232. *The Properties of Freshly Formed Surfaces. Part XXI.* The Influence of Chain Length and Structure on the Surface Potentials of Aqueous Solutions of Alcohols.*

By C. C. ADDISON and D. LITHERLAND.

Orientation and disorientation surface potentials have been measured for aqueous solutions of ethyl, *n*-propyl, *n*-butyl, *n*-amyl, and *n*-hexyl alcohols. When the equilibrium (orientation) potentials ΔV_0 are plotted against surface excess Γ for the C_2—C_5 alcohols, the points lie on a common line. The constant value of the measured dipole moment (μ = 223 mD) indicates that the tilt of the dipole to the surface is independent of chain length over this range. Hexyl and higher alcohols show some deviation; possible reasons for this are considered. The disorientation produced by adsorption ($\Delta V_d - \Delta V_0$) is studied as a function of chain length and surface excess. For any given surface excess, disorientation increases with chain length up to C_5, after which the effect diminishes. The results are interpreted on the basis of the temporary displacement of the dipole from the orientation position, and the disorientation of associated water molecules in the surface. The degree of disorientation produced by further adsorption to a surface carrying an equilibrium film has been studied. For dilute solutions of the shorter-chain alcohols (*e.g.*, *n*-propyl), the disorientation is no more than that equivalent to the increment in Γ. At the higher Γ values given by longer-chain alcohols the disorientation is diminished by mutual interference in the film. The curiously slow rate of orientation of a disoriented film is also discussed.

The influence of chain structure on surface potential is considered in the light of results for *iso*butyl, *iso*amyl, *tert.*-butyl, and *tert.*-amyl alcohols. *tert.*-Butyl alcohol (μ = 460 mD) is unique in that its symmetrical structure renders its vertical orientation to the surface highly probable. On this assumption, the angle of tilt of the dipole to the vertical (θ) is calculated, the value to be attributed to the dielectric constant ε in the application of the Helmholtz equation $\Delta V = 4\pi n\mu$ is deduced, and this value of ε employed in the calculation of θ for the straight-chain alcohols.

Surface potential and tension measurements for ethylene glycol and for butane-1 : 3-diol are presented for comparison with the monohydric alcohols. Each compound gives the same value (*ca.* 850 mD) for the total dipole moment.

THE measurements now described were carried out to determine how far the general relations between surface potential and orientation already outlined are modified by

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* Part XX, preceding paper.

variation in the length and structure of the carbon chain. Frumkin (*Z. physikal. Chem.*, 1924, **111**, 195) and Pankhurst (*Proc. Roy. Soc.*, 1942, *A*, **179**, 393) have determined equilibrium surface potentials for a few alcohols, but the available evidence is insufficient for a comprehensive study. Both orientation and disorientation potentials have therefore been measured for aqueous solutions of the ethyl–hexyl series of straight-chain alcohols at 16°, and the results are collected in Table 1. In each case the concentration range employed is chosen so as to lie wholly, or mainly, below the concentration at which mutual interference of adsorbed molecules will arise, so that the effects observed may be related directly with the structure of the solute molecule concerned. The relevant concentrations are given below:

Alcohol	Ethyl	*n*-Propyl	*n*-Butyl	*n*-Amyl	*n*-Hexyl	*n*-Decyl
Concn., %	(mono-layer)	(mono-layer)	2·0	0·20	0·043	0·00015

These concentrations are calculated on the assumption that the adsorbed molecules lie flat in the surface, and form the diameters of hexagonally close-packed circles. With ethyl and propyl alcohol, the area of such a circle is near the cross-sectional area of the head-group, so that little mutual interference occurs at any concentration. At the highest concentrations used (1·45 and 1·20%, respectively) the Γ values are 1·0 and $2 \cdot 2 \times 10^{-8}$ g./cm.^{2}, compared with 3·5 and $4 \cdot 6 \times 10^{-8}$ g./cm.^{2} for the monolayers.

TABLE 1.

