129. *The Properties of Freshly Formed Surfaces. Part III. The Mechanism of Adsorption, with Particular Reference to the* sec.*-Octyl Alcohol–Water System.*

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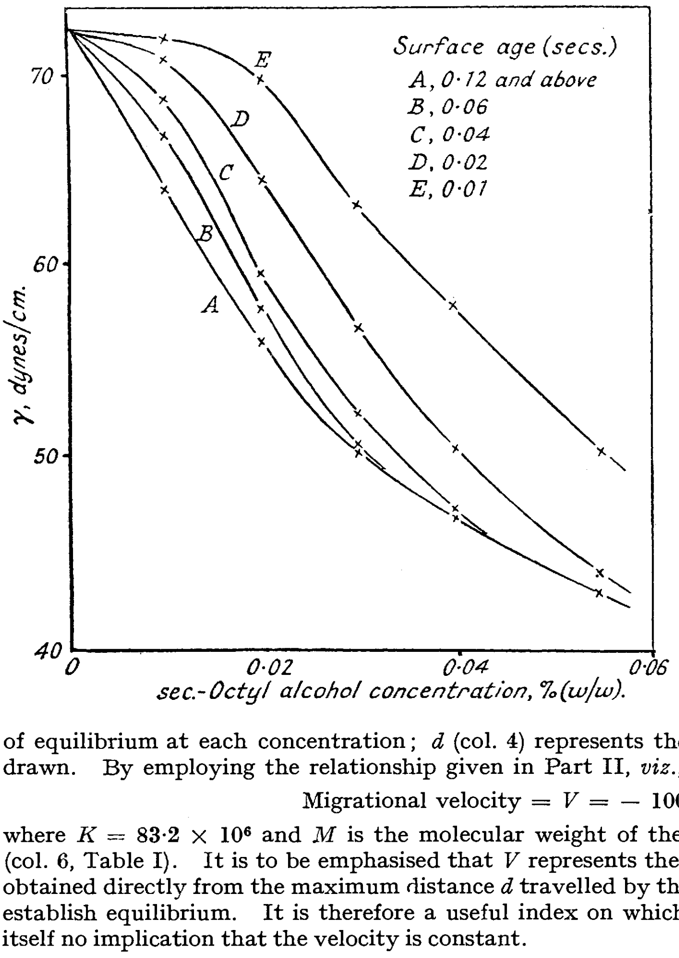
Dynamic surface tensions of aqueous *sec.*-octyl alcohol solutions have been measured by the vibrating-jet method. The extent to which the free energy of the surface can be reduced by the adsorbate at any given concentration is shown to be the major factor controlling the velocity at which the adsorbate molecules migrate to the surface, and the variation in true velocity during adsorption has been determined.

THE vibrating-jet technique described in Part I (J., 1943, 535) was applied in Part II (this vol., p. 252) to the study of the dynamic surface tensions of aqueous solutions of *iso*amyl alcohol, and the mean velocity (termed the migrational velocity) at which molecules of *iso*amyl alcohol migrate from the bulk of the liquid to the surface was determined. The surface age at which equilibrium is established with this alcohol (of the order of 10^{-2} sec.) is so small, however, that the system could not be suitably applied to the study of true velocities of migration. Further work has shown that the range of surface ages available for measurement increases with increasing chain length. The upper limit is set by the solubility of the alcohol in water, which diminishes rapidly with increasing chain length, and the range of dynamic tensions (about 30 dynes/cm.) given by the lower members is not available beyond the C_8 alcohol. *sec.*-Octyl alcohol has been used in the present investigation, and dynamic surface tensions (obtained as shown in Part II) cover surface ages up to 0·12 sec. The results provide information on the variation in true velocity of migration to the surface, which takes place while adsorption is proceeding.

FIG. 1.



Migrational Velocity.—γ–c Curves for *sec.*-octyl alcohol solutions in water at 20° and at various surface ages are given in Fig. 1. The curves are similar in form to those already described for *iso*amyl alcohol. Curve *A*, which represents equilibrium conditions as determined by the vibrating jet, is in ideal agreement with that obtained by drop-weight measurements. The values of $d\gamma/dc$ obtained from this curve have been substituted in the approximate form of Gibbs's adsorption equation, $\Gamma = -c(d\gamma/dc)/\boldsymbol{R}T$, to obtain the maximum amount of adsorbate on the surface at each concentration (col. 3, Table I), it being assumed that, over the range of low concentration chosen, the activity coefficient of the solute does not differ appreciably from unity. By replotting the information in Fig. 1 to show directly the relation between γ and surface age, it is possible to determine the time required (t_1 seconds) for the establishment of equilibrium at each concentration; *d* (col. 4) represents the depth of solution from which the adsorbate is drawn. By employing the relationship given in Part II, *viz.*,

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

where $K = 83{\cdot}2 \times 10^6$ and *M* is the molecular weight of the alcohol, the values of *V* have been calculated (col. 6, Table I). It is to be emphasised that *V* represents the mean velocity of the migrating molecule, and is obtained directly from the maximum distance *d* travelled by the adsorbate molecules and the time t_1 required to establish equilibrium. It is therefore a useful index on which to compare rates of adsorption, and carries in itself no implication that the velocity is constant.

