Flow properties of aluminium soap-hydrocarbon systems

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Organogels prepared from aluminium stearate and liquid paraffin in concentrations of 0·5 to 17·0% by weight were examined using a rotational viscometer fitted with cone and plate. Parameters used to characterize the flow curves of these gels were plastic viscosity, apparent viscosity at fixed rates of shear and the estimated area of the hysteresis loop. The influence of temperature and aluminium stearate concentration on the shapes of the curves was examined. Concentration of aluminium stearate and temperature were found to influence both thixotropic behaviour and the rate of recovery after shear. A minimum concentration of 1·5 to 2·0% by weight of aluminium stearate appeared to be necessary for the formation of the gel structure.

The use of a beeswax-peanut oil base as a vehicle for a repository form of penicillin was described by Romansky & Rittman (1944). Later, Buckwalter & Dickison (1948) described a depot injection containing a suspension of pencillin salts in vegetable oil gelled with aluminium stearate. The viscosity of these gels was found to depend on the aluminium stearate used, its concentration, the type of oil, and the conditions under which the gel was made.

The rheological properties of the aluminium organogels reported by various workers have shown some discrepancies. The effect of concentration of aluminium stearate, and of temperature, on the rheological properties of a range of gels, together with subsequent changes in gel properties on storage and recovery after shear have now been examined.

MATERIALS AND METHODS

Gel preparation

Gels were formed with liquid paraffin B.P. and aluminium stearate (Manox†) in concentrations ranging from 0·5 to 17·0% by weight of the metal soap. Quantities of 300g were prepared with raw materials drawn from the same batch throughout. The method of manufacture followed the principles described by Morrison & Stephens (1967).

The finely powdered aluminium stearate was slowly added to about half the quantity of oil with the aid of a small electric stirrer. After 20 min mixing, the remainder of the oil was added and agitation continued for a further 10 min. With the mixer running, the mixture was heated through 2 to 3°/min to 160°, allowed to cool to between 130 and 140° and maintained within this range for a further hour, any

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entrained air or steam being removed by manipulation of the stirrer. The preparation was then allowed to cool to 120° before removal of the stirrer and insulated to ensure a cooling rate of between 5 and 10°/h from 120° to room temperature.

Rheological examination of the gels

The instrument used was the Haake Rotovisco Rotational Viscometer fitted with cone and plate. Test sample, cone, and plate were allowed to attain test temperature (5 min) and any excess sample extruded was removed before readings were made. Rates of shear were varied manually; temperature was maintained within 0·2° throughout.

Viscosity was measured at 25° on a series of gels ranging in concentration from 0·5 to 9·0% of aluminium stearate by weight using a 15 s time cycle. Readings were then repeated at 10, 37 and 45°. Samples of 3·0 and 9·0% by weight gels were stored at 25° and allowed to remain undisturbed for 2, 7 and 21 days to test for reproducibility of the hysteresis loop.

To determine the effects of gel ageing, material containing 1·0, 3·0 and 9·0% by weight of aluminium stearate was transferred to sealed containers with the minimum of disturbance and stored at 25°. Viscosity at 25° was measured daily for three days and thereafter at weekly intervals for up to two years.

<div align="center">RESULTS</div>

The 0·5 and 1·0% gels gave plastic curves at 25, 37 and 45°. Curves have been characterized by calculated values for plastic viscosity and yield stress; both increased with concentration of aluminium stearate. At 10° curves showed a yield value but were curvilinear and thus a plastic viscosity was not calculated.

The evaluation of yield stress by extrapolation to 0 s^{-1} rate of shear has been shown to provide an additional parameter for comparing curves obtained under standardized conditions of measurement. It is appreciated that if measurements had been possible at very low rates of shear, the curve would incline towards the origin of the graph and, in theory, pass through it at zero rate of shear.

At concentrations of 1·5% by weight aluminium stearate and above, hysteresis loops were formed when shear stress was plotted against rate of shear. Above 9·0% measurements were no longer possible as material was extruded.

The following relations have been established:

1. A non-linear relation was shown between the estimated areas of the hysteresis loop and both temperature and gel concentration. The loop area increased with increase in aluminium stearate concentration, and for a set concentration decreased with temperature (Table 1).

2. Yield stress values increased with concentration of aluminium stearate and decrease with temperature (Fig. 1).

3. At fixed rates of shear a relation between aluminium stearate concentration and apparent viscosity has been demonstrated. At the highest rate of shear used (9923 s^{-1}) the curve is almost linear (Fig. 2); at a low rate of shear on the up-curve (1103 s^{-1}) the curve is sigmoidal. The tangent to the curve is decreased with increase in temperature (Fig. 3).

