229. *The Properties of Freshly Formed Surfaces. Part XVIII.** *Dynamic Surface Potentials and the Adsorption Process: Molecular Orientation in Soluble Films of Decyl Alcohol.*

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The adsorption of long-chain alcohols at a fresh water surface results in a rapid change of surface potential as well as of surface tension. An apparatus is described for the study of continuous changes in potential at fresh surfaces. Experiments on decyl alcohol solutions are recorded in which the rates of adsorption are sufficiently slow to enable rates of change of tension and potential to be compared. When concentration equilibrium between the surface and bulk solution is established, the surface tension shows no further change, but surface potential values show further pronounced changes which are interpreted as reflecting the rate of orientation of the disoriented film produced immediately adsorption is complete. When the soluble film has reached orientation equilibrium, the adsorption of additional solute (by further additions to bulk solution) disorients the film, and the influence of surface excess on rate of disorientation is considered. Unlike surface tension, which is relatively insensitive to changes in orientation, the surface potential of a solution depends as much on the condition of the adsorbed film as on the surface excess.

Previous papers in this series have been concerned with changes in the surface tension of aqueous solutions which occur immediately after the formation of a fresh liquid surface. Throughout this work a close relation has been observed between surface tension and surface excess, the latter being by far the major factor determining the surface tension of a solution. For any given surface excess, surface tension is influenced to a relatively small extent by changes in the orientation of adsorbed molecules. Under conditions (*i.e.*, rapid

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* Part XVII, *J.*, 1950, 3103.

expansion of the surface) in which there must be considerable deviations from the equilibrium orientation, surface tensions are not greatly modified; thus for chain lengths below C_8 (Part XIV, *J.*, 1949, 3406) the relation between γ and Γ for rapidly expanding surfaces is the same as that for stationary surfaces. The disorientation of longer chains is reflected in a slight modification of the surface tension (Part IX, *J.*, 1948, 943; Part XIV, *loc. cit.*) but even then only when surface expansion is rapid and disorientation considerable. It appeared possible, however, that the orientation of an adsorbed molecule with respect to the surface might influence the air–water contact potential to a greater extent than the surface tension; this potential arises from the polar character of the water molecule, and the orientation of the hydrocarbon chains (and thus of the polar groups) in adsorbed molecules is likely to be of importance in determining the extent to which this air–water potential is modified.

It was therefore necessary, in initial experiments, to select a solute giving aqueous solutions in which the accumulation of surface excess is sufficiently slow to be measurable by both surface tension and surface potential techniques. Decyl alcohol is suitable, since adsorption continues for some minutes after formation of a fresh surface, and wide ranges of both surface tension and surface potential are available. The exploratory experiments on such solutions now described illustrate the pronounced sensitivity of surface potentials to orientation changes in adsorbed films of this kind.

EXPERIMENTAL

The apparatus used is indicated in Fig. 1. The contact potentials were obtained from the potential difference between a standard calomel half-cell in contact with the solution, and a radioactive electrode placed immediately above the surface. This potential difference was measured by an electrometer triode unit, incorporating a Wheatstone slide-back bridge circuit and galvanometer. The whole electrical circuit (including the batteries but excluding the galvanometer) was enclosed in an earthed cage of perforated zinc sheet, with detachable front, providing adequate screening from external electrical interference.

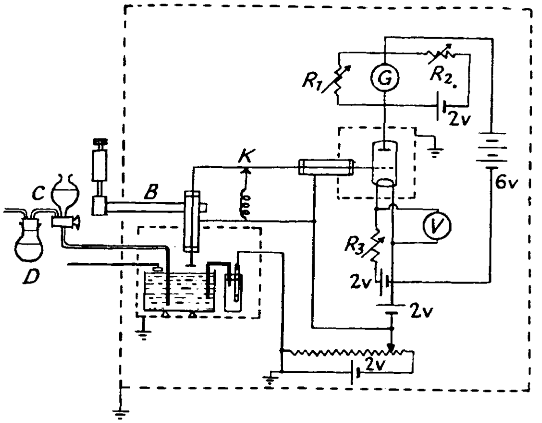


FIG. 1.
R_1 = 250 ohms.
R_2 = 10,000 ohms.
R_3 = 30 ohms.

