

STUDIES IN INORGANO-ORGANIC GELS IN PINENE

Part VI. Viscosity Changes with Time and Shear during the Gelation of Some Soap Systems in Pinene

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IN a recent communication, Prasad and co-workers¹ have determined the viscosity changes that take place during the setting of solutions of sodium oleate and sodium stearate in pinene when they are cooled to different temperatures, using two types of viscometers, namely, the capillary-type Ostwald viscometer and the Falling Sphere viscometer. The regularities observed in the viscosity data obtained by the latter instrument during the process of gel-formation could, according to them, be expressed by the empirical relation $\eta - \eta_0 = ae^{kt}$, whereas the data obtained with the capillary viscometer obeyed the well-known Einstein's equation $\eta/\eta_0 = 1 + k\phi$ within a certain range of temperature only. It is very important to determine the effect of shear on the viscosity values obtained during the sol-gel transformation. An attempt in this direction was made in the case of cellulose acetate gel-forming systems in benzyl alcohol by Mardles² who observed that the values of the apparent viscosity decrease with increasing shear, and the nature of the viscosity-time curve changes its character with a change in the shear applied. He has, however, given no satisfactory explanation for this peculiar behaviour of the gelating systems.

This investigation gives the results of the measurements of the viscosity changes with time of some soap systems in pinene during the process of setting when different shears are applied. The soaps used are sodium oleate, sodium stearate and sodium palmitate, and the viscosity determinations have been made by employing a rotating cylinder viscometer.

EXPERIMENTAL

The sodium oleate and sodium palmitate used were products of the B. D. House, and sodium stearate of Messrs. E. Merck. The pinene used was obtained from Messrs. Eastman Kodak & Co., and was the fraction distilling at 156°.

The rotating cylinder viscometer used was manufactured by Messrs. W. G. Pye & Co., and consisted of a hollow cylinder (3.73 cm. in diameter and 10 cm. in length), which was rotated in a cylindrical vessel containing the gel-forming solution, there being a clearance of 0.678 cm. between the walls of the two cylinders. The inner cylinder was rotated by means of falling weights attached to the ends of a thin tough cord which passed over frictionless pulleys. The effective radius of the drum, D , round which the cord was wound was 1.91 cm. The value of the viscosity was calculated from the relation

$$\eta = \frac{g D (a^2 - b^2)}{8 \pi^2 a^2 b^2} \cdot \frac{MT}{I + k}$$

TABLE I
Sodium oleate in pinene

Soap content (in g.)	Time interval (in mts.)	Relative viscosity values at different rates of shear		
		10 g.	15 g.	20 g.
0.60	0	2.50	2.50	2.50
	1	2.60	2.55	2.55
	2	2.80	2.70	2.65
	3	3.25	2.93	2.84
	4	3.69	3.06	3.02
	5	3.89	3.45	3.20
	10	do	3.73	3.56
	20	do	do	do
	30	do	do	do
	40	do	do	do
	50	do	do	do
0.75	0	3.10	3.10	3.10
	1	3.40	3.25	3.20
	2	3.85	3.45	3.30
	3	4.50	3.70	3.45
	4	4.99	3.85	3.60
	5	5.29	4.00	3.73
	10	5.58	4.35	4.14
	20	do	do	4.35
	30	do	do	do
	40	do	do	do
	50	do	do	do
0.90	0	4.15	4.15	4.15
	1	4.43	4.27	4.21
	2	4.65	4.40	4.27
	3	4.98	4.65	4.36
	4	5.10	4.95	4.62
	5	5.32	5.07	4.75
	10	5.84	5.33	5.00
	20	do	do	do
	30	do	do	do
	40	do	do	do
	50	do	do	do

The radius of the outer and inner cylinders, a and b , were 2.543 cm. and 1.865 cm., respectively; M is the mass applied to the end of the cord and is proportional to shear; T is the time taken (in seconds) for one complete revolution of the cylinder; l is the length of the gel, and k the constant of the instrument ($k = 0.55$).

The solutions of the various sodium soaps in pinene were prepared by dissolving known amounts of the soap in 60 c.c. of pinene as described by Prasad and Hattiangdi³; the results of the various experiments are given in Tables I to III.

