

# EFFECT OF ADDITION AGENTS ON THE SYNERESIS OF SODIUM OLEATE GELS IN PINENE

BY MATA PRASAD, G. S. HATTIANGDI AND S. P. ADARKAR

*(From the Chemical Laboratories, Royal Institute of Science, Bombay)*

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THE earliest attempt for the quantitative determination of the effect of addition agents on the syneresis of gels was made by Lipatov.<sup>1</sup> He investigated the kinetics of syneresis of geranin gels and observed that the addition of small amounts of sodium chloride and alcohol accelerates the syneretic process, whereas alkali and carbon bisulfide have a retarding effect. Prakash and Dhar<sup>2</sup> observed that the addition of electrolytes increases the velocity of syneresis of a number of inorganic gels. The effect of the addition of a series of alcohols on the syneresis of silicic acid gels has been recently studied by Munro and Monteith<sup>3</sup> who observe that the total volume of the syneretic liquid at equilibrium is the same as that of the control and that no adsorption of alcohol takes place.

In a recent communication, Prasad, Hattiangdi and Mathur<sup>4</sup> have mentioned that the addition of certain substances to the solutions of sodium oleate in pinene giving rise to gels, either accelerate or retard their syneretic process. In the present investigation, the effects of a number of addition agents such as soaps, fatty acids, non-aqueous solvents and other organic substances on the syneretic phenomenon exhibited by sodium oleate gels in pinene have been exhaustively studied. A few of these results have been communicated by Hattiangdi<sup>5</sup> in connection with the stability of soap gels in non-aqueous media, but no attempt has been made therein to explain the behaviour of the various addition agents on the phenomenon of syneresis.

## EXPERIMENTAL TECHNIQUE

The sodium stearate used was a Merck's product, whereas sodium oleate, sodium palmitate and potassium stearate were pure products of the B. D. House. The pinene used in the preparation of gels was obtained from Messrs. Eastman Kodak and Co., and was the fraction distilling at 156°. Benzene, toluene, xylene, mesitylene, aniline, phenylene-diamine, oleic acid, stearic acid and palmitic acid were Merck's pure products; the nujol used was a product of Stanco Inc. Co.

The gel-forming solutions of sodium oleate in pinene were prepared in test-tubes of the same diameter ( $2r = 1.45$  cm.) as described by Prasad and Hattiangdi<sup>6</sup> and small known amounts of different substances were added; the hot homogeneous solutions were then allowed to cool, gelate and synerise in a water thermostat maintained at 30° C. The amount of synereticum exuded after a fixed time interval was determined by the method employed by Prasad and co-workers.<sup>4</sup> The results presented in all the tables in this paper are represented on a percentage basis, the amount of synereticum exuded by sodium oleate gel in pinene without any addition agent being taken as a standard for comparison of the degrees of acceleration or retardation.

DISCUSSION OF RESULTS

*Effects of the Addition of Alkali Soaps.*—Experiments on the addition of sodium stearate, sodium palmitate and potassium stearate on the syneretic process were performed on the system consisting of 0.09 g. of sodium oleate in 10 c.c. of pinene. The results show that all these three soaps retard the syneretic process. On plotting the amounts of synereticum exuded at any fixed time interval against the amounts of the soap present in the system, regular smooth curves are obtained which fall rapidly in the beginning and then gradually as the soap content is increased, and finally intersect the concentration axis at some point. The nature of these curves shows that as the concentration of the added soap is gradually increased, the retardation is rapid in the beginning and slows down continuously till a stage is reached at some optimum concentration when the syneretic process is completely stopped. The retarding effects of the three soaps at an interval of one hour from the commencement of experiments are given in Table I.

TABLE I

Amount of soap added (in g.)	Percentage Retardation		
	Sodium stearate	Sodium palmitate	Potassium stearate
0.005	..	62.1	..
0.007	..	70.9	..
0.010	27.9	78.7	70.1
0.015	..	90.0	..
0.020	51.0	..	79.0
0.030	62.7	..	..
0.040	..	..	86.2
0.050	87.5	..	89.1

It will be seen from the results given above that all the soaps retard and finally tend to stop the syneresis of sodium oleate gels in pinene, the retarding effect

being in the order of NaP > KSt > NaSt. It was observed qualitatively that gels of sodium stearate, sodium palmitate and potassium stearate in pinene synerise to a very slight extent and the apparent order is NaP < KSt < NaSt. The parallelism between the retarding effects of the soaps and the synerising capacity of their gels in pinene explains the retarding effect on the syneretic process of sodium oleate gels in pinene when small amounts of either of these soaps are present in the synerising system.

