

Oscillatory testing of o/w emulsions containing mixed emulsifiers of the surfactant-long chain alcohol type: self-bodying action

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Liquid paraffin-in-water emulsions stabilized by cationic (cetrimide) or non-ionic (cetomacrogol) surfactants and cetostearyl alcohol were examined at 25° in oscillatory mode, using the Weissenberg Rheogoniometer with parallel plates coupled to a digital transfer function analyser. Ternary systems, formed by dispersing the mixed emulsifiers in water, were similarly investigated. Each preparation was tested in the linear viscoelastic region, and fundamental rheological parameters, the storage modulus (G') and the real viscosity (η') were derived as functions of frequency over the range 7.91×10^{-4} to 25 Hz. All ternary systems behaved similarly with respect to frequency. As this increased, G' rose and η' fell. These trends were related to the viscoelastic nature of the systems. Both mixed emulsifiers exhibited self-bodying mechanisms, so that emulsion consistency increased as the mixed emulsifier concentration rose. This was shown by increases in G' and η' at each frequency. The shapes of the plots and other rheological properties were related to viscoelastic gel networks formed in the emulsion continuous phases. The ternary system parameters implied that emulsion networks were similar to ternary gels, that is, they formed by the interaction of long chain alcohol and aqueous surfactant solution. The oscillatory data were compared and correlated with creep data derived for similar ionic and non-ionic dispersed systems, previously described.

The self-bodying action of mixed emulsifiers of the surfactant-long chain alcohol type is their ability both to stabilize oil-in-water emulsions and to control their consistencies between wide limits. An essential feature of this action is that a significant elastic component is introduced into the rheological behaviour which distinguishes such emulsions from preparations with simple emulsifiers since these do not exhibit a prominent elastic component.

Many self-bodied emulsions are semisolid and this phenomenon can be investigated by small strain experiments (e.g. creep or oscillatory techniques). In these the systems are examined in their rheological ground states, and the results are analysed on the basis of linear viscoelastic theory to provide fundamental viscoelastic parameters.

Creep experiments provided valuable information about the self-bodying action of various ionic and non-ionic mixed emulsifiers (Barry, 1968; Barry & Saunders, 1970a,b, 1971a,b, 1972a-c). Transient experiments, however, are restricted by the response time of the apparatus and recording system and by the impossibility of applying a truly instantaneous stress at the beginning of each experiment.

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To completely characterize semisolid systems, information over a wide time scale should be obtained (Ferry, 1970). We have examined self-bodying phenomena using the alternative fundamental method of testing, that is, to examine typical ionic and non-ionic systems in oscillatory mode. Oscillatory data provide information corresponding to short creep times, as a periodic experiment at a frequency ω rad s^{-1} is qualitatively equivalent to a transient experiment at time $t = 1/\omega$ s.

THEORY

Many semisolid ointments and creams are viscoelastic liquids, and a suitable representation in oscillation consists of elastic springs and viscous dashpots combined to form a generalized Maxwell model (Fig. 1). At high frequencies of testing, the

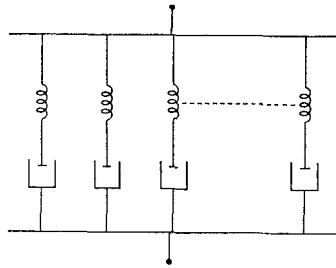


FIG. 1. Generalized Maxwell model used to represent the rheological behaviour of the systems.

springs can elongate and contract under the imposed oscillatory shear, but the dashpots have little time in which to move. The system therefore behaves essentially as an elastic solid of modulus G ; most of the energy is stored and recovered per cycle of deformation. At low frequencies, the springs can elongate, but the dashpots also have time to move, and their extensions greatly exceed those of the springs. Thus the system now behaves as a fluid of viscosity η ; the energy for each cycle is almost completely dissipated. At intermediate frequencies, in the so-called viscoelastic region, both springs and dashpots provide definite contributions.

