

## STUDIES IN INORGANO-ORGANIC GELS IN PINENE

### Part III. Viscosity Measurements of Gel-forming Solutions of Sodium Oleate and Sodium Stearate in Pinene

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THE determination of viscosity is a prominent methodic principle in investigating the properties of colloidal systems. Although the spontaneous increases in viscosity with time have been measured by different workers during the gelation of different hydrosols, a search through literature shows that the sol-gel transformation of gel-forming systems in non-aqueous media has not been studied viscometrically to the same extent in spite of the fact that in the latter case there is an advantage that no disturbing changes corresponding to hydrolysis in aqueous solutions take place and vitiate the results. The only noticeable work in this field has been carried out by Mardles<sup>1</sup> who has systematically studied the reversible sol-gel transformation of the cellulose acetate—benzyl alcohol system viscometrically using different types of viscometers. He observes that the shape of the curve relating viscosity and time is independent of the method of determining viscosity; he has also given an empirical relation which conveniently expresses the regularities observed in the viscosity-time data. Other work on viscosity measurements of organic gels has been prominently done on gels of gelatin in aqueous medium by Levites<sup>2</sup> and Shoji<sup>3</sup>; the former found that the rate of increase of viscosity is nearly proportional to time, whereas the latter has suggested a mathematical relation to represent the viscosity-time curves during the early stages of gelation. Von Schroeder's<sup>4</sup> viscosity-time curves also for gelatin, are smooth, there being a rapid rise with time in the rate of change, whilst in some cases there was a decrease in the last stages of gelation. Biltz and von Vegenack<sup>5</sup> found that the viscosity-time curves with benzopurpurin solutions were sigmoid in shape. A similar result was obtained by Arisz<sup>6</sup> working on glycerine solutions of gelatin.

In the present investigation the viscosity changes during the sol-gel transformation of some soap systems in pinene have been studied, and the effects of the concentration of the soap in the gel-forming systems and of temperature have been determined.

## EXPERIMENTAL

*Methods Employed for determining Viscosity*

In this investigation two types of viscometers have been employed to investigate into the kinetics of the sol-gel transformation of solutions of sodium oleate and sodium stearate in pinene.

(i) *Ostwald type of viscometer*.—This type of viscometer can be used only for low or moderately concentrated solutions or sols and at high temperatures. With the more concentrated sols and at lower temperatures, the drainage error of the viscometer becomes serious and the time of transpiration lengthy, so that during the actual determination, the viscosity may have considerably increased and, in some extreme cases, the transition to the rigid state may have occurred before complete transpiration.

The viscosities of some low and moderately concentrated solutions of sodium oleate and sodium stearate in pinene were determined by this method at several high temperatures.

(ii) *Falling Sphere Viscometer*.—The determination of viscosity of viscous systems such as are obtained in the gel-forming mixtures of organic substances is a matter of some difficulty. For such measurements it has been found that the Falling Sphere Viscometer is simple, accurate and advantageous (*cf.* Sheppard,<sup>7</sup> Mardles,<sup>1</sup> Gibson and Jacobs<sup>8</sup>). The rate of shear is very small when the sphere falls slowly, and the rapid viscosity changes can be conveniently followed until even the last ball remains suspended and the time to take a reading reduced to any extent.

The principle of the method depends upon Stoke's Law and the viscosity is given by the relation

$$\eta = \frac{2gr^2(S-S')}{9v}$$

where  $\eta$  = coefficient of viscosity,  $r$  = radius of the sphere,

$v$  = velocity of fall,  $S$  = density of the sphere,

$S'$  = density of the liquid, and  $g$  = gravitational constant. Ladenburg<sup>9</sup> and Arnold<sup>10</sup> suggested two linear corrections to be applied to the simple Stoke's Law equation, *viz.*, (i) a correction for the wall effect and (ii) a correction for the end effect. The complete modified equation, including both the corrections, is

$$9\eta v (1 + 2.4 X) (1 + 3.3 r/h) = 2 g r^2 (S-S'),$$

where  $X$  = ratio of radius of sphere to that of cylinder, and  $h$  = height of the liquid;

If 'T' be the time taken for the ball to travel a distance 'l', then

$$9\eta l (1 + 2 \cdot 4 X) (1 + 3 \cdot 3 r/h) = 2 g r^2 (S - S') T \quad (1)$$

### EXPERIMENTAL TECHNIQUE

The sodium oleate and sodium stearate used in this investigation were Merck's pure products; the pinene used in the preparation of the gel-forming solutions was obtained from Messrs. Eastman Kodak & Co., and was the fraction distilling at 156°.