*Effect of the Addition of Fatty Acids.*—The effects of the addition of oleic, stearic and palmitic acids on the syneretic phenomenon exhibited by sodium oleate gels in pinene were investigated on a system consisting of 0.09 g. of the soap dissolved in 10 c.c. of pinene. The results obtained are presented Table II.

TABLE II

Amount of acid added (in g.)	Percentage Retardation		
	Oleic acid	Stearic acid	Palmitic acid
0.01	System does not set to a gel ↓ Non-syneretic gel is obtained	System does not set to a gel ↓	8.5
0.02			22.6
0.03			77.5
0.04			93.3
0.05			95.7
0.10			System does not set to a gel

It is interesting to note that the effects of the three closely related fatty acids on the syneretic phenomenon are totally different from one another. Oleic acid when present even in very small quantities prevents the gel-forming system from setting to a gel; the system is transparent when hot but develops considerable opacity on cooling. If the oleic acid content is slowly increased, it is found that in the neighbourhood of 0.1 g., the system sets to a firm transparent gel. This gel does not synerise and neither does it develop opacity when kept for a sufficiently long time. This behaviour of oleic acid is unique.

In the presence of stearic acid, it is found that the system does not set to a gel even when the acid content is varied over a sufficiently large range. A gel is obtained when small amounts of palmitic acid are present in the system and the syneretic process is retarded, the extent of retardation increasing as the acid content is increased from 0.01 g. to 0.05 g. When the acid content is increased slightly beyond 0.05 g., the system yields a loose viscous mass instead of giving a rigid, transparent gel.

It would be interesting to mention here that Miss Laing<sup>7</sup> studied intensively the state of oleic acid and potassium oleate in solution in dry alcohol, and concluded that a small amount of a complex compound is formed in this system, which is responsible for the slight yet distinct tendency of all such solutions towards opalescence and frothing. The development of opacity by mixtures of sodium oleate and the various acids in pinene when they are cooled can probably be explained in the same manner.

*Effect of the Addition of Non-Aqueous Media.*—The results of the experiments on the effects of the addition of a number of non-aqueous media on the syneretic phenomenon exhibited by sodium oleate gels in pinene are given in Tables III, IV and V. The synerising system investigated in all these cases consisted of 0.09 g. of sodium oleate dissolved in 7 c.c. of pinene. The various results have been presented in three different tables for the sake of convenience during discussion.

TABLE III

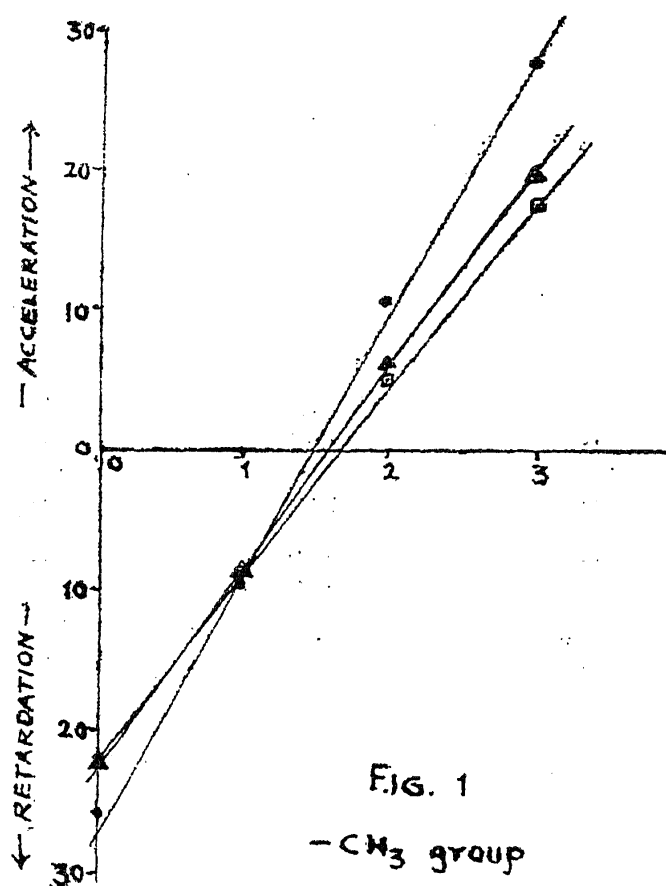
Non-aqueous media added (in c. c.)	Percentage Acceleration or Retardation			
	Benzene (Retardation)	Toluene (Retardation)	Xylene (Acceleration)	Mesitylene (Acceleration)
0.1	2.6	..	11.5	..
0.2	..	12.8	..	..
0.3	13.0	..	16.2	..
0.4	..	11.5	..	..
0.5	20.8	12.2	14.2	17.2
0.6	..	16.1	..	..
0.8	..	12.9	..	..
1.0	25.9	9.4	10.8	27.6
2.0	22.4	9.3	6.1	19.9
3.0	22.4	9.4	5.8	17.8