Valve.—A G.E.C. Type E.T.1 valve (filament voltage 1 v) was employed, enclosed in an earthed, airtight metal box. The valve holder was supported on an antimicrophonic mounting of sponge rubber. The base pins were connected directly to terminals on a Polythene panel on the side of the box. The control grid lead was taken from the box through a guard ring consisting of a 2-cm. brass tube fitted with polystyrene end plugs. (This lead, which was made as short as possible, passed directly and without further support to the air electrode terminal.) Before being fitted into the box, the glass surface of the valve was thoroughly cleaned with sodium-dried ether, and dried in a current of warm air. Before the box was sealed a dish of phosphoric oxide was put into it.

Air Electrode.—Radon needles mounted on copper electrodes were tried in preliminary experiments; ionisation of the air space was inadequate, and the galvanometer readings showed a continual drift. However, satisfactory electrical balance in the apparatus was obtained when sufficient polonium was deposited on the electrode by direct displacement. When this deposition technique was used, copper was found to be unsuitable as an electrode metal, since its electrode potential ($-0{\cdot}34$ v) is below that of polonium ($-0{\cdot}4$ v). Zinc ($+0{\cdot}76$ v) is satisfactory, and the measurements described were carried out with zinc electrodes. A zinc cube (0·5 cm. edge) was soldered to the end of a brass rod (0·15 cm. diam. and 4 cm. long). The upper face and sides of the zinc block and the lower half of the rod were coated with picein wax. The lower face of the block was cleaned by filing it, and then immersed in 50 ml. of dilute hydrochloric–nitric acid solution prepared two years previously, containing $0{\cdot}81 \times 10^{-3}$ g. of radium per litre. Electrodes, dipped for 2, 12, and 27 minutes in this solution and allowed to dry in warm air, were placed 3 cm. from the window of a G.E.C. Type G.M.2 counter, and gave 4000, 9000, and 24,000 counts per minute respectively. (A similar copper electrode dipped for 15 minutes gave less than 1000 counts/min.) It was found that electrodes giving about 8000 counts/min. and upwards produced satisfactory ionisation of the air gap. With such electrodes the contact potential did not vary significantly with variation in the air gap up to about 5 mm. This is in agreement with observations by Harding and Adam (*Proc. Roy. Soc.*, 1932, **138**, *A*, 411). Nevertheless, in the present experiment the air gap was kept within the range 1·5—2·5 mm.

Temperature.—When the aqueous solution under test in the trough was at room temperature (at or near 20°) condensation took place on the air electrode; this resulted in loss of sensitivity and a continuous upward drift in the galvanometer readings. This difficulty was negligible when the solution was cooled, at the beginning of the experiment, to about 5° below room temperature. During an experiment the solution did not warm to room temperature; the sensitivity was checked at intervals during each experiment.

Air Electrode Mounting.—The electrode was coupled to the end of a brass rod (0·3 cm. diam. and 15 cm. long) passing centrally through a guard ring (2 cm. diameter, 10 cm. long) fitted with polystyrene end plugs. The guard ring was attached rigidly to one end of an ebonite bar 15 cm. long (*B*, Fig. 1), the other end of which was clamped to a worm-driven vertical rack mounted on the cage framework. The pitch of the worm drive was 1 mm., permitting accurate adjustment of the electrode position.

Standard Apparatus.—The potentiometer used was a Tinsley model, Type 3387 B, standardised by Weston cell. Since the instrument was used to give continuous readings, its galvanometer terminals were short-circuited and the key was permanently depressed. *G* (Fig. 1) was a Cambridge m/c spot galvanometer, with 16-cm. (centre zero) scale; to eliminate electrical interference, the lamp was run from a 6-v battery rather than a step-down transformer.

All batteries were of large capacity. After recharging, the apparatus was run for several hours to establish steady conditions. No switches were used, and terminals were soldered to short, stout, copper leads.