(i) *Ostwald type of Viscometer*.—The technique employed was the standard one. The viscometer made of good hard glass, was immersed in a liquid paraffin bath for some time till it attained the temperature of the bath; a solution of a known amount of either sodium oleate or sodium stearate in 10 c.c. of pinene was prepared as described in Part I,<sup>11</sup> and was immediately transferred to the viscometer. The temperature of the paraffin bath was maintained at 150°. After the solution in the viscometer had attained a steady temperature, it was sucked up in the capillary end of the instrument and the time taken for a fixed volume of the solution to pass through the capillary was noted by means of a stop-watch. Such readings were taken after different intervals of time and at different temperatures (the paraffin bath was cooled to lower temperatures which were maintained constant) using several concentrations of the two soaps. Aniline was used as a standard; the time taken for the aniline to flow through the capillary of the viscometer was noted at several temperatures, and the values of the density and viscosity of aniline at different temperatures were taken from Beilstein's *Handbuch der Organischen Chemie*. Since the coefficient of viscosity of aniline was known, the coefficient of viscosity (in c. p.) of the soap solutions in pinene were obtained from

$$\eta/\eta' = dt/d't'.$$

The ends were kept open to atmospheric pressure and throughout the experiments, the pressure head was maintained constant.

The data obtained are given in Tables I and II.

(ii) *Falling Sphere Viscometer*.—The apparatus used was similar to the one used by Gibson and Jacobs.<sup>8</sup> The viscometer tube was selected from the best Pyrex glass tubing having a uniform bore and particular care was to see that the walls of the tube contained no rough surfaces. The length taken of the tube, one end of which was closed, was 29 cm. Four marks, each at a distance of 5 cm., and at a distance of 12 cm. from the top, were etched on the tube. To deliver the sphere into the mouth of the tube it was

TABLE I. Viscosity measurements of solutions of sodium oleate in pinene

A (g.)	Temp. (° C.)	$\eta$	$\eta/\eta_0$
0.03	130	0.4146	1.072
	120	0.4932	1.162
	110	0.5996	1.284
	100	0.7685	1.486
	95	0.9126	1.644
0.05	130	0.4284	1.108
	120	0.5306	1.250
	110	0.6806	1.458
	100	0.8523	1.648
	95	1.044	1.882
0.08	130	0.4560	1.152
	120	0.5560	1.311
	110	0.7131	1.528
	100	1.299	2.513
	95	1.744	3.198
0.09	130	0.4724	1.222
	120	0.5828	1.373
	110	0.7519	1.611
	100	1.956	3.784
	95	2.738	4.935
0.10	130	0.4975	1.286
	120	0.6155	1.450
	110	0.7818	1.675
	100	2.515	4.864
	95	4.126	7.435

TABLE II. Viscosity measurements of solutions of sodium stearate in pinene

A (g.)	Temp. (° C.)	$\eta$	$\eta/\eta_0$
0.03	130	0.4146	1.072
	120	0.4782	1.127
	110	0.6094	1.305
	100	0.6985	1.351
	95	..	..
0.05	130	0.4217	1.098
	120	0.5081	1.198
	110	0.6482	1.389
	100	0.7859	1.520
	95	..	..
0.08	130	0.4421	1.142
	120	0.5380	1.268
	110	0.6806	1.458
	100	1.223	2.364
	95	1.621	2.922
0.09	130	0.4604	1.191
	120	0.5530	1.303
	110	0.6936	1.486
	100	1.571	3.040
	95	2.446	3.501
0.10	130	0.4724	1.222
	120	0.5679	1.339
	110	0.7131	1.528
	100	2.166	4.189
	95	2.993	5.395

