

# SYNERESIS OF SODIUM OLEATE GELS IN ORGANIC SOLVENTS

## Part IV. Effect of Concentration on the Syneresis of Sodium Oleate Gels in Pinene and Xylene

BY MATA PRASAD, F.A.SC. AND V. SUNDARAM

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

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HOLMES, KAUFMANN and NICHOLAS<sup>1</sup> were the first to observe that syneresis in silica gels increases with an increase in the concentration of silicic acid. This fact has been confirmed by Ferguson and Applebey<sup>2</sup> and by Bonnell<sup>3</sup>; however, Bonnell has also shown that for very dilute gels (concentration less than 4%) syneresis increases with decrease in concentration.

Lipatov and Korobova<sup>4</sup> have found that the velocity of syneresis of geranin gels increases as the concentration of the gel is increased. Mukoyama<sup>5</sup> has also observed that, at constant alkali content, syneresis of gels of cellulose acetate increases with increase in the concentration. However, Atsuki and Sobue<sup>6</sup> state that more dilute the viscose gel is, the greater is the syneresis.

Prasad, Hattiangdi and Mathur<sup>7</sup> studied the kinetics of syneresis of sodium oleate gels in pinene of concentrations varying from 0.5% to 1.25% and have observed that an increase in the concentration of the soap in the gel decreases the syneresis. In the present investigation an attempt has been made to extend the work of Prasad and co-workers in order to see whether these gels show any effect similar to that observed in the case of silica gels. Also, the effect of concentration on the syneresis of sodium oleate gels in xylene has been investigated for the first time.

### EXPERIMENTAL

Gels of sodium oleate in pinene and xylene were prepared in test-tubes of internal diameter of 1.38 cm. by the method described in Part II.<sup>8</sup> All the gels were allowed to set in a thermostat maintained at  $30^{\circ} \pm 0.1^{\circ}$  C. The amount of syneresis was measured by the method of Prasad and co-workers.<sup>7</sup> The different concentrations studied were 0.05 g., 0.08 g., 0.10 g., 0.15 g., 0.20 g., and 0.25 g. of the soap in 10 c.c. of pinene and 0.05 g., 0.08 g., 0.10 g., 0.15 g. and 0.25 g. of the soap in 10 c.c. of xylene. Higher concentrations of the soap could not be used because at these concentrations the soap dissolves in the two solvents only with very great difficulty and the gels formed are not homogeneous.

## RESULTS

The results obtained are given in the following tables in which  $t$  and  $X$  carry the same meaning as in Part II and  $Q$  in Part III.

TABLE I

*Syneresis of sodium oleate gels in pinene*

$t$ in hours	X for gels containing					
	Q=0.05	Q=0.08	Q=0.10	Q=0.15	Q=0.20	Q=0.25
1	1.261	1.139	0.975	0.720	0.489	0.313
2	1.470	1.281	1.150	0.964	0.691	0.500
3	1.602	1.426	1.322	1.161	0.900	0.685
5	1.846	1.610	1.538	1.290	1.125	0.932
7	1.971	1.750	1.643	1.507	1.337	1.178
10	2.238	1.972	1.848	1.696	1.620	1.466
$\infty$	4.44	3.75	3.60	2.63	1.92	1.51

TABLE II

*Syneresis of sodium oleate gels in xylene*

$t$ in minutes	X for gels containing				
	Q=0.05	Q=0.08	Q=0.10	Q=0.15	Q=0.25
5	1.431	1.330	1.247	1.160	1.025
10	1.720	1.663	1.555	1.459	1.361
15	2.030	1.862	1.780	1.730	1.606
20	2.093	2.017	1.890	1.836	1.821
30	2.417	2.307	2.166	2.107	2.068
$\infty$	3.40	3.28	3.23	3.00	2.63

## DISCUSSION OF RESULTS

It is seen from the above tables that in the case of sodium oleate gels in pinene and xylene the rate of syneresis and the amount of synereticum exuded out in any given interval of time are greater for the dilute gels than

for the concentrated ones, and they gradually decrease with increase in concentration. The graphs of  $X$  against  $t$  are smooth rising curves and not S-shaped in all cases (cf. Parts II and III<sup>8,9</sup>); those for the gels in pinene are shown in Fig. 1.