TABLE II
Sodium stearate in pinene

Soap content (in g.)	Time interval (in mts.)	Relative viscosity value at different rates of shear						
		10 g.	15 g.	20 g.	30 g.	40 g.	50 g.	60 g.
0.60	0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	1	3.34	3.20	3.1	3.07	3.06	3.06	3.05
	2	3.57	3.51	3.25	3.15	3.12	3.08	do
	3	3.81	3.70	3.4	3.25	3.17	3.1	do
	4	3.96	4.12	3.6	3.33	3.20	3.1	do
	5	4.12	do	3.75	3.42	3.25	3.15	do
	10	4.46	do	3.9	3.64	3.50	3.25	do
	20	4.95	do	do	do	do	do	do
	30	do	do	do	do	do	do	do
	40	do	do	do	do	do	do	do
0.75	0	4.2	4.2	4.2	4.2	4.2	4.2	4.2
	1	4.44	4.35	4.33	4.32	4.31	4.3	4.2
	2	4.7	4.55	4.5	4.45	4.33	4.3	4.3
	3	4.95	4.8	4.75	4.64	4.45	4.41	do
	4	5.60	5.2	4.98	4.8	4.55	4.45	do
	5	6.19	5.5	5.25	4.9	4.65	4.5	do
	10	8.42	6.91	6.25	5.52	5.0	4.8	do
	20	8.91	7.76	6.6	do	do	do	do
	30	do	do	do	do	do	do	do
	40	do	do	do	do	do	do	do
0.90	0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	1	5.25	5.15	5.07	5.06	5.06	5.06	5.06
	2	5.59	5.32	5.25	5.11	5.11	5.06	do
	3	6.0	5.54	5.32	5.24	5.15	..	do
	4	6.52	5.8	5.53	5.32	5.2	5.1	do
	5	6.75	6.25	5.71	5.45	5.25	5.2	do
	10	8.69	7.58	6.95	5.95	5.50	5.25	dn
	20	do	do	do	do	do	do	do
	30	do	do	do	do	do	do	do
	40	do	do	do	do	do	do	do
50	do	do	do	do	do	do	do	

TABLE III
Sodium palmitate in pinene

Soap content (in g.)	Time interval (in mts.)	Relative viscosity values at different rates of shear		
		10 g.	15 g.	20 g.
0.60	0	2.6	2.6	2.6
	1	2.8	2.8	2.69
	2	3.1	3.0	2.90
	3	3.42	3.3	3.05
	4	3.8	3.5	3.31
	5	4.25	3.6	3.45
	10	5.1	4.0	3.7
	20	do	do	do
	30	do	do	do
	40	do	do	do
	50	do	do	do
0.75	0	3.5	3.5	3.5
	1	3.6	3.57	3.55
	2	3.99	3.7	3.65
	3	4.5	3.99	3.87
	4	4.85	4.2	4.00
	5	5.05	4.32	4.1
	10	5.51	4.65	4.35
	20	5.82	5.45	do
	30	do	do	do
	40	do	do	do
	50	do	do	do
0.90	0	5.25	5.25	5.25
	1	5.38	5.35	5.30
	2	5.6	5.45	5.35
	3	5.9	5.58	5.45
	4	6.15	5.76	5.55
	5	6.31	5.95	5.70
	10	6.6	6.26	5.95
	20	do	do	do
	30	do	do	do
	40	do	do	do
	50	do	do	do

DISCUSSION OF RESULTS

The effect of shear on the viscosity changes during gelation is very pronounced. The viscosity values decrease with an increasing shear, and the shape of the viscosity-time curves of the same system under different shears goes on changing. As a typical case the decrease in the apparent viscosity value with increasing shear for the gelating system of sodium stearate in pinene (0.75 g. in 60 c.c.) is shown by means of curves in Fig. 1. It will be observed from these curves that for low shears (10 g. to 30 g.) the viscosity-time curves rise slowly at first and then rapidly till they tend to run almost parallel to the viscosity axis; this is the condition when the setting

point is being approached. After this stage the curve takes a sudden turn and runs parallel to the time axis, indicating that the values of viscosity remain constant for any given set of experimental conditions. These curves would therefore appear to be different from those obtained by Prasad, Hattiangdi and Vishvanath¹ in the sense that the last part of the curves parallel to the time axis is absent. This is due to the fact that when the gel is set, there is no longer any velocity gradient in the gel, and the only consequence of the applied shear is a sort of slipping between the outer surface of the inner cylinder and the surface of the gel in contact with it.

