87. *The Properties of Freshly Formed Surfaces. Part V. A Velocity–Time Equation for Adsorption to Dynamic Surfaces.*

By C. C. Addison.

The dynamic surface tensions of aqueous solutions of *n*-alcohols reported in Part IV (this vol., p. 98) have been used to determine the true velocities of migration to the surface over the full time required for equilibrium. The velocity (v) and surface age (t) are shown to be related by the equation $v = a^n t e^{-akt}$; n and k are functions of chain length but are independent of concentration. At infinite dilution a is independent of chain length, and is a direct function of concentration. Hence the surface behaviour of alcohols having chain lengths outside the experimental range can be predicted. The distance travelled by the adsorbate molecules, obtained by integration of the exponential equation, agrees closely with that deduced directly from Gibbs's equation, and provides support for the adsorption mechanism proposed. The results can be used to assess the probable constancy of the migrational velocity at concentrations lower than those which can be studied experimentally.

From the values for the mean velocity of migration to the air–water surface reported for *iso*amyl and *sec.*-octyl alcohols (Parts II and III, J., 1944, 252, 447) and for the *n*-alcohols from amyl to octyl (Part IV, *loc. cit.*), it is clear that this mean velocity, which increases appreciably with chain length, is sufficiently constant for any given alcohol over the available concentration range to be regarded as a property of that particular alcohol. However, apart from their use as a basis on which to compare surface activities, the mean velocities have limited application in the study of the true mechanism of the adsorption process. It therefore became necessary to determine the true velocity of adsorbing molecules under various conditions of chain length and concentration, and over the full range of surface age. It was shown in Part III that the free energy per unit area of the surface at any given surface age (defined as the difference between the surface tension at that age, and the equilibrium value) was the major factor determining the velocity at that moment, and this fact was used to obtain true velocities of migration over a part of the time required for surface equilibrium. The adsorbing molecules undergo acceleration when the surface is first formed (see below), and the true velocities reported in Part III were purposely limited to the later stages of the adsorption.

The dynamic surface tensions of aqueous solutions of *n*-amyl, -hexyl, -heptyl, and -octyl alcohols reported in Part IV have now been used as a basis for the calculation of true velocities of migration over the full time taken to establish equilibrium. The velocity–surface age curves have been interpreted mathematically, and an exponential relationship obtained in which the constants used have a physical significance.

Velocity–Surface Age Curves.—Curves for the above four *n*-alcohols are given in Figs. 1—4. The broken horizontal lines M represent the migrational velocity. The full curves represent the true velocities, and have been calculated for three separate concentrations in each case. The development of Γ with time was first plotted as shown in Part III; the tangent to the Γ–t curve represents the rate of arrival of adsorbate at the surface. Since the velocity is uniform throughout the disc from which the adsorbate is drawn, the rate of arrival at the surface gives directly the velocity of the adsorbing molecules at the base of the disc. This adsorption mechanism, which has been assumed in deducing these curves, receives striking support from the mathematical results given below, and is referred to again in more detail. The curves shown in Figs. 1—4 represent in each case the velocity of the adsorbing molecules most remote from the surface, and thus the velocity reaches zero when adsorption is complete. The velocity of molecules which are at a smaller distance from the surface when it is first formed will be obtained by displacing the curves to the required extent parallel to the time axis. Such molecules may therefore have, on reaching the surface, velocities up to that represented by the peak in the curve, depending on their initial distance from the surface.

FIG. 1.

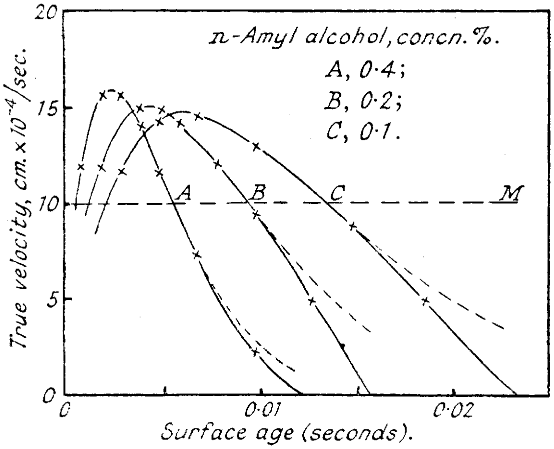


FIG. 2.