The equation of state for a linear elastic liquid undergoing forced harmonic oscillations of small amplitude can be written as (Walters, 1968)

$$\sigma = 2\dot{\gamma} \eta^* \quad \dots \quad (1)$$

where σ is the shear stress, $\dot{\gamma}$ the shear rate and η^* the complex dynamic viscosity which is a function of the frequency of oscillation, ω rad s^{-1} ($\omega = 2\pi n$, $n =$ frequency in Hz) and is in general complex. It is convenient to express η^* in the form

$$\eta^* = \eta' - \frac{iG'}{\omega} \quad \dots \quad (2)$$

where η' is the dynamic viscosity, G' the dynamic rigidity (storage modulus) and i is the square root of -1 . The dynamic viscosity is a measure of energy lost or dissipated as heat per cycle (viscous behaviour) and the storage modulus measures energy stored and recovered per cycle (elastic behaviour). A full discussion of these parameters was given by Ferry (1970).

In oscillatory experiments, the material may be subjected to a small sinusoidal shear stress and the subsequent shear strain measured, or alternatively a small sinusoidal shear strain may be applied, and the resultant shear stress measured. In

steady state equilibrium sinusoidal experiments, the two methods are equivalent. The input strain and output stress method is used with the Weissenberg Rheogoniometer. In each geometry, one of the instrument members in contact with the test material is given a forced sinusoidal oscillation, and the other member (which is also in contact with the test material) is constrained by a torsion bar. If the test material is linearly viscoelastic, the constrained member will also alternate sinusoidally with an amplitude proportional to that of the forced member, but with a phase shift between the waves. The magnitudes of the amplitude ratio between the two waves and the phase shift between them depend on the degree of viscoelasticity exhibited by the material.

Parallel plate geometry is the most convenient from both practical and theoretical considerations for oscillatory testing with a Rheogoniometer. The theory for parallel plate geometry provides the results (Walters & Kemp, 1968).

$$\frac{e^{ic}}{A} = \cos \alpha h + S \alpha h \sin \alpha h \quad \dots \quad (3)$$

$$\text{where } \alpha^2 = \frac{-2\pi n i \sigma}{\eta^*} \quad \dots \quad (4)$$

$$S = \frac{2}{\pi \sigma r^4 h} \left(\frac{K}{4 \pi^2 n^2} - I \right) \quad \dots \quad (5)$$

and $i =$ square root of -1 ; $c =$ phase lag of the constrained plate behind the forced plate (rad); $A = a_1/a_2$ where a_1 is the angular amplitude of the constrained plate and a_2 that of the forced plate; $h =$ distance between the plates (cm); $r =$ radius of the parallel plates (cm); $n =$ frequency of oscillation (Hz); $\sigma =$ density of the sample (g cm^{-3}); $\eta^* =$ complex viscosity (poise); $K =$ torsion constant for the bar (dyne cm rad^{-1}); $I =$ moment of inertia of the constrained member about its axis (g cm^2). When αh is small ($\ll 1$) and fluid inertia is negligible, Equation 3 may be expanded to squared terms only to give

$$\frac{e^{ic}}{A} = 1 + \alpha^2 h^2 S \quad \dots \quad (6)$$

When the real and imaginary parts are separated, equation (6) leads to

$$\eta' = \frac{-2\pi n S h^2 \sigma A \sin c}{(A^2 - 2A \cos c + 1)} \quad \dots \quad (7)$$

$$G' = \frac{4\pi^2 n^2 S h^2 \sigma A (\cos c - A)}{(A^2 - 2A \cos c + 1)} \quad \dots \quad (8)$$

Equations 7 and 8 were employed to provide values for η' and G' used in this work, and were solved using an Atlas computer.

EXPERIMENTAL AND RESULTS

Materials. Cetostearyl alcohol, liquid paraffin, water, cetrinide and cetomacrogol were as described previously (Barry & Saunders, 1970a, 1972a).

Preparation and appearance of the systems. Ternary systems and emulsions were prepared by a standardized procedure according to the formulae in Table 1 (Barry & Saunders, 1970a). In the discussion which follows, ternary systems and emulsions

Table 1. *Composition of emulsions and ternary systems.*

System*	Liquid paraffin	Water	Cetostearyl alcohol	Surfactant (cetrimide or cetomacrogol)
T10	—	360	36.0	4.0 g
T12	—	360	43.2	57.6 g
T16	—	360	57.6	6.4 g
E4	100	300	14.4	1.6 g
E5	100	300	18.0	2.0 g
E6	100	300	21.6	2.4 g
E7	100	300	25.2	2.8 g
E8	100	300	28.8	3.2 g
E9	100	300	32.4	3.6 g
E10	100	300	36.0	4.0 g
E11	100	300	39.6	4.4 g
E12	100	300	43.2	4.8 g
E13	100	300	46.8	5.2 g
E14	100	300	50.4	5.6 g
E15	100	300	54.0	6.0 g
E16	100	300	57.6	6.4 g

* T represents a ternary system formed when the mixed emulsifier disperses in water. E denotes an emulsion.