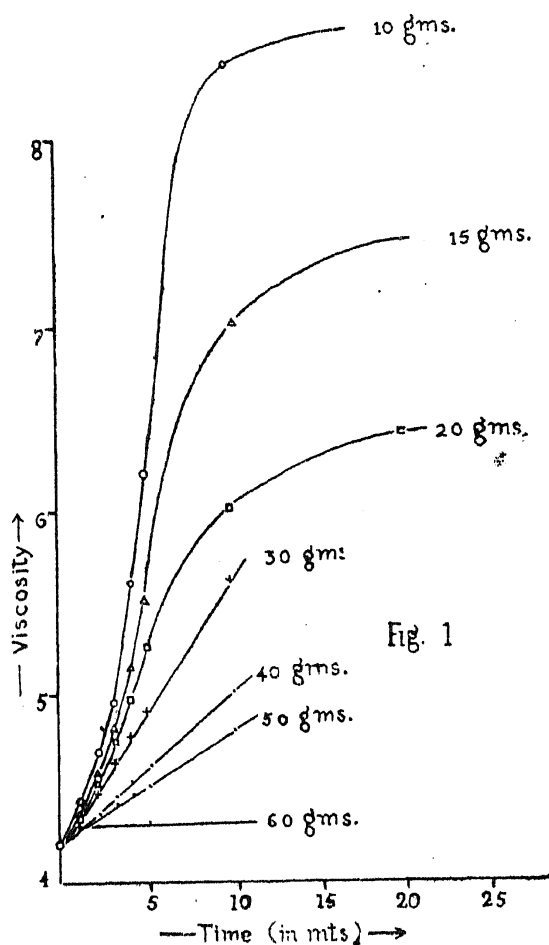


Fig. 1

This slipping is of a similar nature as that of rolling friction and has the same value as the viscosity of the set gel. As the shear is slowly increased, it is found that the apparently S-shaped nature of the curve is maintained, that is, the top part of the curve runs parallel to the time axis due to the constant value of viscosity attained by the gel system. For high rates of shear, however, the viscosity increases linearly with time and then reaches an almost constant value, the position of the straight lines moving towards the time axis as the shear is increased. The results obtained by Mardles² are similar

to these observations. The peculiar phenomenon of anomalous viscosity exhibited by the soap systems during gel-formation can be explained on the basis of the mechanism of the formation of these gels stressed by Prasad and co-workers in a number of papers. According to them, gel-formation results from (i) the gradual increase in the number and size (volume) of the soap micelles which are aggregates of small soap particles, (ii) the solvation of these micelles with the dispersion medium which is a saturated solution of soap in pinene, (iii) the fusion or aggregation of these solvated micelles into fibrils, and (iv) the enclosure of the intermicellary fluid in the interfibrillar space in an adsorbed state due to the attractive or linking forces between the fibrils. Prasad and co-workers have also shown that all the aforesaid processes take place simultaneously in the gel-forming system although some of them may take place preponderantly at one time than the others. Thus when a gel-forming solution of soap in pinene is allowed to cool to a low temperature, there will firstly be, preferably on an average, an increase in the number and size of the micelles and this will be abundantly followed by processes (ii), (iii) and (iv) described above. As a consequence, in the earlier stages of gelation, the structural gel-strength which is linked with the growth of the micelles will be weak and will become stronger as time elapses and the setting point is being approached.

The viscosity-time curves (*cf.* Fig. 1) for low rates of shear bring out the above-mentioned points very clearly. The slow increase in viscosity initially is caused by the increase in the number and the size of the soap micelles; the subsequent fairly rapid rise shows that the increase in viscosity with time is considerably accelerated owing to the large degree of solvation of the soap micelles and their aggregation into fibrils. The very rapid rise in viscosity during the last stage is due to the formation of a structure in the gel which behaves almost like a solid and hence offers a great resistance. These observations lead to the conclusion that the aforesaid behaviour would be shown by the gel-forming systems of soap in pinene if a viscosity-time curve is obtained without the application of any shear (*cf.* the curves obtained by Prasad and others¹).

When the viscosity measurements are made with these gel-forming systems under different shear, two processes take place simultaneously, namely, (i) the occurrence of the processes described above, and (ii) the breakdown of all or some of the functions in the processes due to the shear acting in a direction opposite to the forces which come into play during the gel-formation.

