231. *The Properties of Freshly Formed Surfaces. Part XX.* An Examination of the Use of Dynamic Surface Potentials in the Study of Adsorption Rates.*

By C. C. Addison and D. Litherland.

The discrepancy between the dynamic surface tensions of aqueous solutions of *iso*amyl and *sec.*-octyl alcohols, measured by Addison (Parts II and III, *J.*, 1944, 252, 477) from the dimensions of an oscillating jet of solution, and those deduced by Posner and Alexander (*Trans. Faraday Soc.*, 1949, **45**, 651) from measurements of surface potentials along the liquid jets has been investigated. Measurements of the change in surface potential with time for solutions of these alcohols show that the disorientation potentials operative during and immediately after completion of the adsorption process differ considerably from the equilibrium orientation potentials of these solutions. When Posner and Alexander's potential measurements are translated into dynamic surface tensions by use of the disorientation potential–tension relation characteristic of the jet surface, the dynamic tensions determined by the two methods are in close agreement.

A KNOWLEDGE of the change of surface tension during the accumulation of an adsorbed film at a fresh surface is almost indispensable in studies of adsorption mechanism. Except for extremely dilute solutions, the adsorption process in aqueous solution is normally completed within one second, and special experimental techniques are necessary for measurement of the rapid tension changes involved. The only comprehensive study of these dynamic surface tensions at present available is that described by Addison (Parts I—V, *J.*, 1943, 535, *et seq.*) in which the dynamic surface tensions of aqueous solutions of long-chain alcohols were derived from measurements of the changing wave-lengths along an oscillating jet of solution; various workers, *e.g.*, Blair (*J. Chem. Phys.*, 1948, **16**, 113) and Ward and Tordai (*ibid.*, 1946, **14**, 453), have relied upon the validity of these measurements in their considerations of the adsorption process. However, the dynamic tensions of aqueous solutions of *iso*amyl and *sec.*-octyl alcohols determined by Posner and Alexander (*loc. cit.*) differed appreciably from the values reported in early papers in this series. These authors determined the change in potential along a liquid jet, and translated these potentials into surface tensions by means of a calibration curve derived from static measurements of potential and tension at equilibrium surfaces.

This paper describes an examination of the relation between surface potentials and surface tensions at fresh surfaces of aqueous solutions of these two alcohols. Posner and Alexander's calculations (*loc. cit.*) are in error in that they take no account of the fact that the potential which is operative at the surface of a liquid jet to which solute is adsorbing is a disorientation potential (Part XVIII, *J.*, 1953, 1143), which differs from the value measured at an equilibrium surface by an amount (often considerable) which varies with chain length and concentration of solute. When Posner and Alexander's potential measurements are correctly interpreted, the dynamic tensions derived therefrom are in almost complete agreement with the values calculated directly from jet dimensions (Parts II and III, *loc. cit.*).

RESULTS AND DISCUSSION

iso*Amyl Alcohol.*—Curves *A*, *B*, and *C* (Fig. 1) refer to aqueous solutions of *iso*amyl alcohol. The technique employed has been described in detail in Part XVIII (*loc. cit.*). The curves in Fig. 1 trace the changes in potential which occurred immediately after the addition of the alcohol solution. Equilibrium was established within 10 minutes, and for

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* Part XIX, preceding paper.

each concentration a series of further additions was then made. The concentrations in the trough represented by each section of each curve are given in the following Table :

Curve (Fig. 1)	Concn. (%) of added 25 ml. of *iso*amyl alcohol solution	Trough concn. (%) following :			
		1st addtn.	2nd addtn.	3rd addtn.	4th addtn.
A	0·35	0·0135	0·026	0·039	—
B	0·82	0·032	0·0635	0·0925	—
C	1·84	0·071	0·139	0·203	0·266

The initial rapid adsorption of *iso*amyl alcohol gives a disoriented film, and equilibrium orientation is only reached after several minutes. There is a difference of up to 100 mv in the potential of the surface in its two limiting states. On first addition of alcohol to the trough the minimum potential is reached within 20—30 seconds; the adsorption process is complete within 1 second, but since the apparatus is not able to respond immediately to potential changes of this rapidity, the initial measured rates of potential change are slower than those actually occurring. However, the subsequent rate of increase in potential is so much slower than the initial rate of decrease that the minimum potentials recorded on first addition of alcohol may be accepted as representing the potential of the fully disoriented film. At all stages during the adsorption process the adsorbed molecules are disoriented, and these experimental conditions hold at the surface of a liquid jet to

FIG. 1.

