STUDIES IN INORGANO-ORGANIC GELS IN PINENE

Part V. Gel-Strength Measurements of Gels of Sodium Stearate in Pinene

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THE gel-strength and modulus of elasticity have been considered to be an important and characteristic property of gels. The largest data available on the subject in literature is on gels of gelatin, probably because they are "rigid", and therefore it is easier to work with them than with gels of other substances which are comparatively "soft" and exude liquid and consequently lose their shape completely on an application of a slight stress.

An important investigation on the measurement of this property of gels in non-aqueous media has been carried out by Poole[1] in the case of cellulose acetate gels in benzyl alcohol. He finds that elasticity is approximately proportional to the square of the concentration, indicating that the rigid phase results from a dynamic solvation equilibrium between the cellulose acetate and the solvent. He proposes a Coefficient of Inner Resistance to denote the force which is required to produce unit velocity of "creep" (the increase in deformation with time when a steady stress is applied to a gel) in a unit cube of the gel in the absence of all elastic controlling forces. Lampitt and Money[2] also find that the gel-strength of gelatin gels is linearly related to the square of the concentration of the gel over a limited range.

In the present investigation the gel-strength of sodium stearate gels in pinene has been measured with a view to get some insight into the elastic properties of these soap gels in non-aqueous media. This soap was selected because it was found to give rise to stable and fairly stiff gels.

EXPERIMENTAL

The several methods which have been proposed for measuring or comparing the gel-strengths of gels may be divided into four main classes:

(a) dynamometer methods, in which the forces required to twist a column of the gel through definite angles are measured;

(b) methods involving the breaking of a gel;

(c) measurement of the depression produced by a constant load; and

(d) measurement of the load required to produce a definite depression. Soap gels in pinene are generally weak or "soft" for they lose shape and exude liquid on the application of a slight torsion. Hence dynamometric methods could not be employed to investigate the gel-strength of these gels.

Preliminary experiments made with a gel-testing apparatus similar to the one described by Oakes and Davis[3] showed that this method could be employed with advantage to measure the gel-strength of sodium stearate gels in pinene. In this apparatus, the bottom of one pan of a sensitive balance is attached to a plunger made of good quality glass. This is counter-poised so that the pointer rests at zero on the scale.

Gel-forming solutions containing varying amounts of sodium stearate (Merck's pure product) were prepared in 10 c.c. of pinene as described by Prasad and Hattiangdi[4] and were immediately poured into small weighing bottles in which they were allowed to set. The surface of the gel was then brought into contact with the plunger; weights were slowly added to the pan and the corresponding deflections on the scale as indicated by the pointer were noted. It was found that all small deflections of the pointer were proportional to the depression of the plunger. Such readings were taken till the breaking point or the elastic limit of the gel was reached. Care was taken to see that there was no jerking or oscillation of the plunger while in contact with the gel, and that the pressure was applied perpendi-cularly to the surface of the gel.

According to several earlier workers, all the methods which depend upon the breaking or compression of the gel in open glasses are subject to two sources of error: (a) the glasses usually vary in diameter thus forming a surface of variable area, and (b) there is always a "skin" of greater or less thickness which interferes with the accuracy of the test. The difficulty arising from the first cause was overcome by employing bottles of the same diameter ($2r = 2\cdot4$ cm.). To determine the existence, if any, of a "skin" or "surface" effect and the extent to which it vitiates the values of gel-strength, the plunger was dipped into a gel-forming solution before it was allowed to set; gel-strength measurements were carried out after the gel had set, in the same manner as described earlier.

Some workers recommend the use of a flat-ended plunger in preference to the hemispherically-ended one, since the area in contact with the gel is constant in the former case instead of increasing with depression as it happens if the latter type of plunger is used. In order that a comparison

of the two types of plungers could be made, a flat-ended circular disc-type plunger having a diameter equal to that of a hemispherically-ended one ($2r = 0.8$ cm.) was prepared, and a series of load–deflection curves were obtained.