closed with an India-rubber stopper, bored centrally, and carrying a glass tube (3 mm. internal diameter and 7 cm. long) cut from best Pyrex glass tubing of uniform bore. The height of the solution in the tube was maintained constant such that the delivery tube dipped 3 cm. below the surface of the solution. A hole in the delivery tube at a distance of 2.5 cm. from the top and just below the stopper, served to adjust the pressure inside and outside the tube. Hence when the sphere ball was dropped into the tube, it travelled down very slowly, leaving the end below the surface of the liquid with a minimum disturbance, and then fell along the centre of the tube.

It is very important that the sphere balls should be uniform and, hence very great care was taken in their selection. Steel ball-bearings were found to be satisfactory. These balls have been guaranteed by their makers (S. K. F. Ball-bearing Co.) to be correct within  $\pm 0.0025$  mm. According to the specification of Gibson and Jacobs, the balls of diameter 0.15 cm. were selected. The density of the steel of which the balls were made was found to be 7.66. In order to test the apparatus, the viscosity of castor-oil was measured and the experimental results were found to agree well with the standard values.

The gel-forming solutions of sodium oleate and sodium stearate in pinene were prepared in the 29-cm.-tube itself. The solution in the viscometer tube was well stirred by means of a thin glass stirrer to make it uniform. After the solution was made, the viscometer tube was taken out of the oil-bath and the fractionating column was replaced by the delivery tube, particular care being taken to see that the delivery tube dipped 3 cm. below the surface of the solution in the tube. After the necessary adjustments were made the viscometer was placed in the water-thermostat maintained at constant required temperature. A stop-watch was started immediately and then at some suitable instant, the steel balls were dropped through the delivery tube, and the time taken by the ball to travel the full distance of 15 cm. length was noted by means of a second stop-watch. Such readings were taken at intervals of 15 seconds till the last ball travelled the complete length.

While measuring viscosity by the Falling Sphere viscometer it was observed that in the early stages of gelation the spheres fell steadily in a straight path, but during the latter stages the motion of the sphere became slightly unsteady and there were very small but perceptible deviations from the vertical path. Sometimes, the ball fell through a short distance in an irregular path, remained temporarily suspended, and then sank slowly. It would then roll off sideways as if struck against a clotted mass and dart downwards, rolling and twisting. It may reach another similar portion of the

gel sufficiently resistant to suspend it, when the ball's passage became more difficult and may finally cease altogether. These clotted masses or aggregates are not unattached to each other at this stage since on disturbing a suspended ball, another ball similarly suspended several centimetres lower was moved downwards.

On allowing the balls to fall through different points on the surface of the gel, it was noticed that the time taken for the fall is much larger from the sides of the viscometer tube than from the middle; also the velocity of fall in the upper portion of the tube is much faster than in the lower one. These peculiarities may be due to the fact that during cooling the part of the gel near the side of the tube and at the bottom gets cooled more quickly than the middle portion of the tube, and hence the former portions of the gel will set or will have nearly set, while the latter portions will be far away from the setting stage. These observations support the conclusions drawn from a study of the cooling of gel-forming solutions of certain soaps in pinene.<sup>11</sup> It is probable that the setting of different parts of a gel-forming solution at different intervals may introduce invisible heterogeneities in the gel structure.

To reduce the errors from this source to a minimum in the viscosity measurements, the average of several readings made at the central portion of the viscometer tube was taken.

The viscosities at several intervals of time during gelation were calculated from the equation (i) and the results obtained are given in Tables III-VIII. The time of fall is expressed in seconds, and the values of

TABLE III. *Viscosity measurements of sodium oleate gels in pinene*  
Temp. = 60° C.

