

Rheology of systems containing cetrimide—cetostearyl alcohol: variation with temperature

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The viscoelastic gel in the continuous phase of a liquid paraffin in water emulsion (stabilized by the mixed emulsifier cetrimide—cetostearyl alcohol) is similar to that formed by dispersing cetrimide and cetostearyl alcohol in water. The effect of temperature changes on the rheological properties of the emulsion and ternary system have been examined in continuous shear and in creep, and variations in the viscosities and compliances have been correlated with thermal phase transitions determined microscopically. The emulsion and ternary system were of maximum consistency at approximately 38° and 43° respectively; these temperatures represent the transition from frozen smectic to liquid crystalline phase. At higher temperatures, the compliances rose and the viscosities fell as the network weakened and finally dissolved to form an isotropic solution.

The “self bodying” action of a mixed emulsifier is its ability to form mobile emulsions when present in low concentrations, and semisolid emulsions when present in moderate amounts (Barry, 1969). In the pharmaceutical and cosmetic industry, combinations of anionic, cationic or non-ionic surfactants with a fatty alcohol are widely used to control the rheological behaviour of emulsions by varying the concentration of mixed emulsifier.

The self bodying action of the mixed emulsifiers sodium dodecyl sulphate—cetyl alcohol and of cetrimide—cetostearyl alcohol has been studied (Barry, 1968; Barry & Saunders, 1970). In these emulsions the gel structure responsible for the self bodying phenomenon consists of frozen smectic phase with similar properties to an oil-free ternary system formed by dispersing cetrimide and cetostearyl alcohol in water.

In the present paper, the rheological stability of this gel network to temperature changes is investigated in an emulsion, and when formulated as a comparable ternary system.

EXPERIMENTAL AND RESULTS

Materials

Water, liquid paraffin B.P., cetrimide B.P. and cetostearyl alcohol B.P. were as used by Barry & Saunders (1970).

Penetration temperature

The penetration temperature (T_{pen}) of aqueous cetrimide solution into cetostearyl alcohol was determined by the method described by Lawrence (1959, 1961) and Barry & Shotton (1968). Because of confusion in the literature about the effects of surfactant concentration on the penetration temperature (Barry & Shotton, 1968),

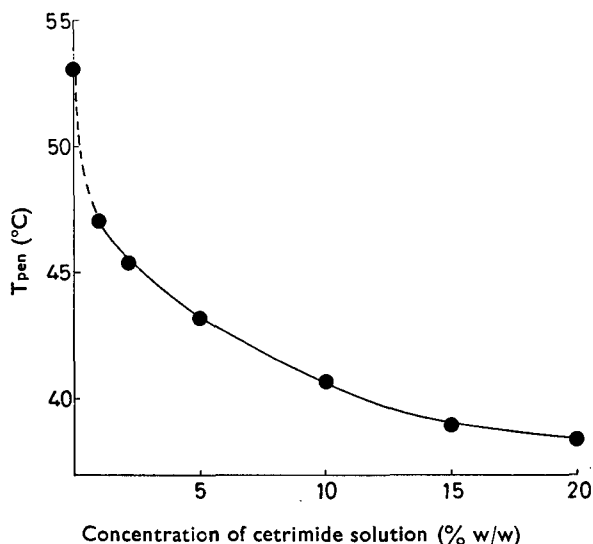


FIG. 1. Penetration temperature, T_{pen} , of aqueous solutions of cetrimide into cetostearyl alcohol.

measurements were made for various concentrations of cetrimide in water. The results (Fig. 1) indicated that variations in penetration temperature were most marked at low cetrimide concentrations.

Preparation and appearance of systems

The ternary system and the emulsion were made by the method of Barry & Saunders (1970) according to the formulae in Table 1. The ternary system was a white glossy semisolid which flowed only slowly under its own weight. The emulsion was a white glossy cream, of similar consistency.

Microscopy

The systems were examined microscopically using a Kofler Micro Hot Stage attached to a polarizing microscope. The ternary system contained scattered deformed globules, which often had the appearance of distorted maltese crosses when viewed between crossed polars. Most of the material became isotropic between 57–59°, and became anisotropic again on cooling.

