

Oscillatory testing of o/w emulsions containing mixed emulsifiers of the surfactant/long chain alcohol type: influence of surfactant chain length

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A Weissenberg Rheogoniometer with parallel plates coupled to a Solartron Digital Transfer Function Analyser was used at 25° in oscillatory mode to investigate liquid paraffin-in-water emulsions stabilized by alkyltrimethylammonium bromides (of C₁₂-C₁₈ chain lengths) and cetostearyl alcohol. Ternary systems, formed by dispersing the quaternary surfactants and cetostearyl alcohol in water, were similarly examined. Each preparation was tested in the linear viscoelastic region and fundamental rheological parameters, the storage modulus (G') and the dynamic viscosity (η'), were derived as functions of frequency over the range 7.91×10^{-4} to 25 Hz. The rheological properties of the emulsions were related to viscoelastic gel networks present in the continuous phases. The corresponding ternary system parameters implied that these networks were formed by the interaction of cetostearyl alcohol and aqueous surfactant solution. Ternary systems and emulsions behaved similarly with respect to frequency. As this increased, G' rose and η' fell, the latter through several logarithmic decades. At low frequencies, G' and η' rose as the quaternary alkyl chain length increased. Formulations containing quaternary surfactants of medium chain lengths (C₁₄ and C₁₆) formed strong viscoelastic networks. The C₁₂ systems contained tenuous networks, and networks formed from the C₁₈ surfactant were not as rigid as predicted by the trend of the lower homologues. The oscillatory data were compared and correlated with creep data described previously.

Recently, continuous shear and creep techniques were employed to examine the influence of surfactant chain length on the rheological properties of emulsions stabilized by mixed emulsifiers of the alkyltrimethylammonium bromide-cetostearyl alcohol type (Barry & Saunders, 1971a, b). These methods, however, were not without disadvantages. Continuous shear tests, although rapid and easy to perform, do not provide fundamental viscoelastic parameters, and creep experiments are limited at short periods 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. Thus, in this work, the rheological investigation of systems prepared with the quaternary mixed emulsifiers is extended to include oscillatory techniques. These experiments provide fundamental viscoelastic parameters. In addition, they yield data corresponding to short creep times as a periodic experiment at frequency ω rad s⁻¹ is qualitatively equivalent to a creep experiment at time $t = 1/\omega$ s.

METHODS AND RESULTS

Materials. Water, liquid paraffin, cetostearyl alcohol and the alkyltrimethylammonium bromides, dodecyl- (DTAB), tetradecyl- (TTAB), hexadecyl- (HTAB) and octadecyl- (OTAB) were as described previously (Barry & Saunders, 1970a, 1971a, b).

Preparation of the systems. Ternary systems and emulsions were prepared (Barry & Saunders, 1970a) respectively according to the formulae: water 360, cetostearyl alcohol 36, alkyltrimethylammonium bromide 4; liquid paraffin 100, water 300, cetostearyl alcohol 28.8, alkyltrimethylammonium bromide 3.2 g.

Oscillatory tests. The behaviour of ternary systems and emulsions in forced oscillation was investigated using an R14 Weissenberg Rheogoniometer modified to bring it up to R16 standards. A Solartron Digital Transfer Function Analyser and a Mechanical Reference Synchronizer coupled to the instrument simplified data collection. The rheogoniometer was employed with parallel plates 7.5 cm in diameter and the platen gap was set to 25×10^{-3} inch. The torsion bar constant was 2.207×10^3 dyne cm^{-1} (or mN m^{-1}) per 0.001 inch movement.

Initial tests for linearity were made by increasing the amplitude of oscillation at representative experimental frequencies. The amplitude ratio [ratio of the amplitudes of the constrained (stress) and forced (strain) oscillations] and the phase shift between the oscillations, were determined. Deviations from linearity were identified by abrupt changes in these values. The systems were then examined in their linear viscoelastic regions by applying sinusoidally varying shear strains at frequencies ranging from 7.91×10^{-4} to 25 Hz. At each frequency, the amplitude ratio and the phase shift were determined and were used to calculate the storage modulus, G' , (representing energy stored and recovered per cycle of deformation) and the dynamic viscosity, η' , (representing energy dissipated) using Walter's equations for parallel plate geometry (Walters & Kemp, 1968; Walters, 1968). Further details of the apparatus and experimental techniques were given by Barry & Eccleston (1973) and by Warburton & Davis (1969) and Davis (1972).

