SYNERESIS OF SODIUM OLEATE GELS IN ORGANIC SOLVENTS

Part II. Effect of time on the syneresis of sodium oleate gels in pinene and xylene

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THE effect of time on the syneresis of silica gels seems to have been first studied by Okatov[1] who suggested that syneresis is a good measure of the maturity of these gels. Ferguson and Applebey[2] have observed that in the initial stages, the velocity of syneresis of silica gel follows an autocatalytic curve. Prasad, Hattiangdi and Mathur[3] have studied the kinetics of the syneresis of sodium oleate gels in pinene and have found that, for the interval of time studied, syneresis follows a relation similar to the imbibition of liquids. The present paper deals with the investigation of syneresis of sodium oleate gels in pinene and in xylene carried out over an extended period of seven days.

EXPERIMENTAL

It has been pointed out in the previous paper[4] that syneresis varies with the surface of the gel. Hence in these investigations test-tubes of the same internal diameter, 1·70 cm., were used throughout. Gels containing 0·10 g. of sodium oleate in 10 c.c. of each solvent were used for the measurement of syneresis. The gels in pinene were prepared in the manner described in Part I.[4] The gels in xylene were prepared in a similar manner by preparing the solution of sodium oleate in xylene at 130° C. All the gels were kept in a thermostat maintained at 30° ± 0·1° C. The amount of syneresis was measured by the method of Prasad and co-workers[3] at different known intervals of time after the gels had just set.

RESULTS

The results obtained are given in the following table in which the following notations have been used:

t = time after the gel had set, and

X = the amount of syneresis in grams.

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TABLE I

t in hrs.	Gels in pinene		Gels in xylene	
	X	$K_m \times 10^6$	X	$K_m \times 10^6$
1	0·600	20·250	1·703	60·900
2	0·795	13·550	1·798	32·370
3	0·923	10·630	1·844	22·200
5	1·088	7·577	1·861	13·460
7	1·165	5·823	1·872	9·658
18	1·317	2·587	..	..
24	1·374	2·031	1·945	2·941
48	1·485	1·107	2·008	1·529
144	..	..	2·074	0·529
168	1·729	0·375	2·090	0·457

DISCUSSION OF RESULTS

It is seen from Table I that the gels in xylene synerise more rapidly than those in pinene. The graphs of the amount of syneresis against time are smooth rising curves (Fig. 1) and are not S-shaped as observed by Ferguson and Applebey.[2] This shows that the process of syneresis of sodium oleate gels both in pinene and in xylene is not autocatalytic.
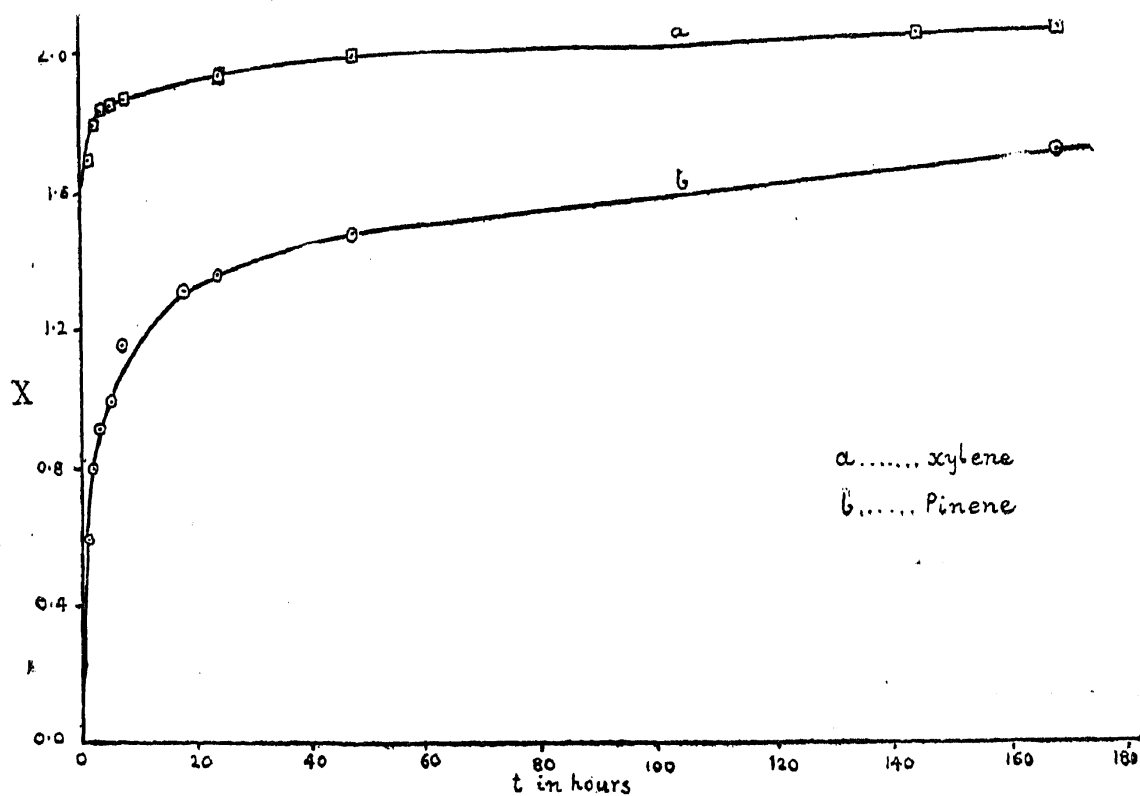

