

SYNERESIS OF SODIUM OLEATE GELS IN ORGANIC SOLVENTS

Part V. Syneresis of Sodium Oleate Gels in Mixtures of Organic Solvents

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

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

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VARIOUS investigators have pointed out the importance of the nature of the dispersion medium on the syneresis of gels. Usually the dispersion medium has been changed by the addition of other substances, such as acids, alcohols and others. Very few investigators have studied the syneresis of the same gel-forming substance in different media. Hardy¹ observed that the syneresis of azomethine gels starts in a few minutes in an ether gel, in a few hours in an alcohol or an aldehyde gel and in a few days in a carbon tetrachloride gel. Le Blanc and Kroger² have noticed that the syneresis of caoutchouc gels in benzene starts earlier than in carbon tetrachloride; the velocity of the main amount exuded in both the solvents is the same but the final amount exuded by the gel in carbon tetrachloride is somewhat greater.

It has been observed in a previous communication³ that gels of sodium oleate in xylene synerise more rapidly than those in pinene. In the present investigation, an attempt has been made to study the syneresis of sodium oleate gels in mixtures of (a) xylene and toluene and (b) xylene and pinene.

EXPERIMENTAL

(a) 0.100 g. of sodium oleate was weighed out into five different test-tubes of the same internal diameter (1.65 cm.) which were filled with several mixtures of xylene (A) and toluene (B). It was observed that if the mixtures contained more than 70% by volume of toluene, the soap does not dissolve completely and the gels obtained are not homogeneous. Hence mixtures containing more than 70% toluene were not used.

(b) 0.100 g. of sodium oleate was weighed out into seven different test-tubes of the same internal diameter (1.65 cm.) which were filled with several mixtures of xylene (A) and pinene (C).

The test-tubes were placed in an oil-bath, the temperature of which was maintained at 120°–25° C. in the case of mixtures of xylene and toluene and at 130°–35° C. in the case of mixtures of xylene and pinene, and the

contents of the test-tubes stirred till all the soap had dissolved. Then a long condensing tube was attached to each test-tube and the test-tubes were allowed to stand in the bath till all the bubbles had disappeared. The test-tubes were then tightly corked and transferred to a thermostat or a thermos flask depending on the temperature at which readings were taken. At definite intervals of time (*t*) after the gels had set, the amount of synereticum (*X*) in each test-tube was measured by the method followed in Part II.³ The temperatures used were 30° C. and 40° C. in the thermostat and 20° C. in the thermos flask.

Sodium oleate used was of the B.D.H. quality and the xylene used was obtained from S. B. Penick & Co., New York. Toluene was obtained from May & Baker, Ltd., and pinene from the City Chemical Corporation, New York.

The results obtained are given in Tables I and II.

DISCUSSION OF RESULTS

It is seen from Table I that in the case of gels in mixtures of xylene and toluene the syneresis increases with an increase in the amount of toluene in the mixture. This fact is seen at all the temperatures. Also, the amount of syneresis at any one composition of the mixture is greatest at 20° C. and decreases as the temperature is increased. The effect of temperature on gels in mixtures of solvents is therefore similar to that on gels in these pure solvents (*cf.* Part III of this series⁴). The graphs of syneresis against composition of the mixture are more or less straight lines for all the time intervals

TABLE I

Values of X for gels in mixtures of xylene and toluene at various intervals

Composition of the mixture		Temperature 20° C.				Temperature 30° C.				Temperature 40 C.			
A	B	15 min.	30 min.	1 hr.	2 hr.	15 min.	30 min.	1 hr.	2 hrs.	15 min.	30 min.	1 hr.	2 hrs.
10 c.c.	0 c.c.	1.850	2.111	2.300	2.416	1.731	1.913	2.054	2.168	1.658	1.784	1.911	2.020
8 c.c.	2 c.c.	1.960	2.232	2.415	2.550	1.827	2.054	2.146	2.290	1.760	1.915	2.075	2.079
6 c.c.	4 c.c.	2.091	2.346	2.553	2.683	1.950	2.184	2.309	2.440	1.894	2.019	2.105	2.174
4 c.c.	6 c.c.	2.207	2.473	2.674	2.805	2.040	2.288	2.411	2.499	1.993	2.139	2.231	2.277
3 c.c.	7 c.c.	2.267	2.555	2.759	2.863	2.100	2.358	2.492	2.600	2.030	2.235	2.320	2.377

