SOME PHYSICAL PROPERTIES OF INTERFACIAL FILMS OF POTASSIUM ARABATE

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The rheological properties of the film formed between solutions of potassium arabate and Light Liquid Paraffin B.P. have been investigated. It is found from preliminary experiments that such a film has plasto-elastic properties and that it becomes more rigid with the passage of time.

It was shown by Plateau that the surface of a liquid appears to offer a greater resistance to the motion of a body than does the bulk liquid. Quantitative measurements were attempted by later workers using oscillating disc pendulums; Stables and Wilson studied saponin solutions in 1883 and showed an enormous increase in resistance to oscillation when the pendulum was in the surface rather than above or below it. Wilson and Ries (1923) used a similar method to investigate the physical properties of certain solutions, concluding that a film existed at the surface having the nature of a plastic solid. In 1955, Criddle and Meader using a biconical oscillating pendulum studied the viscosity and elasticity of films, and the effect of ageing on these properties. Before this Tachibana and Inochudi (1953) had made a different approach to the problem. Using a very light wire ring as pendulum they observed its motion through a comparatively small angle under varying degrees of torque applied by a fine torsion suspension, and the results were interpreted in rheological terms rather than as a viscosity. This method has the advantage of causing less disturbance to any structure that may exist at the surface than the oscillation method, and of being able to detect rapid changes in these properties.

Experimental

Two types of system were investigated using a torsion pendulum, that at the aqueous potassium arabate/air interface and that at the aqueous potassium arabate/light liquid paraffin interface. The brass bob was biconical in shape, of 20° included angle and 5·621 cm. diameter. Before being attached to the torsion wire the bob was thoroughly cleaned, immersed for 5–10 sec. in a dilute nitric acid solution until the surface was etched, and then well washed to ensure it was readily wetted by water. It was suspended by a copper beryllium wire 0·015 cm. diameter, 58 cm. long which had been heat treated for 3 hr. at 320° whilst under tension to straighten it and develop its elastic properties. The torsion constant was 10·77 dynes/cm., and the moment of inertia of the rotating system was 47·46 g./cm.^{2}. At its upper end the wire was secured in a collet which could be adjusted vertically by means of a micrometer screw, and rotated through a known angle.

Rotary displacements of the bob were measured by an optical lever of about 2·7 metres. One millimeter deflection on this scale represents a rotation of about 0·01 degree. Precautions were taken to eliminate the effect of backlash on the rotating and measuring parts. Solutions were made in freshly distilled water and placed in scrupulously clean optical cells 6 × 10 × 10 cm.

The apparatus was set up so that the equator of the pendulum bob was brought to the interface by raising or lowering the cell platform using a slow speed electric driving system, care being taken to ensure that the lower surface of the bob was completely wetted, and the upper surface untouched by the gum solution. At this stage the optical lever was adjusted to the zero of the scale. After the lapse of a suitable time, by rotating the torsion head between adjustable stops, a predetermined twist (either 20° or 45°) was put in the wire and the movement of the optical

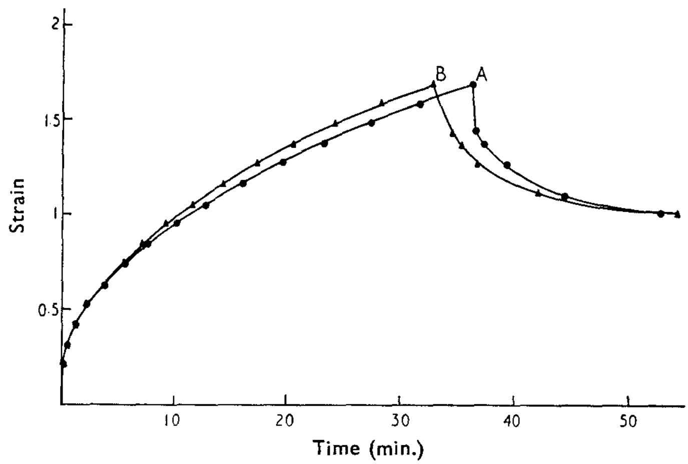

FIG. 1. Strain-time curve for film at interface of 15 per cent potassium arabate solution and A, air; B, light liquid paraffin. Initial torsion 20°.

lever recorded at suitable time intervals. When the bob had rotated about 5° the head was returned to its zero position or to such a position that the wire was free from strain, and subsequent movement recorded. The movement of the pendulum was limited to about 5° of arc to minimise the chance of damage to the film. Only on one occasion, when the degree of wetting of the pendulum was not satisfactory was there any evidence of slip between film and pendulum.