Manipulation.—To standardise the apparatus, the valve-filament heater was first connected, and resistance R_3 adjusted to give a potential drop of 1 v across the filament. With contact *K* closed and resistance R_1 short-circuited, all batteries were connected, bringing the valve grid to -2 v potential. The galvanometer sensitivity was increased by increasing R_1, and R_2 was simultaneously adjusted to maintain zero deflection. When steady conditions were reached (about 1 hour), R_1 was again reduced to protect *G*, the contact *K* was broken, and the air electrode lowered into position; R_1 was then slowly increased to give the desired sensitivity, and the potentiometer adjusted to restore zero galvanometer deflection. The galvanometer readings became steady 2—3 minutes after the air electrode had been lowered. At this stage, solute was added to the water in the trough. The subsequent changes in contact potential may be followed by continuous adjustment of the potentiometer to maintain zero deflection in *G* or by following the changes on the galvanometer scale, previously calibrated. The second (deflection) method was more convenient, and although the guard rings and valve grid may differ slightly in potential the insulating properties of polystyrene are sufficient to prevent leakage. The sensitivity was adjusted so that the 16-cm. galvanometer scale covered a range of ±50 mv, and the potentiometer was adjusted in 100-mv steps when it was necessary to follow larger changes in contact potential.

Trough Arrangement.—A rectangular glass trough, 10·5 cm. deep, with ground and waxed rim was used. When it was filled to the rim, the liquid surface area was $10 \times 6{\cdot}2$ cm.^{2}, and the volume of liquid 650 ml. Before each experiment the trough was cleaned with hot alcohol–nitric acid mixture, and washed with clean tap-water: this gave the same results as distilled water, with less risk of grease contamination of the surface. At the beginning of each experiment the trough, calomel half-cell, and burette device for adding solute (*C*, Fig. 1) were placed in position, and a clean water surface obtained by running a stream of tap-water into the trough for several minutes, with continuous overflowing. In experiments involving direct addition of decyl alcohol to the liquid surface, burette device *C* was not required; a waxed barrier was then fitted to the top of the trough to isolate the half-cell agar bridge, and the surface was swept by a movable barrier operated from outside the screening cage. To exclude draught, the trough was enclosed in an earthed metal box with transparent front.

FIG. 2.

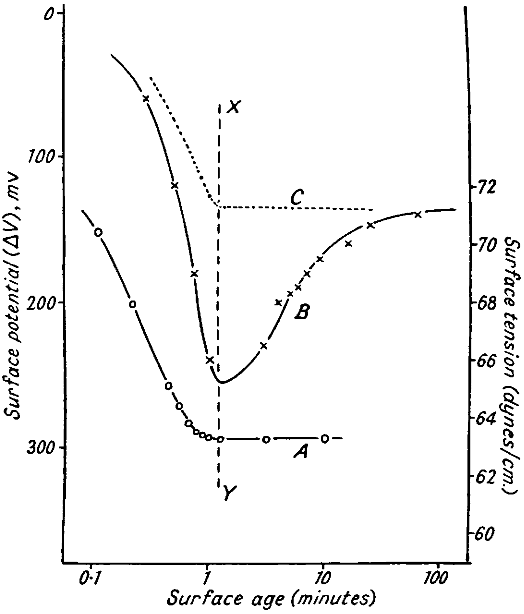
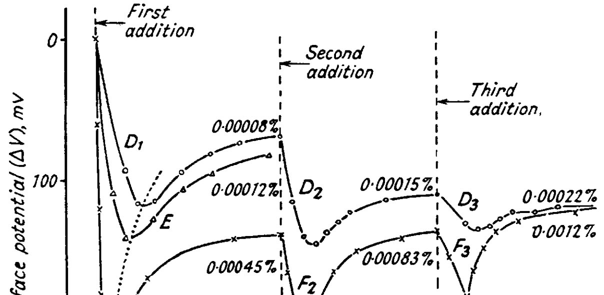


FIG. 3.