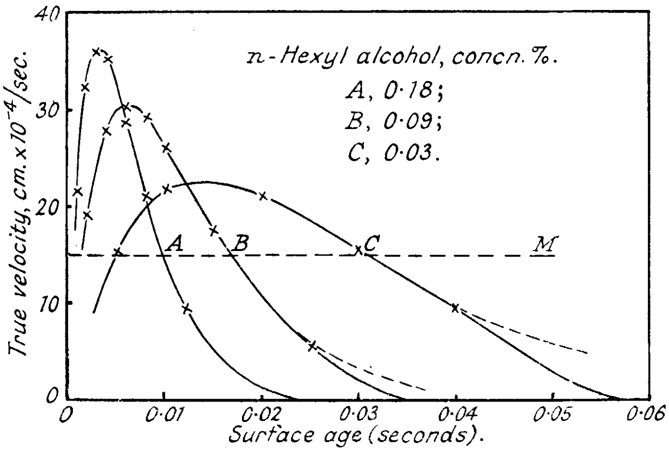
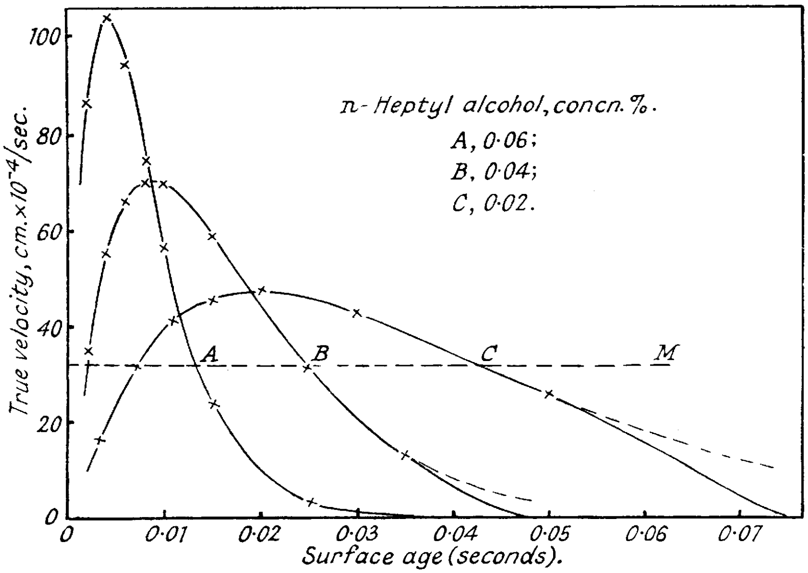


FIG. 3.

