

Hydrophobic bonding in soap-stabilized emulsions

STANLEY S. DAVIS

Pharmaceutics Section, Pharmacy Department, University of Aston in Birmingham, Gosta Green, Birmingham 4, U.K.

The rheological properties of emulsions stabilized by potassium laurate have been measured at different temperatures and in the presence of urea to assess the validity of the concept of aggregation through hydrophobic interactions. The elasticity of the systems, as measured by a Rheogoniometer, increased with increased temperature and decreased with added urea. These results are entirely consistent with hydrophobic bonding. The mechanism of bonding is discussed in terms of interfacial hydrolysis, complex condensed films of acid soap, and polymolecular adsorption of surfactant at the oil-water interface.

Recently the aggregation behaviour of liquid paraffin, oil-in-water emulsions stabilized by potassium laurate was examined by Shotton & Davis (1968a). A maximum state of aggregation in the region of 5% surfactant could not be explained by the classical DVO theory of colloid stability (Derjaguin, 1940; Verwey & Overbeek, 1948). Instead, polymolecular adsorption of surfactant at the oil-water interface, followed by hydrophobic bonding was suggested as a possible alternative. Similar processes of polymolecular adsorption, micellar adsorption or hydrophobic bonding interactions (or both) have been proposed previously for the air-water interface (Dixon, Judson & Salley, 1954; Ross, 1945; Moilliet, Collie & Black, 1961), solid-water interface (Matijevic & Ottewill, 1958; Ottewill & Watanabe, 1958; Somasundarin, Healy & Fuerstenau, 1966), emulsions (Cockbain, 1952; Osipow, Birsan & Snell, 1957; Riegelman, 1962) and surfactant protein interactions (Nemethy, 1967).

Cockbain's original concept of hydrophobic bonding as an effective mechanism of aggregation has been thought improbable (Higuchi, Rhee & Flanagan, 1965; Becher, 1965) and some authors have preferred to restrict their conclusions to vague statements such as "film-film interactions" (Moore & Lemberger, 1963; Lemberger & Mourad, 1965) or "weakly adsorbed, thick hydrophilic layers" (Higuchi & others, 1965).

The liquid paraffin emulsions we used were pseudoplastic in their flow properties. This decrease in viscosity with increased shear rate can be explained in one of two ways. The link formation concept of Goodeve (1939) or the entrappment of continuous phase approach of Mooney (1946). Furthermore, any aggregated emulsion will be sensitive to changes in temperature. The entrappment theory predicts that an increase in temperature will cause partial destruction of aggregate structure and a subsequent fall in relative viscosity (Reiner, 1961). On the other hand, aggregates stabilized by hydrophobic bonds would be expected to increase in stability as the temperature rises due to the endothermic nature of hydrophobic bond formation (Nemethy, 1967). The relative viscosity would therefore increase. Likewise the

addition of a hydrophobic bond breaker, such as urea, should tend to decrease the relative viscosity.

Experiments of this nature have been carried out in the present work, to assess the validity of our suggested mechanism for aggregation.

MATERIALS AND METHODS

Materials and methods were as previously described (Shotton & Davis, 1968a, b; Davis, 1971). Emulsions of 60% liquid paraffin dispersed in potassium laurate of differing concentration, were prepared by initial mixing with a high speed stirrer, followed by homogenization. All emulsions were stored for one month before examination to allow for interfacial equilibrium, release of entrapped air, and possible changes in aggregation state (Sherman, 1967). Particle size distributions were characterized using a Coulter Counter (Model A—Industrial) (Shotton & Davis, 1968b). Rheological studies were performed with a Ferranti-Shirley viscometer and a Weissenberg Rheogoniometer. Bulk solution viscosities were measured by U-tube viscometers.

RESULTS AND DISCUSSION

Continuous phase

The viscosity of soap solutions varies exponentially with concentration:

$$\eta = e^{KC}$$

where K is a constant and C the soap concentration (Davis, 1967). The exponential shape of the curve is due to the association of soap molecules into micellar aggregates (Booij, 1949) and in the region of the critical micelle concentration there is a break. An increase in temperature or added solute would be expected to disturb the equilibrium between micellar and monomeric species and thereby affect viscosity.

