Soap Gels in Non-Aqueous Media. III. The Setting Time, Syneresis, and Gel-Strength of Gels of Some Sodium Soaps in Organic Solvents

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THE physico-chemical and phase behavior of sodium soaps in organic solvents has been investigated to some extent (7-10), and several physical properties of soap gels in pinene have also been reported (2-6). The systems of alkali soaps in toluene and Nujol are reported to gelate faster than those in xylene and pinene (1). An attempt is made in the present investigation to determine the effect of soap and solvent molecules on some physical-chemical properties of the resulting gels.

Materials Used and Experimental Technique

The sodium palmitate and sodium oleate were products of the British Drug Houses and had melting points of 270°C. and 232°C., respectively. The sodium stearate was a pure product of E. Merck and had a melting point of 260°C.

n-Amyl, butyl (n- and iso-), and propyl (n- and iso-) alcohols, and anisole were products of E. D. Haen; toluene, xylene, chlorobenzene, bromobenzene, o-cresol, and glycerol of the British Drug Houses; phenol and p-chlorotoluene of E. Merck; benzyl alcohol of van Ameringen Haebler Inc., cymene of Dr. T. Schuchardt's laboratories; and pinene of E. Kodak and Company. All these solvents were used without further purification other than drying and storing over anhydrous calcium sulfate.

Gel-forming solutions were prepared in Pyrex glass tubes (2r = 1.45 cm.) by dissolving a known amount of a soap in 10 ml. of an organic solvent at a temperature nearabout the boiling point of the latter. An air condenser was attached to prevent evaporation of the solvent, and the system was stirred constantly. When the soap had dissolved completely, the test tubes were placed in a thermostat maintained at 30°C.

The procedural details employed in measuring the setting time (6), syneresis (5), and gel-strength (4), were the same as those used in earlier investigations. The setting time was measured at 30°C. by determining the time which the gel-forming system took to reach a consistency when it did not flow out of the container when it was inverted. The extent of syneresis was determined two hours after the systems had set to the gel state at 30°C. The test tubes were weighed before and after the removal of the syneretic liquid with small rolls of filter paper, and the difference in weights was taken as a measure of the exuded synereticum. In making gel-strength measurements, small weighing bottles (2r = 2.4 cm.) and a flat disc-shaped plunger (2r = 0.8 cm.) were used. The plunger was attached to the bottom of the pan of a balance and was placed gently in contact with the top of the gel; weights were slowly added to the pan and the corresponding deflections on the scale as indicated by the pointer were noted. The load necessary to produce a shift of 10 scale divisions was determined in each case. The temperature, time interval, and other factors were chosen arbitrarily since the main purpose of this investigation is to determine the nature of changes brought about in the physical properties of gels with changes in soap and solvent types rather than to obtain "absolute" values for the same.

The various results of measurements on the setting time, syneresis, and gel-strength are presented in Tables I and II. More data along these lines could not be obtained, first because soap gels of a given composition are not formed always in solvents of different chemical character, and secondly because of difficulty in procuring a larger number of solvents belonging to the same homologous series.

Many of the soap-solvent systems, when freshly prepared, are present as jellies but quickly go over to the gel state when syneresis sets in. Hence, the broad general term "gel" has been used throughout in this paper inasmuch as all the systems might not have been jellies when the various measurements were made.

Results and Their Discussion

It will be seen from Tables I and II that the values of setting time, syneresis, and gel-strength differ considerably from one another for gels of different soaps dispersed in the same solvent as also for gels of the same soap dispersed in different solvents. Prasad *et al.* (7) find that the tendency of the alkali soaps to form gel-like material increases with an increase in the molar polarization of the solvents belonging to a homologous series. It was considered interesting therefore to determine if the physical properties of the gels investigated here are in any manner related to the molar polarization or some similar constitutive property of the solvent molecules.

It will be seen from Table I that for gels in toluene and xylene, an increase in molar polarization or molar volume is accompanied by an increase in the setting time and extent of syneresis, and a decrease in the gel-strength. The gels in the various alcohols do not synerise to any appreciable extent. However, with an increase in the molar polarization of the normal alcohols, there is an increase in the setting time and a decrease in gel-strength. For gels in anisole and phenetole an increase in the molar volume is accompanied by an increase in the setting time and the extent of syneresis and a decrease in gel-strength. Although it is presumptuous to make a broad generalization on the basis of these limited data, it is nevertheless interesting to note that an increase in the molar polarization of solvents belonging to different homologous series indicates, almost always, an increase in the setting time and extent of syneresis and a decrease in the strength of the resulting gels.