The variation of G' and η' with frequency for the ternary systems and emulsions are shown in Figs 1 and 2.

DISCUSSION

In this and previous work, the method of approach was to investigate first the properties of ternary systems, formed when the mixed emulsifiers dispersed in water, and then to examine the four component systems produced when liquid paraffin was added so as to form oil-in-water emulsions. This program indicated that ternary gel networks, formed by surfactant solutions and cetostearyl alcohol interacting in the continuous phases, were responsible for the rheological properties of the emulsions (Barry & Saunders, 1970a, b, 1971a, b, 1972a-c).

During mixing of each ternary system, aqueous quaternary surfactant solution interacted with cetostearyl alcohol to form a liquid crystalline phase. No efforts were made to ensure equilibrium, and when the system cooled below the transition temperature T_{pen}^* , the rate of interaction reduced and the system precipitated to form a viscoelastic gel of low temperature ternary phase. Gel formation by direct low temperature interaction was of minor importance in these alkyltrimethylammonium bromide systems (Barry & Saunders, 1971a, b, 1972c).

* Minimum temperature at which liquid crystals exist.

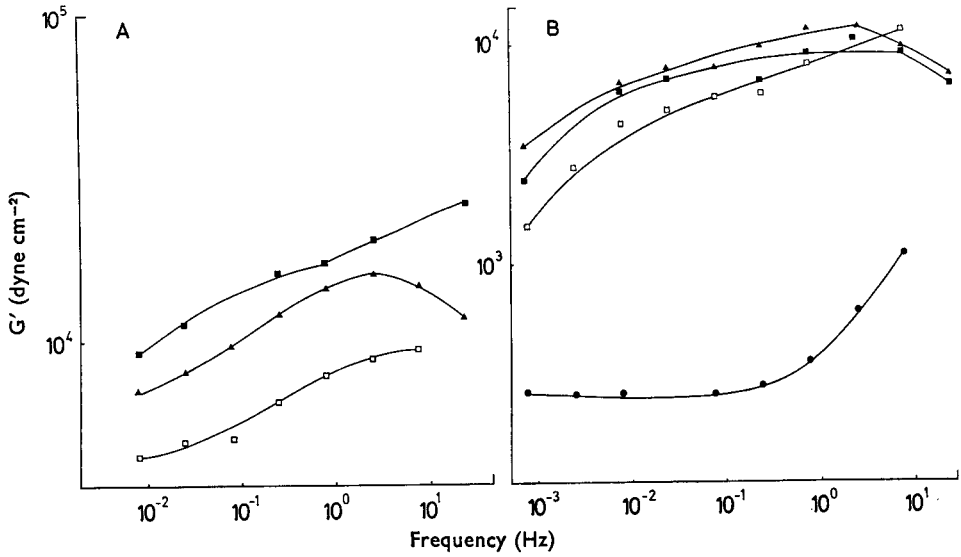


FIG. 1. Variation of storage modulus, G' (dyne cm^{-2}) with frequency (Hz). A, for ternary system TC_{14} (□), TC_{16} (■), TC_{18} (▲). B for emulsions; EC_{12} (●), EC_{14} (□), EC_{16} (■), EC_{18} (▲).