4. Some degree of recovery after shearing was seen and depended upon concentration of aluminium stearate (Table 2).

On storage, the 1·0 and 9·0% gels increased in consistency for the first 188 h after manufacture and then changed negligibly over a 2 year period.   The 3·0% gel increased in consistency during the initial 3 weeks storage and then remained constant (Table 3).

DISCUSSION

Yield stress values were determined from the curves by extrapolation of the "up-curve" to the shear stress axis.   At a given temperature, yield stress increased progressively with concentration throughout the range of gels and for a fixed concentration the yield stress decreased with temperature rise (Fig. 1).   Shiba (1960) described the

Table 1.   *The relation between estimated area of the hysteresis loop and gel strength at varying temperatures.*

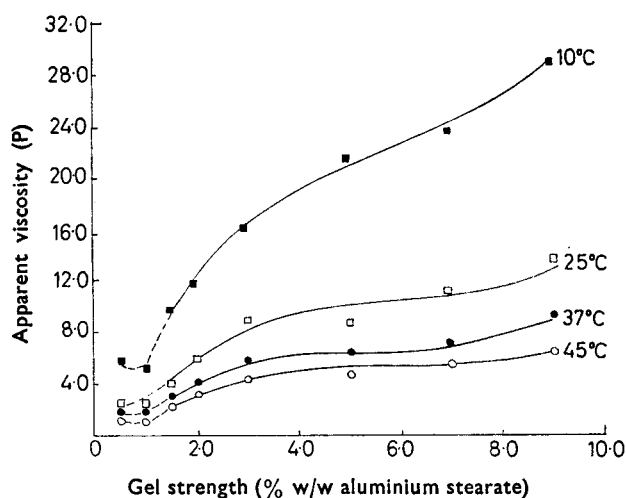| Gel strength (% w/w aluminium stearate)	Measurement temperature (°C)	Estimated area of hysteresis loop (cm²)	Gel strength (% w/w aluminium stearate)	Measurement temperature (°C)	Estimated area of hysteresis loop (cm²)
1·5	10·0	14·3	5·0	10·0	42·0
	25·0	5·80		25·0	16·8
	37·0	8·30		37·0	15·0
	45·0	3·40		45·0	7·00
2·0	10·0	33·0	7·0	10·0	—
	25·0	20·8		25·0	28·2
	37·0	7·50		37·0	22·0
	45·0	6·60		45·0	15·6
3·0	10·0	39·5	9·0	10·0	—
	25·0	21·8		25·0	46·3
	37·0	18·0		37·0	24·5
	45·0	9·60		45·0	11·0

FIG. 1.   The relation between yield stress and concentration of aluminium stearate in liquid paraffin derived by extrapolation of the up-curve to the shear stress axis at 0 s⁻¹ rate of shear.
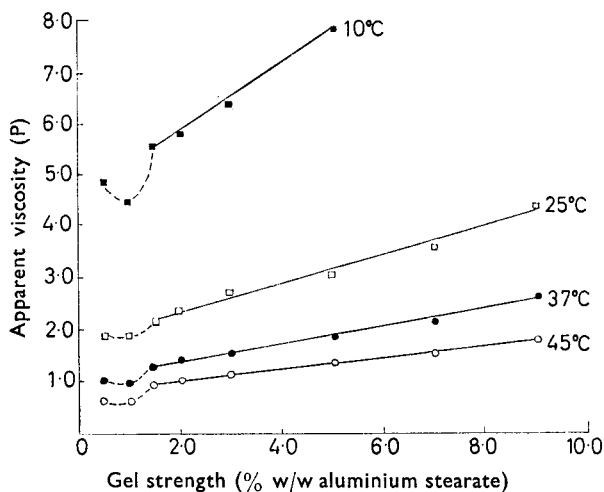
FIG. 2. The relation between apparent viscosity and concentration of aluminium stearate in liquid paraffin at high rates of shear (9923 s⁻¹). Shear rate employed maximum.
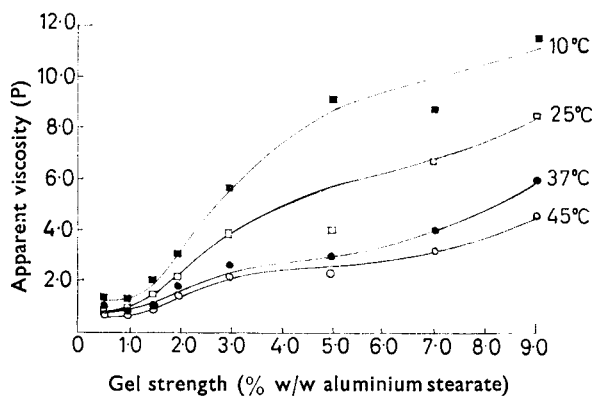