a .... xylene

b .... Pinene

FIG. 1

Lipatov[5] has observed that the velocity of syneresis in geranin gels follows the law of first order reaction, Prasad and co-workers[3] have found

that the unimolecular constants (K_m) calculated for different intervals of time in a given series are not constant but decrease as the time interval is increased, thereby showing that the law of unimolecular reaction is not obeyed in this case. They have also noticed that the graphs obtained by plotting X/t against K_m are straight lines, showing that the relation $X/t = KK_m + C$, where K and C are constants, is followed in this case. Similar results have been obtained in this investigation on the syneresis of sodium oleate gels in pinene as well as in xylene (*cf.*, Columns 3 and 5, Table I).

Prasad and co-workers[3] have found that the relation $X^n = kt$ in which n and k are constants, holds good in the case of sodium oleate gels in pinene. Hence the graphs of log X against log t have been drawn, using the data given in Table I, and the plotted points appear to lie on a pair of intersecting straight lines (*cf.*, Fig. 2). This indicates that (i) two stages are involved in the process of syneresis of gels in xylene and pinene and (ii) the velocity of the second stage is much smaller than that of the first. The existence of the second stage is noticed only after a sufficient amount of the syneretic liquid has been exuded out of the gel. This happens much earlier in xylene than in pinene. The existence of the second stage has not been observed by Prasad and co-workers[3] since the period for which they measured the syneresis was not sufficiently long to bring out this phenomenon.
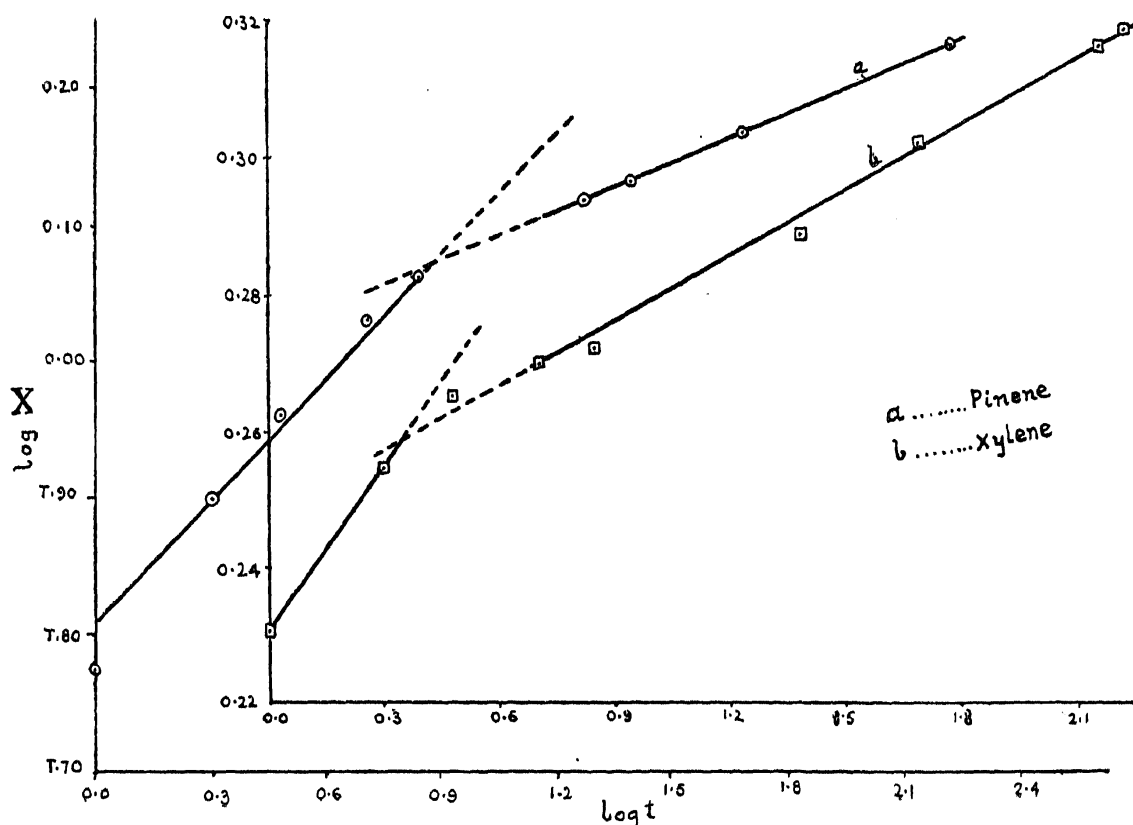

FIG. 2