The numerals indicate the approximate % of mixed emulsifier present with a constant alcohol to surfactant ratio of 9:1; for emulsions this is the emulsion number.

containing cetrimide or cetomacrogol surfactants will be referred to as ionic or non-ionic systems respectively.

The macroscopic and microscopic appearance of the ternary systems and emulsions were described by Barry & Saunders (1970a,b; 1972a,b). The formulations varied in consistency from mobile liquids at low concentrations to glossy semisolids at moderate and high concentrations of mixed emulsifiers.

Oscillatory tests. The behaviour of ternary systems and emulsions in forced oscillation at $25 \pm 0.5^\circ$ was investigated using an R14 Weissenberg Rheogoniometer modified to R16 standards. A Solartron Digital Transfer Function Analyser and Mechanical Reference Synchroniser coupled to the instrument simplified data collection. The torsion bar constant was 2.207×10^3 dyne cm for each 0.001 inch deflection. Each sample was placed between the parallel plates (7.5 cm diam.) and the platen gap was set at 25×10^{-3} inch using a displacement transducer connected to a digital voltmeter calibrated to display gap width directly. The lower platen was oscillated by a variable sine wave generator at frequencies from 7.91×10^{-4} to 25 Hz. At each frequency, the input and output signals were measured by displacement transducers and were fed into two separate direct reading transducer meters. The signals from the meters passed to the digital transfer function analyser where they were resolved and integrated over a preset number of cycles to give direct digital values of amplitude and phase. Further details were as given by Warburton & Davis (1969).

Tests for linearity were performed by increasing the amplitude of oscillation at representative experimental frequencies and measuring the amplitude of the constrained plate and the phase shift. Departure from linearity was easily identified by an abrupt change in these values. The systems were then examined as a function of frequency in their linear viscoelastic regions and values of amplitude

ratio and phase lag were determined. These were used to calculate G' and η' using equations 7 and 8.

The variations of G' and η' with frequency for ternary system and emulsions are shown in Figs 2 and 3 respectively. The values derived for emulsions containing greater than 12% mixed emulsifier were similar at all frequencies, and for clarity only representative emulsions of high emulsion number (see Table 1 footnote) are plotted.

DISCUSSION

In the examination of self-bodying mechanisms, a useful method of approach is to study first ternary systems formed when the mixed emulsifier disperses in water, and then to consider the appropriate four component systems formed when an oil is incorporated to make an emulsion. This approach provided evidence that the rheological properties of liquid paraffin-in-water emulsions stabilized by cetostearyl alcohol and surfactants cetrinide or cetomacrogol depended on viscoelastic networks in the continuous phases, formed by the interaction of cetostearyl alcohol and aqueous surfactant solution (Barry & Saunders, 1970a,b; 1972a,b,c).

During the preparation of each ternary system, aqueous surfactant solution penetrated into molten cetostearyl alcohol to form ternary liquid crystalline phase. No efforts were made to ensure equilibrium between the liquid crystalline and isotropic phases, and as the system cooled below T_{pen} (the minimum temperature at which liquid crystals exist) interaction reduced and low temperature ternary phase

