230. *The Properties of Freshly Formed Surfaces. Part XIX.* Dynamic Surface Potentials and the Desorption Process: the Spreading of Decyl Alcohol Films.*

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When a film of decyl alcohol is spread on water, the adsorbed molecules are disoriented, and the subsequent variations in surface potential reflect the changes in molecular orientation as well as concentration in the adsorbed film. Similar measurements of potential changes during desorption into decyl alcohol solutions show that the extent of molecular disorientation produced in a spread film is determined by the rate of desorption from the film. Changes in potential produced on compression of an adsorbed film, and during subsequent desorption, are compared with those produced by spreading.

PART XII (*J.*, 1949, 3395) reported a study of the desorption of decyl alcohol from soluble films in which the surface excess was increased beyond the equilibrium value either by spreading the alcohol on the surface, or by pouring the aqueous solution of decyl alcohol from one vessel into another. The information available on the behaviour of the adsorbed molecules during the desorption process was limited by the relative insensitivity of surface tension to molecular orientation. Part XVIII * has shown that, for the adsorption process, further important properties of the film can be deduced from a parallel study of surface-potential changes. In view of this, the changes in surface potential occurring during desorption of decyl alcohol have been measured and are now described.

EXPERIMENTAL

The electrical apparatus employed was that described in the preceding paper, and the galvanometer-deflection method was used in measuring the contact potentials. The trough was modified for spreading experiments by removing the burette device used for addition of decyl alcohol solutions; the surface was swept by a waxed glass barrier which was drawn over the surface by means of an attached metal rod extending outside the screening cage. The film was applied by placing a measured quantity (up to 0·1 ml.) of a *n*-hexane solution of decyl alcohol on the surface from a microburette. The surface tension values recorded in Figs. 1, 4, and 5 were obtained by the vertical-plate method (Part VII, *J.*, 1948, 930).

DISCUSSION AND RESULTS

Fig. 1 compares the changes in surface tension and surface potential which occur when 0·1 ml. of a solution containing 0·3 g./l. of decyl alcohol in *n*-hexane is added to a swept water surface at 15°. The surface area of the trough was 56 cm.^{2}, so the decyl alcohol added to the surface was equivalent to 4·4 times the quantity required to form a monolayer ($12{\cdot}2 \times 10^{-8}$ g./cm.^{2}). As the decyl alcohol spreads over the surface it is desorbed into the bulk solution, and the surface condition at any time is determined by the rates of spreading and desorption. When the quantity of alcohol added is eventually dispersed

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* Part XVIII, preceding paper.

throughout the liquid, the bulk concentration is too small to give rise to any appreciable surface excess, so that after an initial rapid fall, both tension and potential return to the value for water. The differing positions of the two minima on the time axis are a characteristic property of this system and have been observed in all experiments. The rise in surface tension follows a smooth curve but the potential curve shows a point of inflexion (*B*) at a surface age of about 20 min. At this stage the potential change is only half completed, whereas the surface tension (point *A*) has almost returned to the water value. It follows that beyond the vertical line *AB*, where the remaining surface excess is small, changes occur in the film which influence the potential to a marked degree, but to which the surface tension is only slightly sensitive.

Fig. 1.

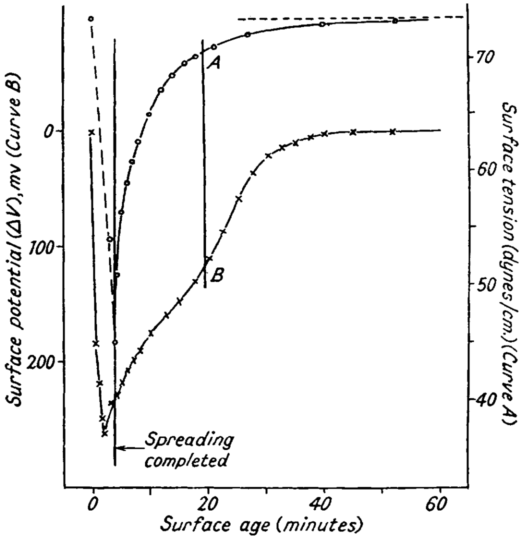


Fig. 2.