Addition of Solute.—When the electrical circuit was steady, 50 ml. of water were drawn from the trough by suction through the two-way tap into vessel *D*, and the solution in *C* (50 ml.) was immediately run into the trough. The latter operation required only a few seconds, but too rapid addition sometimes produced bubbles on the trough surface. Surface ages (Figs. 2 and 3) were timed from the instant when addition of solute was complete. The delivery tube extended to within 2 cm. of the bottom of the tank, and the circulation set up by the jet of liquid flowing from *C* rapidly established uniform concentration in the trough. This form of addition was specifically designed to avoid pouring through the surface, which leads (Part XII, *J.*, 1949, 3395) to the formation of a surface excess greater than that representing concentration equilibrium.

In successive addition experiments (Fig. 3) 50 ml. of decyl alcohol solution were removed from the trough and replaced by 50 ml. of a solution of higher concentration.

Blank experiments were carried out in which 50 ml. of water were withdrawn and replaced. This operation produced only a minor fluctuation of a few mv in the galvanometer reading. Since the introduction of decyl alcohol solution into the trough can give rise to rapid changes in contact potential, the response of the galvanometer readings to potential change was tested frequently.

Surface Tension.—The values recorded in Fig. 5 were determined by the vertical-plate method (Parts VII and XI, *J.*, 1948, 930; 1949, 3387).

DISCUSSION

Curve *A* (Fig. 2) shows the change in surface tension of a 0·00045% solution of decyl alcohol at 15°. Immediately upon formation of a fresh surface, the tension falls, reaching a minimum of 63·3 dynes/cm. after 1 min. Thereafter, no further change occurs in the quantity of decyl alcohol adsorbed at the surface. Curve *B* shows the variations in the corresponding air–solution contact potentials. The potential at first falls rapidly from the air–water value through a range of 250 mv, reaching a minimum at the same surface age (1 min.) as that at which the surface tension becomes constant. However, the contact potential shows a considerable increase at surface ages beyond 1 min.; a steady value is reached within an hour, though the change in potential is almost complete within 30 min. In these papers the term surface potential is applied to the difference (ΔV) in potential between the air–water contact potential and that of the aqueous solution. The potential values are plotted in terms of ΔV, although in discussion of the experimental results it is usually more convenient to refer directly to the air–solution contact potentials.

Comparison of curves *A* and *B* at surface ages above the vertical line *XY* shows clearly that the potential values are influenced to a pronounced degree by some factor other than change in the quantity of alcohol adsorbed at the surface. These measurements may be readily interpreted on the basis that this additional factor is the change in orientation of the adsorbed molecules. During the adsorption process, molecules adsorbed at the surface will be prevented from achieving a state of stable orientation by the continual accumulation of adsorbate at the surface, and when adsorption is complete the film will therefore be in a disordered state. The subsequent rearrangement to a stable orientation involves no change in surface excess (Γ) and thus no change in surface tension, but is reflected in the pronounced rise in contact potential which commences immediately the adsorption process is complete. In earlier papers the term " equilibrium surface " (as opposed to " dynamic surface ") has been employed to signify a surface in concentration equilibrium with bulk solution. It is now necessary to qualify this term. Immediately the accumulation of adsorbate is complete, the surface is in a state of " disorientation equilibrium," and the results in Fig. 2 show that considerable intervals of time may elapse before this state changes to one of " orientation equilibrium."

The initial rapid fall in contact potential (curve *B*) therefore reflects the sum of two factors, *viz.*, surface excess and surface disorientation. If no disorientation occurred, the potential curve would have the form shown by the broken curve *C*. In view of the above, the potential representing orientation equilibrium is a characteristic physical property of the solution. Again, since molecular disorientation is at its maximum immediately the adsorption process is completed, the potential of the surface in this state is also a fundamental property of the solution.

The first section of Fig. 3 includes two additional potential–surface age curves obtained for lower decyl alcohol concentrations. The form of the curves is closely similar to curve *F* (*i.e.*, curve *B*, Fig. 2) so the general nature of the changes in potential occurring at a fresh surface is independent of concentration. The minima in the curves (connected by a broken line) occur at greater surface ages as concentration is decreased, and in each case the minimum occurs at the same surface age as that at which the corresponding surface tension becomes constant. At each concentration, orientation equilibrium is virtually complete within 30 min.; the relative position of the curves indicates that the surface potential both of the disorientated film (ΔV_d) and of the oriented film (ΔV_0) increase with increasing concentration.