This type of experiment was made on solution/air interfaces about 1 hr. old and on solution/oil interfaces of ages varying between 1 and 66 hr.

Materials

The aqueous phase was a 15 per cent w/v solution of potassium arabate prepared by the method described by White (1960).

The oil phase was Light Liquid Paraffin B.P.

Results

When the pendulum was totally immersed in either the solution or the oil it oscillated freely when displaced from its resting position, but when at the interface it moved only in one direction.

In all cases the results were qualitatively similar, the magnitude of the effect depending only on the age and not on the nature of the interface as shown in Figs. 1 and 2.

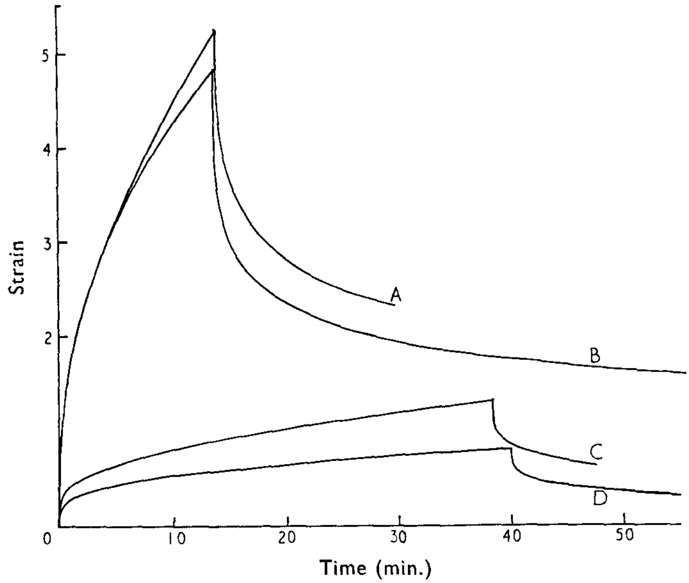

FIG. 2. Strain-time curve for film at the interface of a 15 per cent potassium arabate solution/light liquid paraffin. Initial torque 45°.
Film age: A, 1 hr. B, $1\frac{3}{4}$ hr. C, 22 hr. D, 66 hr.

Discussion

To produce a stable emulsion it is necessary for the globules of the disperse phase to be prevented from coalescing, this is usually achieved either by causing the droplets to be electrically charged, and so mutually repulsive, or by enclosing them in an integument having the necessary physical properties of rigidity, elasticity and cohesive strength. Acacia appears to function largely by this latter method, it is therefore of interest to determine the rheological properties of the interfacial film.

Measurements of interfacial viscosity may be misleading since the film may not be in the liquid state, but be a semi-solid or solid body. This consideration rules out all methods using either flow or a body oscillating through an appreciable arc since excessive vibration would destroy any film structure. If the amplitude of vibration be kept so small that this danger is minimised, then it becomes difficult to maintain the vibration and to measure its rate of damping. However, under such conditions it becomes possible to measure the angle of displacement of the bob of a torsion pendulum and the torque necessary to produce it. From the behaviour of the system whilst under stress and after removal of the stress it is a simple matter to describe qualitatively its rheological properties, but whether or no a quantitative interpretation can be made will depend on the events that take place. In particular plastic flow may cause difficulty.

The form of the strain versus time graph (Figs. 1 and 2) is that typical of visco-elastic and plasto-elastic materials but it does not allow distinction to be made between them. In every case there is a rapid displacement of the bob of the pendulum which may represent an instantaneous elastic response damped by the large moment of inertia of the system, and then a rate of deflection decreasing more rapidly than the torque. Removal of the stress allows a rapid recovery and then a decreasing rate of relaxation