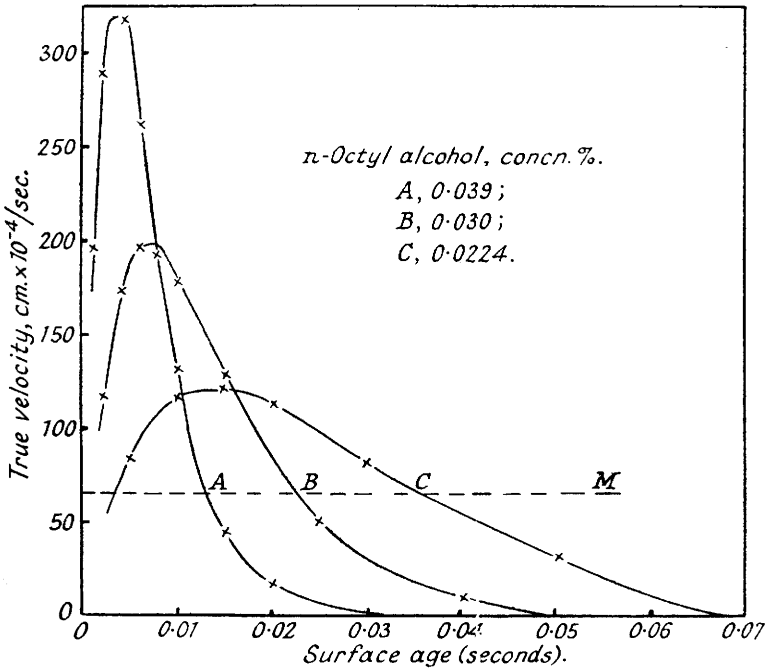


The dynamic surface-tension measurements made by the vibrating jet, from which these curves are calculated, are considered to be accurate to ±0·25 dyne/cm. The Γ–t curves (see Part III, Fig. 2) will therefore have a similar accuracy, and the tangents thereto are considered to be accurate to at least ±2%. The lower limit of surface age at which accurate tension measurement is possible is the age at the second wave, *i.e.*, about 0·004—0·007 second. In Figs. 1—4, the major portion of each curve lies above this lower age limit, and only with the higher concentrations of *n*-amyl alcohol is any significant part of the curve below this limit. Where velocities have been recorded at lower surface ages, they have been obtained by extrapolation of the Γ–t curve to the origin. The error here may therefore be rather greater than at higher surface ages. However, the length of the first wave can be used to confirm fairly accurately the position of the small extrapolated section of the

Γ–t curve. The extent to which this wave is decreased in length by turbulent flow below the equilibrium value for pure water (Addison, *Phil. Mag.*, in the press) is a constant for a given apparatus, and by assuming that a proportionate reduction takes place in dilute solutions also, the surface tension (and thus Γ) at 0·002—0·003 sec. can be obtained with sufficient accuracy to confirm the position of the extrapolated Γ–t curve.

Physical Basis for Shape of Curves.—All the curves show a rapid rise to a peak velocity, followed by a more gradual fall to zero velocity. The peak value increases with increasing concentration, and this effect is more pronounced as chain length increases. These results are consistent with the following mechanism. Before the formation of the surface, the adsorbate molecules are in a state of kinetic agitation. This movement will be distributed over the three dimensions, and the mean velocity in the direction of the surface can be taken as zero. In consequence, the velocity is zero at zero surface age whatever the concentration or chain length. Immediately the free surface energy operates, the molecules will accelerate towards a velocity corresponding to the maximum free surface energy. While this velocity is still small, little adsorption will occur, and little fall in surface tension should take place. That this is, in fact, the case is shown by the results given in Part II, Figs. 3 and 4, and Part III, Fig. 1, where for a short period of time immediately following the formation of the surface, little or no fall in surface tension occurs. The rate of fall then increases as the adsorbate molecules accelerate. During acceleration, the free surface energy is falling owing to the arrival of adsorbate at the surface, until at the peak of the velocity–time curve the adsorbing molecules reach a velocity corresponding to the free surface energy at that age. This energy is highest in more concentrated solutions and increases with chain length, and thus the initial acceleration increases with both concentration and chain length. Again, the rate of fall of free surface energy is greater for concentrated than for dilute solutions. Owing to a combination of these two effects, the peak value increases with concentration, but the peak is reached at a lower surface age. Thereafter, the velocity falls at a rate which decreases with the decreasing free surface energy.

FIG. 4.



Equations of Curves.—The general shape of the curves does not alter with concentration or chain length, and the relation between true velocity (v) and surface age (t) is in all cases of the form

$$v = te^{-t} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If a smooth curve is drawn through the peak points for each alcohol, it is clear that the envelope so formed is almost parallel to the t axis in the case of amyl alcohol, but becomes rapidly steeper as chain length increases. This can be allowed for in Equation (1) by the introduction of two terms, thus

