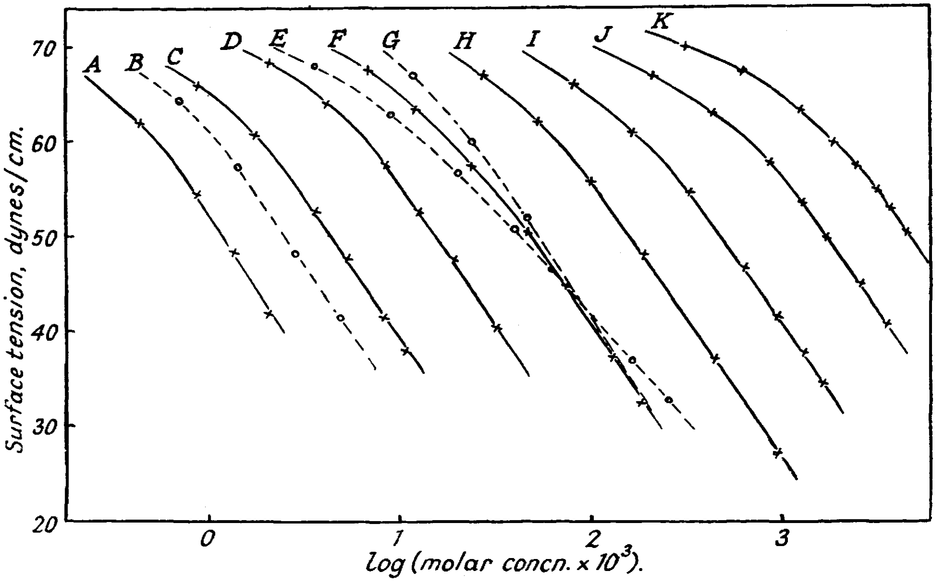
26. *The Properties of Freshly Formed Surfaces. Part IV. The Influence of Chain Length and Structure on the Static and the Dynamic Surface Tensions of Aqueous-alcoholic Solutions.*

By C. C. Addison.

The vibrating-jet technique already described has been applied to the measurement of both static and dynamic surface tensions of aqueous solutions of alcohols containing from one to eight carbon atoms. The static tensions at high concentration have been used to evaluate the Szyszkowski constants, and the work of adsorption has been deduced from the static tensions at great dilution. Dynamic surface tensions are recorded for aqueous solutions of *n*-amyl, *n*-hexyl, *n*-heptyl, and *n*-octyl alcohols over a range of surface ages, and the migrational velocity has been shown to increase with increasing chain length. Branching of the carbon chain (as in *iso*amyl or *tert.*-hexyl alcohol) or alteration in the position of the hydroxyl group (as in *sec.*-octyl alcohol) appears to reduce the migrational velocity, and possible reasons for this are discussed.

The mean velocity of migration of *sec.*-octyl alcohol molecules to the air–water surface reported in Part III (J., 1944, 477) is appreciably greater than that for *iso*amyl alcohol (Part II, *ibid.*, p. 252). Since the structure of the carbon chain differs in the two cases, the values cannot be taken as more than an indication of the influence of increasing chain length. The investigation has now been extended to the measurement of the rate at which equilibrium is established for a range of alcohols in aqueous solution, and the chain-length effect has been accurately determined. The influence of structure on migrational velocity is not yet clear, but the available evidence is now reviewed. Solubility considerations limited the present study to the 1—8 carbon atom range, and although static surface tensions are fairly well established for aqueous solutions of the lower members, fewer previous measurements have been made on the higher members. In some cases the relevant constants have not previously been determined, and the concentration ranges are limited. Preliminary work with the *n*-alcohols indicated that chain length was one of the major factors determining migrational velocity, and that the presence in the alcohol samples of small amounts of impurity of longer chain length seriously impaired the accuracy of measurement. The presence of such impurity is reflected in the static curves also, and the dynamic systems were not studied until it had been confirmed that the static tensions given by the actual alcohols to be used obeyed Traube's rule. Over most of the concentration and chain-length ranges studied, the change in wave-length set up in a vibrating jet by adsorption processes ceased before the end of the jet, and the wave-length reached a steady value corresponding to the equilibrium surface.

Fig. 1.



Alcohols.

A, n-*Octyl.* B, sec.-*Octyl.* C, n-*Heptyl.* D, n-*Hexyl.* E, tert.-*Hexyl* (1 : 1-*dimethylbutyl*). F, n-*Amyl.* G, iso*Amyl.* H, n-*Butyl.* I, n-*Propyl.* J, *Ethyl.* K, *Methyl.*

The technique already described (J., 1943, 535; *Phil. Mag.*, in the press) has been thus applied to the study of both static and dynamic tensions. The static values comply closely with the rules governing an homologous series, and the dynamic tensions obtained have therefore been accepted as a reliable basis on which to assess the influence of chain length and structure.