TABLE I.

c, %.	$-d\gamma/dc$.	$\Gamma \times 10^8$, g./cm.^{2}.	$d \times 10^5$, cm.	t_1, sec.	$V \times 10^4$, cm./sec.
0·01	800	4·30	43·0	0·120	36·0
0·02	640	6·90	34·5	0·095	36·2
0·03	490	7·90	26·5	0·070	37·6

The value of *V* for *sec.*-octyl alcohol is greater than that recorded in Part II for *iso*amyl alcohol (9×10^{-4} cm./sec.) and is again independent of concentration. The general relationship between *V* and chain length will be discussed more fully in a later part.

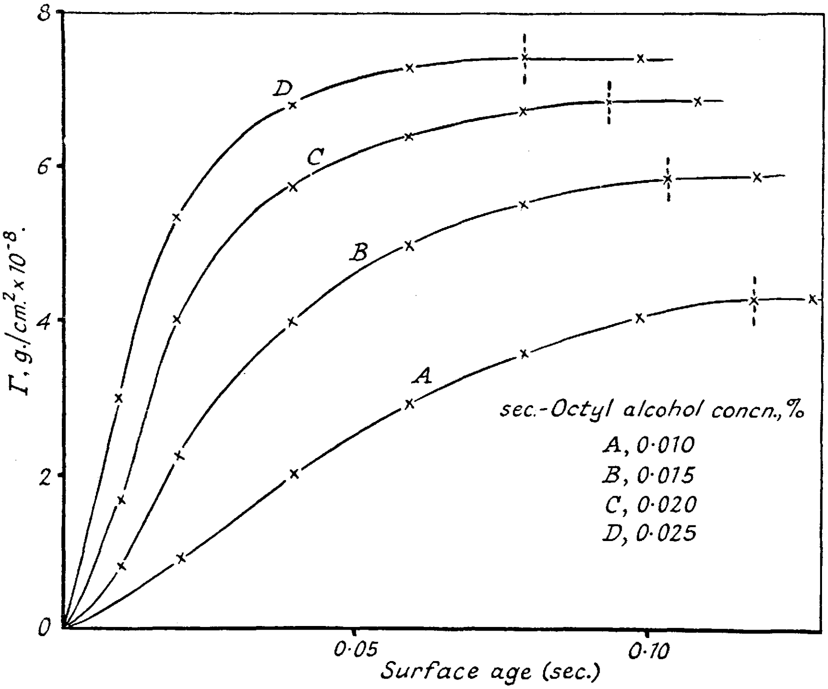
Factors controlling Velocity of Migration to the Surface.—The velocity of an adsorbate molecule migrating to a surface will be determined by a number of factors, including (*a*) the viscosity of the medium, (*b*) the dimensions and polar nature of the molecule, (*c*) the temperature, (*d*) the distance of the molecule from the surface, and (*e*) the free energy of the surface. The influence of the first three factors will vary with each particular case, but factors (*d*) and (*e*) have general application. Their relative significance can be deduced from the results given below.

In selecting the octyl alcohol system for study, the activity coefficient of the alcohol was not expected to deviate appreciably from unity in view of the very low concentrations required to produce large depressions in surface tension. In this case the more accurate form of Gibbs's equation, $\Gamma_2^{(1)} = -\ (\partial\gamma/\partial \log_e fc)/\boldsymbol{R}T$, where

f is the activity coefficient, could have been reduced to the above approximate form for the determination of velocities of migration throughout the available range of concentration. However, the mode of variation of $d\gamma/dc$ over the concentration range 0—0·06% (Curve A, Fig. 1) indicates that even in this system the activity coefficient deviates appreciably from unity at concentrations above 0·03%. Thus, when the equation $\Gamma = -c(d\gamma/dc)/\boldsymbol{R}T$ is applied to Curve A, Fig. 1, the value of Γ increases steadily up to a concentration of 0·03%, and the relation between γ and Γ is almost linear. Thereafter $d\gamma/dc$ falls more rapidly, and decreasing values of Γ are obtained. In the absence of values for the activity coefficients at the higher concentrations, calculation of Γ by the approximate form of Gibbs's equation has been restricted to the concentration range 0—0·03%. Under these conditions of extreme dilution, Γ will approximate closely to the amount of solute in a layer one molecule deep on the surface.

In determining the results in Fig. 2, the assumption has been made that a given value for γ represents a given Γ irrespective of surface age. The development of Γ with age of surface has been calculated on this basis from the values in Fig. 1, and the results are given in Fig. 2 over the concentration range 0·01—0·025%. The broken vertical lines indicate the surface ages at which adsorption is complete. At any given surface age, the slope of the tangent to the curves in Fig. 2 represents the rate of arrival of adsorbate at the surface. 1 cm.^{2} being taken as unit area of surface, the units of $d\Gamma/dt$ are in g./sec. These values are given in Table II, col. 4. The free energy of the surface with respect to the adsorbate molecules is defined for present purposes as the extent to which the surface tension can be lowered by accumulation of adsorbate at the surface. Thus if γ_t represents the surface tension at time t after formation of the surface, and γ_E represents the equilibrium value for that concentration, then the free energy of the surface is equal to $\gamma_t - \gamma_E$.