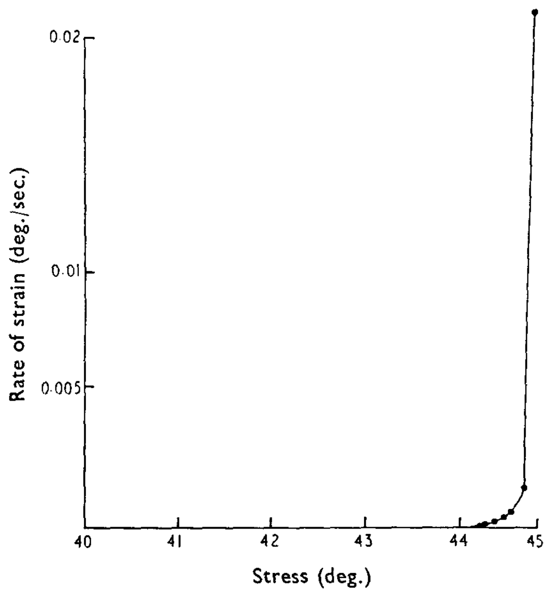

FIG. 3. Rate of shear *vs.* stress for film at interface of 15 per cent potassium arabate/light liquid paraffin.

but in no case did the pendulum return to its original position, clear indication that flow had taken place. Distinction between viscous or plastic flow in the systems can be made by reference to the rate of strain versus stress graph Fig. 3 in which there is an intercept at a substantial value on the stress axis, evidence of the existence of a yield value, hence in the film, of plastic flow. The behaviour of the film under, and free from applied stress, may be depicted in formal fashion with a spring dashpot model incorporating five elements (Fig. 4). This is arranged in three parts and shows the rapid elastic response, the slow recoverable response, and the yield value. Under very low stresses this last element will not function and at higher stresses represents the irrecoverable element of flow. The whole model simulates the behaviour of a plasto-elastic body. The effect of the lapse of time can be shown by the calculation of an Apparent Shear Modulus by the use of

$$n = \frac{K}{4\pi h} \times \left(\frac{1}{R_1^2} - \frac{1}{R_2^2}\right) \times \frac{\delta - \theta}{\theta},$$

(where K = Wire constant 10·7698 dynes/cm., h = Thickness of film = 1500 Å; R_1 = Radius of pendulum bob; R_2 = Radius of dish; δ = Applied torque; θ = Measured deflection) assuming that no plastic flow has taken place. The effect of such an assumption is to reduce slightly the magnitude of δ and more seriously increase that of θ, resulting in a low value for n. The magnitude of the discrepancy decreases with the decrease of θ, i.e., with the age of the film.

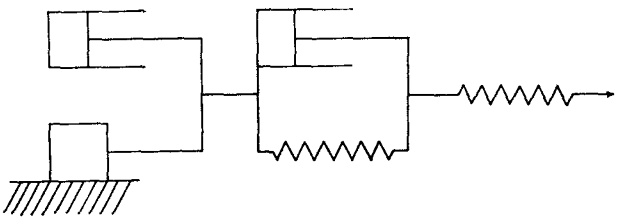

FIG. 4. Spring and dashpot model to represent the behaviour of the potassium arabate film at the oil/water interface.

The only factor in this equation that was not evaluated for this particular case was h the thickness of the film, and for this, White's determination of 0·15 μ for films in the presence of a 15 per cent w/v solution of potassium arabate was used.

TABLE I

APPARENT SHEAR MODULUS OF INTERFACIAL FILMS OF 15 PER CENT W/V POTASSIUM ARABATE/LIGHT LIQUID PARAFFIN

Age of film (hr.)	n
0·5	0·34 × 10^5 dynes/cm.^{2}
1·0	0·32
1·75	0·36
2	0·44
22	1·59
66	2·59

In the case of the film 66 hr. old, since the film reached equilibrium in both parts of the experiment n can be calculated making due allowance for the shift of zero due to the plastic flow, when the value is found to be 4·25 × 10^5 dynes/cm.^{2} and the yield value 1·11 × 10^4 dynes/cm.^{2}. These figures indicate the film to be considerably more rigid than a 10 per cent gelatine gel for which values for n of about 3 × 10^5 dynes/cm.^{2} are quoted by Alexander and Johnson (1950).

The evidence now available shows that solutions of arabates develop an interfacial film as a third phase between the aqueous phase and the adjacent one be it air or liquid. These films all have well marked time dependent plasto-elastic properties which means that they are able to undergo considerable elastic distortion and when the elastic limit is exceeded the film flows plastically and does not break. In addition, any portion of the film which suffers such thinning will gradually regain its original condition. Such physical properties allied to the substantial thickness of film make arabates almost ideal emulsifying agents, their only shortcomings being their liability to microbial attack.

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