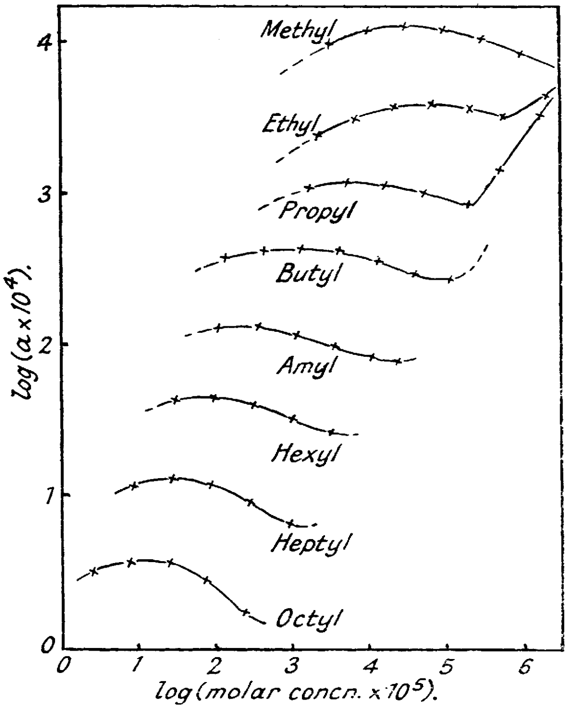
Static Surface Tensions.—The relation between equilibrium surface tension at 20°, and molar concentration for the *n*-alcohols from methyl to octyl is shown in Fig. 1. The tension values have been calculated from the wave-length by using the mathematical technique given in Part I (J., 1943, 535). The results have been checked by the drop-weight method, and in all cases agreement was within experimental error. With the most dilute solutions of the higher alcohols, the time required for establishment of equilibrium was greater than that available in the jet, and this section of the curve was determined by the drop-weight method alone. There was no detectable break where the method of measurement changed. A full review of the static surface-tension measurements which have been made by previous workers on aqueous alcohol solutions is outside the purpose and scope of the present paper. The values available are in many cases on isolated alcohols of unknown purity, but where concentration ranges overlap, the results in Fig. 1 are in good agreement with the most reliable of these (*e.g.*, Traube, *Annalen*, 1891, **265**, 27; Pederson, *Phil. Trans.*, 1907, *A*, **207**, 341; Bond and Puls, *Phil. Mag.*, 1937, **24**, 864). The agreement between values obtained by static methods such as drop weight and capillary rise, and the equilibrium values obtained from the vibrating jet, makes it clear that the condition of surface equilibrium holding when the surface is several minutes old is that which is established immediately adsorption is complete.

Below a tension of about 55 dynes/cm., the surface tension γ is a linear function of the logarithm of the concentration C for each *n*-alcohol, and this part of the curve is represented by the relation

$$\gamma = \alpha - \beta \log C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(where α and β are constants) proposed by Milner (*Phil. Mag.*, 1907, **23**, 102) for acetic acid; β is constant within the accuracy of measurement irrespective of chain length, and has the value 29·6. The curves for *iso*amyl, *sec.*-octyl, and *tert.*-hexyl (1 : 1-dimethylbutyl) alcohols are superimposed as broken lines in Fig. 1 for comparison. Each alcohol is less surface-active than the corresponding straight-chain alcohol. The β values for *iso*amyl and *sec.*-octyl alcohols differ only a little from the straight-chain primary alcohol values, but β for *tert.*-hexyl alcohol falls to about 22. When (1) is combined with the approximate form of the Gibbs equation, *viz.*, $\Gamma = -(C/\boldsymbol{R}T)\mathrm{d}\gamma/\mathrm{d}C$, then Γ_∞ approximately $= \beta/\boldsymbol{R}T$. The limiting amount of adsorbate which can be accommodated on the surface at these higher concentrations will diminish as complexity in the structure of the carbon chain increases the molecular cross-section, and thus the β values for these three alcohols are in general agreement with this theory.

FIG. 2.