Ethyl alcohol

C, %	ΔV_0	ΔV_0 †	ΔV_d
0·385	40	—	60
0·475	47	50	—
0·755	68	—	88
0·792	70	75·5	—
1·105	88	—	110
1·450	100	—	132

n-*Propyl alcohol*

C, %	ΔV_0	ΔV_0 †	ΔV_d
0·028	5	—	28
0·128	34	—	104
0·155	50	—	110
0·240	74	54	140
0·300	92	—	—
0·360	—	—	168
0·470	131	—	170
0·582	—	—	190
0·680	152	—	—
0·885	160	—	214
0·975	176	—	—
1·20	182	187·5	—

n-*Butyl alcohol*

C, %	ΔV_0	ΔV_0 ‡	ΔV_d
0·025	15	—	124
0·060	33	—	149
0·100	60	43	178
0·120	68	—	182
0·240	130	—	226
0·300	144	129	234
0·358	154	—	250
0·470	164	—	252
0·500	171	165	260
0·580	184	—	—
0·690	180	—	—
0·920	200	—	—
1·000	204	209	—

n-*Amyl alcohol*

C, %	ΔV_0	ΔV_0 *	ΔV_d
0·01	20	—	112
0·022	45	—	—
0·030	—	—	203
0·040	80	—	—
0·050	96	85	230
0·061	112	—	246
0·089	144	—	256
0·100	151	113	268
0·118	160	—	—
0·145	174	—	—

n-*Hexyl alcohol*

C, %	ΔV_0	ΔV_0 *	ΔV_d
0·0040	48	—	121
0·0080	62	—	145
0·0195	98	—	210
0·0250	124	—	—
0·0300	127	63	246
0·0375	140	—	—
0·0570	164	—	—
0·0740	175	—	—

* Pankhurst's results (*loc. cit.*) † Frumkin's results (*loc. cit.*).
‡ Adam, Askew, and Pankhurst's results (*Proc. Roy. Soc.*, 1939, *A*, **178**, 485).

Frumkin obtained the quoted values of ΔV_0 for ethyl and *n*-propyl alcohol by using the method of flowing junctions, and Table 1 shows that the results obtained by these two widely differing techniques are in reasonable agreement. Adam, Askew, and Pankhurst (*loc. cit.*) used a radioactive electrode technique similar to that employed in the present work. Except for the very dilute solutions, the ΔV_0 values for *n*-butyl alcohol are in good agreement, but the present values for *n*-amyl and for *n*-hexyl alcohol solutions are greater than the values given by Pankhurst (*loc. cit.*) for these solutions.

Equilibrium (*Orientation*) *Surface Potentials.*—When the equilibrium surface potential values are plotted against the logarithm of the molar concentration, a series of nearly parallel lines is obtained, indicating that Traube's rule is applicable to the surface potentials of this homologous series. The mean molar concentration ratio for each increment in chain length (between C_2 and C_6) is given below for a range of ΔV_0 values :

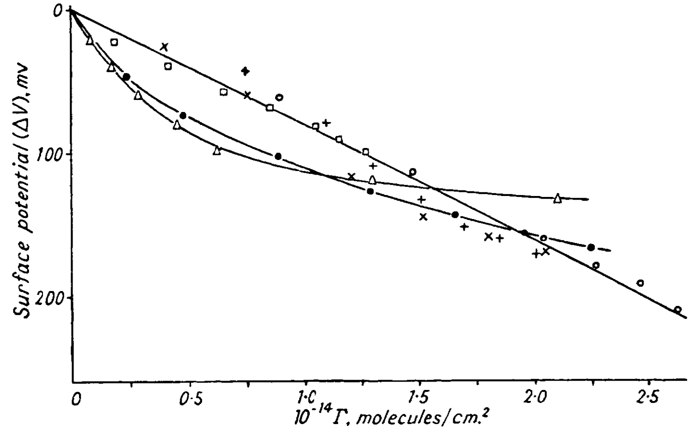
ΔV_0	40	60	80	100
C_{n+1}/C_n	3·81	3·73	3·60	3·65

The concentration–potential curve for decyl alcohol reported in Part XVIII (*loc. cit.*) lies close to the position calculated from the above ratios. Frumkin (*loc. cit.*) obtained a mean value for C_{n+1}/C_n of 3·65 for the straight-chain fatty acids. The mean value of C_{n+1}/C_n determined from the surface tensions of these alcohols (Part IV, *J.*, 1945, 98) is 3·23.