Stepwise Increase in Concentration.—The second and the third section of curves D and F (Fig. 3) show the changes in potential which occur when additional solute is added to solutions which already carry adsorbed films in a condition of orientation equilibrium. The concentrations given on the curves represent the values to which the bulk concentration was increased at 32 and 59 min., respectively. In each case the contact potential shows an initial fall to a minimum, followed by a rise to the steady potential characteristic of orientation surface equilibrium at the new concentration.

FIG. 4.

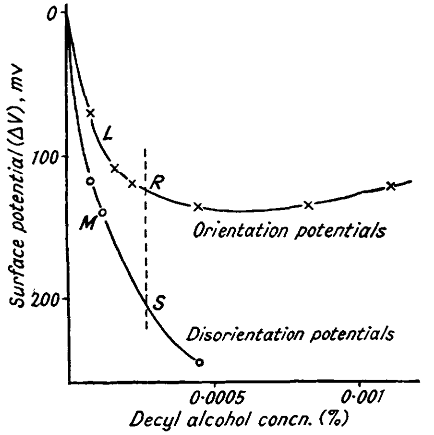


FIG. 5.

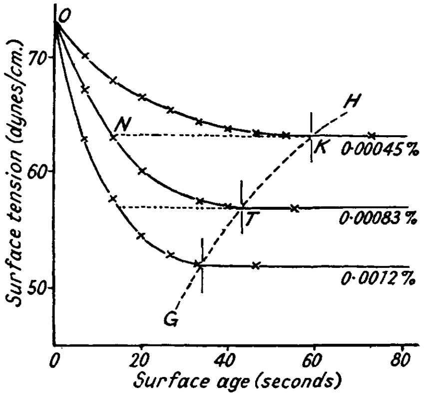


Fig. 4, curve L, shows the relation between V_0 and bulk concentration. Over a wide range of concentration the potential of the oriented film is almost independent of concentration, and only at the lowest concentrations does V_0 decrease with increasing concentration. The minimum cross-sectional area of long-chain primary alcohols, extrapolated to zero compression, is 21·6 Å^2 (Adam, " Physics and Chemistry of Surfaces," 3rd edn., 1941, p. 50). If each molecule is regarded as a cylinder, its diameter is therefore 5·24 Å. A length of 13·5 Å being assumed for the decyl alcohol molecule, the minimum permissible area occupied by each molecule lying flat in the surface is 70·7 Å^2, which is equivalent to a surface excess $\Gamma = 3{\cdot}72 \times 10^{-8}$ g./cm.^{2}. This Γ value corresponds to a bulk concentration of 0·00032% (Part XI, *loc. cit.*), and it is significant that the levelling of the V_0–concentration curve L commences at about this concentration. These results suggest that below this concentration the equilibrium orientation lies between two widely divergent limits, *i.e.*, the horizontal and the vertical positions, and variation in concentration can therefore influence to a considerable degree the mean position, and thus the potential. Above this concentration it is no longer possible for the molecules to achieve the horizontal position; the limits are therefore narrower, and change in concentration then has a small influence on the potential of the oriented film.

Extent of Disorientation.—Curve M, Fig. 4, was determined from measurements on the first addition of solute to water. The differences in potential between curves L and M therefore represent, at any concentration, the maximum possible influence of molecular disorientation. The addition to water of enough solute to bring the concentration immediately to the value represented by RS will cause the potential to decrease initially to S, and then to rise to R. If a solution of intermediate concentration is employed, which has been allowed to reach orientation equilibrium, and enough solute is then added to augment the concentration to RS, the adsorption process resulting from this second solute addition may be unable fully to disorient the film, and in consequence the minimum potential will not fall as far as S.