The S-shaped curves obtained with increasing shear varying from 10 g. to 30 g. show that excepting for the earlier portions, the curves are lowered on increasing the shear, the latter part being lowered more than the earlier one. This shows that the application of the shear causes a general decrease in the rates of the occurrence of the four processes involved in gel-formation of soap-pinene systems, and the decrease is considerably more in the last three processes than the first one. This means that there is not only a decrease in the number and volume of the micelles formed owing to the application of the shear but their extent of solvation and aggregation into fibrils is also decreased, and hence the formation of a structure which causes a gel to set is delayed. This view is supported by the fact that the gel takes slightly more time to set when the shear applied is increased from 10 g. to 30 g.

When the shear is increased to 40 g. and 50 g., it is observed that (i) the viscosity-time curve is a straight line, that is, the acceleration in viscosity entirely disappears, and (ii) the earlier parts of the curves in the two cases are practically coincident. On the basis of the theory outlined above it means that factors which tend to form the essential agents for the formation of gel-structure are prevented from getting into action by the opposing shear. Since the gradients of these straight lines are less than those of the earlier parts of the curves for 10 g. to 30 g., it appears that the increase in viscosity at uniform rate in these two cases takes place mostly owing to the constant rate of increase in the number and the size of the micelles, and possibly, to some extent, to their solvation. This view is supported by the fact that when shears higher than 30 g. are applied, the system does not set to a gel even on keeping it for a sufficiently long time after the application of the shear, probably because the structure has been very badly broken down, and it looks like a suspension of soap in pinene.

On further increasing the shear to 60 g., the viscosity increases slightly in the beginning (during the first one or two minutes) and then attains a constant value. This shows that initially some micelles are formed which give the observed viscosity value to the gel-forming system; later on, the application of the high shear either destroys or prevents completely (i) the formation of more micelles and (ii) their increase either in volume, solvation, or aggregation. The viscosity-time curve for 60 g. of shear therefore represents the condition of the formation of a minimum number of micelles in this particular instance which is not affected by the shear.

This discussion leads us to two important conclusions regarding the application of shear, namely, (i) it can prevent or destroy the formation of gel structure which is responsible for the acceleration of viscosity with time,

and (ii) it can also decrease the rate of formation of the micelles or of the increase in their size or degree of solvation.

According to Goodeve and Whitefield⁴, there is an equilibrium under certain conditions of steady shear between the rate of increase of the concentration of the micelles in a thixotropic system and their breakdown, and the apparent viscosity η of the system is given by the relation

$$\eta - \eta_0 = \frac{\theta}{s},$$

where η_0 is the residual viscosity, s the shear, and θ the coefficient of thixotropy. They also report that on plotting the observed values of viscosity against the reciprocal of shear straight lines are obtained. According to Freundlich, Goodeve and others, thixotropy indicates the isothermal decrease of viscosity with increase in rate of shear. In the light of the above definition, soap gels in pinene may be considered to be thixotropic and hence may conform to the above mentioned relation. This has been found to be so. On plotting the values of the apparent viscosity (η) against the reciprocal of the shear ($\frac{1}{s}$), the curves obtained are straight lines for all the gel-forming systems studied in this investigation. Further according to the relation given above, the intercepts of the straight lines on the viscosity axis must be equal to η_0 , the residual viscosity of the system. The values of η_0 have been determined and have been found to correspond to the state of the soap-pinene systems upto which all the $\eta - t$ curves are coincident. The residual viscosity may therefore be interpreted as the true viscosity of the colloidal system containing soap micelles which have undergone little or no solvation. According to the considerations brought out in the discussion, this part of the viscosity-time curves corresponds to the soap-pinene system which contains practically only the soap micelles in a colloidal state in pinene.

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SUMMARY

Measurements of the viscosity changes with time taking place in the gel-forming systems of certain soaps in pinene yield $\eta - t$ curves which change their shape considerably as the shear applied is varied. It is also found that the shear applied can (i) prevent or destroy the formation of a gel structure which is responsible for the acceleration of viscosity with time,

and (ii) decrease the rate of formation of the micelles or of the increase in their size or degree of solvation. The plots of viscosity against the reciprocal of the shear are straight lines, indicating that the equation $\eta - \eta_0 = \theta/s$ is applicable to these soap-pinene systems.

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