SYNERESIS OF SODIUM OLEATE GELS IN ORGANIC SOLVENTS

Part III. Effect of Temperature on the Syneresis of Sodium Oleate Gels in Pinene

By Mata Prasad, F.A.Sc. and V. Sundaram

(From the Chemical Laboratories, The Institute of Science, Bombay)

Received September 20, 1950

Changes in temperature affect the syneresis of different gels in different manner. In gels of silicic acid, an increase in temperature increases the syneresis. Ferguson and Applebey[1] have observed that the velocity of syneresis of silicic acid gels is approximately doubled for each 10° rise in temperature. Similarly Bonnell[2] has concluded that increased temperature accelerates the syneresis of silicic acid gels and causes it to proceed to a further stage. Prakash and Dhar[3] have also found that not only the syneresis of some inorganic jellies is higher at higher temperatures but also the temperature coefficient of their syneresis at higher temperatures is larger than that at lower temperatures.

The increase in temperatures causes the reverse effect on the syneresis of the geranin gels (*cf.* Lipatov[4]). Prasad and co-workers[5] have observed that the syneresis of sodium oleate gels in pinene also decreases with increasing temperature. In the present investigation the syneresis of sodium oleate gels in pinene has been studied thoroughly and systematically over a long range of temperature.

Experimental

1. *Maintenance of temperature.*—An air thermostat was used for maintaining the temperature at 30°, 40° and 50° C. The temperature inside the thermostat was maintained within $\pm 0{\cdot}1°$.

For maintaining the temperatures at 0°, 15° and 25° C., a thermos flask was used. To maintain 0° C., the test-tubes containing the gels were placed vertically in powdered ice kept in the flask. At frequent intervals water formed in the flask was removed and fresh ice was added. To maintain 15° C., ice was added to water to cool it to the required temperature. The test-tubes were clamped vertically such that the level of the gel in the test-tube was lower than that of water in the flask. Occasionally, a little water was removed from the flask and a small piece of ice was added. The temperature was maintained with an accuracy of $\pm 0{\cdot}4°$ C. A similar procedure was followed for obtaining the temperature of 25° C.

2. *Preparation of the gels.*—The gels were prepared in test-tubes of internal diameter 1·70 cm., by dissolving the requisite quantity of sodium oleate (0·10 g., 0·15 g., 0·20 g.) in 10 c.c. of pinene by the procedure adopted in Part I.[6] The gels were allowed to set in either the thermostat or the thermos flask depending on the temperature at which the syneresis was studied. The amount of syneresis was measured by the method of Prasad and co-workers.[5]

Results

The results obtained are given in the following tables in which Y and t carry the same meaning as in Parts I and II and Q represents the amount in grams of sodium oleate in 10 c.c. of the solvent.

Table I

Q = 0·10

t in hours	Y at various temperatures					
	0°	15°	25°	30°	40°	50°
1	11·58	10·88	8·04	7·03	5·38	3·53
2	14·48	12·54	10·92	9·32	7·26	5·28
3	15·68	15·51	11·60	10·87	10·07	6·49
5	16·81	15·84	13·85	12·77	11·03	8·75
7	17·34	16·28	15·15	13·67	12·84	10·41

Table II

Q = 0·15

t in hours	Y at various temperatures			
	0°	30°	40°	50°
1	9·36	4·72	3·63	2·48
2	12·27	6·84	5·60	3·83
3	13·85	8·05	6·67	4·75
5	14·36	11·10	8·85	6·13
7	15·48	12·89	10·41	8·30

TABLE III

Q = 0·20

t in hours	Y at various temperatures			
	0°	30°	40°	50°
1	7·12	3·46	2·58	1·76
2	9·08	4·92	4·37	2·92
3	10·39	6·28	5·40	3·78
5	12·12	8·08	7·25	4·98
7	12·64	10·43	8·75	6·43

DISCUSSION OF RESULTS

It will be seen from the above tables that for all the three concentrations of the gel studied the amount of liquid exuded is greatest at the lowest temperature, and decreases as the temperature is increased. This observation is similar to that of Prasad and co-workers. The Y–*t* curves in all cases are smooth rising (*cf.* Part II[7]) and their initial rise falls off gradually as the temperature is increased.

At any temperature the values of the unimolecular constant (Km) decrease as the time interval is increased (*cf.* Part II[7]), and at any given interval of the time they increase as the temperature is decreased.

The validity of the relation $Y^n = kt$ for different temperatures was examined by plotting the values of log Y against those of log *t* for gels containing 0·1 g. of the soap. It will be seen that the graphs (Fig. 1) for syneresis at 25° C. and above are straight lines, thereby indicating that the relation is followed for these temperatures. However, the graphs for syneresis at 0° C. and 15° C. are pairs of intersecting straight lines; the change in the direction of the initial line taking place after the syneresis has reached about 16%. This establishes that there are two stages involved in the exudation of the syneretic liquid, the earlier one being more rapid than the latter. The second stage could not be observed at temperatures besides 0° C. and 15° C. because the maximum time interval studied is not sufficient for the syneresis to reach this stage. This view was confirmed when the gels were allowed to synerise for longer period at 30° C. (*cf.* Part II[7]).