TABLE II

Values of X for gels in mixtures of xylene and pinene at various intervals

Composition of the mixture		Temperature 20° C.				Temperature 30° C.				Temperature 40° C.			
A	C	15 min.	30 min.	1 hr.	2 hrs.	15 min.	30 min.	1 hr.	2 hrs.	15 min.	30 min.	1 hr.	2 hrs.
10 c.c.	0 c.c.	1.850	2.111	2.300	2.416	1.731	1.913	2.054	2.168	1.658	1.784	1.911	2.020
9 c.c.	1 c.c.	1.962	2.344	2.464	2.600	1.906	2.118	2.352	2.462	1.814	2.111	2.168	2.250
8 c.c.	2 c.c.	2.022	2.390	2.592	2.652	1.886	2.220	2.485	2.545	1.708	2.126	2.340	2.422
6 c.c.	4 c.c.	1.643	1.979	2.475	2.595	1.471	1.887	2.350	2.513	1.147	1.700	2.104	2.330
4 c.c.	6 c.c.	1.094	1.604	1.944	2.196	1.136	1.326	1.800	2.087	0.640	1.057	1.384	1.867
2 c.c.	8 c.c.	0.894	1.148	1.464	1.742	0.723	0.922	1.338	1.607	0.217	0.520	0.907	1.266
0 c.c.	10 c.c.	0.650	0.858	1.187	1.398	0.460	0.668	1.048	1.189	0.166	0.324	0.635	0.967

studied, indicating the possibility of an additivity law. The graphs of syneresis against composition at 20° C. are shown in Fig. 1. Since no gels are formed in pure toluene with 0.10 g. of the soap, the validity of the additivity law cannot be tested in any case.

It is seen from Table II that on increasing the percentage of pinene in the mixture of xylene and pinene, the amount of syneresis of gels at first increases, reaches a maximum in a mixture containing 80% xylene and 20% pinene, and then gradually falls off. The graphs of syneresis against composition of the mixture are S-shaped for all the time intervals and temperatures studied; those in the case of syneresis at 20° C. are shown in Fig. 2. The amount of synereticum given out by a gel in pure xylene is greater than that given out by the same gel in pure pinene. Hence, it would be expected that on increasing the amount of pinene in the mixture the amount of synereticum should continually decrease.

Palit and co-workers⁵ have shown that in the case of organic mixtures containing a glycol as one component, the solubility of soap reaches a maximum value at intermediate compositions of the mixture. Probably in the mixtures of pinene and xylene the solubility has an optimum value in the mixture containing 80% xylene and 20% pinene. Since the same amount of soap is used in all the mixtures the amount of supersaturation will be least in the mixture of 80% xylene and 20% pinene and hence the gel formed will be weaker (*cf.* Part IV⁶). Therefore the syneresis of the gel in the

