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Kinetics of structure build-up in self-bodied emulsions stabilized by mixed emulsifiers B. W. BARRY AND G. M. SAUNDERS

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The semi-solid properties of emulsions prepared with surfactant-long chain alcohol mixed emulsifiers are due to viscoelastic networks present in the continuous phases. These networks have similar properties to ternary systems formed by dispersing the mixed emulsifiers in water (e.g. Barry & Saunders, 1970). In this work, the differences between the mechanisms which operate to form ionic and non-ionic networks were investigated.

Ternary systems and emulsions prepared with anionic (sodium dodecyl sulphate), cationic (cetrimide) or non-ionic (cetomacrogol) surfactants and cetostearyl alcohol were examined in creep and in continuous shear rheometry at a storage temperature of 25°. Systems were tested frequently during the first 24 h after preparation, and then regularly for 3 months. Short time creep tests were analysed to derive continuous spectra of retardation times, using a second order approximation method (Leaderman, 1958), equation 1,

$$L(\tau) \sim \frac{d}{d/nt} \left[J(t) - \frac{dJ(t)}{d/nt} \right] t = 2\tau$$
 1

where $L(\tau)$ is the value of a retardation spectrum, which is of the nature of a distribution function, although it has the dimension of compliance, and J(t) is the total compliance at time t. For each surfactant the results obtained were correlated with the mechanisms by which gel networks formed.

With age, anionic and cationic ternary systems and emulsions behaved similarly with respect to total compliance, retardation spectra and continuous shear parameters. Additional structure, although not extensive, formed within the first 2 h storage. This was indicated in creep by initial falls in total compliance values and decreases in spectral heights, and in continuous shear by corresponding increases in apparent viscosities and hysteresis loop areas. Thereafter negligible new structure formed, and thus spectra for systems tested after 2.5 and 24 h storage were similar, and there was little variation in total compliances, apparent viscosities and loop areas. The essentially constant position of spectral maxima indicated that the high temperature interaction which occurred during the preparation of ionic systems was the major mechanism which operated to form gel networks. The low temperature interaction occurring during the first 2 h storage was insignificant.

Cetomacrogol systems behaved differently. Structure built up rapidly during the first 24 h storage. This was shown in creep by marked reductions in total compliances and spectral heights, and in continuous shear by changing complex flow properties. The movement of maxima in the spectra to longer times indicated that mechanisms which operated to form gel networks at the storage temperature produced structures which differed at a molecular level from those formed at high temperatures.

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