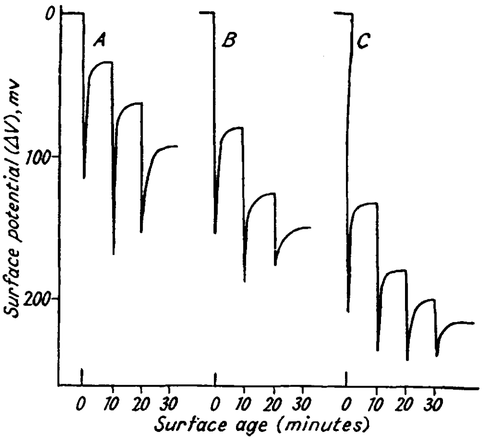
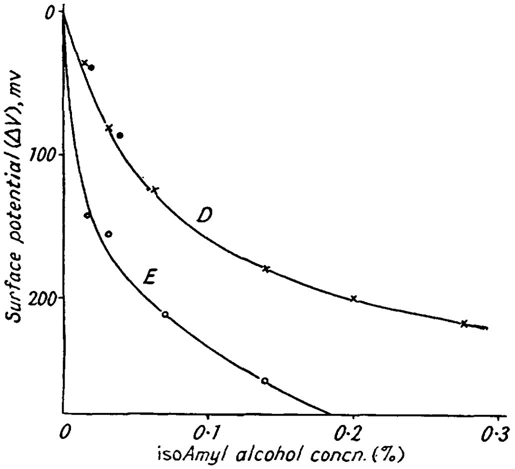


FIG. 2.



× × Orientation potentials (this work).
● ● Surface potentials (Posner and Alexander).
○ ○ Disorientation potentials (this work).

FIG. 3.

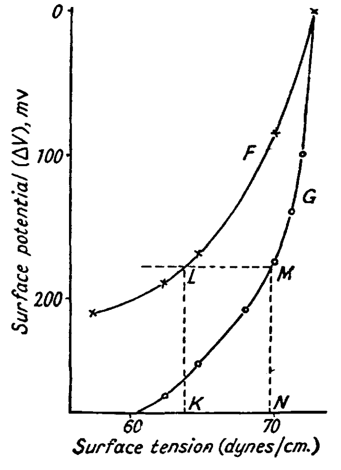
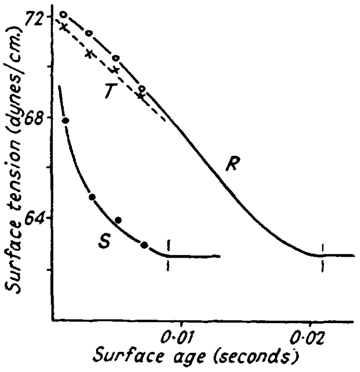


FIG. 4.



which solute is being adsorbed. Although the state of orientation has little influence on surface tension (and thus on the physical dimensions of an oscillating jet), the potential at the jet surface will differ considerably from that at a surface at which the same quantity of adsorbate has been allowed to reach orientation equilibrium.

From experiments of the type illustrated in Fig. 1, the orientation potential–concentration curve has been determined, and is shown in Fig. 2 (curve *D*). The equilibrium values determined by Posner and Alexander (*loc. cit.*) are superimposed in Fig. 2, and lie close to curve *D*. Curve *E* (Fig. 2) is the disorientation potential–concentration curve, determined from first additions of *iso*amyl alcohol to water. Except in the most dilute solutions (*e.g.*, second addition, curve *A*, Fig. 1) the adsorption of *iso*amyl alcohol is not able to bring about complete disorientation of a surface at which an oriented film already exists; as with decyl alcohol (Part XVIII, *loc. cit.*) the disorientation potentials obtained by successive addition of alcohol to the same solution lie between curves *D* and *E* (Fig. 2).