In the emulsion, distorted oil globules often contained anisotropic crystals along the straight sides. Remnants of an ordered anisotropic filamentous matrix were visible surrounding larger globules and often enclosing aggregates of smaller globules (c.f. Barry & Saunders, 1970). Much of the anisotropic material inside or very close to the oil globules became isotropic between 38–40°. Although at about 50°,

Table 1. *Composition of ternary system and emulsion*

	Liquid paraffin	Water	Cetostearyl alcohol	Cetrimide
Ternary system	—	360	36	4.0 g
Emulsion	100	300	28.8	3.2 g

the filamentous matrix appeared unaltered in ordinary light, it was less ordered in polarized light: the matrix became completely invisible at 59°.

On cooling the emulsion, the matrix reappeared enveloping some of the larger globules. It did not regain the ordered anisotropic structure and on further cooling, acicular crystals often appeared inside the globules; these were similar to those photographed by Talman & Rowan (1968).

Continuous shear

The ternary system and the emulsion were tested at each temperature using a Ferranti Shirley Cone and Plate Viscometer (Barry & Shotton, 1967; Barry & Saunders, 1970). The apparent viscosity at 1671 s⁻¹ was derived, and the approximation being made that the systems under the conditions of testing behaved as simple liquids, an apparent relative viscosity was defined as:

$$\eta'_{\text{rel}} = \frac{\text{Apparent viscosity at } 1671 \text{ s}^{-1} \text{ at } T^{\circ}}{\text{Viscosity of water at } T^{\circ}}$$

The viscosity of water at T° was obtained from tables (Lange, 1961). This procedure eliminated the effect on the consistency of the system of a fall in the viscosity of water due solely to a rise in temperature.

Figs 2 and 3 show plots of η'_{rel} against temperature for the ternary system and the emulsion respectively.

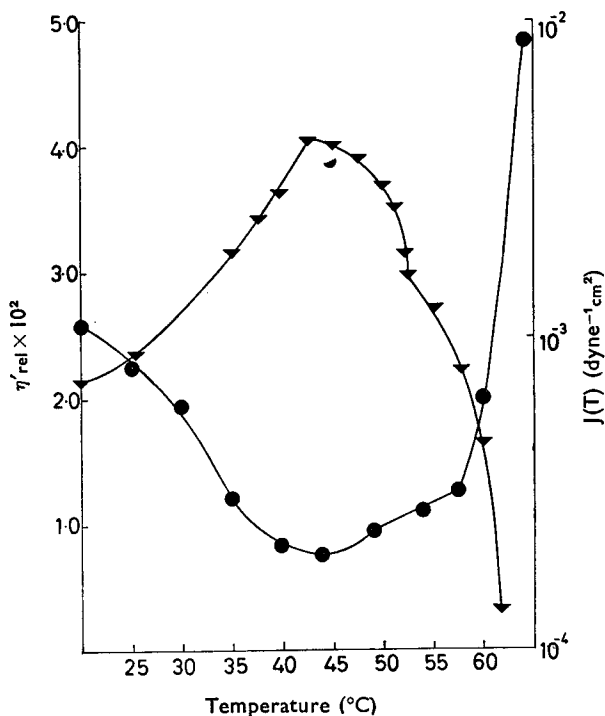


FIG. 2. Ternary system. Total compliance $J(T)$ after 50 min creep (dyne⁻¹ cm²) —●— and apparent relative viscosity η'_{rel} —▲— versus temperature.

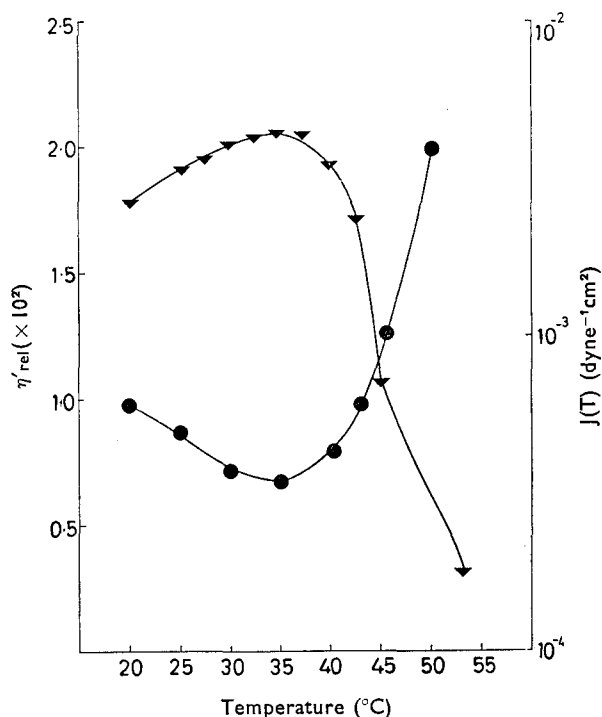


FIG. 3. Emulsion. Total compliance $J(T)$ after 50 min ($\text{dyne}^{-1} \text{cm}^2$) —●— and apparent relative viscosity η'_{rel} —▼— versus temperature.