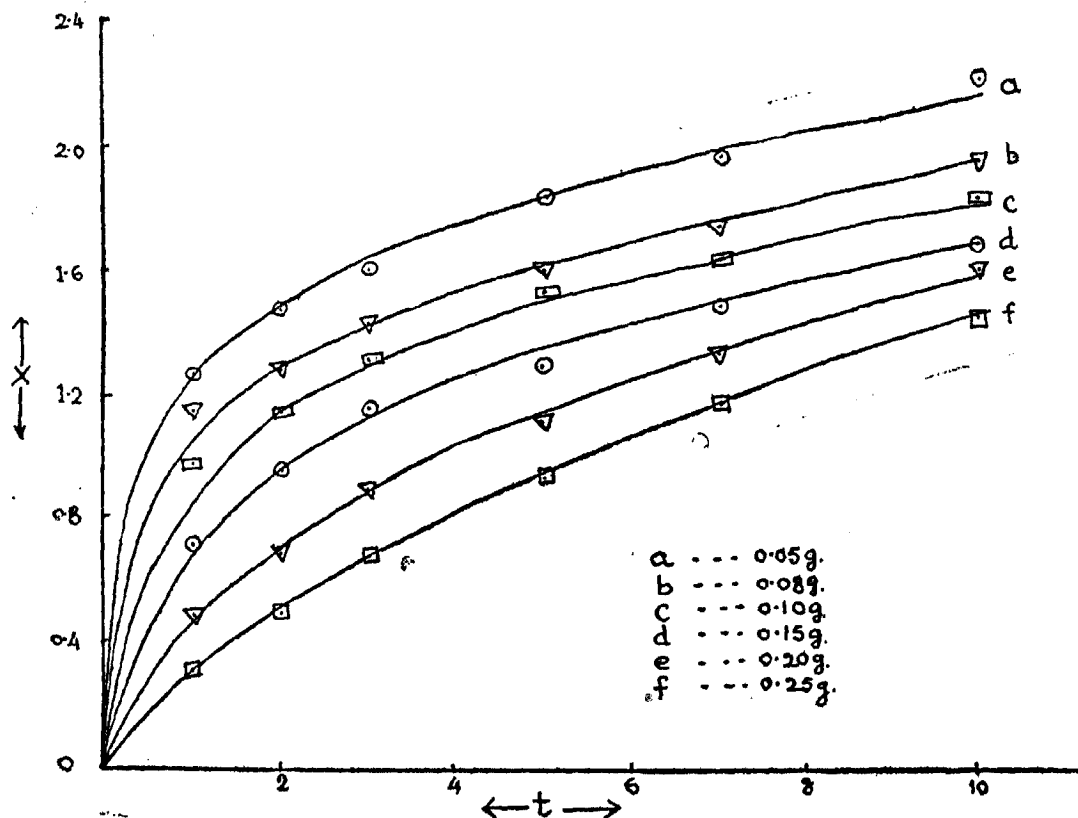


FIG. 1

The relation  $X^n = kt$  has been found to hold good for gels of all concentrations in xylene and pinene. The values of  $n$  calculated from the graph are given in the last row of Tables I and II. The values of  $n$  are not 2 in all cases and decrease as the concentration is increased.

Gapon<sup>10</sup> has expressed the relation between syneresis and concentration by the equation  $\frac{X_s}{(P_0 - P)} = H$ , where  $X_s$  is the amount of syneresis expressed as percentage of the initial quantity of the solvent for the concentration of the solute  $P$ ,  $P_0$  is the concentration at which no syneresis takes place, and  $H$  is the syneresis constant. It follows from this that graphs of  $X_s$  against  $P$  must be straight lines, as  $P_0$  can be assumed to be constant for a particular gel system. If the same amount of the solvent is taken in each case, then  $X_s$  can be replaced by  $X$ , the amount of syneresis actually obtained in this investigation and  $P$  is the same as  $Q$ . To test the validity of this

relation in the case of sodium oleate gels in pinene and xylene, the values of  $X$  after the same interval of time were plotted against  $Q$  and the graphs obtained were definitely not straight lines. Gapon's equation is, therefore, not applicable to the syneresis of sodium oleate gels in pinene and xylene and hence cannot be taken as a general equation.

The most important result obtained in this investigation is that the gels of lower concentration synerise more than those of higher concentration, that is, syneresis decreases with an increase in the concentration of the gel. This may be due to one or more of the following causes:

(i) It has been stated in the previous paper (*cf.* Part III<sup>9</sup>) that (a) gelation of a gel-forming system takes place at its gelation temperature because of certain equilibrium conditions present in the system at that temperature and (b) that when a gel is cooled below its gelation temperature, due to the changes in equilibrium conditions caused by the lowering of temperature, the gel structure becomes unstable causing syneresis. It is quite possible that the equilibrium conditions necessary for gel-formation are different at different temperatures. It has been observed experimentally that the gelation temperature increases with increase in concentration that is, a gel-forming system of a higher soap content sets at a higher temperature than one of a lower soap content. Hence, the equilibrium conditions in which a gel of higher concentration has been formed are different from those of the formation of gel of lower concentration and therefore the structure of the entities forming the gel in the two cases will be different. This difference in structure probably results in increasing the ability of gels of higher concentrations to withstand the deviations in equilibrium conditions caused by the lowering of temperature below the gelation temperature. Hence, when cooled to the same temperature, the gels of higher concentration synerise less than those of lower concentrations, although the changes in the equilibrium conditions may be greater in the case of gels of higher concentrations than in those of lower concentrations because of their higher gelation temperatures.

(ii) It is observed during the preparation of these gel-forming systems that an increase in the concentration of soap in the solvent increases the viscosity of the solution to a large extent. Since a viscous system offers a larger resistance to forces of shear and deformation, it appears that the increased viscosity of the more concentrated gel-forming system gives rise to a gel structure which offers greater resistance to changes in equilibrium conditions than gels of lower concentrations, and hence favours a decrease in syneresis with increase in concentration.

(iii) When an aqueous solution of calcium acetate is poured into alcohol, a gel results which rapidly breaks up into crystals. The addition of sodium oleate to this system prevents crystallisation and the gel obtained remains stable. This has been attributed to the fact that sodium oleate inhibits crystallisation of calcium acetate. In the systems of sodium oleate in pinene, it has been observed that below a concentration of 0.4% gels are not formed and crystallisation occurs. Increasing the amount of sodium oleate to about 0.5% results in gel-formation. This may also be due to the same cause as in the case of calcium acetate gels. Hence further increase in the amount of sodium oleate can be expected to increase the stability of the gel thereby decreasing syneresis.

#### SUMMARY

The effect of concentration on the syneresis of sodium oleate gels in pinene and xylene has been investigated. The initial rate of syneresis and the total amount of synereticum given out in a given interval of time since the commencement of syneresis are larger for gels of lower concentrations and decrease with an increase in the concentration of the gels. An explanation has been advanced for this behaviour.

#### REFERENCES

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