The values of ΔV_0 given in Table 1, together with the decyl alcohol values, are plotted in Fig. 1 against the corresponding molecular surface excess; the latter values were determined by applying Gibbs's equation to the surface-tension data given in Part IV (*loc. cit.*). The points for all alcohols up to C_5 lie close to a straight line passing through the origin. Substitution of the slope of this line in Helmholtz's equation $\Delta V/n = 4\pi\mu$ (where $n = \Gamma$ when the latter is expressed as molecules/cm.^{2}) gives a value of 223 mD for the dipole moment μ, which agrees closely with the value of about 230 mD found from insoluble monolayers of the higher homologues (Adam, " The Physics and Chemistry of Surfaces," Oxford Univ. Press, 1941, 3rd edtn., p. 136) and from other soluble alcohols

FIG. 1.

□ □ Ethyl alcohol.
× × *n*-Propyl alcohol.
○ ○ *n*-Butyl alcohol.
+ + *n*-Amyl alcohol.
● ● *n*-Hexyl alcohol.
△ △ *n*-Decyl alcohol.

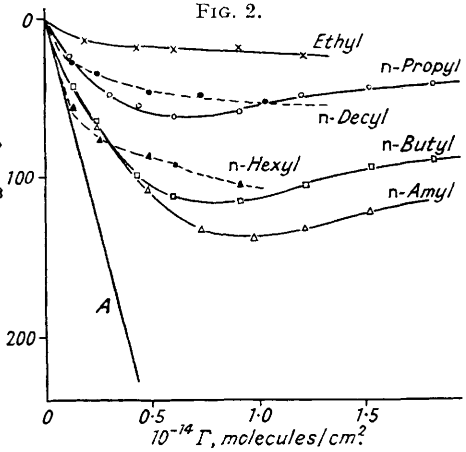


(Sawai, *Trans. Faraday Soc.*, 1935, **31**, 765). For these shorter-chain alcohols in the very dilute concentrations employed, the orientation of the polar group with respect to the liquid surface is little influenced by variation in chain length. The points for hexyl alcohol lie on a curve which deviates somewhat from the straight line. Similar deviations were observed by Posner and Alexander (*Trans. Faraday Soc.*, 1949, **45**, 651) for *sec.*-octyl alcohol; the best straight line through the available experimental points gave 226 mD. The decyl alcohol curve (Fig. 1) shows that this deviation increases with increasing chain length. Posner and Alexander (*loc. cit.*) determined Γ values from Gibbs's equation, and also from the equation of state $\pi(A - A_0) = xkT$ (where π is the surface pressure, A_0 is constant for a given homologous series, and x is specific to the solute) and obtained points lying above the standard line at the lower concentrations. It is presumably for this reason that these authors treated the deviations observed at lower concentrations as dependent upon the method used in calculating Γ rather than as representing a true molecular property. However, the additional evidence obtained in this work justifies a reconsideration of these deviations. Previous parts in this series (*e.g.*, Part XIV, *J.*, 1949, 3406) have shown that the behaviour of decyl alcohol follows closely that predicted by calculations based upon the applicability of Gibbs's equation. For this reason, the values derived from Gibbs's equation are preferred to those calculated from the equation of state, and the deviations observed at chain lengths of C_6 and above are considered to represent a real surface property of the molecules concerned. The initial slopes of the ΔV–Γ curves for hexyl and decyl alcohols give μ values of about 560 and 640 mD, respectively. If the addition of carbon atoms beyond C_5 involved no more than the lengthening of a straight chain, there is no apparent reason why the orientation of the dipole with respect to the surface should change, since the chains are regarded as lying flat on the surface in these very low concentrations. The reason is perhaps to be found in the variation in the shape assumed by the carbon chain with increasing chain length. From a study of the physical properties of the hydrocarbons, Ward (*Trans. Faraday Soc.*, 1946, **42**, 399) noted that above C_8 the addition of each CH_2 group causes a constant increase in the molecular volume and surface area; below C_8 the same regularity does not occur. It is clear from Fig. 1 that at about C_6 some change in the equilibrium shape or position of the adsorbed molecule occurs which is sufficient to change the surface orientation of the polar group.