Szyszkowski's empirical equation (*Z. physikal. Chem.*, 1908, **64**, 385)

$$\gamma/\gamma_0 = 1 - B \log (C/a + 1) \quad . \quad . \quad (2)$$

can be written in the form

$$\gamma = \gamma_0(1 + B \log a) - \gamma_0 B \log C \quad . \quad (3)$$

for the higher concentrations over which Milner's equation holds. Hence $\beta = \gamma_0 B$, and $B = 0{\cdot}407$. This agrees closely with the value 0·411 found by Szyszkowski for the fatty acids, and is consistent with the slightly larger area occupied by the alcohol molecule in a condensed insoluble film at zero compression, *i.e.*, 21·6 sq. A. per molecule compared with 20·5 for the fatty acids (Adam, " Physics and Chemistry of Surfaces," Oxford Univ. Press, 2nd Ed., p. 50). The value of *a* in (2) varies with concentration, and is only approximately a constant for a given alcohol. Since the surface tensions of the pure alcohols themselves are similar, the values of *a* must approach a standard figure irrespective of chain length as the percentage concentration approaches 100. After a slight rise at great dilution, *a* falls as the concentration increases, and this fall would be exaggerated by the introduction of an activity coefficient. The values of *a* have been determined for each *n*-alcohol at 20° over the available concentration range, and are given in Fig. 2. For chains of more than four carbon atoms, the final rapid rise in *a* is not obtained because of the solubility barrier, but a uniform system clearly holds throughout. The peak values of *a* which occur at low concentration have been used as a basis on which to compare the alcohols, and are listed in Table I, col. 2, together with the values reported by Szyszkowski for fatty acids of equal chain length (col. 4). The short-chain alcohols are a little more surface-active than the acids of equal chain length because of the enhanced water solubility of the carboxyl group, but increase in chain length will minimise this effect. Thus it is reasonable that the *a* values for the shorter-chain alcohols should be lower than those for the corresponding acids, but approach the acid value at greater chain length. This is found to be the case; and the ratios of the values of *a* for alcohols differing by one carbon atom are a little below that for the acids. Agreement with Traube's rule has been confirmed by measuring the con-

TABLE I.

C atoms in *n*-alcohol molecule.	*a*.	a_n/a_{n-1}.	*a* for acid molecule (Szyszkowski).	a_n/a_{n-1} (Szyszkowski).	Molar concn. at 55 dynes/cm.	$C_n\ C_{n-1}$.
1	1·290	—	—	—	3·16	—
2	0·400	3·24	—	—	1·05	3·02
3	0·126	3·16	0·165	—	0·316	3·31
4	0·0407	3·09	0·051	3·24	0·100	3·16
5	0·0135	3·02	0·015	3·40	0·0309	3·24
6	0·00447	3·02	0·0043	3·49	0·0100	3·09
7	0·00135	3·31	—	—	0·00295	3·39
8	0·000407	3·31	—	—	0·000832	3·39
		Mean 3·16		Mean 3·38		Mean 3·23

centration of each alcohol required to lower the surface tension to 55 dynes/cm. These values are quoted in col. 6, and the ratios for alcohols differing by one carbon atom (col. 7) are in quite close agreement with the *a* ratios.

The results in Table I confirm that the increase in surface activity with chain length is regular for the alcohols used at the higher concentrations. However, the dynamic studies must frequently be restricted to dilute solutions, and this regularity has been shown to extend to infinite dilution by determining the work of adsorption for each alcohol. Langmuir (*J. Amer. Chem. Soc.*, **1917**, **39**, 1883 *et seq.*) has shown that the work done in transferring 1 g.-mol. of the solute from the bulk of the liquid to the surface increases for each additional carbon atom in accord with the equation

$$\lambda_n - \lambda_{n-1} = RT \log (\Gamma/\tau C)_n/(\Gamma/\tau C)_{n-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where τ is the thickness of the surface layer. The mean value of C_n/C_{n-1} given in Table I, when substituted into this equation, gives $\lambda_n - \lambda_{n-1} = 687$ cals. per g.-mol.

The work of adsorption λ has been calculated from the Langmuir equation

$$\lambda = RT \log \Gamma/\tau C \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

the thickness of the surface layer being assumed to be 6 A. throughout. λ is a constant property of any given adsorbate so long as Γ is proportional to C, which is the case in very dilute solutions only. The Γ–C curve was therefore determined separately for each alcohol, and the value of Γ/C obtained from the slope of the tangent to this curve at the origin. The values of Γ/C, and λ deduced therefrom, are given in Table II. The values of λ were substituted into the equation

$$\lambda = \lambda_0 + \kappa n \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