Creep compliance with time at a constant low shear stress

To apply the creep test, a concentric cylinder reaction air turbine viscometer was used, in which an air bearing centred and supported the inner cylinder, and turbine air applied a constant torque. A Kent recorder registered the development of strain with time as a continuous trace. The apparatus was calibrated in the vertical position (Barry & Saunders, 1969).

The viscometer was loaded and left overnight for stresses to relax and for temperature to equilibrate, and each test was performed in the linear region. Curves were analysed by the method of Warburton & Barry (1968), and could be represented by a mechanical model of a Maxwell Unit in series with three Voigt Units. The creep compliance was represented by the equation

$$J(t) = J_0 + \sum_{n=1}^3 J_n (1 - e^{-t/\tau_n}) + \frac{t}{\eta_0}$$

$J(t)$ = total creep compliance at time t , where J is the ratio of shear strain to shear stress. J_0 = residual shear compliance. J_1, J_2, J_3 = shear compliances of elastic parts of Voigt Units 1, 2, 3 respectively. τ_1, τ_2, τ_3 = retardation times of Voigt Units 1, 2, 3 respectively. η_0 = residual shear viscosity. Figs 2 and 3 include plots of total compliance against temperature for the ternary system and the emulsion. Table 2 includes the creep parameters for the ternary system. Figs 4–7 are plots of the residual and Voigt Unit compliances and viscosities for the emulsion.

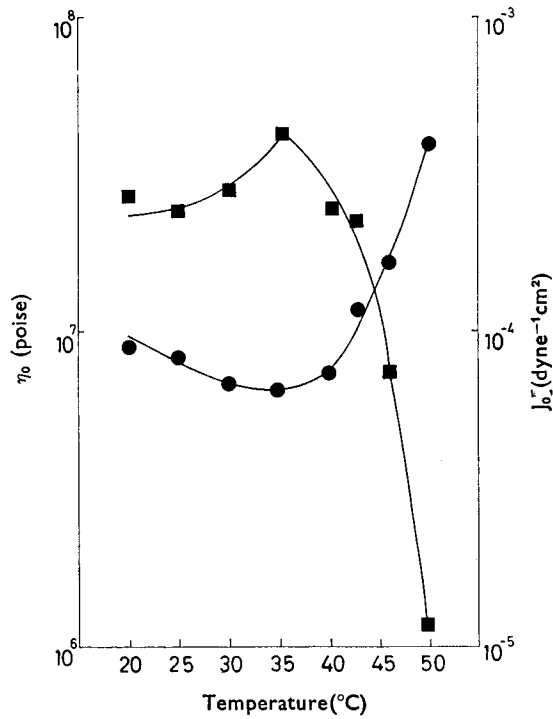


FIG. 4. Residual compliance J_0 (dyne⁻¹ cm²) —●— and residual viscosity η_0 (poise) —■— versus emulsion temperature.

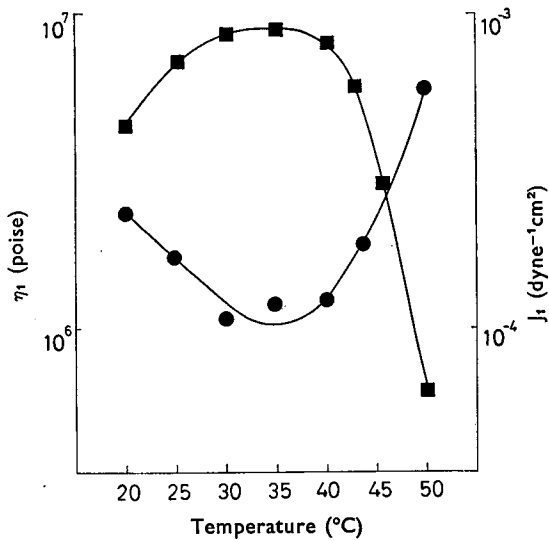


FIG. 5. Compliance J_1 (dyne⁻¹ cm²) —●— and viscosity η_1 (poise) —■— of Voigt Unit 1 versus emulsion temperature.