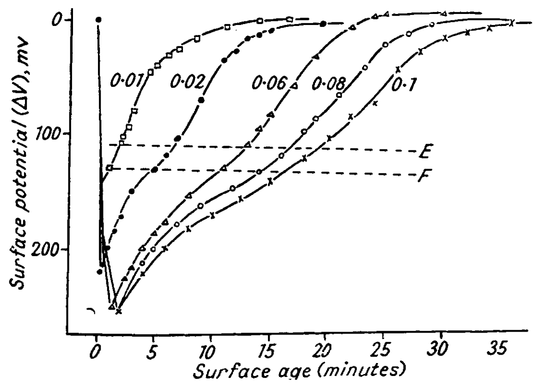


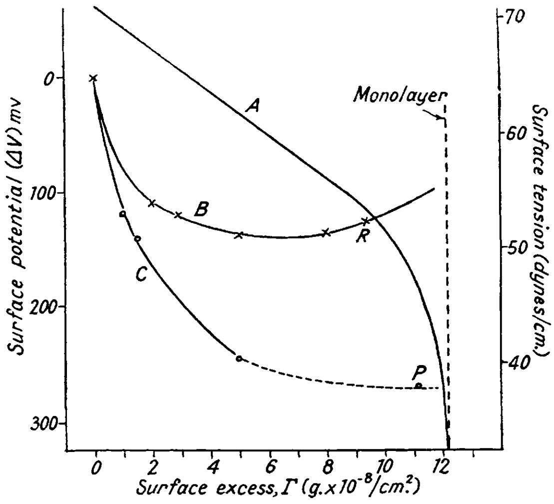
Fig. 2 shows the effect of spreading various quantities of decyl alcohol on water; the numbers on the curves refer to the volume (ml.) of decyl alcohol solution spread on the surface. For added quantities up to 0·02 ml. the minimum potential decreases, but thereafter the minimum is almost independent of the quantity of decyl alcohol spread. The times to reach minimum potential are given below :

Decyl alcohol solution added, ml.	0·01	0·02	0·04	0·06	0·08	0·10
Time to reach minimum (secs.)	<10	20	60	90	110	120

Each curve shows pronounced inflexion, and the position of the point of inflexion is a function of the potential (and thus the surface condition) rather than of the age of the surface.

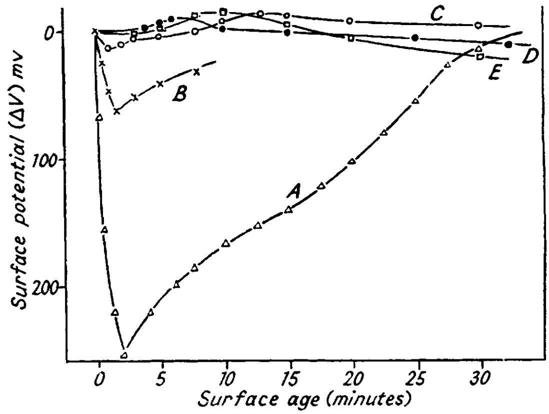
In order to interpret the potential changes, it is first necessary to consider the relative effect of surface excess on surface tension and potential (Fig. 3). The tension curve *A* is

Fig. 3.



derived from data given in Part XI (*J.*, 1949, 3387), and the orientation and disorientation potential curves (*B* and *C*, respectively) are derived from data in this and the preceding paper. At low Γ values the slope of curve *A* changes only slightly, but at high Γ values the curve approaches asymptotically the monolayer Γ value. Curve *B* illustrates the greater sensitivity of the orientation potential at low Γ values. The slope rapidly diminishes, and over a wide Γ range the orientation potential is not greatly influenced by change in surface excess; as the monolayer is approached, curve *B* rises again. Beyond point *R*, the position of curve *B* is determined from the desorption curves for high concentrations given in Fig. 5.