The various load-deflection results obtained for these gels are shown graphically in Figs. 1–4.
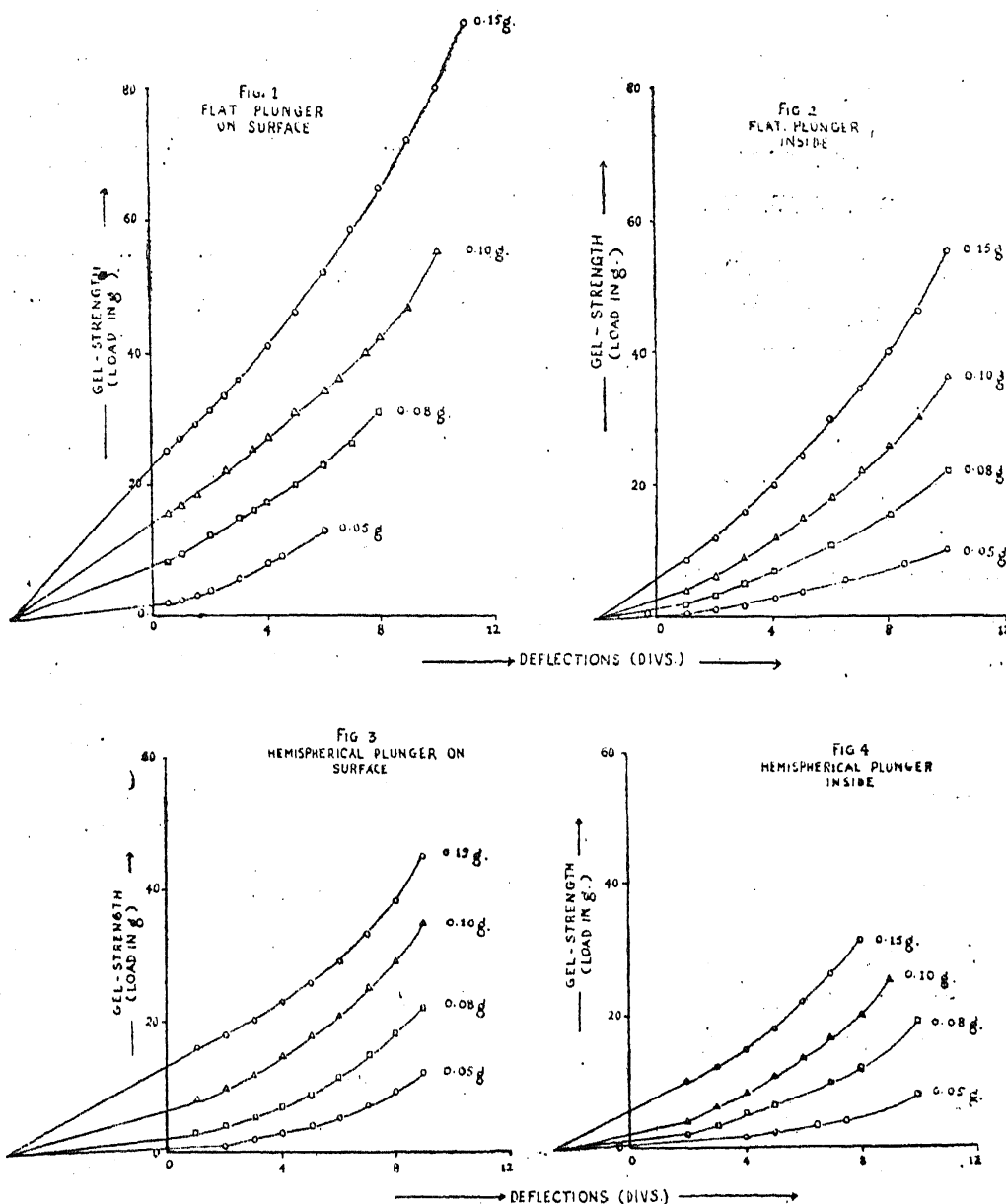
DISCUSSION OF RESULTS

A comparison of the data obtained with the two types of plungers acting (i) on the surface of, and (ii) inside the gel, shows that

(a) both plungers give an almost linear loading curve until the elastic limit is exceeded;

(b) the deflection produced for a given load is much smaller in the case of a flat plunger than when the hemispherical plunger is used; this is due to the fact that the hemispherical plunger has a greater weight in proportion to the surface directly opposed to the gel, and is therefore better able to overcome the resistance of the gel. Thus the velocity of the hemispherical plunger is assisted and a greater range for the same load is obtained;

and (c) the elastic limit of the gel is reached with a smaller depression (deflection) of the flat plunger than that of the hemispherically-ended one; this is a direct consequence of the observation and behaviour mentioned in (b).