There does not seem to be any direct relationship between the amount of syneresis and temperature at which a gel synerises. However, an interest-

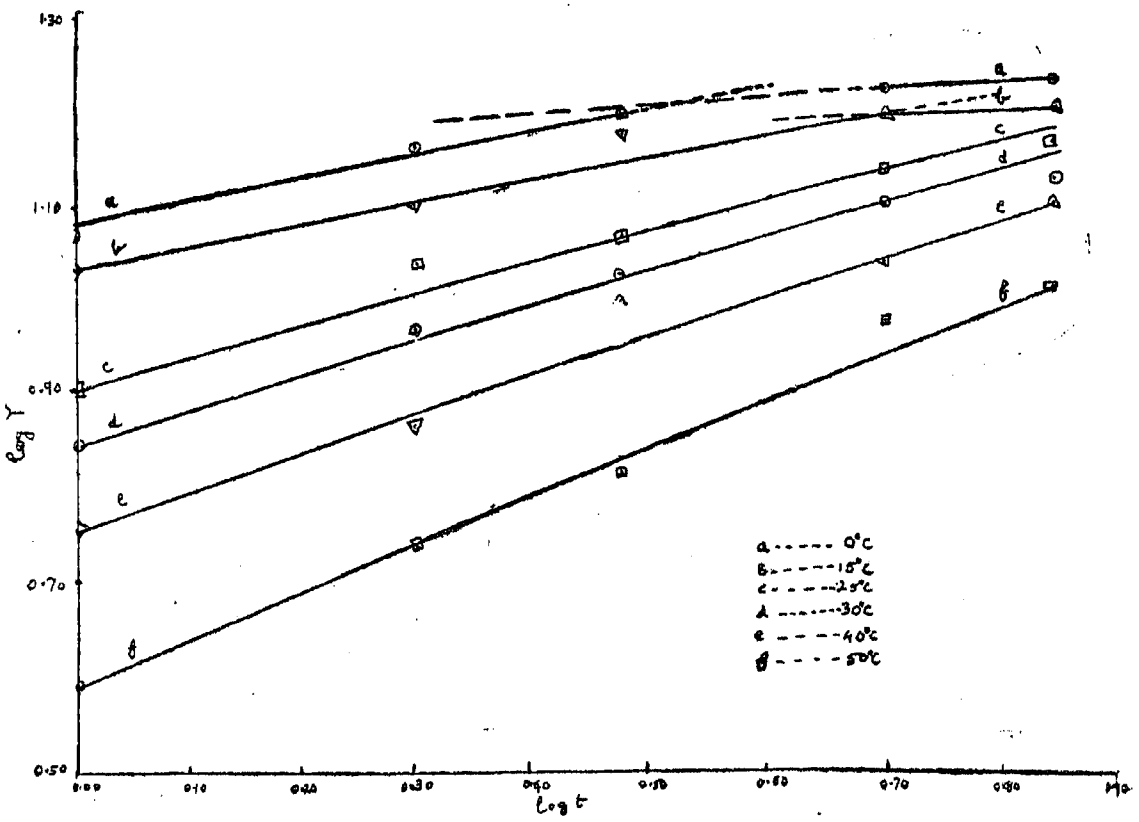

FIG.

ing observation is made when the values of Y at each time interval are plotted against temperature in the case of 1% gel. The points for each time interval lie on a curve and all the curves appear to converge and meet the temperature axis at one point (*cf.* Fig. 2). This shows that at this temperature,