A (g.)	T	$\eta$	$\eta - \eta_0$	$\log(\eta - \eta_0)$
0.4812	5-0.7	0.3268	0.3018	- 0.5204
	0.8	0.3778	0.3528	- 0.4579
	1.25	0.5834	0.5584	- 0.2531
	2.5	1.167	1.142	0.0577
	14	6.534	6.509	0.8135
	40	18.67	18.65	1.2707
0.5500	5-0.7	0.3268	0.3018	- 0.5204
	0.8	0.3778	0.3528	- 0.4579
	2.0	0.9335	0.9085	- 0.0417
	2.8	1.307	1.282	0.1079
	6.7	3.127	3.102	0.4917
	17.75	8.285	8.260	0.9170
0.6500	5-0.75	0.3501	0.3251	- 0.4880
	1.4	0.6534	0.6284	- 0.2017
	3	1.401	1.376	0.1386
	11.1	5.135	5.110	0.7084
	54.5	25.44	25.42	1.4051

TABLE IV. *Viscosity measurements of sodium oleate gels in pinene*  
Temp. = 70° C.

A (g.)	T	$\eta$	$\eta - \eta_0$	$\log (\eta - \eta_0)$
0.5500	5-0.5	0.2334	0.2084	- 0.6813
	0.65	0.3034	0.2784	- 0.5554
	0.75	0.3501	0.3251	- 0.4880
	0.85	0.3968	0.3718	- 0.4327
	1.1	0.5135	0.4885	- 0.3112
	1.5	0.7001	0.6751	- 0.1706
	2.1	0.9802	0.9552	- 0.0199
	3.25	1.517	1.492	0.1738
	3.75	1.750	1.725	0.2367
	5.15	2.404	2.379	0.3764
	12.0	5.602	5.577	0.7464
	37.75	17.62	17.60	1.2455
0.6500	5-0.5	0.2334	0.2084	- 0.6813
	0.6	0.2801	0.2551	- 0.5935
	0.75	0.3501	0.3251	- 0.4880
	0.9	0.4200	0.3950	- 0.4034
	1.75	0.8168	0.7918	- 0.1015
	2	0.9335	0.9085	- 0.0417
	2.6	1.214	1.189	0.0753
	3.8	1.774	1.749	0.2427
	10.75	5.019	4.994	0.6985
	26.75	12.48	12.46	1.0955
0.8019	5-0.6	0.2801	0.2551	- 0.5935
	1.0	0.4667	0.4417	- 0.3549
	1.3	0.6067	0.6042	- 0.2189
	2.1	0.9802	0.9777	- 0.0098
	2.7	1.260	1.235	0.0916
	4.75	2.217	2.192	0.3408
	26	12.13	12.11	1.0831

TABLE V. *Viscosity measurements of sodium oleate gels in pinene*  
Temp. = 80° C.

A (g.)	T	$\eta$	$\eta - \eta_0$	$\log (\eta - \eta_0)$
0.5500	5-0.375	0.1750	0.1500	- 0.8239
	0.5	0.2334	0.2084	- 0.6813
	0.55	0.2568	0.2318	- 0.6349
	0.6	0.2801	0.2551	- 0.5935
	0.65	0.3034	0.2784	- 0.5554
	0.7	0.3268	0.3018	- 0.5204
	0.75	0.3501	0.3251	- 0.4880
	1.5	0.7001	0.6751	- 0.1706
	2.05	0.9570	0.9320	- 0.0306
	2.75	1.284	1.259	0.1000
	3.0	1.401	1.376	0.1386
	3.75	1.750	1.725	0.2367
	5.25	2.451	2.426	0.3849
	11.0	5.135	5.110	0.7084
	22.35	10.43	10.41	1.0174
	54.25	25.32	25.30	1.4031

TABLE V—(Contd.)