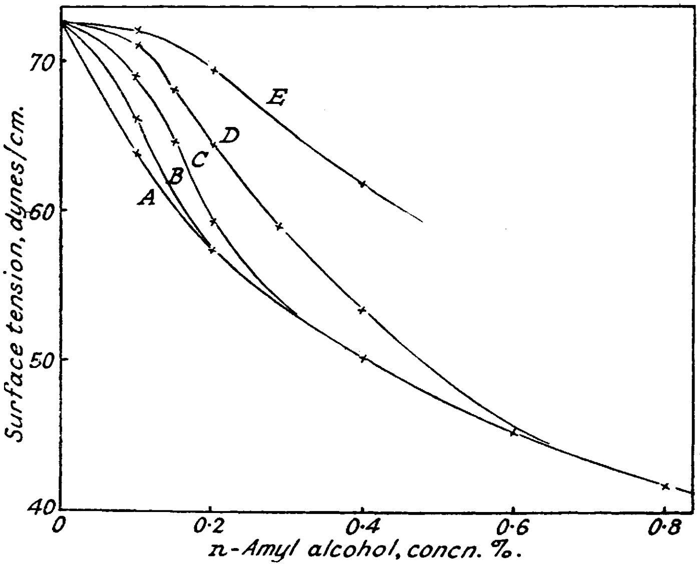
where n is the number of carbon atoms in the molecule and κ is a constant. It has been found that λ_0 varies appreciably if the value of $\lambda_n - \lambda_{n-1}$ obtained from equation (4), *i.e.*, 687 cals./g.-mol., is substituted for κ in equation (6). Langmuir (*loc. cit.*) found for a number of series that λ_0 was reasonably constant if $\kappa = 625$, and this value has been used in determining λ_0 (Table II, col. 4). The small increase in λ_0 with chain length is not significant in view of the calculation errors involved. The mean value is 597 cals./g.-mol., in good agreement with Langmuir's primary alcohol value of 575.

TABLE II.

C atoms in *n*-alcohol molecule.	Γ/c, cm. × 10^6.	λ, cals./g.-mol.	λ_0, cals./g.-mol.	C atoms in *n*-alcohol molecule.	Γ/c, cm. × 10^6.	λ, cals./g.-mol.	λ_0. cals./g.-mol.
1	0·45	1180	555	5	36·0	3750	625
2	1·32	1810	560	6	105	4380	630
3	4·00	2460	585	7	300	4990	616
4	11·20	3070	570	8	900	5630	630

FIG. 3.

n-Amyl alcohol.



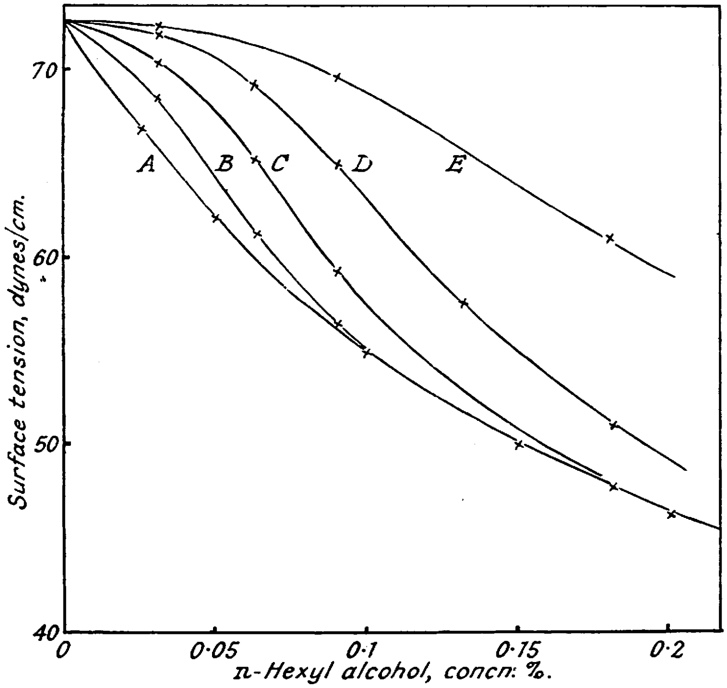
Surface age (*secs.*): A, *Equilibrium curve*. B, 0·016. C, 0·012. D, 0·008. E, 0·005.

Dynamic Surface Tensions.—An attempt has been made to determine the migrational velocity of each alcohol by measurement of the vibrating jet formed from the aqueous solution. The plate orifice described elsewhere (Addison, *Phil. Mag.*, in press) was used, with a mean orifice radius of 0·055 cm. Variation in wave-length due to turbulent flow was thus restricted to the first wave. The head of pressure on the orifice was adjusted, to a degree depending on the density of the test liquid, in order to maintain the flow rate constant throughout at 1·99 ml./sec.

With methyl, ethyl, *n*-propyl, and *n*-butyl alcohols, no variation in wave-length after the first wave was apparent at any concentration; the measurement of dynamic tensions for these alcohols in aqueous solution is therefore beyond the scope of the vibrating-jet method. The migrational velocity is a direct ratio between the distance travelled by the adsorbate molecules and the time taken, and if the concentration of these first members of the series is decreased until the time taken is large enough to be measurable in the jet, the equilibrium surface tension of the solution is so near to the pure water value that the variation in wave-length in

FIG. 4.