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TABLE I

Effect of Solvent Molecules on the Physical-Chemical Properties of Gels
(Concentration of soap = 7.8 g. per liter of solvent)

Solvent	Molar polarzn. $\left(\frac{\epsilon-1}{\epsilon+2}\right)$ V	Molar volume	Sodium oleate gel			Sodium stearate gel		
			Setting time	Syneresis	Gel-strength	Setting time	Syneresis	Gel-strength
Toluene	33.8	106.2	0′ 20″	1.38 g.	6	....	......	......
Xylene	38.4	122.5	1′ 20″	3.67	4	1′ 03″	2.27 g.	7
Cymene	49.1	152.1	4′ 06″	0.10	6	3′ 48″	......	7
Pinene	57.4	158.6	1′ 40″	1.81	16	1′ 12″	0.83	24
Chlorobenzene	60.7	101.7	2′ 55″	2.98	1.2	....	......	......
Bromobenzene	62.3	104.7	3′ 11″	3.67	1.1	2′ 55″	3.07	1
p-Chlorotoluene	......	118.3	1′ 10″	2.78	2.5	0′ 45″	0.07	4
n-Propyl alcohol	64.9	74.7	8′ 33″	......	17	2′ 30″	......	175
i-Propyl alcohol	65.1	76.2	6′ 10″	......	24	....	......	......
n-Butyl alcohol	77.7	91.6	18′ 15″	......	4	10′ 44″	......	125
i-Butyl alcohol	76.5	91.7	6′ 55″	......	9	3′ 10″	......	60
n-Amyl alcohol	89.9	108.1	....	......	......	18′ 50″	......	100
Anisole	......	108.2	9′ 15″	1.17	2	....	......	......
Phenetole	......	126.4	2′ 05″	6.44	0.4	1′ 45″	1.16	6
o-Cresol	63.5	103.2	....	......	......	6′ 55″	......	25
Glycerol	70.9	73.1	....	......	......	20′ 35″	......	300
Benzyl alcohol	80.9	102.9	....	......	......	6′ 40″	......	85

When a hot gel-forming solution of a sodium soap in an organic solvent is allowed to cool and gelate, the soap separates out of solution on account of its decreasing solubility at lower temperatures. The rate of cooling determines largely both the number and the size of these soap particles formed during initial cooling. Subsequent cooling results in the separation of more soap particles as also in the aggregation of the initially-formed primary colloidal particles into secondary aggregates. These, in their turn, link together by secondary valence forces to form fibrils. At about this stage solvation of the soap also takes place and the "free" dispersion medium is almost entirely enmeshed in the network of soap aggregates. The system thickens and sets to a jelly or crystallizes to a gel. X-ray investigations (11) show that gel-formation does not affect the structure of the soap crystallites and is therefore probably a surface phenomenon or an arrangement of the gross particles with respect to each other leaving the fine structure of the particles essentially unchanged. These studies also reveal that the intensity and width of the long and short spacing lines for the soap and of the "halo" for the oil are dependent upon a) the molecular weight of the soap in a homologous series (cationic or anionic), and b) the constitutive nature of the solvent.

The arrangement of molecules of alkali soaps and organic solvents in a gel-forming solution would essentially be with the former tending to stick their hydrocarbon tails towards layers of the latter. If the solvent molecules are very polar, the extent of orientation of the soap molecules would be large enough to retard the formation of secondary and tertiary aggregates, and the setting time would consequently be lengthened. The high polarity of the solvent molecules would continue to distort the positions of the soap particles and readjust the arrangement of the structural units even after the system has set to a jelly. The system would consequently shrink (crumple down in some extreme cases) and exude syneretic liquid.

It is interesting to note that this mode of reasoning is applicable to data for soap gels in certain other groups of solvents. For example, with sodium oleate gels in chlorobenzene and bromobenzene, increased polarity seems to result in an increase in the setting time and extent of syneresis and a decrease in the gel-strength. However, for gels in chlorobenzene and p-chlorotoluene, an increase in molar volume is accompanied by a decrease in setting time and syneresis and an increase in gel-strength. A different type of behavior is found with gels in toluene and p-chlorotoluene: with an increase in molar volume there is an increase in setting time and syneresis, but the gel-strength increases slightly instead of decreasing. This is evidently due to certain other factors, pertaining probably to the constitutive nature of the soap-solvent systems, being responsible in determining the physical-chemical properties of gels in organic solvents.