A (g)	T	$\eta$	$\eta - \eta_0$	$\log(\eta - \eta_0)$
0.5876	5-0-375	0.1750	0.1500	- 0.8239
	0.5	0.2332	0.2082	- 0.6813
	0.6	0.2800	0.2550	- 0.5935
	0.7	0.3267	0.3017	- 0.5204
	0.8	0.3734	0.3484	- 0.4579
	0.95	0.4434	0.4184	- 0.3784
	1.0	0.4667	0.4417	- 0.3549
	1.3	0.6070	0.5820	- 0.2351
	1.5	0.7001	0.6751	- 0.1706
	1.8	0.8403	0.8153	- 0.0886
	2.25	1.050	1.025	0.0107
	2.4	1.120	1.095	0.0395
	3.0	1.401	1.376	0.1386
	3.5	1.633	1.608	0.2062
	4.5	2.100	2.075	0.3171
	5	2.332	2.307	0.3630
	6.5	3.034	3.019	0.4799
	39.5	18.44	18.42	1.2653
0.6500	5-0-375	0.1750	0.1500	- 0.8239
	0.5	0.2332	0.2082	- 0.6813
	0.6	0.2800	0.2550	- 0.5935
	0.7	0.3267	0.3017	- 0.5204
	0.8	0.3734	0.3484	- 0.4579
	0.95	0.4434	0.4184	- 0.3784
	1.1	0.5135	0.4885	- 0.3112
	2	0.9335	0.9085	- 0.0417
	2.5	1.167	1.142	0.0577
	3	1.401	1.376	0.1386
	3.9	1.821	1.796	0.2544
	5	2.332	2.307	0.3630
	7.8	3.641	3.616	0.5582

TABLE VI. Viscosity measurements of sodium stearate gels in pinene  
Temp. = 40° C.

A (g.)	T	$\eta$	$\eta - \eta_0$	$\log(\eta - \eta_0)$
0.2250	5-0.5	0.2332	0.2082	- 0.6813
	0.6	0.2800	0.2550	- 0.5935
	0.9	0.4200	0.3950	- 0.4034
	1.75	0.8166	0.7916	- 0.1015
	3.5	1.633	1.608	0.2060
	5	2.333	2.308	0.3632
	10	4.667	4.642	0.6667
	28	13.07	13.05	1.1155
0.3750	2-0.7	0.3267	0.3017	- 0.5204
	0.8	0.3734	0.3484	- 0.4579
	1.2	0.5601	0.5351	- 0.2715
	2.8	1.307	1.282	0.1079
	4.5	2.100	2.075	0.3171
	8	3.734	3.709	0.5692
	14	6.533	6.508	0.8137
	24	11.20	11.18	1.0483
0.6000	1-0.9	0.4200	0.3950	- 0.4034
	1.5	0.7000	0.6750	- 0.1707
	4	1.867	1.842	0.2653
	10	4.667	4.642	0.6667
	29	13.53	13.51	1.1306

TABLE VII. *Viscosity measurements of sodium stearate gels in pinene*  
Temp. = 50° C.

A (g.)	T	$\eta$	$\eta - \eta_0$	$\log (\eta - \eta_0)$
0.2250	6-0.4	0.1866	0.1616	- 0.7916
	0.6	0.2800	0.2550	- 0.5935
	0.7	0.3267	0.3017	- 0.5204
	0.9	0.4200	0.3950	- 0.4034
	2	0.9334	0.9084	- 0.0418
	4	1.867	1.842	0.2653
	8.5	3.967	3.942	0.5957
	12.7	5.927	5.902	0.7710
	32	14.93	14.91	1.1735
0.3750	3-0.7	0.3267	0.3017	- 0.5204
	1.2	0.5601	0.5351	- 0.2715
	2.8	1.307	1.282	0.1079
	5	2.332	2.307	0.3630
	11	5.134	5.109	0.7084
	21	9.797	9.772	0.9900
	35	16.31	16.29	1.2125
0.6000	1-0.5	0.2332	0.2082	- 0.6813
	0.8	0.3734	0.3484	- 0.4579
	1.25	0.5833	0.5583	- 0.2532
	3.8	1.773	1.748	0.2425
	14	6.533	6.508	0.8137
	40	18.67	18.65	1.2706

TABLE VIII. *Viscosity measurements of sodium stearate gels in pinene*  
Temp. = 60° C.