An interesting observation was made during the actual experimentation. Initially the pointer is at rest at zero on the scale when the surface of the gel is brought into contact with that of the plunger. When a very small load is applied, the plunger actually rises up instead of being forced down, and the pointer immediately starts oscillating. On applying small increasing loads, the upthrust of the plunger is gradually countered till a stage is reached when the pointer is once again at rest at zero, and subsequently the plunger moves downwards only if still greater loads are applied. The initial upthrust of the plunger is an evidence of the existence of a " surface " effect which behaves like an elastic membrane and whenever the loads applied are small the upward reaction is quite noticeable; in the absence of such an effect, the plunger would have pressed down against the surface of the gel on the application of even a very small load. An attempt was made to determine the magnitude of this " surface " effect by increasing the load till it could just break the surface film.

In the case of a flat plunger, the expression for the tension can be mathematically derived on the considerations that the rim of the flat plunger is in contact with the film to be broken and the tension will act perpendicularly to the line of contact. Usually in liquids, some angle (the angle of contact) is made with the direction of the tension and the line of contact. No angle was, however, observed when a rod was immersed vertically inside the gel, and hence the angle of contact was taken as zero. The total force acting upwards is therefore $2\pi rT_F$, where r is the radius of the plunger, and this is balanced by mg the force necessary to break the film. Therefore,

$$2\pi rT_F = mg,$$

$$\text{or} \qquad T_F = mg/2\pi r. \tag{I}$$

The expression in the case of the hemispherical plunger can be derived as follows. As increasing loads are applied, the plunger presses more and more against the surface of the gel, and near about the point when the skin is pierced the hemisphere is closely and completely surrounded by the membrane on the top of the gel. At this stage the extended membrane has an area $2\pi r^2$, where r is the radius of the sphere; the area of the membrane before this extension took place was only πr^2, and therefore the increase in area due to the action of the plunger is πr^2. Therefore the surface energy is equal to $\pi r^2 T_H$. This energy is derived by the work done by the weight mg in moving through a distance r, the buoyancy effect being neglected. Hence,

$$\pi r^2 T_H = mgr,$$

or $\qquad T_H = mg/\pi r.$ \hfill (II)

The values of the tension T_F and T_H were calculated for gels of different concentrations of sodium stearate using the relations (I) and (II), and are given in columns 2 and 3 of Table I.

TABLE I

Values of the Surface Effect " T "

Soap content (in g.)	Determined from the limiting value of the load on the surface of the gel		Determined by the graphical method	
	Flat-ended plunger T_F	Hemispherical plunger T_H	Flat-ended plunger T_F'	Hemispherical plunger T_H'
0·05	1290	1169	2078	2027
0·08	3959	3945	4937	4755
0·10	6238	6238	6366	6239
0·15	8470	8055	8445	8420

The existence of the " surface " effect can be evidenced on different considerations altogether. If there were no such effect, the shear required to produce any strain should be the same wherever the plunger may be acting, on the surface or inside. The various curves in Figs. 1 and 2, and 3 and 4, however, show that the load required to produce a certain deflection is larger when either type of plunger is acting on the surface than when it is inside the gel. The difference between these two values of loads can be reasonably assumed to be the force which is necessary to counter the " surface " effect. The correctness of this assumption was verified by

determining the actual magnitude of the effect as follows. If L_1 is the load required to produce a certain deflection when the plunger is acting on the surface of the gel, and if L_2 is the load which produces the same deflection when the plunger is inside the gel, then $(L_1 - L_2) g$ is the force required to overcome the surface effect. Substituting $(L_1 - L_2) g$ for mg in equations (I) and (II), the values of T_F' and T_H' were calculated, and are given in columns 4 and 5 of Table I.