FIG. 3. The relation between apparent viscosity and concentration of aluminium stearate in liquid paraffin at low rates of shear (1103 s⁻¹) on the up-curve.

relation between yield stress and concentration as approximately linear. Results obtained in this study showed a sharp increase in yield stress at concentrations of aluminium stearate of 1·5% and higher.

Determinations of apparent viscosity at both high and low rates of shear showed that in the first case the apparent viscosity increased linearly with increasing concentration of aluminium stearate; at low rates of shear the curve was sigmoidal (Figs 2 and 3). A family of curves was obtained in both cases, the slope increasing in temperature. These observations were made for concentration of aluminium stearate greater than 1·5%. Shiba (1960) described the relation between apparent viscosity and concentration as approximately linear with aluminium stearate concentrations of 0·5 to 4·0% and maximum rates of shear of 1 × 10³ s⁻¹. Differences between results obtained by Shiba and those obtained in this study may be attributed to several factors. These include: variations in instruments used; the maximum soap

Table 2. *Recovery behaviour of 3·0 and 9·0% gel after shearing.* Up-curve +, down-curve o.

Rate of Shear (s⁻¹)	Shear stress (10⁻¹ N m²)											
	t = 0		t = 18 h		t = 0		t = 7 days		t = 0		t = 21 days	
	+	o	+	o	+	o	+	o	+	o	+	o
						3·0% gel						
61	5440	2720	3570	2890	4590	2720	2720	2380	4930	2890	2890	2720
123	5950	3230	3400	3230	5270	3230	3230	2720	5270	3060	3570	2890
184	6630	3570	3740	3400	5780	3400	3400	3060	5780	3230	3740	3060
368	7990	4250	4590	4250	6970	4080	4080	3740	6970	4080	4420	3740
551	8670	4760	5100	4760	7820	4590	4420	4080	8160	5270	5100	4420
						9·0% gel						
61	9690	3740	3570	3400	8840	3400	3560	3400	8610	2665	2635	2550
123	11 220	4080	4080	3910	10 030	3740	3470	3520	10 650	3115	3145	3060
184	10 030	4590	4420	4420	10 030	4420	4360	4240	9800	3740	3740	3655
368	11 790	5270	5270	5100	11 300	5150	5150	4980	11 270	4535	4505	4505
551	12 240	6290	6290	6120	11 810	6180	6130	6120	12 070	5725	5695	5525

Table 3. *Consistency changes in gels on storage at 25°.*

Gel concentration (% w/w aluminium stearate)		Time after preparation								
		18 h	24 h	48 h	72 h	7 days	14 days	21 days	7 weeks	2 years
1·0	Plastic viscosity (Poise)	1·80	1·76	1·69	1·65	1·85		1·82		2·05
	Apparent viscosity (Poise) (1103 s⁻¹ rate of shear)	2·67	2·65	2·71	2·65	2·77		2·77		2·86
	Apparent viscosity (Poise) (9923 s⁻¹) rate of shear)	1·89	1·85	1·78	1·75	1·82		1·91		2·16
3·0	Estimated area of hysteresis loop (ergs cm⁻³ s⁻¹ × 10⁷)	3·84	2·96	2·46	2·18	2·30	2·42	2·18	2·94	4·25
	Apparent viscosity (Poise) (1103 s⁻¹ rate of shear)	15·2	8·32	9·02	9·63	10·2	10·1	8·79	10·3	16·1
	Apparent viscosity (Poise) (9923 s⁻¹ rate of shear)	1·95	2·36	2·42	2·73	2·77	2·70	2·78	2·81	3·7
9·0	Estimated area of hysteresis loop (ergs cm⁻³ s⁻¹ × 10⁷)	4·42	4·56	4·70		4·42		4·63		5·40
	Apparent viscosity (Poise) (1103 s⁻¹ rate of shear)	13·8	13·4	13·6		13·9		13·5		15·4
	Apparent viscosity (Poise) (9923 s⁻¹ rate of shear)	4·53	4·46	4·41		4·51		4·41		4·93

All determinations made at 25·0°

concentration used; the purity of the soap; the rate of cooling of the gel during preparation.