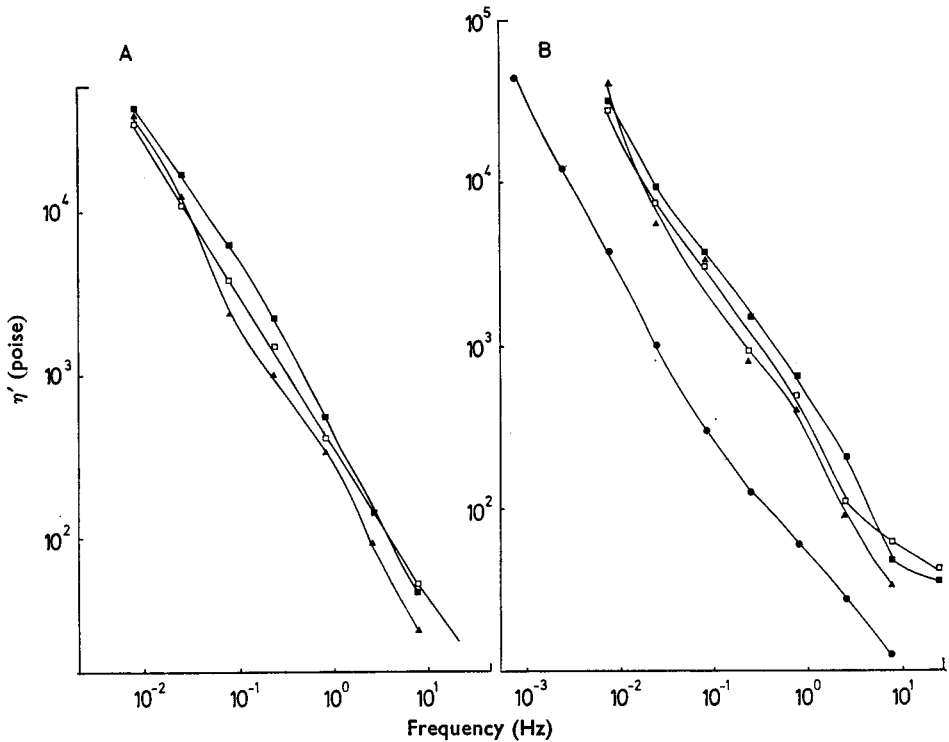


FIG. 2. Variation of dynamic viscosity η' (poise) with frequency (Hz). A for ternary systems; TC_{14} (□), TC_{16} (■), TC_{18} (▲). B for emulsions; EC_{12} (●), EC_{14} (□), EC_{16} (■), EC_{18} (▲).

In each emulsion, as the ingredients cooled, cetostearyl alcohol diffused from the liquid paraffin into the micellar environment and interacted with quaternary surfactant to form liquid crystals; a small proportion of liquid paraffin was also solubilized. Thus essentially, each cooled emulsion consisted of an alkyltrimethylammonium bromide-cetostearyl alcohol-water gel in which liquid paraffin droplets were dispersed.

The phenomenological behaviour of individual systems in oscillation will be considered briefly before the effect of varying the surfactant chain lengths is studied. The changes in G' and η' with frequency for all ternary systems and emulsions were similar (Figs 1–2). As the frequency increased G' rose and η' fell, the latter through several logarithmic decades. Any discrepancies in the curves at frequencies close to resonance (10.2 Hz) were not significant; they were probably due to the magnification of small experimental errors (Jones & Walters, 1971). The dynamic behaviour conformed with the generalized Maxwell model analogy described by Barry & Eccleston (1973), since the magnitudes of G' and η' at each frequency depended on the molecular rearrangements that could take place within the period of oscillatory deformation (Ferry, 1970). At high frequencies, elastic behaviour dominated as there was little time available for viscous deformation, and values of G' and η' were high and low respectively. At the time period increased, viscous behaviour became increasingly prominent and thus η' rose and G' reduced with decrease in frequency. At very low frequencies, viscoelastic theory predicts that the dynamic viscosity, η' , will approach η_0 , the residual viscosity derived in creep. Table 1 indicates that η' calculated at the

Table 1. 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^{-3} Hz for each ternary system and 7.91×10^{-4} Hz for each emulsion. (T = Ternary System, E = Emulsion.)

System	η_0 (poise $\times 10^7$)	η' (poise $\times 10^5$)
TC ₁₄	2.48	0.359
TC ₁₆	5.76	0.441
TC ₁₈	7.32	0.419
EC ₁₂	0.440	0.460
EC ₁₄	2.63	2.18
EC ₁₆	6.17	3.01
EC ₁₈	6.65	7.98

* Barry & Saunders, 1971a.

lowest experimental frequencies, 7.91×10^{-4} Hz for the emulsions and 7.91×10^{-3} Hz for ternary systems (equivalent to creep times of approximately 200 and 20 s respectively) were often a hundredfold or more lower than the corresponding creep viscosities. This was because at these frequencies elastic mechanisms still influenced rheological behaviour. Similar results were obtained when η' for cetrimide systems were compared with the corresponding creep residual viscosities (Barry & Eccleston, 1973). (For comments on low frequencies see Barry & Eccleston, 1973, p. 250.)