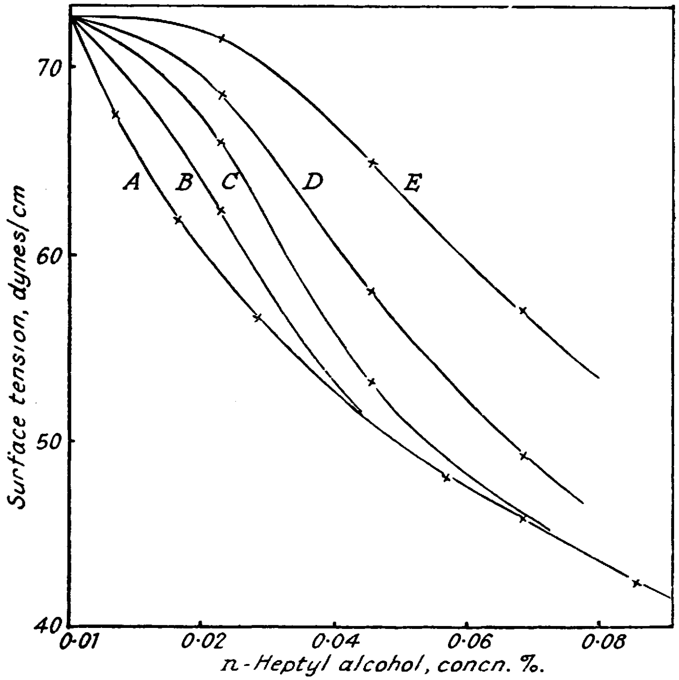
n-*Hexyl alcohol.*



Surface age (*secs.*) *:* A, *Equilibrium curve.* B, 0·06. C, 0·02. D, 0·01. E, 0·005.

FIG. 5.

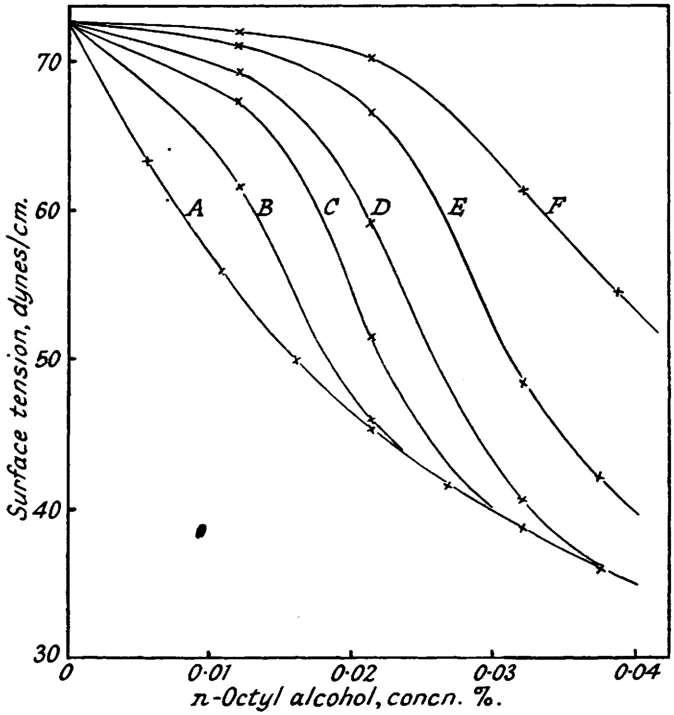
n-*Heptyl alcohol.*



Surface age (*secs.*) *:* A, *Equilibrium curve.* B, 0·05. C, 0·03. D, 0·02. E, 0·01.

the jet is within the experimental error of measurement. As the chain length is increased, the range of surface tension available with the dilute solutions is also increased, so that the wave-length varies along the jet to a measurable degree. This is first apparent with amyl alcohol, and change in wave-length is progressively more pronounced as chain length increases. Surface tension–concentration curves at 20° for *n*-amyl, -hexyl, -heptyl, and -octyl alcohols at various surface ages are recorded in Figs. 3—6. In contrast to the behaviour of the methyl–butyl alcohols, the minimum concentration of *n*-octyl alcohol required to give an accurately measurable change in wave-length is so small (and thus the distance from which adsorbate is drawn is so large) that equilibrium is not established before break-up of the jet.

FIG. 6.
n-*Octyl alcohol.*



Surface age (*secs.*) : A, *Equilibrium curve.* B, 0·10. C, 0·06. D, 0·04. E, 0·02. F, 0·01.

