66. *The Properties of Freshly Formed Surfaces. Part II. The Rate of Adsorption of* iso*Amyl Alcohol at the Air–Water Surface.*

By C. C. Addison.

The vibrating-jet technique has been applied to the study of the rate at which surface equilibrium of *iso*amyl alcohol–water mixtures is established. Dynamic tensions at surface ages of the order of 10^{-2} second are recorded for various concentrations, and the velocity at which adsorbate molecules migrate to the surface is calculated.

When amphipathic solute molecules are adsorbed from solution to the air–water surface, the surface tension is lowered to a value lying between that for pure water and that corresponding to full adsorption, and is a function of surface age. Although the properties of equilibrium adsorbed layers have been very fully investigated, no case is known in which the rate of development of this equilibrium has been studied. The vibrating-jet technique (see Part I, J., **1943**, 535) has now been applied to the study of surfaces to which surface-active molecules are in the process of migrating. The term " surface equilibrium " is used in this work to imply the surface state attained as soon as the concentration of surface-active molecules in the surface is such that migration no longer takes place, and when dipole orientation of adsorbed molecules is complete. This equilibrium is normally achieved within one second, and is distinct from the slow change in surface tension of the type reported by Adam and Shute (*Trans. Faraday Soc.*, **1935**, **31**, 204), which takes place with certain long-chain colloidal electrolytes over periods of days after the initial equilibrium has been established. The rate of development of this equilibrium depends (*inter alia*) on the following factors.

1. *Concentration of Surface-active Solute in the Water Phase.*—The excess of concentration at the surface over that in the bulk of liquid can be made up in a concentrated solution by migration of surface-active molecules from the immediate neighbourhood of the surface. The velocity at which this effect operates is determined by the repulsive forces acting between the aqueous medium and the hydrophobic carbon chain, and provided that the required number of surface active molecules be available within a few molecular radii of the surface, equilibrium will be established rapidly. Diffusion from the bulk of the liquid to the region of low concentration immediately below the surface can then take place without influence on surface properties. As concentration decreases, surface equilibrium is progressively more dependent upon migration to the phase boundary of solute molecules from the bulk of the liquid, and the time necessary for the establishment of final equilibrium will increase accordingly.

2. *Length of Carbon Chain.*—The factors controlling dipole orientation are both electrical and mechanical. The mutual attraction between carbon chains at the surface will increase with increasing chain length; the rate of increase of surface pressure (or decrease of surface tension) will therefore be enhanced by increasing chain length although the mechanical resistance to movement, which is also a function of chain length, will operate to counteract this tendency. As to velocity of migration to the surface, the repulsion between the aqueous medium and the hydrophobic carbon chain can be regarded as the restricting influence operating to set up a form of Donnan membrane equilibrium, and thus as the factor determining the distribution of solute

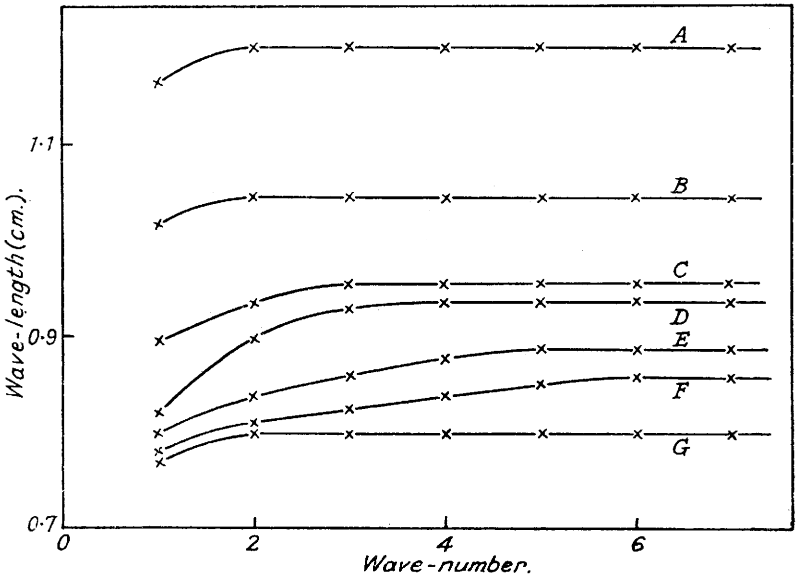
across some arbitrary bounding surface only a few molecular radii from the true physical surface. The speed at which this distribution is completed has been shown to be a function of chain length, and this will be the subject of a later communication.