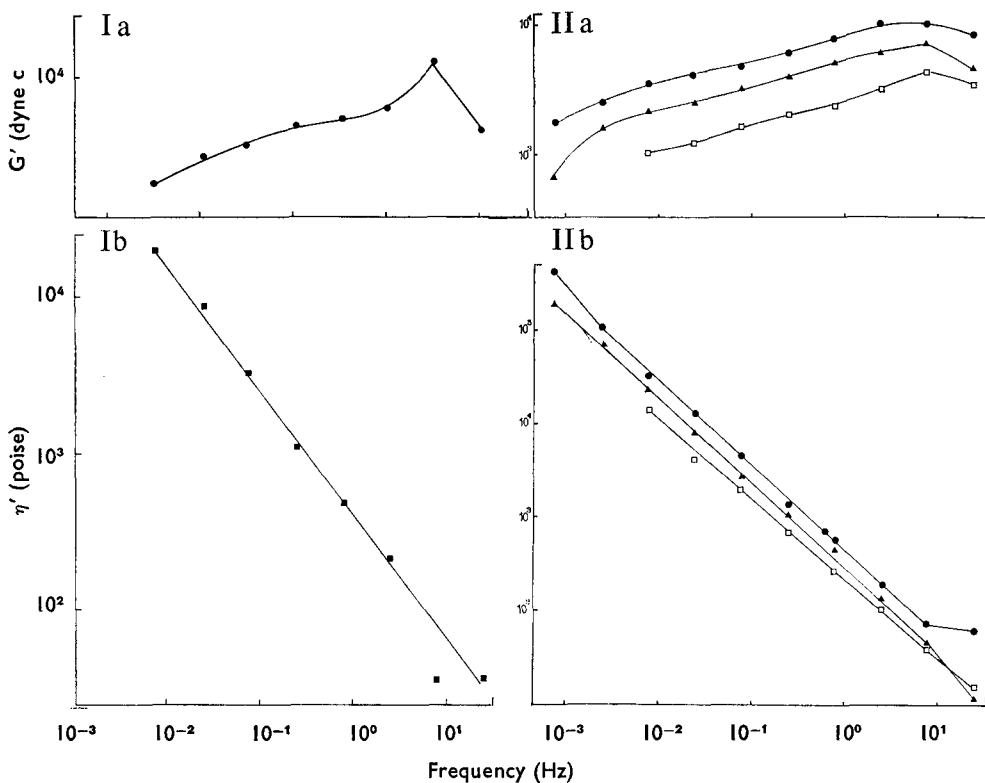


FIG. 2. Ternary systems: I cetrinide, II cetomacrogol. The variation of (a) storage modulus, G' , and (b) dynamic viscosity, η' , with frequency. T10 = \square , T12 = \blacktriangle , T16 = \bullet , for II.