A (g.)	T	$\eta$	$\eta - \eta_0$	$\log (\eta - \eta_0)$
0.2250	8-0.45	0.2100	0.1950	- 0.7100
	0.6	0.2800	0.2550	- 0.5935
	0.7	0.3267	0.3017	- 0.5204
	1.25	0.5833	0.5583	- 0.2532
	1.8	0.8401	0.8151	- 0.0887
	3.8	1.773	1.748	0.2425
	7.5	3.500	3.475	0.5409
	12	5.601	5.576	0.7464
	25	11.66	11.64	1.066
0.3750	4-0.6	0.2800	0.2550	- 0.5935
	0.8	0.3734	0.3484	- 0.4579
	1	0.4667	0.4417	- 0.3549
	3.5	1.633	1.608	0.2062
	5	2.332	2.307	0.3630
	10	4.667	4.642	0.6667
	23	10.74	10.72	1.0302
0.6000	1-0.45	0.2100	0.1950	- 0.7100
	0.7	0.3267	0.3017	- 0.5204
	0.9	0.4200	0.3950	- 0.4034
	2.1	0.9797	0.9547	- 0.0200
	4.8	2.240	2.215	0.3454
	13	6.066	6.041	0.7811
	38.2	17.83	17.81	1.2506

viscosities are expressed in c.g.s. units. Such measurements were made with solutions containing different amounts of the gel-forming substance (Ag. in 75 c.c. of pinene) at several temperatures. In the table of results 'T' the average time when the viscosity reading was taken, is expressed as 5-0·4 which means that the first reading was taken 5 mts. after the viscometer tube had been placed in the thermostat, and 0·4 is the time of fall in seconds.

#### DISCUSSION OF RESULTS

In Part II of this series of papers,<sup>12</sup> it has been shown that the solutions of soaps in pinene at temperatures near about the boiling point are true molecular solutions. Hence an attempt was made to see if the well-known Einstein equation  $\eta/\eta_0 = 1 + k\phi$  is applicable to these systems. Consequently the values of  $\eta/\eta_0$  were plotted against  $\phi$  (the proportion of the disperse part to the entire volume, or in other words, the concentration of the solution) and the curves obtained in the case of sodium oleate are shown in Fig. 1. It will be noticed that straight lines are obtained for all solutions at temperatures above about 110°. This shows that the values of viscosity recorded above 110° are those for true molecular solutions or for sols with little or no aggregation of dispersed particles. This conclusion is supported by the observation that the viscosities of these solutions are largely independent of time, thermal history and mechanical treatment.

Incipient gelation of sols was detected by the abnormal increase in viscosity with time in the case of solutions of all concentrations between the temperature range 110°–100° and below. This can be clearly seen from the curves in Fig. 1; at temperatures 100° and below, steep curves which rise slowly are obtained instead of straight lines. It was observed that below 90° the time of transpiration was long and in certain cases the viscosity increased considerably during the actual determination. The remarkable increase in viscosity with (i) the lowering of temperature (upto and near about 90°) and (ii) the increase of soap content, can be seen from Tables I and II. For instance, the value of  $\eta/\eta_0$  for solutions containing 0·1 g. of sodium oleate at 95° is nearly six times of that at 130°. It therefore appears that on cooling the soap solution in pinene below 110°, small colloidal particles or micelles or loose or open aggregates are formed, and their number increases either on increasing the soap content or on further cooling. The observed increase in viscosity is due to the increased shear imposed by these aggregates upon the solvent for a given amount of flow.

The values of viscosity observed at different intervals of time during the sol-gel transformation of the soap solutions at lower temperatures give rise to  $\eta-t$  curves which are very similar in general characteristics; those