Migrational Velocities.—The measurements recorded in Figs. 3—6 have been used to calculate the mean velocities of migration to the surface (V) by using the relation (Part II)

$$V = -100M(d\gamma/dC)/KTt$$

Relevant figures are listed in Table III, and the *tert.*-hexyl results are included for comparison with *n*-hexyl alcohol.

TABLE III.

Alcohol.	C, %.	$-d\gamma/dC$.	$\Gamma \times 10^8$, g./cm.^{2}.	$d \times 10^5$, cm.	t, secs.	$V \times 10^4$, cm./sec.
n-Amyl	0·10	65	2·35	2·35	0·023	10·2
	0·20	45	3·25	1·62	0·016	10·1
	0·40	32	4·62	1·15	0·012	9·6
n-Hexyl	0·03	206	2·59	8·63	0·055	15·7
	0·06	154	3·86	6·43	0·041	15·7
	0·09	120	4·52	5·02	0·034	15·0
	0·12	100	5·01	4·17	0·026	15·9
	0·18	80	6·03	3·35	0·023	14·6
n-Heptyl	0·02	520	4·95	24·7	0·074	33·5
	0·04	340	6·47	16·2	0·048	32·8
	0·06	240	6·85	11·4	0·037	31·1
	0·08	188	7·16	8·95	0·029	30·6
n-Octyl	0·0224	800	9·55	42·7	0·068	62·8
	0·030	650	10·40	34·7	0·052	66·7
tert.-Hexyl	0·06	98	2·46	4·10	0·035	11·6
	0·09	75	2·82	3·14	0·028	11·2
	0·14	54	3·16	2·26	0·019	12·0

The mean value of V for each alcohol is plotted against the chain length in Fig. 7. The failure of the practical technique sets the lower limit for the *n*-alcohols at five carbon atoms. Above eight carbon atoms, the solubility is so small that, although an appreciable range of surface tension is available with saturated solutions of nonyl and decyl alcohols, equilibrium is not established, even with saturated solutions, before the end of the jet. These systems can be used for the determination of true rates of migration during a part of the total time required for equilibration (see Part III), but a method capable of measuring a wider range of surface ages is needed before the time to equilibrium, and thus the migrational velocity, can be determined. However, from the smooth curve drawn through the available *n*-alcohol values it is clear that $\mathrm{d}V/\mathrm{d}n$ increases rapidly with increasing chain length. The curve can be extrapolated to give migrational velocities of neighbouring alcohols with fair accuracy.

It is of interest that, although the migrational velocity increases with chain length, the time t taken to establish equilibrium under the available experimental conditions also increases with chain length, since the solubility diminishes at a rate exceeding the rate of increase of V. The approximate times are given below for concentrations equal to one-tenth of the solubility at 20°.

n-Alcohol	Amyl.	Hexyl.	Heptyl.	Octyl.
t (sec.)	0·015	0·035	0·07	>0·1

Influence of Chain Structure.—The values of V for *iso*amyl, *sec.*-octyl, and *tert.*-hexyl alcohols are included in Fig. 7, from which it is clear that the structure of a molecule has a definite effect on its migrational velocity.

FIG. 7.

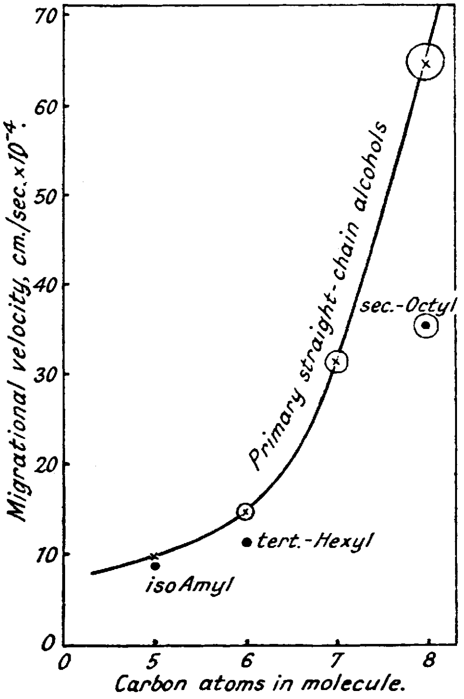
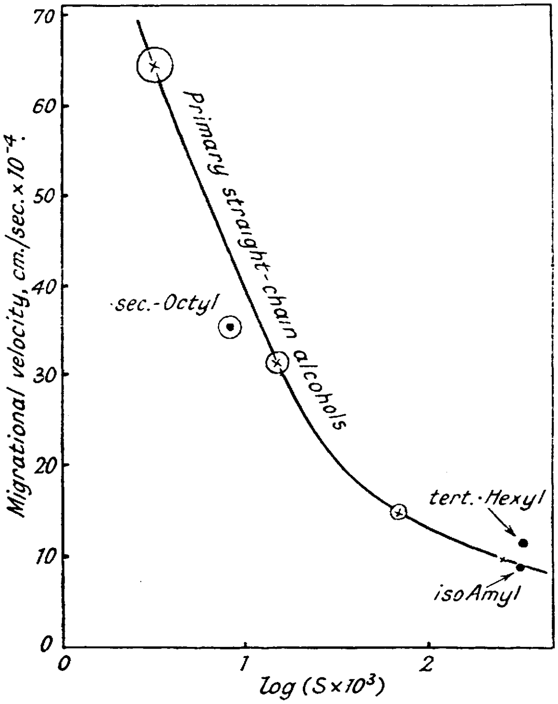


FIG. 8.