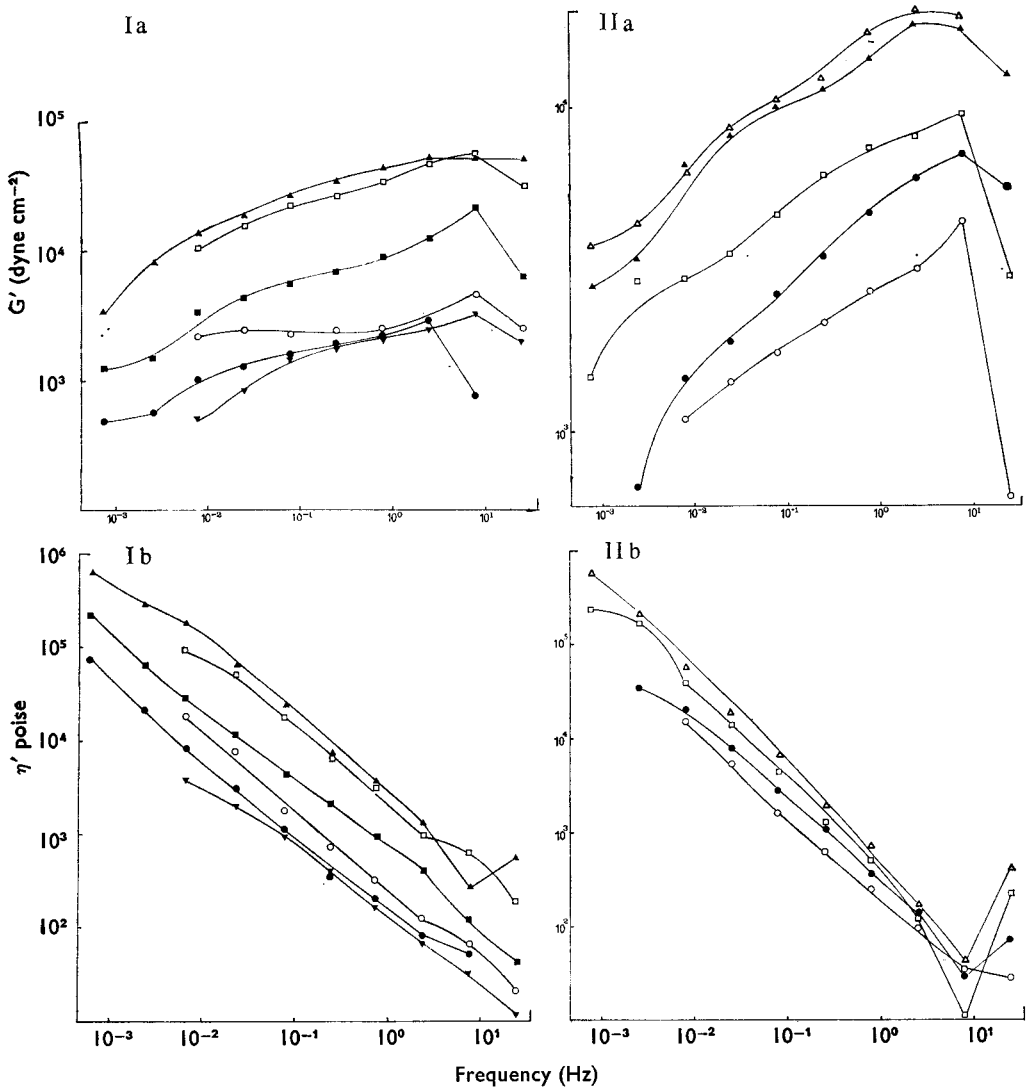


FIG. 3. Emulsion: I cetrimide, II cetromacrogol. The variation of (a) storage modulus, G' , and (b) dynamic viscosity, η' , with frequency. E4=▼, E6=● (I only), E7=○, E8=■ (I only, ● in II), E10=□, E14=▲, E16=△.

precipitated. This phase was gel-like; the hydrocarbon chains were rigid although molecular packing was relatively loose. Below T_{pen} , unreacted surfactant solution penetrated slowly into crystalline alcohol to form additional network structure.

The concentrations of mixed emulsifiers used in the preparation of the emulsions were in excess of those required to form complex, condensed, monomolecular films at the oil-water interfaces. As the ingredients cooled, excess alcohol diffused into the continuous phase of each emulsion and formed liquid crystals; a small proportion of liquid paraffin was also solubilized. Thus, each cooled emulsion consisted essentially of a ternary surfactant-cetostearyl alcohol-water gel containing dispersed liquid paraffin droplets.

High temperature interaction (i.e. above T_{pen}) between cetrimide solution and cetostearyl alcohol was extensive and thus cetrimide networks were fully formed soon after the systems cooled to the storage temperature. In contrast, interaction between cetomacrogol and the alcohol at high temperature was not extensive, and low temperature interaction (which may take several days) was also of considerable importance in the formation of non-ionic networks (Barry & Saunders, 1972c). In the present work, all the ternary systems and emulsions were examined after approximately 3 months storage at 25° to ensure that penetration was essentially complete and all the networks were fully formed.

For clarity, the behaviour of individual ternary systems and emulsions is examined in oscillation before discussing the variation of oscillatory parameters with emulsifier concentration. Phenomenological results only will be considered, as at the present time complete information is not available concerning the detailed molecular structure of the heterogeneous ternary system and emulsion networks (Barry & Saunders, 1972c).

The variations of G' and η' with frequency for all ternary systems and emulsions were similar (Figs 2, 3). As frequency increased, G' increased and η' fell monotonically through several decades. This behaviour conforms with the mechanical model described in the theory section. Fig. 2I, which is simplified because the data for only one experimental system were plotted, illustrates these trends. Discontinuities occurred in many of the curves at frequencies close to the natural frequency of the constrained member of the Rheogoniometer (10.2 Hz). Other workers also observed irregularities in plots of G' and η' in this region (e.g. Warburton & Davis, 1969; Weeks & Reid, 1970; Jones & Walters, 1971). The last authors considered that small experimental errors were magnified at frequencies close to resonance, and thus the anomalous behaviour may be discounted.

Although it is doubtful whether a meaningful comparison may be made between oscillatory data derived for solutions of amorphous polymers of high molecular weight and for the multiphase systems examined, the trends whereby G' increased and η' fell monotonically as frequency increased, were similar (cf. Ferry, 1970). Creep data supported the comparison; both categories of material exhibited a residual viscosity, η_0 , derived within a relatively short time.