$$v = a^n te^{-at} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where n determines the slope of the envelope, and a the position of the peak on the envelope. There is also a wide variation in the actual peak velocities with chain length (cf. 14—16 × 10^{-4} cm./sec. for amyl, and 120—320 × 10^{-4} cm./sec. for octyl alcohol). This can be allowed for in equation (2) by the introduction into the index of a further term, thus

$$v = a^n te^{-akt} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where *k* determines the dimensions of each set of curves. By adjusting the values of *a*, *n*, and *k* the practical curves can be reproduced with accuracy, and equation (3) appears to be a fundamental relationship controlling the establishment of surface equilibrium. The curves obtained by experiment are shown in Figs. 1—4 by full lines, and where deviations do occur, the curves deduced from equation (3) are shown as broken curves leaving the experimental curves. Such discrepancies as do occur are at small velocities, where adsorption is almost complete. For hexyl, heptyl, and octyl alcohols, the discrepancy is almost negligible; with amyl alcohol a large part of each curve is duplicated by equation (3), and the deviation at high surface ages is not serious in view of the small velocities involved.

The values of *a*, *n*, and *k* for any given chain length and concentration were readily determined by virtue of the fact that the effect of each term on the general form of the curve is independent of variations in the other two terms. Thus by giving *k* an arbitrary value (say 100) the shape of the envelope connecting the peaks was determined for a range of values of *n*; this term was therefore determined first for each alcohol; *a* was then obtained from the position of the peak on the envelope (*i.e.*, from the initial slope of the curve), and finally *k* was adjusted to bring the theoretical curve to the same dimensions as the experimental curve. The values found for *k*, *n*, and *a* are given in Table I.

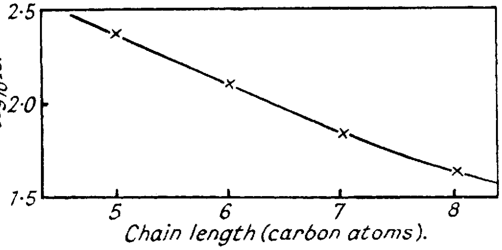
TABLE I.

n-Alcohol.	Concentration, %.	*k*.	*n*.	*a*.	*n*-Alcohol.	Concentration, %.	*k*.	*n*.	*a*.
Amyl	0·1	240	1·1	0·65	Heptyl	0·02	68	1·5	0·74
	0·2	240	1·1	0·95		0·04	68	1·5	1·68
	0·4	240	1·1	1·70		0·06	68	1·5	3·75
Hexyl	0·03	130	1·3	0·56	Octyl	0·0224	44	1·7	1·68
	0·09	130	1·3	1·25		0·030	44	1·7	3·33
	0·18	130	1·3	2·30		0·039	44	1·7	6·84

Physical Significance of k, n, *and* a.—It is clear from Table I that *n* is a constant for any given alcohol, is independent of concentration, and increases by a regular increment of 0·2 for each additional carbon atom in the chain. Hence, if *l* is number of carbon atoms in the chain

$$n = 0{\cdot}1 + 0{\cdot}2l \qquad (4)$$

FIG. 5.



Similarly, *k* is also a constant for each alcohol and is independent of concentration, but its value diminishes rapidly with increasing chain length. The relation between $\log_{10} k$ and *l* is shown in Fig. 5. The points for amyl, hexyl, and heptyl alcohols are closely linear; that for octyl alcohol deviates slightly, and evaluation of *k* at chain lengths greater than 8 (not possible by the present practical technique) will be required to determine whether this is the beginning of a true departure from linearity. This aspect is being studied. Linearity being assumed, the relation between *k* and chain length, can be written with sufficient accuracy for present purposes as