It will be seen from the above table that although small amounts of benzene or toluene retard the syneretic process, yet the effect is not great in as much as syneresis is not stopped. On increasing the amounts of any one of these substances, the percentage retardation first increases and then decreases to a constant value. Xylene and mesitylene, even when present in small quantities, accelerate the syneretic process of the system and in this respect behave differently from benzene and toluene. The acceleration which is noticed in the presence of small amounts of xylene or mesitylene is not largely affected by the addition of larger amounts of these substances.

It has been qualitatively observed that sodium oleate gels in benzene and toluene synerise but the extent of syneresis is not so pronounced as in the case of pinene; the addition of increasing amounts of either benzene

or toluene would, therefore, tend to exert a slightly retarding effect on the syneresis of the system, but the actual process of exudation of liquid is not stopped altogether. The gels of sodium oleate in xylene and mesitylene have been observed to synerise more profusely than those in pinene, and hence on the basis of the aforesaid considerations, the syneresis of the sodium oleate gels in pinene is slightly accelerated by the addition of small amounts of either of these substances.

An interesting observation can be made from the data presented in Table III, that whereas there is retardation of the syneretic process in the presence of benzene, the percentage retardation decreases on the addition of the same amount of toluene, and xylene and mesitylene actually accelerate the syneretic process. Thus, the addition of benzene, toluene, xylene



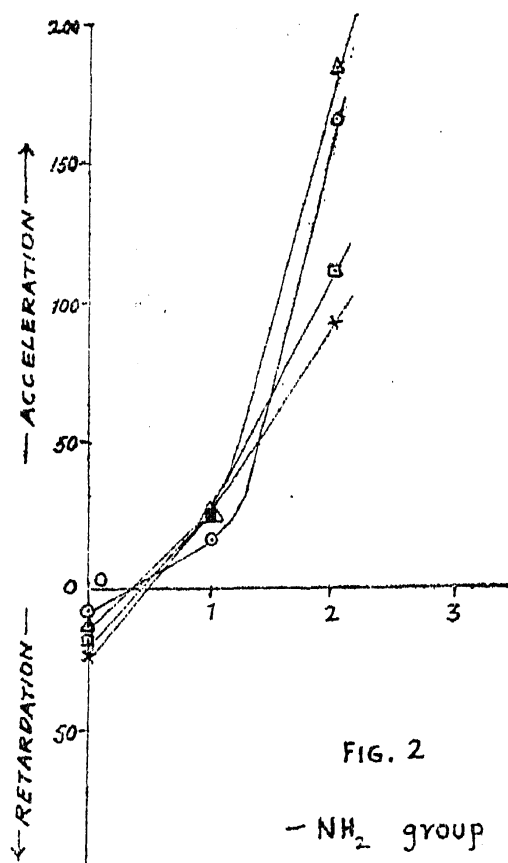
and mesitylene which differ from each other in the increasing number of  $-\text{CH}_3$  groups modifies the syneretic process of sodium oleate gels in pinene in a definite manner. In order to determine the relationship between the percentage retardation or acceleration for the same amounts of benzene, toluene, xylene and mesitylene and the number of  $-\text{CH}_3$  groups contained in these substances, the values of the two have been plotted and the curves obtained are shown in Fig. 1. In all cases, these curves are straight lines which shows the existence of a linear relationship between the two factors.

The effect of the addition of aniline and phenylene diamine on the syneretic phenomenon exhibited by sodium oleate gels in pinene is given in Table IV.

TABLE IV

Amount of substance added (in g.)	Percentage Acceleration or Retardation		
	Benzene (Retardation)	Aniline (Acceleration)	Phenylene diamine (Acceleration)
0.0224	10.3	17.1	167.1
0.0600	19.0	25.0	186.7
0.1468	22.6	32.5	112.5
0.2368	25.0	38.1	94.7

It will be seen from the above table that whereas benzene retards the syneretic process slightly, aniline and phenylene diamine accelerate it, the latter having a greater accelerating power than aniline. In this respect, their behaviour is analogous to that of xylene and mesitylene.



