenon analogous to the imbibition of liquid by non-swelling gels (*cf.* Hardy[15]). The most important work on the imbibition of liquids by gels is that of the rise of water in strips of filter-paper. It has been found in most cases that the relation between the height x, to which a liquid rises in time t, is to a great extent represented by the relation

$$x^a = kt \qquad \text{(i)}$$

where a is approximately equal to 2.

According to the fibrillar theory of gel structure a gel consists of fine capillaries. This view has been confirmed by Bell and Cameron[16] who showed that the velocity of rise of liquid in a gel is governed by the same laws which hold for the flow of a liquid in capillaries and the relation (i) is also applicable. It is, therefore, reasonable to expect that the relation (i) will also hold for the exudation of liquid from the capillaries of a gel. On plotting the values of log x (x is the amount of synereticum exuded in time t) against log t, straight lines were obtained in all cases; this shows that the above relation (i) holds true in the case of the syneresis of gels of sodium oleate in pinene.

TABLE V

Values of 'a'

Concentration c (in g.)	- 10° C.	30° C.	40° C.	50° C.	60° C.	70° C.
0·05	5·29	5·31			5·35	5·26
0·08	4·08	4·42	4·09	4·17	4·07	4·17
0·09	3·89	3·75	4·08	3·85	3·85	4·03
0·10	3·52	3·54	3·38	3·51	3·64	3·64
0·125	3·30	3·29	3·06	3·23	3·33	3·23
0·15	3·12	3·14	2·93	3·17	3·17	3·23

The values of a (given in Table V) obtained from the slopes of the various straight lines vary from 3 to 5 as the soap content in the system is decreased; it will be noticed, however, that for the same soap content the value of a appears to be constant at all temperatures. While attempting to see if there exists any relationship between the soap content c of the gel and the term a, it was observed that a varies with c as

$$a = \frac{k_1}{c} + k_2, \qquad \text{(ii)}$$

where k_1 and k_2 are constants; their values were computed and found to be 0·17 and 1·93 respectively. Hence the relation (i) is represented as

$$x^{\left(\frac{k_1}{c} + k_2\right)} = kt \qquad \text{(iii)}$$

For large values of c, a will be nearly equal to 2. The equation (iii) is of a more general character than the equation (i).

An attempt was made to see if the exudation of liquid from the sodium oleate gels follows the law of the first-order reaction. For this purpose, the values of the uni-molecular constant (K_m) were calculated for different intervals of time in a given experiment and it was found that these values decrease as the period of syneresis increases. It was also noticed that the velocity (x/t) of syneresis decreases with time. Consequently the values of x/t were plotted against K_m and the curves obtained were found to be straight lines.

The velocity of syneresis is, therefore, given by

$$\frac{dx}{dt} = \frac{k_3 (a - x)}{a - x - k_4}, \qquad \text{(iv)}$$

where a = amount of pinene initially present;

x = amount of pinene exuded at time t;

k_3, k_4 = constants.

This is an equation which is similar to that of an inhibited change. The inhibition of the velocity of syneresis of sodium oleate gels in pinene can be explained as follows.

It has been stated earlier that the synereticum exuded at any interval of time and at any temperature by a gel of any concentration is merely a saturated solution of sodium oleate in pinene, and as the soap is sparingly soluble, we can assume that the soap content of the remaining gel is very nearly constant. Supposing the initial concentration of the gel is C_0, then at any interval of time t_1 after syneresis has started the concentration of the gel C_1 is greater than C_0 due to the exudation of the syneretic liquid; hence, the exudation of synereticum by this gel of concentration C_1 will be less than that of the original gel (concentration C_0) because, as has already been found experimentally, the concentrated gels exude less liquid than the dilute ones. Thus at successive intervals of time the velocity of syneresis goes on continuously diminishing which appears as an inhibition of the initial velocity of syneresis of the gels.

SUMMARY

The phenomenon of syneresis exhibited by gels of sodium oleate in pinene has been systematically investigated. The velocity of syneresis increases as (i) temperature is lowered and (ii) concentration is decreased. The nature of the synereticum has been examined. A theory has been suggested which explains the effects of several factors on the kinetics of syneresis of these gels. The law which holds for the imbibition of liquids is also applicable to the phenomenon of syneresis. Also, the kinetics of syneresis of these gels obey an equation which is similar to that of an inhibited reaction.

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