3. *Nature of Polar Group.*—The electrical attractions and repulsions operating between neighbouring adsorbed molecules have a pronounced effect on equilibrium surface tension. Any body (such as an added ion of opposite charge) capable of affecting these electrical forces modifies the surface tension considerably (Powney and Addison, *Trans. Faraday Soc.*, 1937, **33**, 1253). It is not to be expected, however, that the nature of the polar group will have any appreciable effect on the rate of establishment of dipole orientation; but since the affinity between the aqueous phase and the long-chain carbon compound depends as much upon the nature of the polar group as on the chain length, the effect of the polar group on rate of migration to the surface should be appreciable.

4. *Temperature.*—Although the surface tension of pure liquids falls with increasing temperature, the opposite effect is obtained with solutions of a highly surface-active solute, and this has been explained on the assumption that less solute enters the surface at higher temperatures (*idem, ibid.*, p. 1243). Since the liquid is also less viscous, it would be expected that migration into the surface would be accelerated at higher temperatures.

FIG. 1.

iso*Amyl alcohol.*



Concentration, %: *A*, 1·624; *B*, 0·812; *C*, 0·406; *D*, 0·325; *E*, 0·203; *F*, 0·122; *G*, *nil.*

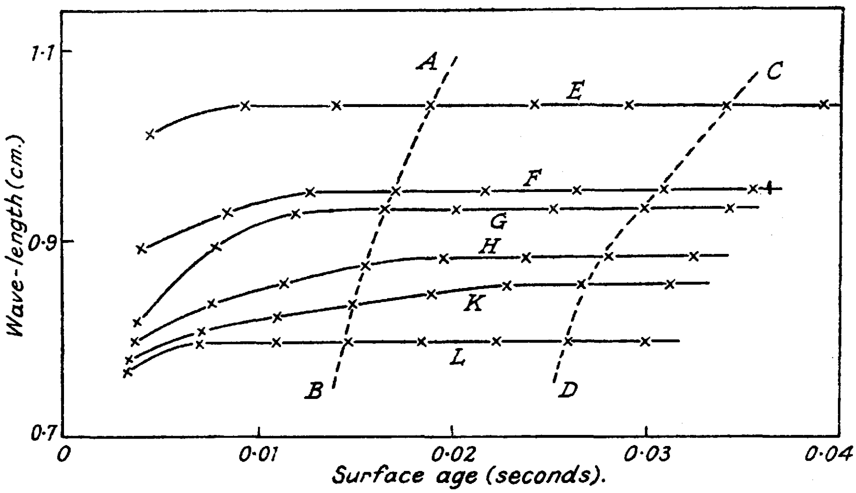
The influence of chain length, concentration, etc., is being studied, but the methods by which the dynamic surface tension, surface age, and migrational velocity are deduced are now recorded, together with their application to only one surface-active substance, *viz.*, *iso*amyl alcohol.

Results and Discussion.—Fig. 1 shows the variation in wave-length which occurs along vibrating jets of water–*iso*amyl alcohol mixtures at 20°. The curves were obtained by using the experimental technique outlined in Part I with a uniform flow rate of 1·990 ml./sec. Since change in surface tension takes place within the first few waves, an improved orifice (described elsewhere) was used which reduced the variations in wave-length at the beginning of a jet of pure liquid from four waves to one wave, and true wave-lengths representative of the surface tension operating at that point in the jet were thus obtained for all but the first wave. Again, as equilibrium is established rapidly, it was not essential to obtain the maximum length of unbroken jet, and the curves shown in Fig. 1 were all obtained by using the jet in a horizontal position. The upper limit for *iso*amyl alcohol concentration is set by its solubility in water at 20°. At the lower concentrations employed, the establishment of surface equilibrium will be largely dependent on migration of *iso*amyl alcohol molecules to the surface from the bulk of the liquid, and for 0·122% alcohol the wave-length changes up to the sixth wave. At a concentration of 0·406% of alcohol, surface equilibrium is reached at the end of the second wave, and at 0·812% the equilibrium is established so rapidly that the wave-length–wave-number curve is similar in form to that for pure water. Adsorption at this and higher concentrations will be complete within the first wave. Since turbulent flow, etc., reduces the length of the first wave below the value corresponding to the operative surface tension, it is not yet possible to measure the tension at a surface age below that corresponding to the end of the first wave, and the 0·812% curve in Fig. 1 represents limiting conditions for the measurement of dynamic tensions.