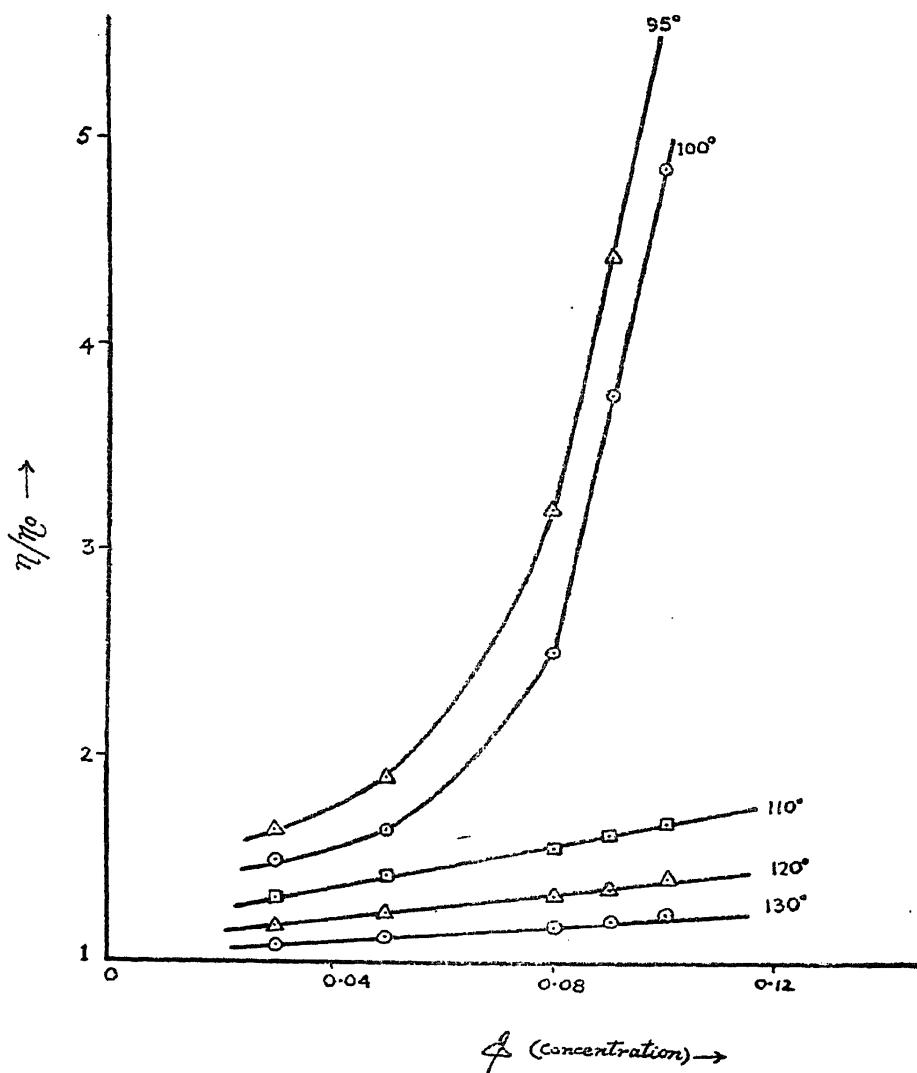
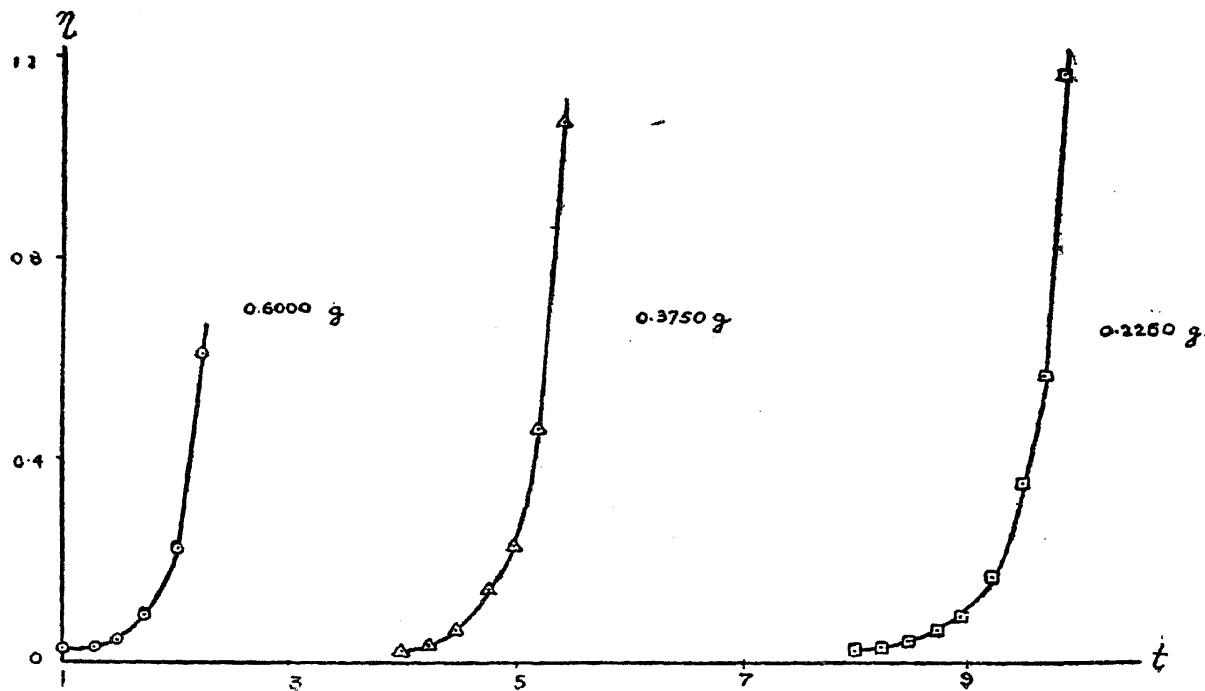