As concentration increases, the slope of the curves for hexyl and decyl alcohol (and thus μ) decreases. The concentration values given on p. 1160 are equivalent to Γ values of $1{\cdot}6 \times 10^{14}$ and $0{\cdot}65 \times 10^{14}$ molecules/cm.^{2} for hexyl and decyl alcohols, respectively, and in consequence mutual interference occurs within the Γ range studied. This must necessarily result in a mean position of orientation differing from that taken up by an independent molecule, and a consequent alteration in the orientation of the dipole.

Disorientation Surface Potentials.—Disorientation potentials (ΔV_d) are listed in Table 1; the effect of disorientation of the surface film is considerable, and persists down to ethyl alcohol. Even with methyl alcohol a slight disorientation effect was observed, of the order of a few mv. Values of $\Delta V_d - \Delta V_0$, which represent directly the effect of disorientation, are plotted against Γ in Fig. 2. The curves show two important features: (*a*) The values of $\Delta V_d - \Delta V_0$ increase with increasing chain length up to C_5; thereafter, the disorientation effect diminishes, and the values of $\Delta V_d - \Delta V_0$ diminish with increasing chain length. (*b*) For any given alcohol, the $\Delta V_d - \Delta V_0$ values rapidly level off with increasing Γ.

FIG. 2.



Concerning (*a*), dipole-moment values calculated from surface-potential measurements are rarely greater than a quarter of the values for molecules containing the same end groups measured by the ordinary methods (Adam, *op. cit.*, p. 38; Frumkin and Williams, *Proc. Nat. Acad. Sci.*, 1929, **15**, 400). For the aliphatic alcohols, μ is about 1700 mD. The low measured values of μ arise partly from the fact that in the application of Helmholtz's equation the dielectric constant cannot be considered as unity (Rideal and Bosworth, *Physica*, 1937, **4**, 925), and partly from the orientation of the adsorbed dipoles at angles of other than 90° to the liquid surface. If we ignore the dielectric considerations, the necessary values of $\Delta V_d - \Delta V_0$ which would be required to augment the 223 mD value to the full value of 1700 mD, would lie along the line *A* shown in Fig. 2. Such values are not obtained experimentally, although as chain length increases up to C_6, the curves approach line *A* asymptotically at very low concentrations. The results may be interpreted satisfactorily if we consider that the disorientation of adsorbed molecules also involves simultaneous disorientation of water molecules in the surface of the solution. It is reasonable to suppose that, for a given surface excess, the longer the chain length of a molecule arriving at the surface the greater is the number of water molecules undergoing temporary (kinetic) disorientation; each disoriented water molecule will make its contribution to the measured value of $\Delta V_d - \Delta V_0$. The combined effect of tilt and water disorientation appears to reach a maximum at about C_5. Although the disorientation of water molecules continues to increase with chain length, it becomes more difficult to alter the angle of tilt of the longer chains; the latter factor outweighs the former beyond C_5, so that $\Delta V_d - \Delta V_0$ then decreases with increasing chain length.

Feature (*b*) (above) is common to all curves. When mutual interference of adsorbed molecules occurs (which is the case over the Γ range studied), the values of $\Delta V_d - \Delta V_0$ should be proportional to Γ, whereas the experimental curves show departure from such linearity. Under these conditions this cannot be the result of change in Γ *per se*, but results rather from change in the velocity of arrival of adsorbing alcohol molecules at the surface, which is known (Part V, *J.*, 1945, 354) to diminish with increasing bulk concentration. It is feasible that the variation in angle of tilt from the equilibrium angle, and also the extent to which the water molecules in the surface undergo temporary kinetic disorientation, should both become less pronounced when the adsorbing molecules arrive more slowly at the surface. This change in adsorbing velocity provides a suitable explanation for the departure of the $(\Delta V_d - \Delta V_0)$–$\Gamma$ curves from linearity, and also for the minima which occur in some of the curves.