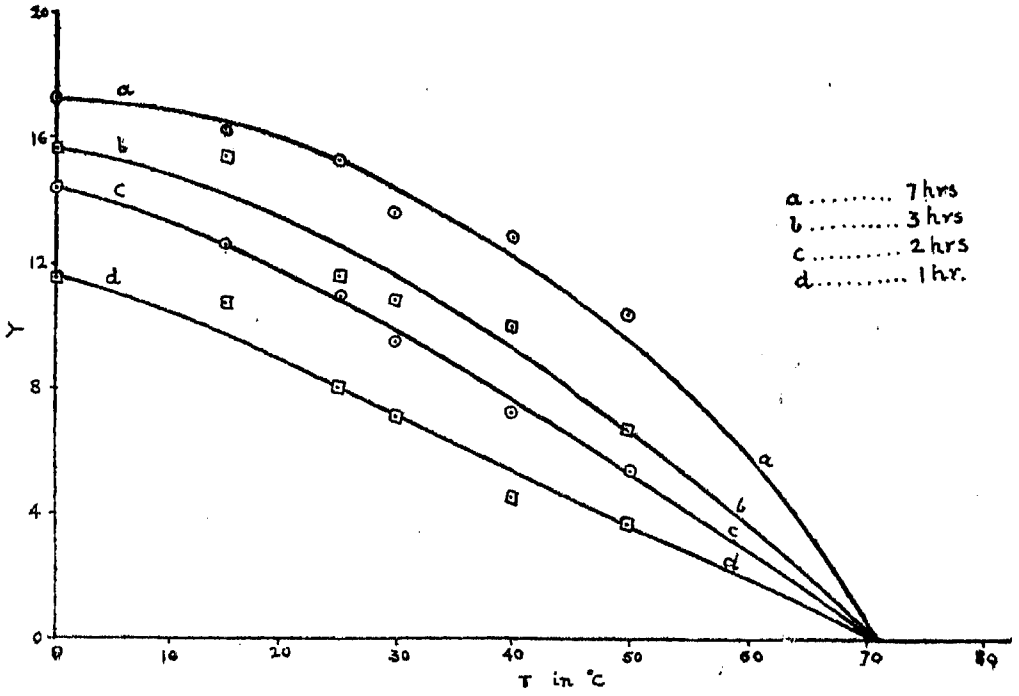

FIG. 2

namely 71° C., no syneresis takes place whatever be the time interval for which the gel is maintained at this temperature. This conclusion has been experimentally verified., Curiously enough it has been found experimentally that the gelation temperature, that is, the temperature at which the gel-forming solution of this concentration just sets to a gel, is 70° C. It may therefore be generalised that if a gel is maintained at its gelation temperature, no syneresis would at all take place, that is, the gel would be most stable.

The above discussion shows that two important observations have been made in this investigation, namely, (i) the gels of sodium oleate in pinene do not synerise at their gelation temperatures and (ii) the amount of synereticum exuded in a given interval of time since the commencement of syneresis increases with a decrease in the temperature, at which the syneresis is studied.

It is known that the gels of the soaps of various metals in organic solvents are prepared in an identical manner, namely, by dissolving a certain amount of the soap in the solvent at a high temperature, near about the boiling point of the solvent, and then cooling the resulting solution. Hence, it will not be far from truth if it is assumed that the mechanism of formation of all these gels and probably their structure are more or less the same. However, only some of these gels, such as gels of sodium oleate in pinene or xylene, exhibit the phenomenon of syneresis, while others, such as gels of sodium oleate in Nujol or of sodium stearate in pinene, are non-syneretic. This indicates that syneresis is a special property of some gels and is not dependent on the mechanism of gel-formation or the gel structure. The special characteristic of a syneretic gel is the instability of its structure formed when the gel sets; this condition would be determined essentially by the nature of the gel-forming substance and the dispersion medium, but it may be effected by the rate of cooling of the solution of the gel-forming substances in the dispersion medium, and its concentration.

Sodium oleate and pinene give rise to an unstable system. It is observed that this system remains quite stable when a solution of sodium oleate in pinene made at 140° C. is cooled to the gelation temperature, that is, the temperature at which the system sets to a gel. It is probable that certain optimum conditions prevail at this temperature which maintain the system in an equilibrium state, that is, the system remains unaltered so long as the temperature is maintained at the gelation temperature of the system, and hence no syneresis is observed at the gelation temperature.

If these gels are allowed to cool below the gelation temperature, the changes in equilibrium conditions caused by the lowering of the temperature

are in the direction of reduced stability. Hence the structure formed at the gelation temperature becomes unstable and syneresis results on account of the displacement of the system to attain stability at that temperature. The lower the temperature to which the gel is cooled, the greater is the deviation from the equilibrium conditions prevailing at the gelation temperature. Hence at lower temperatures the unstability of gel structure formed at the gelation temperature is greater causing a larger amount of syneresis.

It is observed in the previous paper[6] that the exudation of liquid is rapid in the early stages of syneresis but subsequently it slows down. On keeping these gels for a very long time (several months) it is found that ultimately almost all the liquid is exuded and only a small flake of the solvated soap settles down at the bottom. This shows that once the syneresis commences, the equilibrium point is very remote, that is, the equilibrium is attained only after a long lapse of time, indicating that not only the structure of the fibrils which go to form the soap gels is broken but even the structure of the entities which go to form the fibrils at the lower temperature is more or less completely smashed.

Summary

The syneresis of sodium oleate gels in pinene has been found to increase with a decrease in the temperature at which they are allowed to synerise. There does not seem to be any direct relation between syneresis and temperature. When the graphs of syneresis against temperature for each interval of time are extrapolated, all the graphs meet the temperature axis at a single point which agrees closely with the gelation temperature of the gel; this leads to the inference that no syneresis takes place at the gelation temperature which has been actually verified. An explanation has been advanced for the observed results.

References

1. Ferguson and Applebey .. *Trans. Faraday Soc.*, 1930, **26**, 642.
2. Bonnell .. *Ibid.*, 1932, **28**, 12.
3. Prakash and Dhar .. *J. Indian Chem. Soc.*, 1930, **7**, 417.
4. Lipatov .. *Kolloid Z.*, 1927, **43**, 396; 1928, **48**, 62.
5. Prasad, Hattiangdi and Mathur *Proc. Ind. Acad. Sci.*, 1945, **21 A**, 105.
6. ——— and Sundaram .. Part I of the Series—Communicated for Publication.
7. ——————— .. Part II—Communicated for Publication.