Temperature. The viscosity of potassium laurate solutions falls monotonically with increased temperature over the range 25–40° (Fig. 1). This is qualitatively in

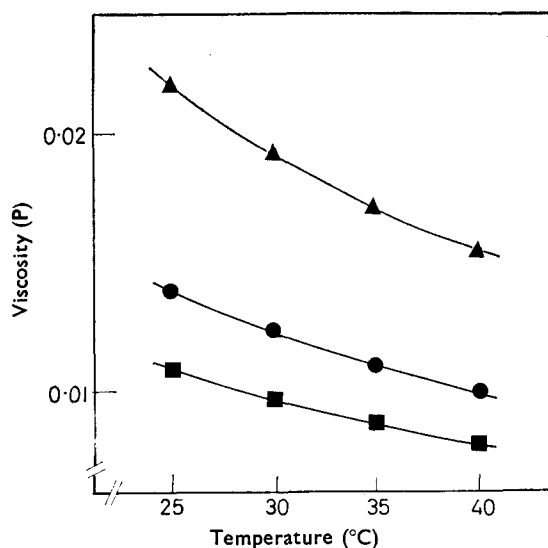


FIG. 1. Viscosity temperature relations for potassium laurate solutions above the critical micelle concentration. Potassium laurate concentration (% w/w). ■ 2.5. ● 5. ▲ 10.

accord with an empirical relation analogous to the Arrhenius equation of chemical kinetics:

$$\eta = Ae^{E/RT}$$

where A is a constant and E is the activation energy (Martin, Swarbrick & Cammarata, 1970). The curves are not truly exponential because the concentrations of the two dissolved species, monomer and micelle are highly dependent on temperature. In general, for ionized surfactants such as potassium laurate, an increase in temperature results in an increase in the number of monomeric species and a reduction in the size and number of micelles (Shinoda, Nakagawa & others, 1963). A slight concomitant fall in viscosity would therefore be expected.

Urea. Urea produces a rise in viscosity and above a concentration of 2M there is a linear relation between viscosity and urea concentration (Fig. 2). The addition

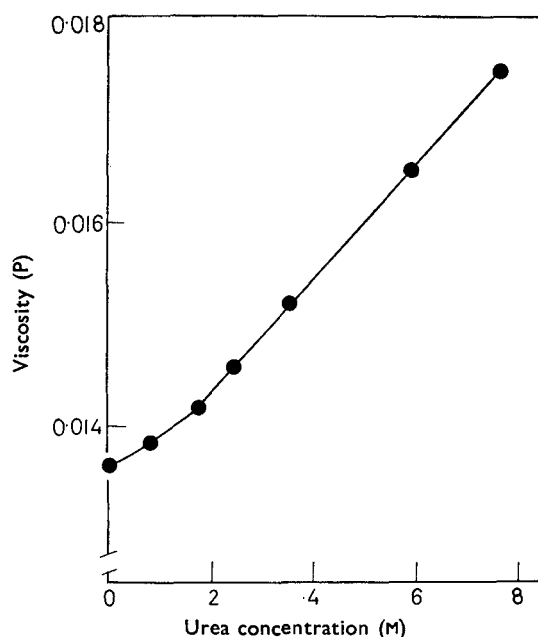


FIG. 2. The effect of urea on the viscosity of 5% potassium laurate (25°).

of urea to a soap solution above its c.m.c. will have two opposing effects on viscosity. It will raise the dielectric constant of water (Wyman, 1936) and should therefore promote micelle formation by decreasing the repulsive forces between the ionic heads of the laurate molecules. However urea has been shown to break up micellar structure due to its effect on hydrophobic bonds (Emerson & Holtzer, 1967; Bruning & Holtzer, 1961; Mukerjee & Ray, 1963), and would therefore be expected to reduce solution viscosity. On the other hand the addition of a solute, at high molar concentrations, will increase the viscosity on simple hydrodynamic grounds. The result of these two opposing effects is clearly shown in Fig. 2. At low concentrations (below 2M) micellar breakdown is occurring, and the gradient of the viscosity concentration relation is smaller than that at high urea concentrations where added urea is having a hydrodynamic effect only.

The effect of temperature on emulsion stability

Cone and plate viscometer. Samples of emulsion, stabilized by different concentrations of potassium laurate, were examined at temperatures in the range 25–40°. In all cases the flow curves were pseudoplastic and there was no evidence of thixotropy. The instrument was programmed to effect a compromise between instrumental effects at short sweep times and evaporation at longer sweep times (Davis, Shotton & Warburton, 1968). Rheograms were characterized by *apparent viscosity* (ratio of shear stress to shear rate at the highest shear rate of 1700 s⁻¹) and *limiting viscosity* (calculated from gradient of linear portion of flow curve). Both parameters fell with increase in temperature but the calculated relative viscosities increased with temperature. Relative apparent viscosity values are shown in Fig. 3. The relative limiting viscosities were similar.