At low frequencies, η' for each experimental system was high. At very low frequencies, viscoelastic theory indicates that η' should approach η_0 , the residual viscosity derived in creep. The lowest frequency we used (7.91×10^{-4} Hz) was equivalent to a creep time of only approximately 200 s. After this time, retarded elastic mechanisms still strongly influenced the creep behaviour of both ionic and non-ionic systems (Barry & Saunders, 1970a, 1972a). This explains why the dynamic viscosities, η' , for each system calculated at the frequency 7.91×10^{-4} Hz were approximately a hundredfold lower than corresponding residual viscosities obtained in creep (Table 2). Approximate calculations indicated that an oscillation frequency as low as 2.5×10^{-5} Hz would be required to obtain values of η' that approach η_0 closely. Working at such low frequencies involves experimental problems. The transfer function analyser required one cycle to lock onto the input sine wave, and then an additional cycle to compare input and output sine waves. The long experimental times required for this at low frequencies increased evaporation errors, especially for parallel plate geometry. These problems illustrate the importance of employing both creep and oscillatory tests to derive data equivalent to a wide range of

Table 2. Comparison of the residual shear viscosity, η_0 , derived in creep experiments* with the dynamic viscosity, η' , calculated at an oscillatory frequency of 7.91×10^{-4} Hz.

Surfactant	System†	η_0 (poise $\times 10^7$)	η' (poise $\times 10^5$)
Cetrimide	E6	1.2	0.97
	E8	2.0	2.2
	E9	3.5	4.2
	E12	5.5	7.5
	E14	7.9	6.9
Cetomacrogol	E10	4.4	2.3
	E12	6.2	4.4
	E14	5.2	4.3
	E16	5.4	6.0

* Barry & Saunders, 1970a, 1972a.

† See Table 1.

frequencies. Thus Davis (1971) defined three different frequency regions for testing semisolid ointments and creams: (a) $\omega > 10^{-1}$, oscillatory testing only; (b) $4 \times 10^{-3} < \omega < 10^{-1}$, creep or oscillatory methods; (c) $\omega < 4 \times 10^{-3}$, creep testing only.

The self-bodying phenomenon was illustrated by the way in which storage moduli and dynamic viscosities increased as the mixed emulsifier concentration rose throughout the measured frequency range. Thus the emulsion plots in Fig. 3 were in ascending order of emulsion number with respect to the G' or η' axes. Similarly plots were also in ascending order for cetomacrogol ternary systems prepared with increasing concentrations of mixed emulsifier. The similarities between all ternary systems and corresponding emulsion plots were significant, and supported the view that the ternary networks, formed by the interaction of mixed emulsifiers and water, were responsible for the rheological properties of the emulsions. As the variation of oscillatory data with mixed emulsifier concentration was the main interest when examining self-bodying phenomena, the data in Fig. 3 were collated to provide plots of G' and η' versus emulsion number at each frequency. From these plots, a more detailed examination of the self-bodying action of each mixed emulsifier was possible. Selected plots of G' and η' versus cetrimide and cetomacrogol mixed emulsifier concentration at representative high, low and intermediate frequencies are given in Fig. 4.

As cetrimide mixed emulsifier concentration increased, a corresponding rise occurred in emulsion consistency caused by gel networks which built-up in the continuous phases. This was shown at each frequency by rises in both η' and G' for cetrimide emulsions of approximate mixed emulsifier concentration increasing from 4–10%. At high frequencies, linearity limits were restricted in emulsions prepared with low concentrations of mixed emulsifier and data were scattered. This restriction accords with the proposition that networks in systems of low emulsion number were not extensive and that they were easily irreversibly disrupted. Once built-up, further additions to the network had less marked effects and the graphs formed plateaux above approximately 10% mixed emulsifier concentration. A second inflexion in G' and η' plots occurred at low frequencies only ($\leq 7.91 \times 10^{-3}$ Hz) in emulsions containing greater than 14% mixed emulsifier concentration. Similar trends were apparent