The similarities between ternary system and corresponding emulsion plots supported the view that ternary networks, formed by the interaction of quaternary surfactant, cetostearyl alcohol and water, were responsible for the rheological properties of the emulsions. It was not possible to formulate ternary systems equivalent exactly to the continuous phases of the corresponding emulsions. In the latter, the precise quantities

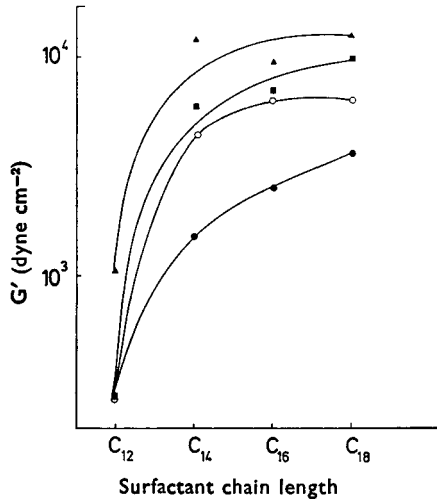


FIG. 3. Emulsions. Variation of storage modulus, G' (dyne cm^{-2}) with surfactant chain length, derived at the stated frequencies (Hz). 7.91×10^{-4} (●), 7.91×10^{-3} (○), 2.5×10^{-1} (■), 7.91 (▲).

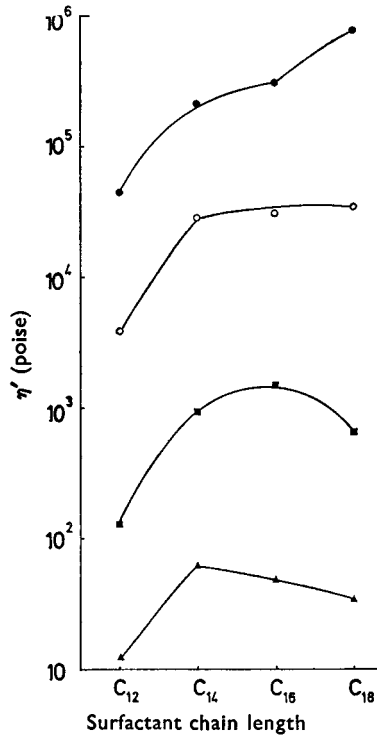


FIG. 4. Emulsions. Variation of dynamic viscosity, η' (poise) with surfactant chain length, derived at the stated frequencies (Hz). 7.91×10^{-4} (●), 7.91×10^{-3} (○), 2.5×10^{-1} (■), 7.91 (▲).

of alcohol diffusing into the continuous phases could not be determined simply, neither could the calculation allow for the influences of particle size distributions on the magnitudes of η' and G' . However, the absence of trends in emulsion plots that might be associated with the disperse phases suggests that liquid paraffin emulsion globules may be considered simply as the inert diluent of a ternary gel.

The consistencies of ternary systems and emulsions rose as the surfactant chain length increased, except for the C_{18} homologue. Thus, throughout the measured frequency range, G' and η' generally increased with increase in quaternary chain length, and the plots in Figs 1 and 2 were usually in ascending order of surfactant chain length with respect to the G' or η' axes. Comparable trends were shown in creep, when compliances decreased and viscosities increased in a similar manner (Barry & Saunders, 1971a, b). However, discrepancies in this general trend occurred, mainly at high frequencies. To examine these in more detail, data from Figs 1 and 2 were collated to provide plots of G' and η' versus chain length at each frequency. Selected plots for the emulsions at representative high, low and intermediate frequencies are shown in Figs 3 and 4. Ternary system plots (not shown) revealed similar trends.

The DTAB ternary system was non-linear in oscillation even at low amplitudes and low frequencies. Thus, data were scattered and were not included in Figs 1A and 2A. Satisfactory results were obtained for the DTAB emulsions, although the values of G' and η' derived at each frequency were much lower than those of the other homologues (Figs 1B, 2B, 3 and 4). This confirmed creep results, which also suggested that the DTAB networks were tenuous, were of low elasticity and were easily disrupted in shear (Barry & Saunders, 1971a, b).