FIG. 2.



If the velocity of migration of adsorbate molecules is dependent upon the free energy, but is independent of distance from the surface, the value of $d\Gamma/dt$ should be proportional to $\gamma_t - \gamma_E$. If distance from the surface is a significant factor in determining velocity, this will not hold true. Values of $\gamma_t - \gamma_E$ are listed in Table II, col. 3, and the ratios are given in col. 5.

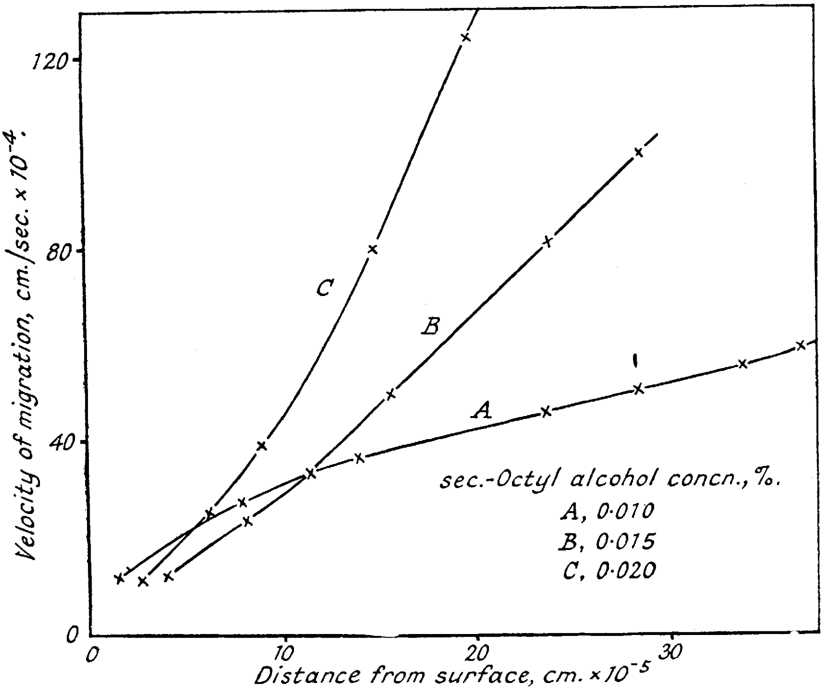
TABLE II.

c, %.	Surface age, sec.	$\gamma_t - \gamma_E$, dynes/cm.	$10^8 d\Gamma/dt$, g./sec.	$[10^8 d\Gamma/dt]/(\gamma_t - \gamma_E)$.
0·01	0·10	0·9	10·5	11·7
,,	0·08	2·1	25·0	11·9
,,	0·06	3·2	37·0	11·6
,,	0·04	4·4	46·5	10·6
0·015	0·07	1·3	16·3	12·5
,,	0·05	2·0	23·7	11·9
,,	0·03	4·9	51·3	10·5
0·02	0·08	0·8	11·5	14·4
,,	0·06	1·7	24·5	14·4
,,	0·04	3·5	52·0	14·9
,,	0·03	5·5	80·0	14·6

The ratios are sufficiently constant to indicate that free energy of surface is the major factor controlling migration velocity, and that distance from the surface is not significant. In view of the small velocities involved, and the high resistance to movement, the relative insignificance of the distance is feasible. The actual value of the ratio in Table II will be a function of concentration, and the above conclusions will hold true so long as the ratios are constant for any given concentration.

It is now possible to determine the actual velocities of the migrating molecules at any required distance from the surface. For example, at a concentration of 0·02%, solute is drawn from the bulk of the liquid to a depth of $34{\cdot}5 \times 10^{-5}$ cm. before an equilibrium surface layer is obtained. At a surface age of 0·04 sec., $d\Gamma/dt$ is 52×10^{-8} g./sec. for 1 cm.^{2} of surface, which corresponds to a velocity of 26×10^{-4} cm./sec. at this concentration. This value will be uniform throughout the full depth of migrating molecules. Again, Γ has reached the value $5{\cdot}75 \times 10^{-8}$ g./cm.^{2} at 0·04 sec., and the adsorbate molecules which were initially most remote from the surface will have advanced $28{\cdot}3 \times 10^{-5}$ cm., *i.e.*, they will be $6{\cdot}2 \times 10^{-5}$ cm. from the surface. This reasoning being used, results for three separate concentrations are recorded in Fig. 3. For each concentration, the curve given represents the variation in velocity of those adsorbate molecules most remote from the surface when adsorption commenced. The velocity of molecules at a distance smaller than *d* from the surface when adsorption commenced may be obtained by displacing the curve parallel to the distance axis to the required extent.

FIG. 3.



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