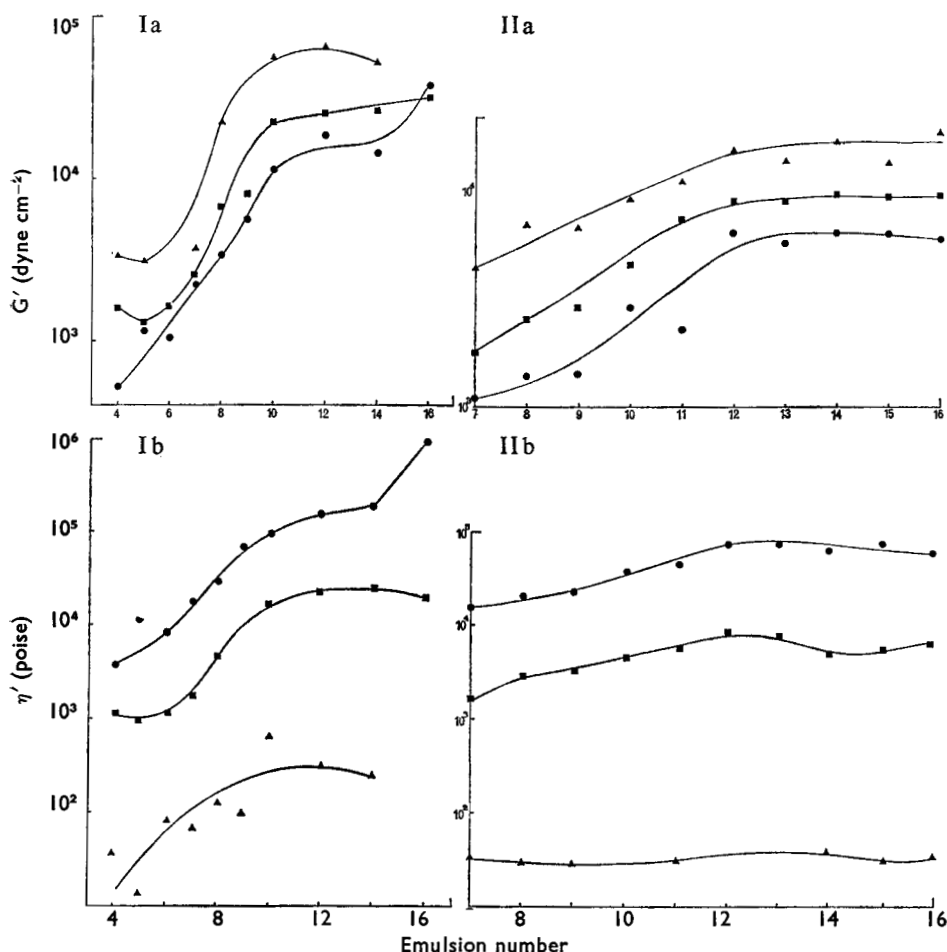


FIG. 4. Emulsions: I cetrimide, II cetromacrogol. The variation of (a) storage modulus, G' , and (b) dynamic viscosity, η' , with emulsion number, measured at the stated frequencies. $\bullet = 7.91 \times 10^{-3}$, $\blacksquare = 7.91 \times 10^{-2}$, $\blacktriangle = 7.91$.

when creep parameters were plotted against mixed emulsifier concentration (Barry & Saunders, 1970a). However, in creep the trends occurred at lower mixed emulsifier concentrations. For example, the creep plateau region was between 6–10% mixed emulsifier concentration and was followed by a second inflexion at higher concentrations of mixed emulsifier. This, when considered with the fact that the second inflexion in oscillatory parameters was observed only at low frequencies (when the time scale of the experiment was approaching that of creep experiments), suggested that important processes associated with self-bodying phenomena were apparent only at long times of testing, and thus were most easily examined in creep.

Self-bodying phenomena were not as marked in cetromacrogol emulsions. There was a comparatively slight initial increase in emulsion consistency, shown by increases in η' and G' as mixed emulsifier concentration increased from 7–12%. At higher concentrations the plots levelled out (Fig. 4II). Similar trends were shown when the creep parameters were plotted versus emulsion number (Barry & Saunders, 1972a). The slight initial increase in consistency was because of the comparatively high mixed

emulsifier concentrations employed. These amounts were necessary to prevent creaming and coalescence because non-ionic networks required a long time to form (Barry & Saunders, 1972c). Thus all results were obtained close to the plateau region and the expected prominent initial rise was absent.

Acknowledgements

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