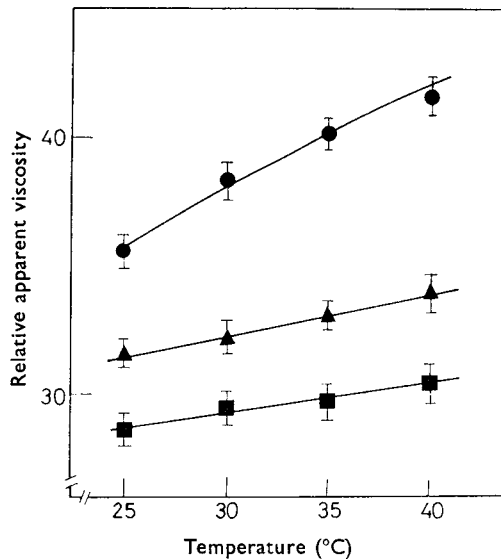


FIG. 3. The effect of temperature on the relative apparent viscosity of potassium laurate stabilized liquid paraffin emulsions (phase volume = 60%). Potassium laurate concentration (% w/w). ■ 2.5. ● 5. ▲ 10.

The rise in relative viscosity suggests that hydrophobic bonding interactions are indeed probable. Since the Ferranti-Shirley Viscometer is known to suffer from spurious effects due to evaporation, even when fitted with the manufacturers anti-evaporation unit (Davis & others, 1968), a further method of testing was selected.

Weissenberg Rheogoniometer. The emulsions under study were highly aggregated systems that demonstrated measurable elasticity when tested at very low shear rates. For a linear viscoelastic material undergoing forced harmonic oscillation of small amplitude

$$\sigma = 2\eta^*\dot{\gamma}$$

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 (W rad. s⁻¹) (Walters, 1968). We can express η^* as real and imaginary parts

$$\eta^* = \eta' - i(G'/W)$$

where η' is the dynamic viscosity, G' the dynamic rigidity, and $i = \sqrt{-1}$.

Samples of emulsion stabilized by 5% potassium laurate (the most highly aggregated system) were contained in parallel plate geometry and oscillated at small strain amplitude and low frequency (shear rate). The measured data, phase angle between stress and strain sine waves, and amplitude ratio were obtained using a Transfer Function Analyser (Warburton & Davis, 1969). These data were subsequently treated by digital computer using the equations of Walters & Kemp (1968).

A frequency of 0.5 rad. s^{-1} and an accurately known gap of around 0.06 cm were used for all experiments. The maximum shear rate was $8.5 \times 10^{-3} \text{ s}^{-1}$ and the maximum shear strain 2×10^{-2} . All experiments were performed as quickly as possible to avoid evaporation effects. Initially, viscoelastic properties were measured at 25° at weekly periods to monitor any storage change in G' and η' (Sherman, 1967). When constant reproducible results had been obtained, measurements were made over the temperature range $22.5\text{--}35^\circ$. Each temperature was held constant for three days before testing. Finally the system was re-examined at 25° .

The elasticity (G'), and (η') increased with temperature over the whole range studied (Fig. 4). This was a reversible increase since on returning to the original

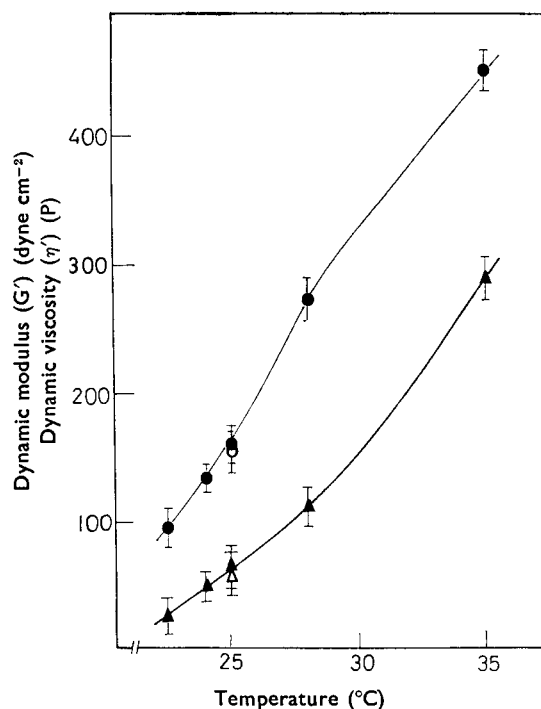


FIG. 4. The effect of temperature on the viscoelastic properties of a potassium laurate stabilized liquid paraffin emulsion (phase volume = 60%, soap concentration = 5% w/w). ● Dynamic viscosity. ▲ Dynamic modulus. Open symbols refer to repeat test after temperature cycle completed.