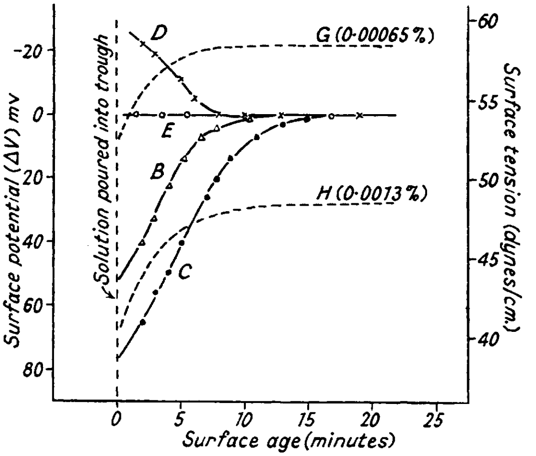
Fig. 4.



At small Γ values, when the adsorbed molecules have ample space in which to depart from equilibrium orientation, experimental conditions under which the position of the disorientation-potential curve *C* can be determined are readily obtained. However, as the molecules become more close-packed it is difficult to envisage conditions under which the film could undergo appreciable disorientation while still maintaining monolayer form, and at the limit it is not feasible to consider a disoriented monolayer. For this reason the part of curve *C* covering higher Γ values is shown as a broken line. Point *P* (curve *C*) represents the lowest potential obtained by spreading on water (Figs. 1 and 2); *P* bears no relation to curve *B*, but clearly falls on the disorientation curve *C*. Since *P* therefore represents a surface excess near the monolayer quantity which is fully disoriented, it must be assumed that when a decyl alcohol film is spread on water, the disturbance to which the surface film is subjected at the point of minimum potential is sufficiently vigorous to destroy a normal monolayer, and that the diffuse film is therefore more than one monolayer thick. It has been shown in Part XII (*loc. cit.*) that desorption from a decyl alcohol film into water is extremely rapid, and this is considered to be responsible for the disorganisation of the film.

The changes in tension and potential shown in Figs. 1 and 2 may be interpreted satisfactorily on this basis. It is known from visual observation that the minimum in the surface-tension curve (Fig. 1) coincides with the disappearance of the added lens of decyl alcohol–hexane solution. During the first 4 min., hexane is evaporating from the surface of the solution; this process, together with rapid desorption, will maintain complete disorientation of the surface film, and it is significant that the potential reaches its minimum value during the course of the spreading (*i.e.*, after 2 min.) rather than when the lens disappears. The minimum surface tension reached is equivalent to a surface excess near that of a monolayer. That the film at this stage is a diffuse one rather than a monolayer of vertically oriented molecules is indicated by the subsequent potential changes. After the disappearance of the lens, the surface excess diminishes, but the rate of increase in potential is much greater than would result from change in surface excess alone (curve *C*, Fig. 3). The major factor is considered to be the change from a diffuse layer towards an oriented film, *i.e.*, the potential moves from curve *C* towards curve *B* (Fig. 3). However, the presence of a point of inflexion in the potential curve indicates that the orientation process does not proceed regularly. Whatever the quantity of decyl alcohol added to the surface, the point of inflexion lies (Fig. 2) within the band defined by the two horizontal broken lines *E* and *F*. Line *E* represents a surface excess of $1{\cdot}67 \times 10^{-8}$ g./cm.^{2}, which is the upper limit at which the adsorbed molecules are free from mutual interference. Line *F* ($\Gamma = 3{\cdot}72 \times 10^{-8}$ g./cm.^{2}) represents the maximum surface excess at which the molecules can lie horizontally in the surface when packed as parallel cylinders; under these conditions it is still possible for maximum disorientation to occur but some mutual interference will no doubt arise. The change is slope of the potential curves (Fig. 2) may therefore be explained in two closely related ways. (*a*) Up to the band *EF* the surface excess is high, and is in the Γ range where variation in this excess has little influence on the poten-

FIG. 5.



tial values. The change in potential is then due almost entirely to the orientation factor. When Γ is reduced to the *EF* band region, both orientation and disorientation potentials are sensitive to surface excess (Fig. 3), so the surface concentration effect is added to the orientation effect, and the increase in potential becomes more rapid. (*b*) Below the band *EF*, the rate of orientation is reduced by the mutual interference of adsorbed molecules. As Γ passes through the band *EF*, the adsorbed molecules become free from mutual interference, with consequent increase in the orientation rate.