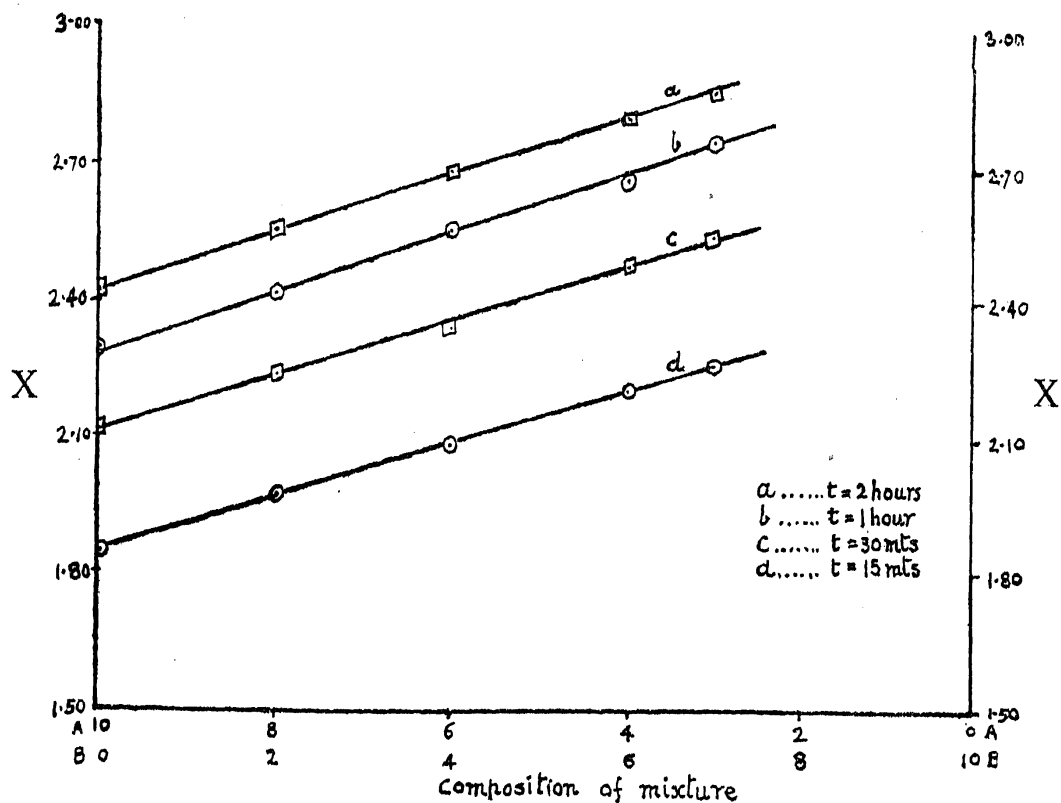


FIG. 1

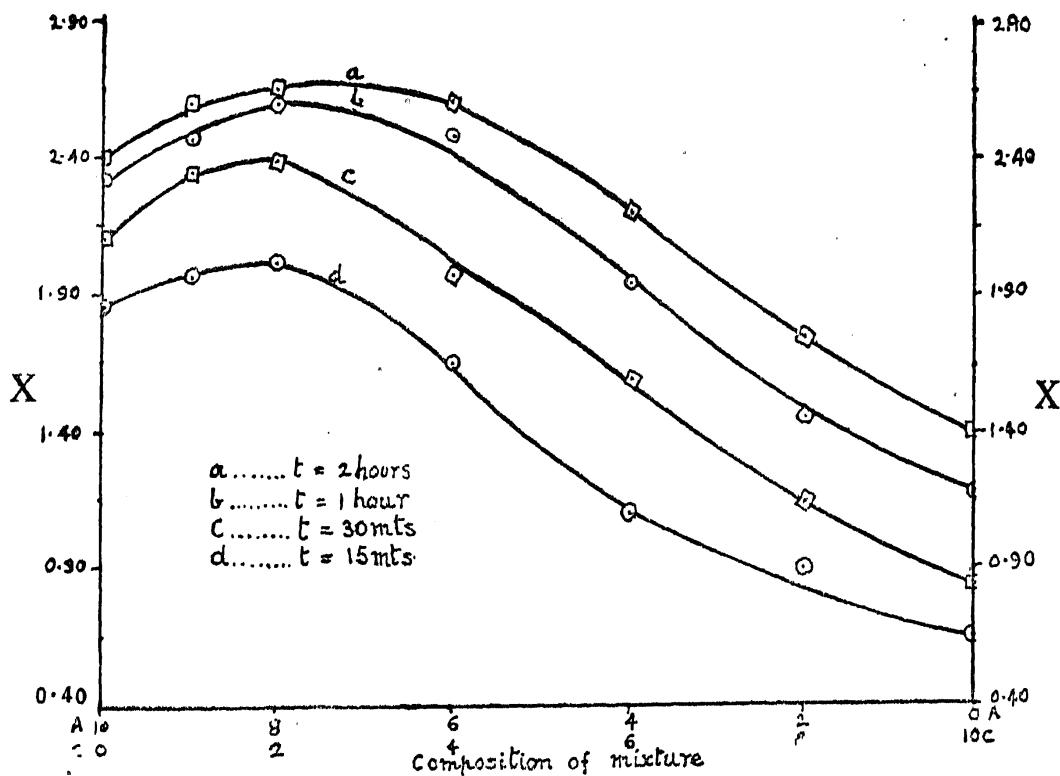


FIG. 2

mixture of 80% xylene and 20% pinene would be maximum. Such an effect is not observed in the mixtures of toluene and xylene, probably because both these solvents belong to the same homologous series and the solubility in these solvents probably follows the additivity law,

It is also observed, as in the case of gels in mixtures of xylene and toluene, that syneresis at a lower temperature is greater than at higher ones.

Further work for the examination of the behaviour of soap gels in mixtures of organic liquids is in progress.

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SUMMARY

The rates of syneresis in mixtures of (1) xylene and toluene and (2) xylene and pinene have been investigated. In the case of xylene-toluene mixtures, syneresis seems to be additive whereas in the case of xylene-pinene mixtures, syneresis shows a maximum value in a mixture of 80% xylene and 20% pinene.

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