Adsorption to an Equilibrium Film.—When Γ in the equilibrium film is sufficiently large for mutual interference of adsorbed molecules to occur, it is to be expected that the arrival of additional adsorbate will give rise to a potential representing disorientation of the newly arrived molecules ($\Delta\Gamma$), together with the partial disorientation of some, or all, of the molecules already adsorbed and at equilibrium orientation. Even at Γ values a little below that required for mutual interference, newly arriving molecules are likely to strike many of those already adsorbed, again giving rise to a disorientation potential greater than that equivalent to $\Delta\Gamma$. This condition applied to the most dilute solutions of decyl alcohol considered in Part XVIII (*loc. cit.*). In contrast, at small Γ values the newly arriving molecules are unlikely to strike those already adsorbed, and the disorientation potential obtained on successive additions of solute should be no more than that equivalent to the $\Delta\Gamma$ value resulting from each addition. These limiting conditions are typical of dilute solutions of solutes of low surface activity, and are illustrated by the results in Fig. 3. Fig. 3(*a*) shows the changes occurring when *n*-propyl alcohol is added in successive stages to the solution in the trough, and the relevant concentrations are given in Table 2(*a*).

TABLE 2.

Addition number	Trough concn., %	$10^{-14}\Delta\Gamma$, molecules/cm.^{2}	$\Delta V_d - \Delta V_0$ (from first additions)	$\Delta V_d - \Delta V_0$ (from successive additions)
(*a*) *n*-Propyl alcohol.				
—	0·0			
1	0·154	0·533	63	—
2	0·302	0·4	57	52
3	0·444	0·275	50	45
4	0·581	0·255	44	36
5	0·713	0·2	36	30
6	0·840	0·165	32	28
7	0·960	0·12	26	26
8	1·076	0·09	22	22
(*b*) *n*-Hexyl alcohol.				
—	0·0			
1	0·019	1·37	103	—
2	0·038	1·225	100	90
3	0·057	0·985	93	74

Col. 3 shows the increment in Γ resulting from each addition, and col. 4 the influence of disorientation on the potential values, it being assumed that in each case the quantity $\Delta\Gamma$ was adsorbed to a clean water surface. The agreement between the values in cols. 4 and 5 is sufficiently close to indicate that under these conditions the disorientation potential values represent disorientation of the incremental surface excess $\Delta\Gamma$ only, and that the molecules already adsorbed undergo no disturbance as a result of the further adsorption.

Some departure from these limiting conditions is observed with increase in chain length. With butyl alcohol solutions, for example, the successive disorientation potentials are appreciably greater than those equivalent to $\Delta\Gamma$ only. Further increase in the chain length brings the concentration required to give mutual interference in the surface within the experimental concentration range. The results obtained on successive addition of *n*-hexyl alcohol [Fig. 3(*b*)] illustrate the effect. Cols. 4 and 5, Table 2(*b*), show that the observed disorientation potentials are now less than those corresponding to full disorientation of $\Delta\Gamma$, and the effect is observed to a more pronounced degree with the concentrated *n*-decyl alcohol solutions discussed in Part XVIII (*loc. cit.*).

Rate of Reorientation.—One of the most curious features observed in this work is the very slow rate at which the disoriented film undergoes reorientation. Typical curves, collected in Fig. 4, show that the time required for orientation diminishes as chain length is decreased. Because of the practical limitations of the apparatus it is difficult to determine the true orientation times in the case of butyl and lower alcohols, but they are of an entirely different order from those required for initial adsorption. If the alcohol molecules, and some of the water molecules, present in the surface when the film is first formed, are regarded as merely displaced from their equilibrium position, then it would be expected that normal kinetic agitation would re-establish the equilibrium orientation almost instantly. Since reorientation occurs after the establishment of the adsorbed film, no considerations involving the surface-energy barrier (be it electrical or kinetic) are likely to be applicable. It seems more probable that reorientation involves the breaking of some form of chemical bond. If strong hydrogen bonding at the surface exists, then reorientation of both alcohol and water molecules may involve the breaking of some of these bonds and the re-forming of others. A less attractive possibility is that the initial adsorbed film is not homogeneous and that during reorientation associated molecules become separated to give a truly gaseous film.