It will be seen from Table I that (i) there is a good agreement between the values of T_F and T_H and T_F' and T_H' over the range of concentrations studied, indicating that the value of T is almost independent of the nature of the plunger used, and (ii) there is a very good agreement between the values of T_F, T_H, T_F' and T_H' for 0·10 g. and 0·15 g. content of sodium stearate in the gel-systems, but the two sets of values are widely divergent for lower soap contents. The values obtained by the graphical method are higher than those obtained by the other method, but they are more correct for the following reasons. In the graphical method the value of m taken in calculating T for any concentration is the mean of several values computed from the graphs, while in the other method only one value of m can be available for calculation and a slight variation in the value of m would considerably affect the value of T. Hence the error is considerably minimised in the graphical method.

The development of a skin or membrane on the surface of the gel can be, in the first instance, very clearly seen when the gel-forming solution is being cooled. Further, it was observed that if the skin of a well-formed gel is pierced by a glass rod or plunger, the pierced portion of the surface appears like a fresh wound when the rod or plunger is withdrawn, and no fresh skin is formed on this spot even on keeping the gel for a sufficiently long time. This shows that a skin is formed during the process of setting of the gel. Its probable mode of formation is as follows. When a hot homogeneous solution of sodium stearate in pinene is allowed to cool, there is a rapid radiation of heat from the surface which brings about (i) an immediate inhomogeneity in the distribution of the solute in the dispersion medium, and (ii) a quick evaporation of the pinene due to which a semi-dry skin or membrane is formed on the surface of the gel. The skin or membrane is thus formed only during the process of setting of the gel, and not at any stage afterwards.

Previous workers have shown that Hooke's law holds true in the case of gels, that is the load–displacement curve is a straight line passing through the origin, and its slope is proportional to elasticity. The earlier portions

of the curves in Figs. 1–4 are straight lines, thus showing that Hooke's law is obeyed up to certain loads only; but with increasing loads these lines bend into a curve which shows that the elastic limit or the fatigue point has been exceeded. If the straight lines are produced backwards, they do not meet at the origin but some point which may be taken as the true origin of the load-deflection co-ordinates. The shape of these curves and the abovementioned behaviour are similar to those reported by Oakes and Davis[3] and Sheppard and Sweet[5] in the case of gelatin gels, using similar plunger methods. The difference in the nature of the earlier portions of the curves in the soap–pinene systems and gelatin gels may be caused by the varying surface of contact of the plunger employed in the latter case.

The gel-strength can be measured either from the slope of the straight lines which converge to a point, or by comparing the loads required for the same deflection. The values of gel-strength were calculated from the slopes of the load–deflection curves shown in Figs. 2 and 4, that is, when the plunger is placed inside the gel, and are given in the following table.

TABLE II.

Values of Gel-Strength (arbitrary units)

Soap content (in g.)	Flat-ended plunger	Hemispherical plunger
0·05	0·75	0·75
0·08	1·75	1·50
0·10	2·75	2·20
0·15	3·75	2·80

The above results show that the gel-strength increases as the soap content of the gels is increased; the slight variation in the actual values when the two types of plungers are used is mainly due to the fact that when the hemispherical plunger is acting, the micelles get more opportunity to orientate themselves in such a way as to reduce the resistance and to increase the strain, and hence the gel-strength values are slightly smaller. Although it is an anomaly to say that a physical property like elasticity is different when different methods are used, it is not surprising to find such a behaviour in these gel systems where the binding forces between the micelles are of such a small order as could be destroyed by mere mechanical agitation.

Poole and others have found that the plots of the logarithm of elasticity or gel-strength (E) against the logarithm of the concentration (C) are approximately straight lines in several cases, and the value of the slope does not

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exceed 2. On plotting the values of log E against log C, obtained from the data given in Table II, it was found that the several points lie very nearly on a straight line whose slope is equal to $1\cdot8$ which closely approximates to 2. This observation is in accordance with the fibrillar theory of gel-structure developed by Poole. It has, however, to be remarked that the variation of elasticity or gel-strength as the square of the concentration, according to the theory, does not appear to hold true in the case of soap-pinene systems for higher concentrations.

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SUMMARY

The gel-strength of gels of sodium stearate in pinene has been measured by the plunger method under several conditions. The values of elasticity have been calculated from the load–deflection curves, and it is found that log E varies linearly as log C, the slope of this straight line being very nearly equal to 2. The existence of a skin or membrane on the surface of the gel which vitiates the values of gel-strength has been critically examined, and its approximate magnitude has been determined.

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