The manner in which the setting time, syneresis, and gel-strength of gels in a given solvent are modified by using different soaps as the disperse phase is shown in Table II. With a few exceptions both the setting time and the extent of syneresis of gels in various solvents decrease in the order

$$NaOl > NaStr > NaP,$$

TABLE II

Effect of Soap Molecules on the Physical-Chemical Properties of Gels
(Concentration of soap = 2.8 g. per liter of solvent)

Solvent	Setting time			Syneresis (g.)			Gel-strength		
	NaOl	NaStr	NaP	NaOl	NaStr	NaP	NaOl	NaStr	NaP
Cymene	7′ 10″	6′ 55″	6′ 25″	0.14	0.10	......	3	4	7.3
Pinene	9′ 12″	8′ 58″	1′ 30″	2.19	1.97	1.78	3.5	4.4	8
Xylene	3′ 55″	3′ 38″	1′ 05″	4.48	3.98	3.64	3.3	3.6	4
Bromobenzene	6′ 15″	5′ 55″	3′ 05″	5.99	4.42	8.94	0.6	0.6	0.7
p-Chlorotoluene	4′ 25″	4′ 19″	2′ 10″	3.14	2.96	0.05	0.7	0.8	1
o-Cresol	....	8′ 08″	6′ 45″	......	......	......	......	4.2	7
Glycerol	....	27′ 03″	40′ 40″	......	......	......	......	5.5	2
Phenetole	2′ 50″	2′ 45″	1′ 45″	8.54	6.79	1.16	0.2	1.2	3

whereas the gel-strength increases in the order

$$NaOl < NaStr < NaP.$$

Summary

1. The setting time, syneresis, and gel-strength of gels of sodium palmitate, sodium stearate, and sodium oleate in toluene, xylene, cymene, pinene, chlorobenzene, bromobenzene, p-chlorotoluene, n-amyl, n- and i-butyl, n- and i-propyl, and benzyl alcohols, o-cresol, glycerol, anisole, and phenetole, have been measured.

2. For gels in any given solvent the setting time and extent of syneresis decrease with different soaps in the order, NaOl > NaStr > NaP, and the gel-strength increases in the order, NaOl < NaStr < NaP. For solvents belonging to a homologous series the setting time and extent of syneresis of soap gels increase and the gel-strength decreases as the series is ascended.

3. An explanation for this behavior is offered in terms of the constitutive properties of the solvent molecules.

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Reactions of Fatty Materials With Oxygen. IV.[1] Quantitative Determination of Functional Groups[2]

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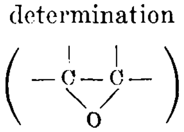
ALTHOUGH it is generally agreed that the conventional analytical procedures for the quantitative determination of functional groups are unreliable when applied to unfractionated oxidation reaction mixtures (4, 6, 9, 24, 25), the basis for such a broad generalization is not readily ascertained from the literature. Except in a few isolated cases the magnitude of the errors has not been reported, nor has any systematic attempt been made to demonstrate which analytical methods are reliable and which are not. In studying the mechanisms of the reaction of fatty materials with oxygen, it is essential to determine accurately the distribution of absorbed oxygen among the various types of oxygen-containing groups known to be present, and it is also essential that the sum of the percentages of oxygen determined analytically on the mixture equals the known oxygen content of the material determined by combustion analysis. As will be shown later, in certain types of mixtures the sum of the percentages of oxygen determined by conventional techniques considerably exceeds the known oxygen content.

In a previous publication (20) we described a procedure for the determination of oxirane oxygen



$$\left(-\overset{|}{C}-\overset{|}{C}-\right)\text{ with O bridging}$$

and indicated which functional groups in oxidation mixtures would interfere. The present investigation had three objectives: a) To prepare pure compounds containing one or, at most, two functional groups encountered in oxidation reaction mixtures and to analyze each of these compounds by the conventional techniques employed in studying oxidation reactions (acid number, saponification number, iodine number, oxirane oxygen, hydroxyl oxygen, carbonyl oxygen, and peroxide oxygen). In this way the magnitude of the interference (if any) of each functional group on each of the analytical methods could be readily determined. b) To prepare synthetic mixtures of known composition from these pure compounds and re-analyze the mixtures to determine the combined effect of numerous functional groups on the analytical techniques. c) When possible, to modify and improve those analytical procedures found to be in error, thus permitting a more accurate accounting of the total oxygen content. It is a sad commentary on research in this field that in more than 100 years of intensive study, resulting in numerous publications, a systematic investigation of this type has not been previously published.

Experimental

(All distillations were conducted in an atmosphere of nitrogen.)

Preparation of Pure Materials. Methyl oleate, b.p. 181-2°/3.6 mm. and n_D^{30} 1.4485, was prepared by fractional crystallization of olive oil fatty acids, followed by esterification with methanol and fractional distillation (1, 21, 27). 9,10-Epoxystearic acid, m.p. 59.6-59.8°, was prepared from pure oleic acid by epoxidation with peracetic acid (5). 9,10-Dihydroxystearic acid, m.p. 95°, was prepared from oleic acid by hydroxylation with hydrogen peroxide in acetic acid solution (19). Methyl ricinoleate, b.p. 187°/2 mm. and n_D^{30} 1.4592, was prepared by fractional distillation of the methyl esters obtained by methanolysis of castor oil (11). Oleyl alcohol, m.p. 7-8°, b.p. 188-90°/4.6 mm. and n_D^{40} 1.4540, was prepared from

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[1] The previous papers in this series are references 20, 22, and 23.

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