$$\log_{10} k = 3{\cdot}75 - 0{\cdot}275l \qquad (5)$$

Hence both *k* and *n* are functions of chain length only. Since the term *a* determines the position of the peak velocity on the envelope, it was anticipated that *a* would be a function of the concentration *c*. The relation between *a*/*c* and *c* is shown in Fig. 6 in logarithmic units. The manner of variation of *a* with *c*, over the concentration range used, alters appreciably with chain length, but the values of *a*/*c* appear to approach at infinite dilution a constant value which is independent of chain length. The relation between *a*/*c* and chain length is plotted in Fig. 7 at four selected concentrations. The sections of the curves shown by broken lines were obtained by extrapolation from the curves in Fig. 6. The point of intersection is common to each of the curves; at a concentration of 0·02% the influence of chain length on *a*/*c* is slight, and it is most probable that at higher dilution the chain length effect will disappear. The value of *a*/*c* will then be represented by the point of common intersection of the curves in Fig. 7, whence

$$\log_{10} a/c = 1{\cdot}45 \text{ or } a = 28c \qquad (6)$$

Application of Exponential Equation.—By employing the relationships given above, it is possible to determine the velocity–surface age curves for alcohols which are at present beyond the range of the vibrating jet method. It is hoped to extend equation (3) to cover a wider range of conditions by the introduction of further terms related to temperature, chain structure, and hydrophilic group. The accuracy with which velocities can be predicted is largely determined by the accuracy with which *a* can be determined, which in turn depends on the concentration. At low concentrations the *a*/*c*–*l* curves in Fig. 7 can be extrapolated to other chain lengths with suitable accuracy, but the accuracy of extrapolation decreases as concentration increases.

As chain length increases, decrease in water solubility outweighs the increase in velocity of migration. The time required for the establishment of surface equilibrium therefore increases with chain length, ultimately beyond the age limit of the vibrating jet (Part IV), and methods of measuring surface tension over periods up to one minute are being developed. Predicted results from equation (3) on alcohols higher than octyl have not therefore been confirmed by experiment, but measurements on aqueous decoic acid solutions confirm the order of time for equilibrium predicted by equation (3). In this calculation, the values of k, n, and a given above are assumed to apply to the acids of equal chain length also, in view of the similarity in surface activity between the alcohols and acids (Part IV). Until this is confirmed, the following results for decoic acid are to be regarded as significant in order only. By extrapolation to C_{10}, $n = 2{\cdot}1$, and $k = 10$. At a concentration of 0·002%, $a = 0{\cdot}056$; and at 0·0011%, $a = 0{\cdot}031$. The velocity–time curves calculated on these values rise to a peak at about 2 and 4 seconds, respectively, and fall back to zero (thus representing complete adsorption) at 12 and 22 seconds, respectively. These times are considerably longer than any previously recorded in this work, and it appeared possible that drop formation might exhibit unusual features with such solutions. An attempt was therefore made to measure the surface tension of the solutions by the drop-weight method, using an orifice radius of 0·12 cm. Whereas with the shorter-chain alcohol systems in which equilibrium is established within 0·1 sec., the drop weight was constant so long as mechanical errors were eliminated by allowing each drop at least 12 seconds to form, the weight of the drop of decoic acid solution was found to be a function of the rate of flow of liquid into the drop (and thus of the rate of expansion of the surface) and did not become constant until the drops were allowed more than 2 minutes to form. This phenomenon is regarded as indicating that several seconds are required before surface equilibrium at a static surface is established, and that, except in the case of the very slow flow rates, the rate of arrival of adsorbate molecules at the surface does not exceed (and at high flow rates is much less than) the rate of fall of surface concentration resulting from expansion of the surface. Harkins and King (*Kansas State Agric. Coll. Tech. Bull.* No. 9) found changes in the surface tension of a 0·0011% decoic acid solution occurring up to 30 minutes after the formation of the surface; it is possible, however, that film rearrangements of the type reviewed by Alexander (*Trans. Faraday Soc.*, **1941, 37, 15**) take place at a static surface to alter tension after the completion of adsorption, but are unlikely to occur at an expanding surface. Accurate data on adsorption at expanding surfaces would materially assist the study of adsorption mechanism, and these novel systems will be discussed more fully in a later part.

FIG. 6.