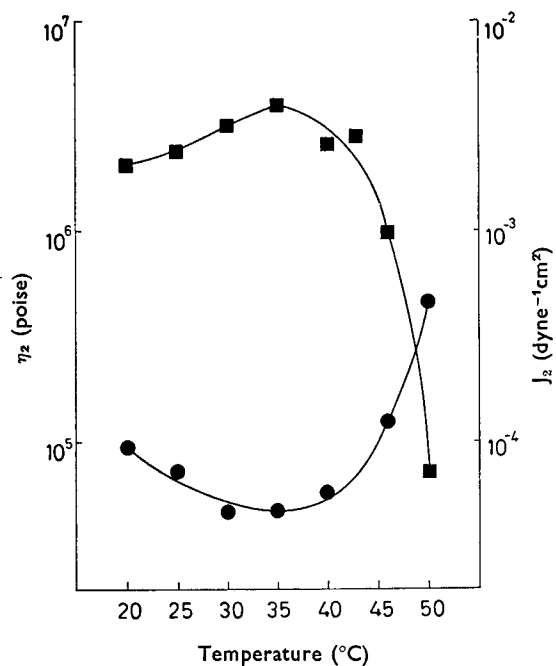


FIG. 6. Compliance J_2 ($\text{dyne}^{-1}\text{cm}^2$) —●— and viscosity η_2 (poise) —■— of Voigt Unit 2 versus emulsion temperature.

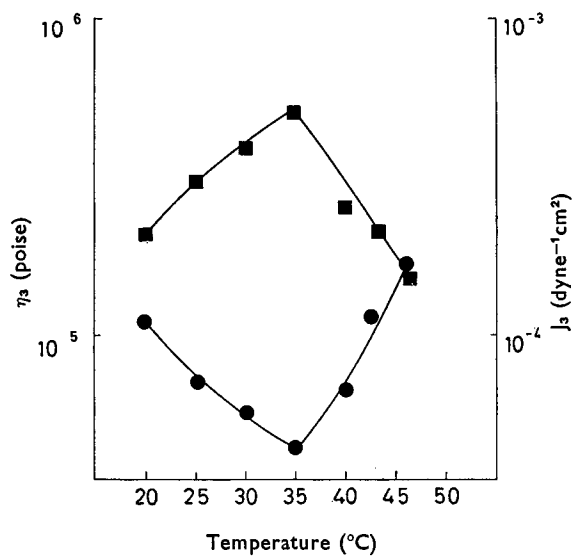


FIG. 7. Compliance J_3 ($\text{dyne}^{-1}\text{cm}^2$) —●— and viscosity η_3 (poise) —■— of Voigt Unit 3 versus emulsion temperature.

DISCUSSION

From the penetration temperature experiments, the minimum temperature for interaction between 1% cetrimide solution and cetostearyl alcohol to form liquid crystals is 47°. During mixing of the ternary system, molten alcohol streamed through the mixture and cetrimide solution penetrated it to form liquid crystals. As the system rapidly cooled to below the penetration temperature, interaction was greatly reduced and the system precipitated to form a three dimensional viscoelastic gel network. When viewed between crossed polars, anisotropic structures often failed to become isotropic at the melting point of the cetostearyl alcohol but did so at a higher temperature. They were thus frozen smectic phase: similar, though larger, structures have been reported in anionic ternary systems (Barry & Shotton, 1967).

During the preparation of the emulsion, as the ingredients cooled, the alcohol diffused into the continuous phase and formed liquid crystals; a small proportion of the liquid paraffin was also solubilized. Thus the cooled emulsion consisted essentially of a ternary cetrimide-cetostearyl alcohol-water gel with liquid paraffin droplets dispersed in it. When the emulsion was diluted, remnants of this gel were visible microscopically as an anisotropic filamentous matrix which surrounded large oil globules and aggregates of smaller globules. Microscopic examination showed that this gel network melted and dissolved to form an isotropic solution over a temperature range of approximately 38° to 59°.

These thermal phase transitions in the ternary system and the emulsion are important for an explanation of the rheological properties of the formulations.