temperature, the two parameters had not changed significantly. The particle size distribution remained effectively the same throughout the tests. [Potassium laurate emulsions, although highly aggregated are known to be extremely stable to changes in particle size and particle size distribution (Shotton & Davis, 1968a, b)]. The results with the rheogoniometer confirm that the emulsions become more highly

aggregated as the temperature is increased. Using the Goodeve theory of pseudo-plastic flow we can consider that the interparticulate linkages become stronger with increase in temperature.

The process of hydrophobic bond formation (Nemethy, 1967; Kauzmann, 1959; Nemethy & Scheraga, 1962) has been compared thermodynamically with the solution of hydrocarbons in water (Kauzmann, 1959; Nemethy & Scheraga, 1962) and at room temperature has the following properties: $\Delta F_H < 0$, $\Delta S_H > 0$, $\Delta H_H > 0$.

The unfavourable enthalpy of formation is more than counterbalanced by the positive entropy term which results in a favourable free energy. Entropy is the most important factor in bond formation which can be profitably discussed in terms of water structure and the Frank & Evans (1945) concept of "ice-berg" formation around non-polar regions of dissolved species. The endothermic nature of the process causes the bonds to become stronger as the temperature rises to approximately 60°.

The effect of urea on emulsion stability

Quantities of high purity urea were added at 25° to emulsions stabilized by 5% potassium laurate. The systems were agitated for 2 h and then G' and η' measured as before. Both parameters were reduced by urea, the major effect being in the concentration region 0–2M (Fig. 5).

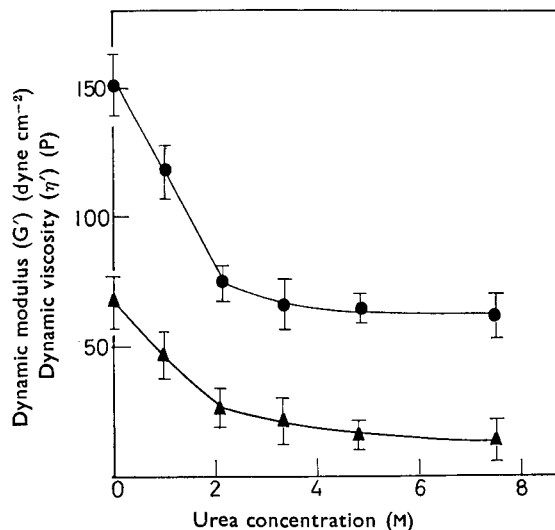


FIG. 5. The effect of added urea on the viscoelastic properties of potassium laurate emulsion in Fig. 4 (25°). ● Dynamic viscosity. ▲ Dynamic modulus.

Urea is known to break hydrophobic bonds (Kauzmann, 1959; Nemethy & Scheraga, 1962), although the exact mechanism is not clear. Frank & Franks (1968) and Mukerjee & Ray (1963) have pointed out that urea can hydrogen bond strongly with water and will therefore alter the water structure that presumably forms around hydrocarbon groups. That is, the "ice-berg" structures will be modified and hydrophobic interactions will be reduced. Kauzmann (1959) has also suggested the formation of urea–hydrocarbon clathrates as a possible mechanism. Urea concentrations in the range 0–2M are sufficient to cause breakdown of most of the hydrophobic bonds in the emulsion systems as well as the laurate micelles (Fig. 2).