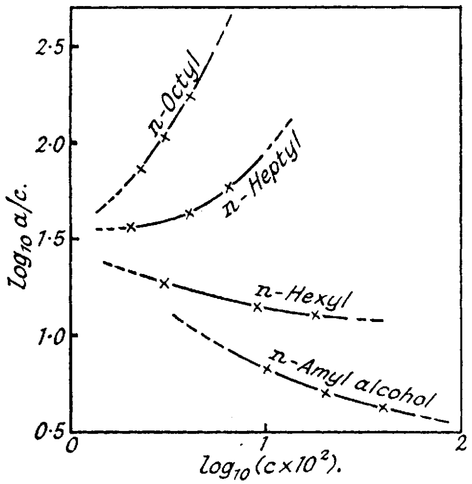
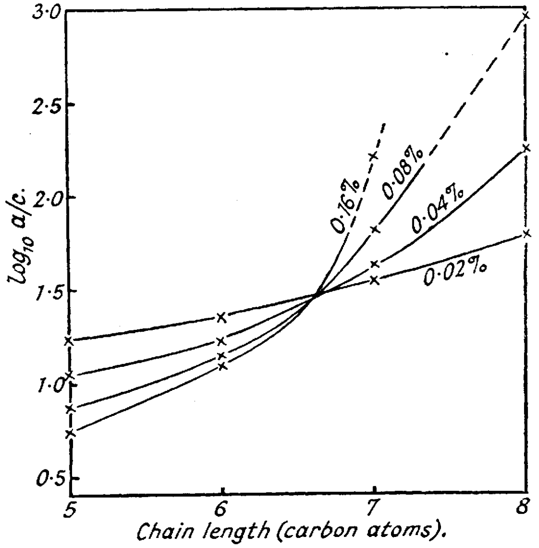


FIG. 7.



Adsorption Mechanism.—The mass of adsorbate (in g.) attached to 1 cm.² of surface at equilibrium can be regarded as being drawn by surface forces from a disc of solution 1 cm.² in cross section, placed with one face in the surface and having thickness d cm. The mass concerned is minute, and though d is appreciable in terms of molecular dimensions, it is very small in comparison with the diameter of the disc. This distance d is thus a function of the bulk concentration c, and can be determined with or without the assumption of an adsorption mechanism. The close agreement between the two provides support for the validity of the mechanism.

(a) *Calculation of* d *without reference to adsorption mechanism.* The approximate form of the Gibbs equation $\Gamma = -(c/\boldsymbol{R}T)\mathrm{d}\gamma/\mathrm{d}c$ is known to be inapplicable to the adsorption of large molecules, particularly where the concentration is sufficient for the formation of colloidal micelles (Gibby and Addison, J., 1936, 119, 1306), and is generally accepted as applicable only to the adsorption of a single component from a solution in which its behaviour is ideal with respect to concentration. However, the alcohols used in the present work are of comparatively short chain length, and practical considerations made it necessary to work with solutions of great dilution, where the relation between γ and Γ is almost linear. Since the activity coefficient f approaches unity at great dilution, the accurate form of the equation $\Gamma_2^{(1)} = -(1/\boldsymbol{R}T)\mathrm{d}\gamma/\mathrm{d}\log_e fc$ has been used in the above approximate form for the determination of Γ at equilibrium (and thus d) in these low concentrations. Values of d so obtained are given in Table II, col. 3.

(b) *Calculation of* d, *adsorption mechanism being assumed.* The following steps used in deriving the curves given in Figs. 1—4 outline the mechanism suggested in this work. (1) The variation of surface tension with surface age was obtained from the vibrating jet. (2) For any given alcohol, it was assumed that under conditions of great dilution a given surface tension represented a fixed Γ irrespective of surface age, and irrespective of whether or not equilibrium was established. (3) From the γ–t relation, the rate of increase of Γ was obtained, and Γ–t curves derived for various concentrations. (4) The tangent to the Γ–t curve at a given time was taken as representing the rate of arrival of molecules at the surface. (5) Evidence was submitted in Part III that in the case of *sec.*-octyl alcohol the distance of the adsorbing molecule from the surface was not significant in determining its velocity. This has been assumed to be the case with all the alcohols studied. Hence the rate of migration of all adsorbing molecules has been taken as uniform throughout the disc. (6) The variation in the slope of the tangent to the Γ–t curves was therefore taken as representing the variation in velocity of migration throughout the disc. As a result, the curves in Figs. 1—4 represent the velocity of the most remote migrating molecules, and any error in the mechanism assumed will be reflected in these curves.