FIG. 3.

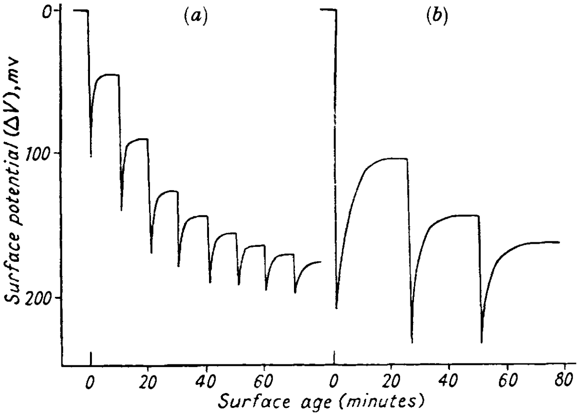
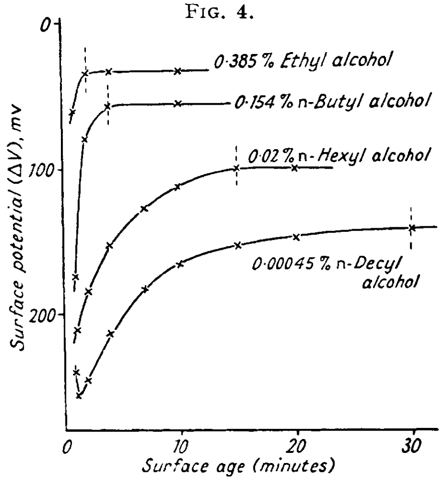


FIG. 4.



Influence of Chain Structure.—The influence of chain structure on surface potentials has been studied with reference to the isomers of butyl and amyl alcohol. Attention has been directed in particular to the influence of chain structure on the apparent dipole moment of the molecule. Tables 3 and 4 give surface-tension and surface-potential data respectively for three of the alcohols studied.

tert.-*Butyl Alcohol.*—The ΔV_0–Γ points for this alcohol lie on a straight line (*B*, Fig. 5) passing through the origin. The slope is much greater than that for the normal alcohol (line *A*) and corresponds to $\mu = 460$ mD. There are features in the structure, $CMe_3{\cdot}OH$, which give it a particular significance. With the straight-chain alcohols, free rotation round the several available bonds precludes a rigid derivation of the vertical components of the dipoles concerned. In calculations of the effective vertical component for long-chain carboxylic acids, Adam and Harding (*Proc. Roy. Soc.*, 1932, *A*, **138**, 411) pointed out the hypothetical nature of the assumptions it was necessary to make concerning the distribution of the C, H, and O atoms of the polar group. With *tert.*-butyl alcohol, three CH_3 groups are disposed symmetrically round the C–O bond; this symmetry renders it highly probable that the molecule will be orientated with the C–O bond vertical to the surface as shown below, since the only forces determining orientation in this case arise from the hydrophilic character of the OH group. Free rotation round the C–O bond, or around any of the three CH_3–C bonds, does not disturb the symmetry. Again, free rotation of the H atom round the C–O bond as illustrated does not alter the direction of the O–H dipole to the surface. This is therefore one of the few cases where comparison of the observed

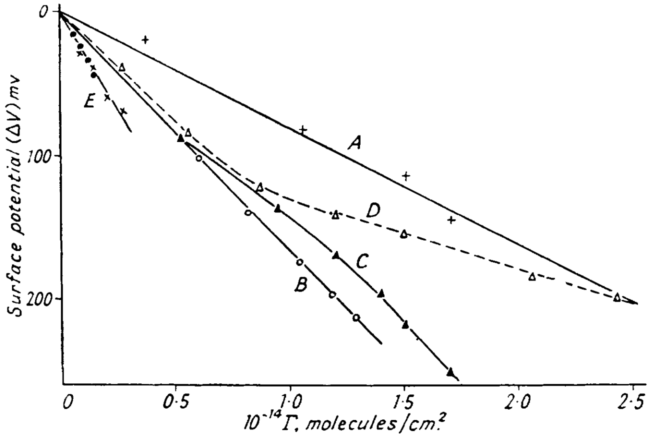


FIG. 5.