The above observations can be explained as follows: When a solution of sodium oleate in pinene or xylene is cooled, at some temperature the soap goes over to the colloidal state due to super-saturation. On further cooling, the colloidal particles of the soap agglomerate in the form of fibrils. During the formation of colloidal particles and their agglomeration, a part of the dispersion medium gets attached to the particles due to solvation. This part of the dispersion medium corresponds to the bound liquid in gels (*cf.*, Hardy[6]). The fibrils form the gel structure enclosing the remaining dispersion medium (called free liquid by Hardy) within the interfibrillary spaces. When the gel starts synerising either due to the collapse of the structure as a whole or due to the fibrils coming closer to each other, the liquid within the interfibrillary spaces gets exuded; this corresponds to the initial stage of rapid syneresis. Subsequently, due to the structural changes taking place in the gel, probably a breakdown of the individual fibrils themselves, some of the bound liquid is also exuded; this corresponds to the second stage of syneresis. Since the structural changes in a gel take place comparatively slowly, the second stage of syneresis is a slow process.

Summary

The effect of time on the syneresis of sodium oleate gels in pinene and xylene has been investigated. The graphs of synereticum against time are smooth rising curves and are not S-shaped as is the case with silica gels. The rate of syneresis is large in the initial period and falls off continuously with time. The progress of syneresis does not follow the law of first order reaction observed in the case of geranin gels. The plots of log X against log *t* for the gels in both the solvents give, in each case, a pair of intersecting straight lines indicating the existence of two different processes of syneresis. An explanation has been advanced for this behaviour.

References

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