The flow properties of the gel changed with time and they depended upon concentration of aluminium stearate and storage temperature. The consistency of non-Newtonian samples may only be accurately compared using the complete flow curves. However, to provide a numerical comparison between samples, values for the plastic viscosity, apparent viscosity at high and low rates of shear on the "up-curve" and the estimated area of the hysteresis loop have been calculated (Table 3). Shiba (1960) considered that consistency reached a maximum some 4 h after gel preparation, but his study was restricted to a 2% gel only. Matsumura, Iguchi & others (1958) also found that storage temperature influenced structural formation. A refrigerated sample of 2% aluminium stearate-peanut oil gel required some 38 days to reach a constant viscosity whereas similar material stored at 37° reached equilibrium in 4 days. These results are not strictly comparable with those in the present study since the aluminium content and oil used differed, but it may be concluded that gels stored at 25° should be allowed to age for a minimum period of 3 weeks to reach equilibrium.

The rate of gel formation appeared to be related to the aluminium stearate content. At 1·0% aluminium stearate concentration, sufficient soap was present for the structure to form within 18 h. Above a concentration of 1·5% a more complex structure existed and its rate of formation appeared to depend upon the amount of metal soap present. With 9·0% of aluminium stearate, structural formation was rapid and complete within 18 h, but at 3·0%, structural formation occurred at a slower rate, insufficient material being present for a rapid build-up of the gel and some three weeks were necessary for consistency to reach equilibrium.

There is a disagreement in the literature about the time effects of flow behaviours on aluminium-hydrocarbon systems. Complete recovery was reported by Goldberg & Sandvik (1947), and Carver & van Wazer (1947). Evans & Matthews (1954) considered that permanent change in the structure of the gel was produced after shearing. Shiba (1960) thought that the paraffin gels were thixotropic at high temperatures or under very low rates of shear. Results in this paper show that a gradual recovery did occur with the 3·0% gel and that the system was thixotropic. No evidence of recovery was observed with the 9·0% gel; it is suggested that recovery may in fact occur, but at an extremely slow rate due to the viscosity of the system (Table 2).

Yield stress is an important factor. From results obtained, systems containing 0·5 and 1·0% of the aluminium stearate behaved as dilute suspensions of the metal soap dispersed in oil and they possessed a yield value. This yield value provided evidence of a weak structure. At soap concentrations above 1·5% the sharp rise in yield stress value coupled with the formation of hysteresis loops has provided evidence of a strong structural build-up (Fig. 1).

One possible explanation for the shape of the flow curves is as follows. At 10° both 0·5 and 1·0% gels yielded a curvilinear flow curve with yield values of 102 and 97 N m^{-2}. These values were within the limits of experimental error. It is suggested that at this temperature the thermal energy of the system was so low that some degree of molecular structure was present even under shearing conditions. On raising the temperature to 25° this weak structure was broken down and plastic flow resulted.

In an attempt to explain the shape of the curvilinear flow curve it is suggested that under low rates of shear the tendency of the long chain molecules to align in the direction of flow was negligible. They remained in a random state in which case the

rate of shear remained proportional to the shearing stress. As the rate of shear was increased, the molecules aligned. The frictional resistance between adjacent layers was reduced and a greater rate of shear was obtained for a given stress than would have occurred otherwise. The curve became concave to the stress axis.

Shearing material with concentrations of aluminium stearate of 1·5% and above resulted in the formation of a hysteresis loop. It is suggested again that under low rates of shear the molecules remained in a random state. At high rates of shear the molecules were aligned linearly and the shearing stress fell markedly. As the shearing rate was then decreased, the molecules required an appreciable time, in excess of the measuring cycle (total time 5 min) to regain their former state of entanglement. The results showed that loop area decreased with increase in temperature showing that thermal energy will break down structure; also the loop area increased with soap concentration thus showing the formation of a more rigid structure.

On the basis of the rheological studies it is possible to suggest evidence of gel structure. The aluminium soap was composed mainly of aluminium hydroxy di-soaps with small amounts of aluminium hydroxide, free fatty acid and a trace of water. The polymeric nature of the soap has been illustrated by the ability to make molecular chains when aluminium stearate in concentrations greater than 1·5% was dispersed by heat in liquid paraffin. These polymer chains imparted a rigid structure to the gel and the consistency increased with concentration. The rigidity of the structure increased lowering the temperature. Results also illustrated that at concentrations of soap less than approximately 1·5%, insufficient material was present to form and maintain such a coherent structure.

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