+ + *iso*Butyl alcohol.
○ ○ *tert.*-Butyl alcohol.
△ △ *iso*Amyl alcohol.
▲ ▲ *tert.*-Amyl alcohol.
● ● Ethylene glycol.
× × Butane-1 : 3-diol.

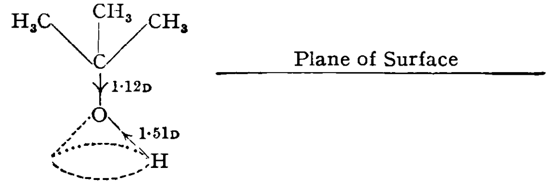
TABLE 3.

Concn., %	d_4^{16}	γ, dynes/cm.	Γ, g. × 10^{-8}/cm.^{2}	Concn., %	d_4^{16}	γ, dynes/cm.	Γ, g. × 10^{-8}/cm.^{2}
			tert.-Butyl alcohol.				
8·22	0·9856	36·55, 36·75	—	0·150	—	65·8, 66·0	1·20
2·05	0·9959	49·85, 49·75	3·35	0·075	—	68·15, 68·35	0·96
0·600	0·9990	59·6, 59·6	1·94	0·0375	—	70·15, 70·15	0·72
0·300	—	62·65, 62·8	1·50				
			*iso*Butyl alcohol				
5·04	0·9931	32·95, 32·95	6·04	0·315	—	58·65, 58·9	1·73
2·52	0·9964	40·7, 40·7	4·00	0·157	—	63·2, 63·2	1·54
1·26	0·9983	48·05, 48·1	3·00	0·079	—	64·8, 64·8	1·14
0·630	0·9992	53·6, 53·7	2·43	0·039	—	67·5, 67·5	0·72
			tert.-Amyl alcohol				
5·33	0·9931	35·30, 35·50	—	0·133	—	65·0, 65·1	1·60
1·33	0·9981	49·25, 49·15	3·00	0·067	—	67·25, 67·3	1·10
0·53	0·9992	56·3, 56·6	2·55	0·0335	—	70·0, 70·1	0·55
0·266	—	61·2, 61·25	2·14				

TABLE 4.

tert.-Butyl alcohol			*iso*Butyl alcohol			*tert.*-Amyl alcohol		
C, %	ΔV_0	ΔV_d	*C*, %	ΔV_0	ΔV_d	*C*, %	ΔV_0	ΔV_d
0·025	62	130	0·031	20	96	0·0246	52	148
0·048	100	—	0·123	83	200	0·0485	98	—
0·071	116	160	0·242	114	—	0·0716	116	—
0·095	140	—	0·358	146	—	0·0940	136	—
0·116	152	178				0·123	152	200
0·246	188	208				0·242	214	—
0·358	208	216				0·358	246	—
0·470	230	235						

dipole with the dipole found by other methods may be made without the uncertainty usually associated with angle of tilt of the dipole.



The dipole moment for the O–H bond is 1510 mD (Syrkin and Dyatkina, " Structure of Molecules and the Chemical Bond," Butterworth, 1950, p. 206); that for the C–O bond will be near its value in methyl alcohol (1120 mD), since the total moments of methyl and *tert.*-butyl alcohol molecules are 1690 and 1650 mD, respectively. On using these values, it is found that the resultant dipole for the *tert.*-butyl alcohol molecule under these conditions is inclined at an angle of 63° to the vertical. The vertical component of the dipole is 750 mD, compared with the value 460 mD obtained from surface-potential measurements. The difference between these two values represents the real discrepancy between the μ value obtained from measurements by other methods, and that obtained by direct application of Helmholtz's equation $\Delta V = 4\pi n\mu$, particularly since the present system is not complicated by the presence of added ions. The difference between calculated and observed values of μ for an equilibrium surface will arise largely from the permanent change in orientation of water molecules brought about by the presence of adsorbed alcohol molecules in the film. This effect may be expressed quantitatively in terms of the dielectric constant ε, where $\mu\varepsilon = \bar{\mu}\cos\theta$ (Adam, *op. cit.*, p. 38); $\bar{\mu}\cos\theta$ is 750 mD, whence $\varepsilon = 1{\cdot}63$.