FIG. 5.

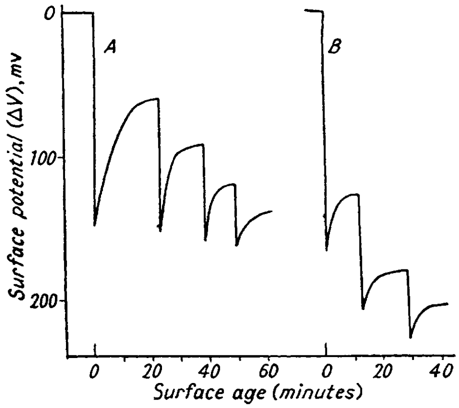
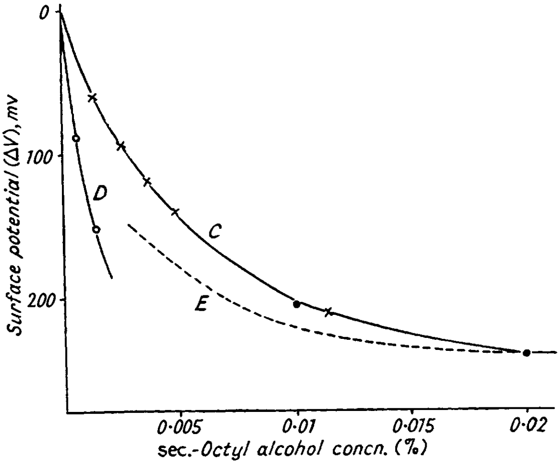


FIG. 6.



× × Orientation potentials (this work).
● ● Surface potentials (Posner and Alexander).
○ ○ Disorientation potentials (this work).

Curve *F* (Fig. 3) is the calibration curve relating the orientation potentials and surface tensions determined in these experiments. Posner and Alexander (*loc. cit.*) do not give all the relevant experimental data, but the calibration curve employed would lie close to curve *F* (Fig. 3). These authors were in error in employing this curve, and the operative dynamic tensions should be obtained by using the disorientation potential–tension curve *G*. The true dynamic tensions have therefore been obtained from Posner and Alexander's data as follows. The reported dynamic tension value (*K*, Fig. 3) is assumed to have been obtained from a measured potential represented by point *L*. Curve *G* being used instead of *F*, point *L* is transferred to *M*, giving a true dynamic tension shown by point *N*.

Curve *R* (Fig. 4) was determined (Part II, *loc. cit.*) from the change in wave-length along an oscillating jet of 0·162% *iso*amyl alcohol solution. Curve *S* shows the tensions reported by Posner and Alexander (there is a discrepancy of 2·6 dynes/cm. between the two equilibrium values for the surface tension of this solution, and Posner and Alexander's values have been advanced on the tension axis by this amount to facilitate direct comparison). Curves *R* and *S* give widely differing values for the time required to complete the adsorption process (0·021 and 0·009 second, respectively). However, when the points on curve *S* are translated in the manner described, curve *S* moves to the position shown by the broken curve *T* (Fig. 4), which is very close to curve *R*. It follows that in the *iso*amyl alcohol system, adsorption rates determined from both jet dimensions and surface potentials are in agreement provided that the variation in surface potential with surface condition is recognised.

sec.-Octyl Alcohol.—Surface potential–time curves for *sec.*-octyl alcohol are given in Fig. 5. The orientation process is slower than with *iso*amyl alcohol. The trough concentration after each addition is given in the following table :

Curve (Fig. 5)	Concn. (%) of added 25 ml. of *sec.*-octyl alcohol solution	Trough concn. (%) following : 1st addtn.	2nd addtn.	3rd addtn.	4th addtn.
A	0·0335	0·0013	0·0025	0·0037	0·00485
B	0·103	0·004	0·0077	0·0115	—

The disorientation produced by successive additions of *sec.*-octyl alcohol to the same solution is again less than the maximum possible. The orientation potential–concentration curve is shown as curve *C*, Fig. 6. Posner and Alexander's equilibrium values have been superimposed, and show exact agreement. It was not possible to extend the disorientation potential curve *D* beyond the low concentration range shown; when the surface excess becomes sufficiently great to involve lateral adhesion of adsorbed molecules, the adsorption process does not produce complete disorientation. In consequence, the rise from the first minimum in curve *B* (Fig. 5) is much less than in curve *A*. The disorientation curve *E* (Fig. 6) illustrates the comparatively small disorientation effect produced over the higher concentration range.