For each interval of time dt, the distance travelled by the molecule is $v_1 \, . \, \mathrm{d}t$, where v_1 is the actual velocity at that instant. Hence the total distance d is given by $d = \int_0^t v_1 \, . \, \mathrm{d}t$, where t is the total time required to establish equilibrium. Since $v_1 = a^n t \mathrm{e}^{-akt}$,

$$d = \int_0^t a^n t \mathrm{e}^{-akt} \mathrm{d}t = -(a^{n-2}/k^2)\mathrm{e}^{-akt}(akt + 1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The depth of the disc is therefore represented by the area enclosed between the v–t curve and the t axis. The values of d thus obtained are given in Table II, col. 4.

TABLE II.

n-Alcohol.	*c*, %.	$d \times 10^5$, cm. (from Gibbs's eqn.).	$d \times 10^5$, cm., from (7).	*n*-Alcohol.	*c*, %.	$d \times 10^5$, cm. (from Gibbs's eqn.).	$d \times 10^5$, cm., from (7).
Amyl	0·1	2·35	2·56	Heptyl	0·02	24·7	25·2
	0·2	1·62	1·82		0·04	16·2	16·7
	0·4	1·15	1·08		0·06	11·4	11·1
Hexyl	0·03	8·63	8·80	Octyl	0·0224	42·7	44·2
	0·09	5·02	5·10		0·030	34·7	36·0
	0·18	3·35	3·30		0·039	28·7	29·0

The agreement obtained by the two methods is striking, and though it does not serve as conclusive proof (since other v–t curves could contain the same area) the results obtained nevertheless provide strong support for the mechanism suggested.

Constancy of Migrational Velocity.—In previous papers, use has been made of the mean velocity of migration (V) of adsorbing molecules, termed the migrational velocity. This was derived from the expression $V = -(100M\mathrm{d}\gamma/\mathrm{d}c)/KTt$; practical conditions necessarily confine the range of concentration over which V can be measured within fairly narrow limits. At low concentrations, either equilibrium is not established in the jet, or the change in wave-length is too small to be accurately measurable. At high concentrations, equilibrium is established within the first wave, and t cannot be determined. Within these limits, dγ/dc has been found to be closely proportional to t, and thus V is constant. The results reported above now enable an estimate to be made of the probable constancy (or otherwise) of V over a concentration range wider than that available experimentally.

(a) *High concentrations.* The low values of dγ/dc which are obtained at the higher concentrations are not suitable for substitution into the expression for V without the introduction of an activity coefficient. Until such coefficients are available, there are no reasons for anticipating that V will deviate, at high concentrations, from the values already reported.

(b) *Low concentrations.* At greater dilution dγ/dc is almost constant. As concentration diminishes t increases, and thus from the expression for V above it appears that, if measurements were possible at greater dilution, V would be found to decrease eventually with decreasing concentration. This is supported by the curves in Figs. 1—4. If the applicability of equation 3 be extended to infinite dilution (and there is at present no objection to this procedure) then the maximum true velocity must eventually, at great dilution, fall below the value reported for the migrational velocity. In the systems studied so far, the concentrations at which this is likely to occur are beyond the range available experimentally. With amyl alcohol, this condition is not nearly approached experimentally since n is only slightly above 1. As chain length increases, the fall in peak velocity with decreasing concentration is more rapid, but the available concentration range is also diminished. If the chain length is increased until n approaches 2 (*i.e.*, above nonyl alcohol), the value of d given in the integral in equation (7) is independent of a, and thus of concentration. However, at such chain lengths the alcohols are approaching complete insolubility, and the surface film passes from a soluble to an insoluble one.

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