An attempt was made to see if any relationship exists between the percentage retardation or acceleration and the number of  $\text{-NH}_2$  groups. The plot of the values of the two factors is shown in Fig. 2. It is apparent that in no case is the linear relation obtained. This behaviour is to be expected

because whereas the retardation in the case of benzene and the acceleration in the case of aniline proceed regularly, that is slowly increase, the acceleration in the presence of phenylene diamine proceeds in the reverse manner, that is it goes on decreasing instead of increasing from the very beginning.

Attempts were then made to establish definitely the truth of these empirical relationships by employing compounds containing different number of  $-OH$  groups. It was found that among the aromatic compounds containing  $-OH$  groups only phenol is miscible in pinene whereas other substances (resorcinol, pyrogallol and phloroglucinol) charred on slight warming with the gel-forming solution. The aliphatic compounds, namely the alcohols, were miscible in pinene in all proportions, but even very small amounts of either of the alcohols were observed to increase the solubility of the soap to such a great extent that it remained in solution and did not set to a gel even after keeping for a very long time.

The data regarding the effect of the addition of nujol on the synerising system of sodium oleate in pinene is given in Table V.

TABLE V

Amount of nujol added (in g.)	Percentage Retardation
1.0	45.7
2.0	82.2
2.5	89.2
2.7	91.5
2.9	93.2
3.0	94.4
3.5	96.2
4.0	97.6

It is evident that small amounts of nujol considerably retard syneresis and if the nujol content is slowly increased the retardation goes on increasing till a stage is reached when syneresis is completely stopped. In this respect the retarding effect of nujol can be compared to that of either of the soaps discussed earlier. The behaviour of nujol may possibly be explained on the basis that gels of sodium oleate in this medium are quite firm and synerise to a very slight extent. Hence, with increasing amounts of nujol present in the system, the syneretic process is considerably retarded in the earlier stages and tends to stop completely in the presence of higher nujol content.

Prasad and co-workers<sup>4</sup> have explained the syneretic phenomenon exhibited by sodium oleate gels in pinene on the consideration that (i) the colloidal particles in the gel-forming solution are bound to each other by

residual valencies more loosely than in a crystal, and (ii) when the arrangement of the structural units of the gel is unstable, that is, the forces of residual valencies are weak, the gel shrinks due to progressive association and probably due to the orientation of the structural units, ultimately resulting in the exudation of interstitial liquid. On this hypothesis, the observed effects (acceleration and retardation) of the various addition agents on the syneretic process can be explained as follows.

The presence of small amounts of certain addition agents (soaps, acids, etc.) in the gel-forming system of sodium oleate in pinene favours the formation of complex compounds which brings about changes in the internal packing, depending upon the constitutive nature of the added substance. The addition agents also considerably influence the binding forces and consequently the shrinkage of the gel due to association of the structural units which depends upon these forces and the consequent exudation of the liquid is also correspondingly modified. If the binding forces are increased due to the addition of certain substances (soaps, nujol, etc.) the system becomes more stable and is less susceptible to shrinkage and therefore retards the syneretic process. Addition of other substances such as xylene, mesitylene, etc., apparently tends to weaken the forces of attraction between the micelles and hence the structure becomes more unstable and shrinks more spontaneously exuding a considerably large amount of the interstitial liquid in this process.

#### SUMMARY

The effect of a number of addition agents on the syneretic phenomenon exhibited by gels of sodium oleate in pinene has been investigated. The addition agents employed are sodium stearate, sodium palmitate, potassium stearate, oleic acid, stearic acid, palmitic acid, benzene, toluene, xylene, mesitylene, aniline, phenylene diamine and nujol.

The soaps retard and tend to stop the syneretic phenomenon, the retarding effect being in the order of  $\text{NaP} > \text{KSt} > \text{NaSt}$ . The effects of the three closely related fatty acids on the syneretic phenomenon are totally different from one another. Benzene and toluene retard the syneretic process but xylene and mesitylene accelerate it. There appears to exist an approximately linear relationship between the percentage retardation or acceleration for the same amount of benzene, toluene, xylene and mesitylene, and the number of  $-\text{CH}_3$  groups contained in these substances. No such relationship can be observed in the case of amino compounds among which benzene retards and aniline and phenylene diamine accelerate the syneretic process.



The retarding effect of nujol, a heavy paraffin oil, on the syneretic process is analogous to that of either of the soaps used in this investigation inasmuch as syneresis is retarded and there is a tendency to stop it altogether.

An attempt has been made to explain the various behaviour on theoretical considerations.

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