The *iso*amyl value falls below that for *n*-amyl alcohol by little more than the experimental error, but both *tert.*-hexyl and *sec.*-octyl alcohols are well below the value for the primary straight-chain alcohol. It is proposed to undertake a more extended investigation into the true and migrational velocity of complex molecules, to obtain direct information on the orientation of the carbon chains during their journey to the surface. The force propelling an amphipathic molecule to the water surface is the resultant of (*a*) the attraction between the medium and the hydrophilic group, and (*b*) the repulsion between the medium and the carbon chain. Thermal agitation will prevent the molecule maintaining any fixed direction during its migration, but these forces may orientate a straight-chain molecule so that the mean direction of the carbon chain is towards the surface. If the surface forces are entirely without orientating influence, the adsorbate molecule could be regarded as occupying, under thermal agitation, a sphere having diameter equal to the length of the carbon chain. The viscous resistance to movement would then increase appreciably with chain length. However, if the molecule advanced in a mean direction perpendicular to the surface, the viscous resistance to movement would depend on the cross-sectional area of the carbon chain, which is independent of chain length, and only the comparatively negligible frictional resistance would vary with chain length. The rise in migrational velocity with chain length found experimentally does not in itself provide proof of orientation, for if the solubility of the alcohols in water be taken as some measure of the repulsive forces operating on the carbon chain, it is probable that the forces propelling the carbon chain increase at a much greater rate than the viscous resistance to unorientated movement. The branching of the carbon chain would probably have little effect in the absence of orientation, but might be expected to reduce appreciably the velocity of an orientated molecule. Also, the orientating influence would be diminished as a result of the transfer of the hydrophilic group from the end to some other position in the chain. A knowledge of the actual forces operating on the alcohol molecule is therefore necessary to determine where between the two limits the actual orientation lies. This force is being determined from the acceleration of the alcohol molecules which takes place when the free surface energy first operates (see Part III) and this will be the subject of further communications.

The structure of each of the three alcohols is such that the centres of hydrophobic and hydrophilic attraction are closer than in the straight-chain alcohol. The solubilities in water are therefore greater, and the forces promoting migration are less, than for the straight-chain alcohol of equal carbon content, and it seemed possible that this effect alone might account for the smaller velocities. If such were the case, all the alcohols should lie on the same velocity–solubility curve. The information available in the literature on the solubilities of the alcohols above amyl is meagre, and the solubilities have therefore been determined on the actual samples used in the tension measurements. Because of the low order of solubility, it was not possible to determine visually whether a drop of the alcohol added to a large volume of water dissolved during stirring, or remained attached to the walls of the vessel as a separate phase. The surface tension of the solutions was therefore utilised as follows.

Sufficient excess of the alcohol was added to 100 ml. of water in a stoppered flask to form a separate lens on the surface. The mixture was then swirled gently (too vigorous agitation gave a semi-permanent emulsion which upset the tension readings). After settling, a small sample of the clear aqueous solution was withdrawn into a drop weight pipette, and the surface tension determined. The swirling was continued until a steady tension was obtained. The tension–concentration curve was known, and required only slight extrapolation (the logarithmic scale was very convenient) to the concentration corresponding to the steady saturation tension. It should be stated here that, before static or dynamic tension measurements were commenced on any of the alcohols above amyl, the surface tension at saturation was determined. The concentrated stock solution was then prepared by adding a weighed quantity of the alcohol to a known volume of water, and stirring until a steady tension was obtained. Provided that this was higher than the saturation value, the absence of undissolved alcohol was confirmed.