FIG. 7.

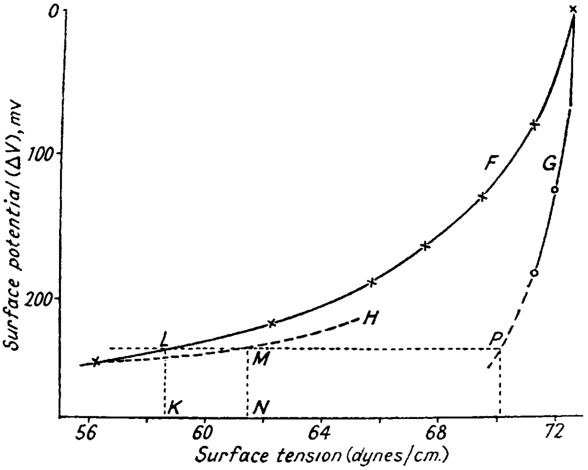
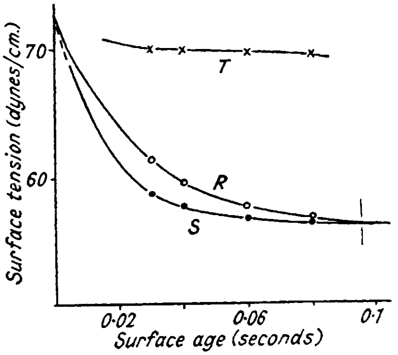


FIG. 8



The corresponding potential–surface tension calibration curves are shown in Fig. 7; the difference between dynamic tensions deduced by using orientation or disorientation potentials clearly depends upon the concentration of the solution under test. Posner and Alexander observed, in the case of *sec.*-octyl alcohol solutions, only small differences between tensions calculated from orientation potentials and those determined directly from jet dimensions; this arises from the fact that at the particular concentration employed (0·02%) the disorientation potential curve *H* (Fig. 7) lies close to the orientation potential curve *F*. The dynamic surface tension–time curve obtained from wave-length measurements (Part III, *loc. cit.*) is shown as curve *R* in Fig. 8. After adjustment on the tension axis to allow for a 2·9 dynes/cm. discrepancy in the equilibrium tension of the solution, the results deduced by Posner and Alexander from an orientation potential–tension calibration curve are shown as curve *S*, Fig. 8. The difference between the curves is small compared with the case of *iso*amyl alcohol, and each curve indicates that adsorption is complete at about 0·1 second. The experimental values on curve *S* (Fig. 8) may be translated as described for *iso*amyl alcohol solutions. The reported tension value *K* (Fig. 7) was derived from the measured potential *L*. If *L* is translated to point *M* on the disorientation curve *H*, then the small increase in tension from *K* to *N* is sufficient to raise curve *S* (Fig. 8) into a position in almost exact agreement with curve *R*. If the full disorientation curve *G* (Fig. 7) is extrapolated to the higher concentration range, translation of point *L* (Fig. 7) to point *P* involves a large increase in tension, and raises curve *S* (Fig. 8) to the position shown by curve T. It is clear therefore that at the high concentration used the state of the surface is correctly represented by the calibration curve H (Fig. 7). It follows from these considerations that if Posner and Alexander had applied their technique to the dilute solutions where full surface disorientation was possible, a larger discrepancy would have been observed between their derived dynamic tensions and those measured directly from jet dimensions.

It is necessary, in conclusion, to compare the suitability of these two techniques for the determination of dynamic surface tension. Posner and Alexander state that the potential method " with its freedom from the theoretical difficulties associated with the oscillatory-jet technique, is more likely to give the correct results." When the state of the surface under test is known, and the appropriate potential–tension relation employed, the two methods yield the same results. The potential method, however, has the disadvantage that it is necessary in all cases to carry out a separate study, often of some complexity, into the nature of the surface involved, before it is possible to translate the measured potentials into dynamic tensions.

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