Spreading on Decyl Alcohol Solutions.—When a film is spread on water, the disorientation of the film arises predominantly from the high rate of desorption. It follows that if the rate of desorption can be reduced there should be less disorientation in the film, and a smaller change in potential. The rate of desorption can be suitably reduced by spreading the decyl alcohol film on an aqueous solution of the alcohol instead of on water. Evidence given in Part XII (*loc. cit.*) showed that the rate of desorption is determined by the difference $\Delta\Gamma$ between the actual surface excess and that representing equilibrium with the bulk solution. The following results give the desorption rates which are observed when a film approximating to a monolayer is spread on decyl alcohol solutions of different concentrations :

Curve (Figs. 4 & 5)	Decyl alcohol concn., %	Equilibrium Γ (g. $\times$ 10^{-8}/cm.^{2})	$\Delta\Gamma$	Desorption rate $-d\Gamma/dt$ (g. $\times$ 10^{-11}/cm.^{2}/sec.)
A	Nil	0	12·2	Very rapid
B	0·00016	1·9	10·3	84
C	0·00065	6·7	5·5	20
D	0·0013	9·9	2·3	7
E	0·0026	12·1	0·1	1

The desorption rates are decreased considerably with increasing concentration of decyl alcohol in bulk solution, and the influence of this decrease is shown in Fig. 4, where the dynamic potentials obtained on spreading 0·1 ml. of the decyl alcohol–hexane solution on aqueous solutions of the alcohol are compared with the results of spreading on water. Even with the most dilute solution employed (curve *B*), disorientation by desorption is considerably diminished, and at 0·00065% the initial decrease in potential on spreading the film has almost vanished. At higher concentrations no disorientation occurs, and the spreading of the film has little influence on the potential of the surface.

Disorientation of Adsorbed Film by Pouring.—The desorption studies in Part XII (*loc. cit.*) showed that the surface excess could also be increased above the equilibrium value by pouring the decyl alcohol solution from one vessel into another. To compare the two methods of producing a high Γ value (*i.e.*, spreading and pouring) solutions having the concentrations employed for curves *B*, *C*, *D*, and *E* (Fig. 4; above table) were each poured steadily into the trough, and the electrode was lowered rapidly into position; the changes in potential observed are shown in Fig. 5. The four curves are referred to a common equilibrium potential (although the actual contact potentials differed) since the surface potentials (ΔV) may then be compared directly with the values in Fig. 4. At the lower concentrations (curves *B* and *C*) the large increase in the potential values indicates some disorientation in the original film, but at higher concentrations (curves *D* and *E*) no rise occurs, and the pouring process is evidently unable to bring about disorientation. As with the spreading process, the nature of the potential changes is fundamentally altered by change in bulk concentration, although the general nature of the surface-tension curves *G* and *H* superimposed in Fig. 5 is not correspondingly influenced by concentration change.

It may be deduced from the surface-tension data that the pouring of solutions *B* and *C* (Fig. 5) produces initial Γ values of about 5·0 and 9·3 $\times$ 10^{-8} g./cm.^{2}, respectively. If these quantities were fully disoriented, Fig. 3 indicates that the subsequent increases in potential would be 130 and 160 mv, respectively. The observed potential changes are 55 and 80 mv, so the compression of the surface film by pouring is inadequate to bring about complete disorientation. The compression produced by pouring solution *D* raises Γ from the equilibrium value of 9·9 to 11·9 $\times$ 10^{-8} g./cm.^{2}. With surface excess of this order it is not possible by this technique to produce disorientation in the film, and the small decrease in potential which is shown in curve *D* (Fig. 5) is entirely a surface concentration factor, and corresponds with the slope of the orientation potential curve *B* (Fig. 3) in this Γ range. The equilibrium Γ for solution *E* is $12{\cdot}1 \times 10^{-8}$ g./cm.^{2}. Compression by pouring, and subsequent desorption, is therefore small in the case of this near-monolayer, and in consequence no change in potential is detectable.

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