Alcohol.	γ of saturated solution, dynes/cm.	Solubility at 20°, % w/w.	Alcohol.	γ of saturated solution, dynes/cm.	Solubility at 20°, % w/w.
n-Amyl	28·2	2·21	*iso*Amyl	26·8	2·66
n-Hexyl	29·9	0·706	*tert.*-Hexyl	30·0	3·23
n-Heptyl	31·6	0·172	*sec.*-Octyl	34·1	0·106
n-Octyl	33·4	0·042			

The solubilities of the seven alcohols on which dynamic measurements have been made, determined by the above method, are listed above. For the *n*-alcohols there is an almost linear relation between chain length and the surface tension of the saturated solution. The relation between solubility and migrational velocity is plotted in Fig. 8, where S = solubility in g.-mol./l. *iso*Amyl alcohol can be regarded as lying almost on the smooth curve given by the *n*-alcohols, but both *sec.*-octyl and *tert.*-hexyl alcohols still lie well away from the curve. Therefore when the structure of an alcohol of given carbon content is altered, other factors in addition to the solubility factor operate to alter the migrational velocity. If the carbon chains are orientated towards the surface during adsorption, complexity of structure and the position of the hydrophilic group will also influence the rate of adsorption, and may explain these results. These possibilities are being studied further.

EXPERIMENTAL.

Limits of Experimental Error.—Where surface tensions have been measured by the drop-weight method, high accuracy (to at least 0·1 dyne/cm.) is achieved. Where the vibrating jet and the simplified mathematical treatment given in Part I have been used, the results are considered to be accurate to ± 0·25 dyne. Since the tensions measured have been of the order of 40—70 dynes, the error does not exceed ± 0·6%, and is not significant in Figs. 1—6. The surface ages recorded in Figs. 3—6 are obtained by direct linear measurement of the jet, with an accuracy of 0·01 cm. The possible error is thus of the order of ± 0·5% at the beginning of the jet but becomes negligible at higher surface ages. The solubilities reported above are based on drop-weight measurements of surface tension, and are therefore regarded as being of the same high order of accuracy.

The experimental error becomes more significant in considering the migrational velocities, particularly where small differences in velocity are compared. Since V is a function of $(d\gamma/dC)/t$, the percentage error in V may be as high as the sum of the maximum errors in $d\gamma/dC$ and t. $d\gamma/dC$ is obtained from the equilibrium γ–C curve, which can be obtained accurately from drop-weight measurement. Errors in reading the slope of the tangent at any particular concentration can be minimised by smoothing the $d\gamma/dC$–C curve, and it is considered that the error in the reported values of $d\gamma/dC$ nowhere exceeds 1%. The greatest source of error lies in the measurement of t, since the rate of change of tension falls rapidly as surface equilibrium is approached. Again, measurement is least accurate with the weaker solutions, *i.e.*, at greater surface ages, and the possible error increases up to about 0·0025 sec. at surface ages of 0·08—0·10 sec. Thus the maximum experimental error in the determination of V from a single measurement may rise to ± 3%, although this error may be reduced by increasing the number of determinations at a given concentration. The results in Table III (and Parts II and III) indicate that values of V for a given alcohol over a range of concentrations may occasionally vary up to ± 5%. It is possible that some physical cause (so far undetermined) may be partly responsible for this wider variation. However, for present purposes the whole of this variation has been assumed to be due to experimental error, and is the basis on which the experimental error in Figs. 7 and 8 has been assessed. The limits of error are indicated for convenience by the size of the points (or by circles drawn round the points where the error is sufficiently large), without implying any error in the horizontal axis.

Purity of Alcohols.—Neither density nor refractive index alone was reliable as a measure of purity. Boiling point provides a more sensitive index, and the purity of each alcohol was assessed by measurement of all three physical properties. The refractive index was determined by an Abbé refractometer, sodium light being used. In some cases the pure alcohols supplied required no further purification; impure alcohols were purified by fractional distillation. The middle fraction from a normal distillation was redistilled through a fractionating column, and the appropriate fraction collected. In some cases this fraction, although of correct b. p., gave a density and/or refractive index differing appreciably from published values. Azeotrope formation was regarded as probably reponsible, and a number of samples were rejected for this reason. Samples were not used for the adsorption measurements until all three properties were in suitable agreement with published values; measured values on the samples used are given below.

Alcohol.	$d_{4^\circ}^{20^\circ}$.	B. p.	$n_D^{20^\circ}$.	Alcohol.	$d_{4^\circ}^{20^\circ}$.	B. p.	$n_D^{20^\circ}$.
Methyl	0·7924	65·0°	1·3294	*n*-Heptyl	0·8220	176·5°	1·4241
Ethyl	0·7898	78·5	1·3610	*n*-Octyl	0·8244	194·5	1·4291
n-Propyl	0·8040	98·0	1·3856	*iso*Amyl	0·8127	131·5	1·4075
n-Butyl	0·8101	118·0	1·3993	*tert.*-Hexyl	0·8048	122·0	1·4120
n-Amyl	0·8154	138·0	1·4102	*sec.*-Octyl	0·8200	178·0	1·4255
n-Hexyl	0·8194	157·5	1·4182				

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