Since wave-length changes along the jet, wave-number cannot be regarded as proportional to surface age, and it is necessary to determine separately the surface age corresponding to each wave at each concentration. The radius of the circle equivalent in area to the orifice ellipse used was 0·055 cm., giving rise to a linear flow rate of 210 cm./sec. The relation between λ and surface age is given in Fig. 2. For comparison with Fig. 1, points of equal wave-number are connected by the broken lines *AB* and *CD*. In the absence of any adsorption phenomenon, the first wave is smaller than the true value, owing to an overall reduction in average translational velocity rather than to a smaller oscillation period. The latter is probably similar to that given under conditions of true two-dimensional oscillation later in the jet. However, in cases where wave-length is changing due to adsorption, no standard exists on which to assess the extent to which turbulent flow reduces the length of the first wave below its true value. In deducing the results shown in Fig. 2, the age assigned to the jet at the end of the first wave is that determined from the linear velocity under streamlined flow given above, and the measured wave-length. The error involved is of the order of 10^{-4} sec., representing a negligible error of less than 1% on the surface ages under consideration. By using the mathematical treatment given in Part I, the change in surface tension with time has been deduced from the results given in Fig. 2. The length of the first wave cannot be used for calculation of surface tension, and the surface-tension–surface-age relationships shown in Fig. 3 are calculated for the second wave onwards. At zero surface age the surface will contain no higher concentration of alcohol molecules than does the bulk. In view of the low concentrations concerned, the tension at such a surface will not differ appreciably from that of pure water. The curves obtained by calculation (shown as continuous lines in Fig. 3) have therefore been extrapolated (by broken lines) towards $\gamma = 72{\cdot}8$ dynes/cm. for zero surface age. The time required before equilibrium is established is shown in Fig. 3 by short vertical lines cutting the curves; the time required diminishes with increasing concentration.

FIG. 2.

iso*Amyl alcohol.*



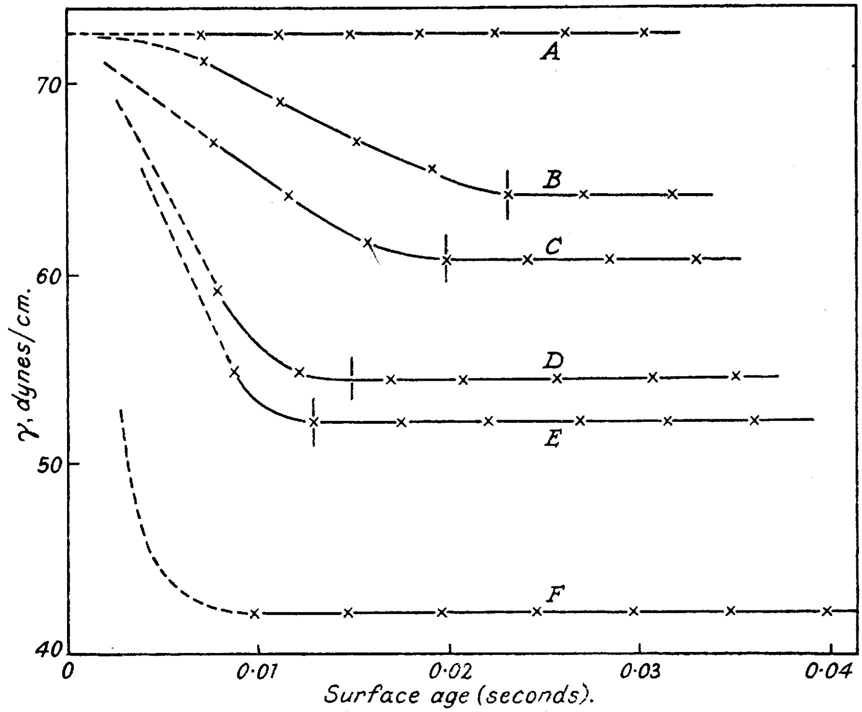
Concentration, % : *E,* 0·812 ; *F,* 0·406 ; *G,* 0·325 ; *H,* 0·203 ; *K,* 0·122 ; *L, nil.*