FIG. 1

for sodium stearate are shown by means of curves in Fig. 2. All these curves are smooth, that is, they show no irregularities during the process of



They show that the soaps in solutions in pinene between the boiling point and 110° are in a molecular state, but they go over to the colloidal state and form a dilute or concentrated soap sol in pinene owing to the supersaturation of the solution as it is cooled to lower temperatures. Further cooling results in the agglomeration of these colloidal particles into bigger ones and the formation of a gel-structure with consequent immobilisation of the dispersion medium.

#### SUMMARY

Viscosity measurements during the sol-gel transformation of gel-forming solutions of sodium oleate and sodium stearate in pinene have been made using two types of viscometers. Results obtained with the Ostwald type of viscometer follow the Einstein equation within a certain range of temperature. The regularities observed in the viscosity-time data obtained by the Falling Sphere viscometer during the sol-gel transformation of soap-pinene systems can be conveniently expressed by the empirical relation  $\eta - \eta_0 = ae^{kt}$ .

The viscosity data has been employed for the purpose of drawing inferences regarding the mechanism of sol-gel transformation of soap-pinene systems.

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#### REFERENCES

1. Mardles .. *Trans. Farad. Soc.*, 1923, **18**, 327.
2. Levites .. *Koll. Z.*, 1907, **2**, 210.
3. Shoji .. *Biochem. J.*, 1919, **13**, 227.
4. von Schroeder .. *Z. physik. Chem.*, 1903, **45**, 75.
5. Biltz and von Vegesack .. *Ibid.*, 1910, **73**, 506.
6. Arisz .. *Koll. Chem. Beih.*, 1915, **7**, 19.
7. Sheppard .. *J. Ind. Eng. Chem.*, 1917, **9**, 34.
8. Gibson and Jacobs .. *J. C. S.*, 1914, **117**, 473.
9. Ladenburg .. *Ann. Phys.*, 1907, **22**, 287.
10. Arnold .. *Phil. Mag.*, 1911, **22**, 753.
11. Prasad and Hattiangdi .. *Proc. Ind. Acad. Sci.*, 1945, **21**, 1.
12. Prasad, Hattiangdi and Vishwanath .. *Proc. Ind. Acad. Sci.*, 1945, **21**,
13. ——— and co-workers .. *J. Phys. Chem.*, 1932, **36**, 1384; *J. Indian Chem. Soc.*, 1936, **13**, 128; 1940, **17**, 508; *Proc. Ind. Acad. Sci.*, 1940, **11**, 282.