Ternary systems and emulsions prepared with higher quaternary homologues contained strong viscoelastic networks. The rigidity of the networks increased, and thus G' and η' at each frequency generally increased as the homologous series was ascended. Discrepancies in this general trend, however, were apparent with the C_{18} plots, especially at high frequencies. Storage moduli and dynamic viscosities for the C_{18} emulsion were sometimes lower than those of the corresponding C_{16} emulsion, and for the C_{18} ternary system they were sometimes lower than those of the C_{16} and C_{14} systems (Figs 1–4). This confirmed creep data, which also suggested that systems prepared with OTAB were not as rigid as might be expected from the trends shown by the lower homologues of increase in consistency with increase in surfactant chain length (Barry & Saunders, 1971a).

The tenuous nature of the C_{12} networks was not related to the concentration of the surfactant, but rather to the difference between the DTAB and cetostearyl alcohol chain lengths, and to steric hindrance by the large cationic head group. These factors prevented the formation of strong molecular complexes. The total van der Waals force between alcohol and surfactant molecules in each complex increased as the number of carbon atoms in the surfactant chain rose. Strong networks formed with homologues of chain lengths greater than C_{12} , as the additional hydrophobic bonds were sufficient to counteract steric effects of the cation. Thus the C_{16} network was stronger than that of the C_{14} , and values for G' and η' for HTAB systems were higher than those for the corresponding TTAB systems. The comparatively low rigidity of the C_{18} network was possibly caused by the high Krafft point of this homologue (Barry & Saunders, 1971a). Although this transition temperature was lowered by additives, probably it was close enough to the storage and testing temperatures of 25° to hasten crystallization of the network.

Conclusions

The dynamic behaviour (Weissenberg Rheogoniometer) of liquid paraffin-in-water emulsions stabilized by alkyltrimethylammonium bromides (of C₁₂-C₁₈ chain lengths) and cetostearyl alcohol correlated with that of the corresponding ternary systems formed when the quaternary surfactant and cetostearyl alcohol dispersed in water.

Ternary systems and emulsions behaved similarly with respect to frequency. Storage moduli (G') rose and dynamic viscosities (η') fell as frequency increased. Discrepancies in these trends occurred at frequencies close to resonance.

Ternary system and emulsion consistencies generally increased as the surfactant chain length increased. This was shown at each frequency by rises in G' and η' values, and was related to the nature of the viscoelastic networks present in each formulation.

Strong viscoelastic networks were present in systems prepared with surfactants of medium chain lengths (C₁₄ and C₁₆). Formulations containing the C₁₂ surfactant formed tenuous networks, and the C₁₈ systems were not as rigid as expected. The strength of each network was related to the influence on the formation of molecular complexes of both the cationic head group and the surfactant chain length.

Oscillatory data were correlated with creep results derived in previous experiments and it was concluded that a combination of both techniques was valuable for this study.

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REFERENCES

- BARRY, B. W. & ECCLESTON, G. M. (1973). *J. Pharm. Pharmac.*, **25**, 244-253.
BARRY, B. W. & SAUNDERS, G. M. (1970a). *J. Colloid Inter. Sci.*, **34**, 300-315.
BARRY, B. W. & SAUNDERS, G. M. (1970b). *J. Pharm. Pharmac.*, **22**, Suppl. 139S-146S.
BARRY, B. W. & SAUNDERS, G. M. (1971a). *J. Colloid Inter. Sci.*, **35**, 689-705.
BARRY, B. W. & SAUNDERS, G. M. (1971b). *Ibid.*, **36**, 130-138.
BARRY, B. W. & SAUNDERS, G. M. (1972a). *Ibid.*, **38**, 609-615.
BARRY, B. W. & SAUNDERS, G. M. (1972b). *Ibid.*, **38**, 616-625.
BARRY, B. W. & SAUNDERS, G. M. (1972c). *Ibid.*, **41**, 331-342.
DAVIS, S. S. (1972). *Rheol. Acta*, **11**, 199-202.
FERRY, J. D. (1970). *Viscoelastic Properties of Polymers*, 2nd edn, London: John Wiley & Sons, Inc.
JONES, T. E. R. & WALTERS, K. (1971). *Rheol. Acta*, **10**, 365-367.
WALTERS, K. (1968). *Basic Concepts and Formulae for the Rheogoniometer*, published by Sangamo Controls Ltd., Bognor, England.
WALTERS, K. & KEMP, R. A. (1968). *Rheol. Acta*, **7**, 1-8.
WARBURTON, B. & DAVIS, S. S. (1969). *Ibid.*, **8**, 205-214.