Rheological examination

At all temperatures the flow curves from the continuous shear experiments were hysteresis loops, with the down curves to the left of the up curves. These loops were caused by breakdown of structure on shearing, and thus the results obtained in this work were a measure of the ability of the systems to resist structural breakdown in continuous shear; they also reflect the relation between this ability and temperature. In creep, the method of testing does not significantly alter the structure, and thus systems were examined in their rheological ground state.

Upon raising the temperature, the consistency of the ternary system increased to a maximum at 43°. This was shown in continuous shear by the maximum viscosity at 43°. In creep, similar maxima were obtained for all the viscosities and corresponding minima for all the compliances at this temperature (Table 2, Fig. 2).

Table 2. *Ternary system: analysis of creep curves*

Temperature °C	Residual Dashpot η_0 (poise $\times 10^3$)	Residual spring J_0 (dyne ⁻¹ cm ² $\times 10^{-5}$)	Voigt Unit 1			Voigt Unit 2			Voigt Unit 3		
			η_1 ($\times 10^7$)	J_1 ($\times 10^{-5}$)	τ_1 (s)	η_2 ($\times 10^6$)	J_2 ($\times 10^{-5}$)	τ_2 (s)	η_3 ($\times 10^5$)	J_3 ($\times 10^{-5}$)	τ_3 (s)
20	0.71	9.14	0.38	26.1	1010	1.26	10.70	136	2.05	15.90	32
25	0.97	10.4	0.32	29.8	958	1.34	10.9	145	2.40	8.81	21
30	1.77	10.4	0.64	17.2	1100	2.98	8.10	241	3.77	9.4	35
35	5.29	5.6	1.03	11.4	1180	3.50	4.48	157	4.24	4.35	18.5
40	7.11	3.99	1.43	8.32	1190	6.17	2.99	185	6.53	3.54	23
44	4.89	3.63	2.11	5.44	1150	5.20	3.06	159	5.66	3.00	17
49	6.23	3.82	1.38	7.88	1090	4.59	4.24	195	7.12	4.35	31
54	4.29	5.06	1.47	10.1	1480	6.41	4.03	258	5.13	4.59	24
57.5	2.74	4.71	8.11	9.88	871	4.08	4.12	168	5.00	5.12	26
60	1.59	8.63	7.28	21.8	1580	1.57	11.1	174	2.75	8.87	24

$$\text{dyne}^{-1} \text{cm}^2 = \text{N}^{-1} \text{m}^2 \times 10^1$$

Such a gradual increase in consistency up to 43° may be caused by increased Brownian movement in the system. This is believed to bring free ends of strands into contact with the main meshwork so as to form new linkages and strengthen the network. As the retardation times did not change markedly with rise in temperature (Table 2) the nature of any such secondary bonds would not alter, although their number would increase.

The temperature for maximum consistency was close to the transition temperature from frozen smectic to liquid crystalline phase, and this temperature was lower than the penetration temperature of 1% cetrimide solution into cetostearyl alcohol. As the temperature increased above 43°, the consistency decreased as the network became true smectic phase. This phase was still viscoelastic and thus there were shoulders on the continuous shear and creep curves between approximately 50° and 57°. Above 57°, significant quantities of the smectic phase dissolved to form an isotropic solution and the network disintegrated causing a steep fall in viscosity with a rise in compliance (Fig. 2).

In the emulsion, as in the ternary system, there was an initial increase in consistency as the temperature increased. This was shown in the continuous shear results, and by the viscoelastic parameters obtained in creep. From the positions of the maxima and minima in Figs 3-7 the transition temperature from frozen smectic to smectic phase in the emulsion was about 37°, i.e. several degrees lower than the transition temperature for the ternary system. Such a shift is attributed to the liquid paraffin in the emulsion, which lowers the temperature for phase transitions. Davis (1969) has obtained similar results for a commercial sample of cetrimide cream B.P.C., although the maxima and minima were not as well defined.

Further evidence that the gel network in the continuous phase of the emulsion was similar to the network in the ternary system was obtained from the plots of total compliance against temperature (Figs 2 and 3). The shapes of the curves are almost identical, although the emulsion plot is shifted along the temperature axis towards lower values, due to the lowering of phase transition temperatures by the liquid paraffin.

The similarities were less marked in the continuous shear results, which showed a very rapid reduction in viscosity above the transition temperature (Fig. 3). At high shear rates and high temperatures the rheology was complicated as oil globules coalesced.

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