Hydrophobic bonding in emulsions

The experiments on temperature effects and added urea are consistent with the premise that emulsions stabilized by potassium laurate are aggregated through a hydrophobic bonding mechanism. Cockbain's (1952) suggestion that aggregation could be accounted for by hydrophobic bonding was based on the assumption that a secondary layer of surfactant was adsorbed at the interface at concentrations just above the cmc. Single surfactant molecules would then be adsorbed with their hydrocarbon chains orientated towards the aqueous phase. Such particles in an aqueous medium would be hydrophobic and aggregation would occur through hydrophobic bonding. However, polymolecular adsorption of surfactant at interfaces is thought to occur only when two or more surface-active materials react to form a complex film (Moilliet & others, 1961). Indeed, Riegelman (1962) has proposed micellar adsorption of surfactant at the oil-water interface when a co-emulsifier is present. Polymolecular adsorption with "pure" surfactants can be considered improbable. The problem remains one of defining a pure surfactant when dealing with fatty acid soaps. The stability of soap emulsions has been attributed to the formation of acid soap by hydrolysis at the interface to give a complex condensed film (Martin & Hermann, 1941; Davis & Bartell, 1943). Such interfacial hydrolysis can occur even at high pH when bulk hydrolysis is negligible (Cook & Talbot, 1952; Eagland & Franks, 1957) so that the emulsions in the present study can be assumed to have complex interfacial films of ionized soap and free lauric acid. This type of film will have a greater stability than a single component film. The mechanism of interaction between the two components is still uncertain, as is its stoichiometry (Goddard, Smith & Kao, 1966). Three alternative suggestions can be made: (i) Van der Waals attraction between hydrocarbon chains and the repulsive forces between charged heads screened by intervening carboxylic acid groups (Spink, 1963), (ii). The negative character of the carboxylate ion leads to strong hydrogen bonding interactions (Alexander, 1941-42) and (iii) Ion-dipole interaction between charged and uncharged head groups (Marsden & Schulman, 1938). As yet the position is unresolved but nevertheless it is clear that complex films are more stable than their one component counterparts and that coulombic repulsion between charged heads is considerably suppressed.

At this stage we can propose a tentative model for polymolecular adsorption and hydrophobic bonding based on interfacial hydrolysis of potassium laurate and the formation of a complex condensed film of soap and free acid (Fig. 6). Similar mechanisms could apply to other "pure" ionic surfactants such as sodium dodecyl sulphate. Here the mixed film would be available from either interfacial hydrolysis or incomplete sulphonation in manufacture.

The process of bond formation can be considered similar to the dimerization of long chain surface active ions described by Mukerjee, Mysels & Dunlin (1958). The structure of the dimer is visualized as one in which the ionic heads are far apart and the flexible chains intertwined. The reduction in the amount of hydrocarbon surface exposed to water is estimated as being approximately equivalent to the removal of 8CH_2 groups from aqueous environment. At 25° the change in free energy upon transfer of one CH_2 group from a non-polar organic phase to water is in the region of 3.6 kJ mol^{-1} ($0.85 \text{ kcal mol}^{-1}$) with $\Delta H = 1.7 \text{ kJ mol}^{-1}$ ($0.4 \text{ kcal mol}^{-1}$) (Davis & Higuchi, unpublished observation). Such values can be used to calculate the energetics of hydrophobic bond formation (Nemethy, 1967) if we bear

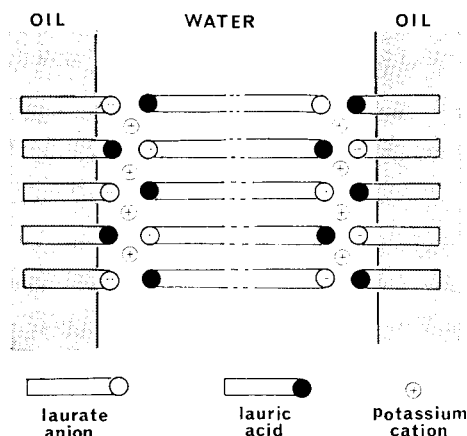


FIG. 6. A model of the mechanism for hydrophobic bonding aggregation in emulsions stabilized by potassium laurate.

in mind that the CH_2 groups in the bond will be much more constrained than in the liquid hydrocarbon and have a lower entropy (Mukerjee, 1967). A more realistic ΔF value for the CH_2 group is obtained from the thermodynamics of micellization of non-ionic surface active agents [$\Delta F_{\text{CH}_2} = 2.9 \text{ kJ mol}^{-1}$ ($0.7 \text{ kcal mol}^{-1}$)]. Hence at 22.5° $\Delta F_{\text{H}} = -23.0 \text{ kJ mol}^{-1}$ ($-5.5 \text{ kcal mol}^{-1}$).

We are currently exploring the possibilities of using aggregated soap emulsions as model systems for the systematic study of hydrophobic interactions. The hydrophobic bond is known to be of great influence in determining secondary and tertiary structure of protein molecules and other polymers as well as in the non-specific interaction of drugs at enzyme surfaces and with receptor sites (Belleau & Lacasse, 1964; Hansch, 1968).

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