Sufficient information was not available at this point to decide whether this change of tension with time was due to dipole orientation of the molecules already in the surface or available within a few molecular radii of the surface, or whether the rate of change at different concentrations was a reflection of the rate of migration of molecules far removed from the surface. If the latter case holds true, the surface tensions represented by the level parts of the curves in Fig. 3 should be typical of a surface at which adsorption is complete, and should equal the values obtained by other methods of measurement (such as drop weight, ring method, etc.) in which the surface is at least several seconds old before a measurement can be performed. Fig. 4 shows the relation between surface tension and alcohol concentration at various surface ages. The broken curve *E* shows the probable conditions at 0·005 sec. At all measured surface ages above 0·025 sec. the curve *A* is obtained, and all other curves approach *A* at higher alcohol concentrations. Equilibrium surface tensions for the same system were obtained by the drop-weight technique described by Powney and Addison (*loc. cit.*), Harkins and Brown's correction factors (*J. Amer. Chem. Soc.*, **1919**, **41**, 499) being used; 12 seconds were allowed for the formation of each drop. The results obtained are superimposed on curve *A* in Fig. 4. The agreement obtained is almost ideal, and confirms that the surface of the vibrating jet is in a state of final equilibrium as soon as the drift in wave-length ceases, and that migration of surface-active molecules to the surface is then complete. Again, as no breaks have been found in that part of the curves (Fig. 3) covering the period of change, it is probable that with short-chain molecules such as *iso*amyl alcohol the orientation at the surface takes place almost instantaneously. The fall in tension is therefore regarded in this particular case as being dependent on the time necessary to accumulate the required number of active molecules in the surface.

A knowledge of the actual concentration of active molecules at the surface would enable migration to be

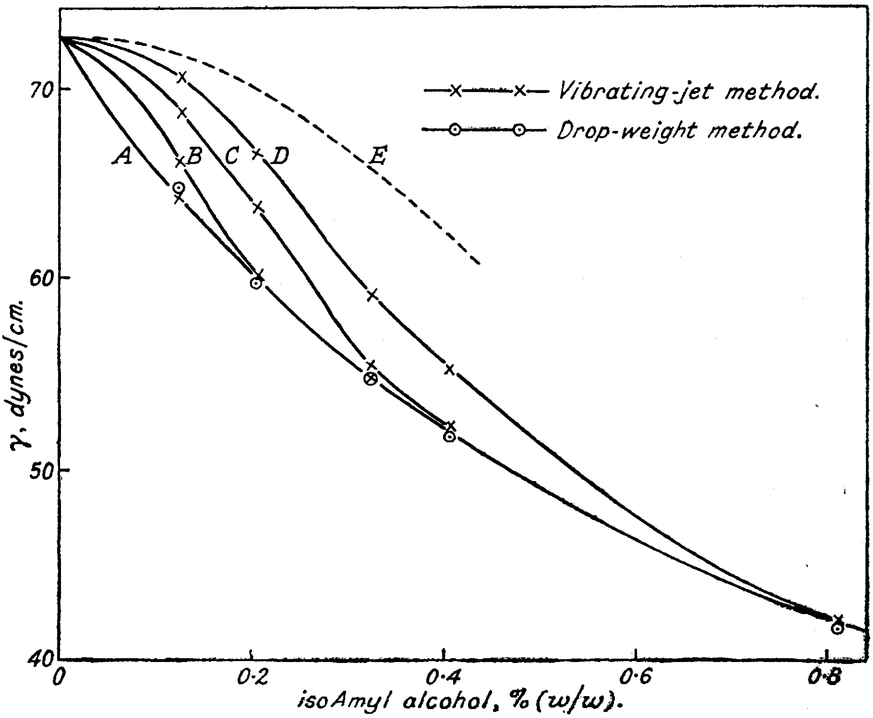
FIG. 3.

iso*Amyl alcohol.*



Concentration, %: *A, nil*; *B*, 0·122; *C*, 0·203; *D*, 0·325; *E*, 0·406; *F*, 0·812.