The results show that full disorientation can only occur when the adsorbed molecules are without mutual interference; any overlapping leads to lateral adhesion, which in turn restricts the disorientation of an oriented film. The maximum surface excess which can be achieved without mutual interference between the adsorbed molecules is represented by a state in which the molecules lie in the plane of the surface, and occupy hexagonally close-packed circles whose diameter is equal to the length of the molecule. Calculation shows that for a decyl alcohol film in this state $\Gamma = 1{\cdot}67 \times 10^{-8}$ g./cm.^{2}, equivalent to a bulk concentration of 0·00015%. This is therefore the maximum concentration at which adsorbed molecules are independent of one another, and capable of maximum disorientation. This is illustrated by the results in Fig. 3. At the initial concentration of 0·00008%, the full disorientation effect is observed. On increase of concentration to 0·00015%, maximum disorientation is again observed, and the decrease in potential is equal to that which would be produced by the single-stage formation of a 0·00015% solution (Fig. 4). The third addition of solute gives a concentration (0·00022%) at which the adsorbed molecules must necessarily suffer some mutual interference. Opportunity for lateral adhesion then arises, and the possible disorientation of the adsorbed film by new adsorbing molecules is restricted. In consequence, the potential fall is small, and with each successive addition it continues to decrease. The same effect is apparent in the corresponding curves F_1, F_2, and F_3 obtained over a higher concentration range. Again, since high values of Γ necessarily limit the extent of possible disorientation, it is not possible to extrapolate curve M (Fig. 4) indefinitely. The particular conditions under which this curve may be extended to higher Γ values are discussed in the following paper.

Rates of Orientation and Disorientation.—The times required for the establishment of orientation equilibrium after the second and third addition of decyl alcohol are only a little less than the times (about 30 min.) within which orientation is substantially complete after the first addition. The small decrease in the orientation time may be related to the fact that (in curves D_3, F_2, and F_3, at least) the disorientation produced by addition of solute is not the maximum possible. In contrast, the rate at which an orientated film can be disorientated is much more rapid. Since in sections D_3, F_2, and F_3 (Fig. 3) the extent of disorientation is indefinite (lying somewhere between the curves L and M, Fig. 4), these falling sections of the curves are most appropriately interpreted by reference to the periods of time required to reach minimum potentials.

In experiments involving second and third additions of solute, it was first necessary to determine the time required for re-establishment of the equilibrium surface excess. The method employed is illustrated in Fig. 5, which shows full γ–surface age curves (15°) corresponding to the three concentrations employed in obtaining curves F_1, F_2, and F_3 (Fig. 3). The surface tensions are unchanged beyond the broken line GH. The surface excess present at the end of stage F_1 (Fig. 3) corresponds to the surface tension value of point K (Fig. 5), and the state of the surface immediately after the addition of a second quantity of solute is represented by point N (Fig. 5). As adsorption proceeds, the surface tension decreases along line NT, and the distance NT on the time axis gives the period necessary for re-establishment of the new surface excess. Similar conditions apply to subsequent additions. In the table below, the times required for disorientation of the adsorbed films are compared against the adsorption times for the concentrations involved in the curves D and F (Fig. 3).

Concn. increment (%)	Fig. 3 curve	Interval of time (seconds): (1) for adsorption of increment in Γ	(2) to reach minimum potential	Ratio (2)/(1)
0—0·00008	D_1	480	480	1
0·00008—0·00015	D_2	170	300	1·76
0·00015—0·00022	D_3	100	360	3·6
0—0·00045	F_1	60	60	1
0·00045—0·00083	F_2	48	240	5
0·00083—0·0012	F_3	20	300	15

Curves D_1 *and* F_1. The minimum potential is reached when adsorption is complete. Adsorbed molecules are disoriented as they arrive at the surface, and no disorientation time is therefore involved.

Curves D_2 *and* D_3. The adsorbed molecules in the oriented film at the beginning of D_2 have space for independent movement in any position. Nevertheless, the new molecules being adsorbed at the surface are not able to disorient the film immediately, and the minimum potential is reached over a period which is almost twice that required for the adsorption process. Slight mutual interference (and lateral adhesion) occurs at D_3, and this is reflected in an increase in the disorientation/adsorption time ratio to 3·6

Curves F_2 *and* F_3. At these concentrations lateral adhesion in the equilibrium film is pronounced. The adsorption times in these cases represent a small proportion of the total time required for disorientation. The differing concentration levels in experiments D and F are reflected in the considerable difference in the rate at which the disorientation/adsorption time ratio increases on successive additions of decyl alcohol.

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[*Received, September* 30*th*, 1952.]