FIG. 4.



Surface ages (*seconds*) : *A*, 0·025 *and over*; *B*, 0·018; *C*, 0·012; *D*, 0·008; *E*, 0·005.

studied quantitatively. The results set out below are calculated by assuming the applicability of Gibbs's theorem to small molecules, and the migrational velocities given form a valuable basis on which to assess the influence of chain length, etc., on rates of adsorption.

Gibbs (" Scientific Papers," Vol. I, p. 235) deduced the relationship $\Gamma = -\mathrm{d}\gamma/\mathrm{d}\mu$, where Γ is the surface excess of solute, γ the surface tension, and μ the potential of the adsorbed component. In the dilute solutions described here, the activity of the solute may be equated to its concentration c, whence $\Gamma = -c(\mathrm{d}\gamma/\mathrm{d}c)/\boldsymbol{R}T$. The quantity Γ has the dimensions of mass per unit area, and thus represents the mass of adsorbed component actually attached to unit area of the surface; $\boldsymbol{R}$ has the value $83{\cdot}2 \times 10^6$ ($=K$) for 1 g.-mol. of adsorbate, whence $\Gamma = -cM(\mathrm{d}\gamma/\mathrm{d}c)/KT$, where M is the molecular weight of the adsorbate. If the terms of this equation are expressed in c.g.s. units, the value of Γ obtained represents the mass of adsorbate (in g.) attached to 1 cm.^{2} of surface. Since the mass concerned is minute, it can be regarded as being drawn by surface forces from a disc 1 cm.^{2} in cross-section placed with one face in the surface, and having thickness of d cm. Although the distance d is appreciable in terms of molecular dimensions, it is very small in comparison with the diameter of the disc. Surface equilibrium will be complete when the whole of the original solute content of the disc reaches the surface, and the time (t_1 seconds) indicated by experiment as necessary for this equilibrium to be established (Fig. 3) can be equated to the time taken by the last migrating molecules reaching the surface (*i.e.*, those from the opposite face of the disc) to travel d cm. As concentration is expressed in % by weight, then

$$d = 100\,\Gamma/c = -\,100M(\mathrm{d}\gamma/\mathrm{d}c)/KT$$

The *mean* velocity at which the adsorbate molecules travel to the surface wlll be termed the " migrational velocity." As this equals d/t_1 cm./sec., then

$$\text{Migrational velocity} = V = -\,100M(\mathrm{d}\gamma/\mathrm{d}c)/KTt_1$$

Relevant figures used to determine migrational velocities for *iso*amyl alcohol at 20° are given in the table.

c, %	0·122	0·203	0·325	0·406	0·812
$-\mathrm{d}\gamma/\mathrm{d}c$	60	48	36	30	18
$\Gamma \times 10^8$, g./cm.^{2}	2·64	3·52	4·22	4·40	5·28
$d \times 10^6$, cm.	21·7	17·3	13·0	10·8	6·5
t_1, sec.	0·023	0·020	0·015	0·013	<0·01
$V \times 10^4$, cm./sec.	9·4	8·7	8·7	8·4	>6·5

The assumption has been made (see above) that the variation in t_1 with concentration is a result of the varying distances d through which surface-active molecules must migrate to the surface. As a consequence, migrational velocities should be independent of concentration. Any variation of surface tension with time caused by dipole orientation rather than migration would be reflected in discrepant values for migrational velocity. The results in l. 6 of the table indicate that migration is at least the major (if not the only) factor determining surface tension changes over the experimental range of surface ages. The slight fall in velocity which occurs with increasing concentration may be due to mutual interference between migrating molecules, which will also increase with concentration.

The forces producing migration, and the mutual interference, should both increase with increasing chain length. These aspects of the problem will be considered when results over a range of chain length are available.

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