It is now possible to determine with some degree of accuracy the angle of tilt of the dipole for the straight-chain alcohols up to C_5, provided that it can be assumed that this value of ε does not vary appreciably with the length and structure of the carbon chain. This assumption is reasonable, since the polar group, rather than the carbon chain, will be responsible for the rearrangement of the water molecules. (This water disorientation is distinct from that caused at the non-equilibrium surfaces discussed in connection with Fig. 2, where the temporary water disorientation is kinetic rather than electrical in origin.) Again, the ΔV_0–Γ points for the C_2—C_5 alcohols all lie along a single line (Fig. 5); it follows that if ε was not constant, the change in ε would be balanced exactly by a corresponding change in the angle of tilt with chain length, which is most improbable. Therefore the unique feature of the *tert.*-butyl alcohol molecule lies solely in its vertical orientation, and there is no reason to suppose that the value of ε determined with this alcohol should differ from that operating in the straight-chain alcohol films. The values for the total dipole moment $\bar{\mu}$ of the C_2—C_5 alcohols are 1·70, 1·64, 1·66, 1·65, respectively (Syrkin and Dyatkina, *op. cit.*, p. 215). Substituting the mean value into expression

$$\Delta V_0/n = (4\pi\bar{\mu}\cos\theta)/\varepsilon$$

where $\Delta V_0/n$ is the slope of line *A*, Fig. 5, we find that θ, the inclination of the dipole to the vertical, is 78°, compared with 63° for *tert.*-butyl alcohol.

iso*Butyl Alcohol.*—The ΔV_0–Γ points for this alcohol are given in Fig. 5 and are seen to lie very close to line *A* which is standard for the normal alcohol. It is consistent with the above treatment that the inclination of the dipole in a molecule having the structure $CHMe_2{\cdot}CH_2{\cdot}OH$ should agree with that of the straight-chain alcohol rather than with the symmetrical *tert.*-butyl isomer.

tert.-*Amyl Alcohol.*—Curve *C*, Fig. 5 (almost a straight line), shows the ΔV_0–Γ relationship for this alcohol. The slope of a straight line drawn through the points is a little less than for *tert.*-butyl alcohol, corresponding to $\mu = 405$ mD, and the dipole is inclined at an angle of 66° to the vertical. *tert.*-Butyl alcohol being considered as standard, the extent to which the dipole of similar molecules will deviate from an angle of 63° to the vertical will depend upon the extent to which substitution of the CH_3 groups introduces dissymmetry round the C–O bond. The substitution of one CH_3 group by a C_2H_5 group (as in *tert.*-

amyl alcohol) introduces a relatively small degree of dissymmetry. The surface orientation therefore resembles that of *tert.*-butyl alcohol, except that the dipole undergoes a small further tilt from 63° to 66°. If two CH_3 groups in *tert.*-butyl alcohol are replaced by H atoms, the symmetry is destroyed to such an extent that the dipole takes up the 78° position typical of straight-chain alcohols.

iso*Amyl Alcohol.*—The behaviour of this alcohol is somewhat anomalous. Analogy with the results discussed above would suggest that the ΔV_0–Γ points should lie along line *A*, Fig. 5, but this is the case at the higher concentrations only (curve *D*).

Surface Potentials of Solutions of Dihydric Alcohols.—For comparison with the behaviour of the monohydric alcohols given above, the surface potentials of aqueous solutions of two dihydric alcohols have been measured, and the results, together with surface tension data, are given in Table 5. The ΔV_0–Γ points for the two glycols lie close to a common line (*E*, Fig. 5).

TABLE 5.

Concn., %	γ, dynes/ cm.	$10^{-14}\,\Gamma$, molecules / cm.^{2}	ΔV_0	ΔV_0 †	μ, mD
Ethylene glycol.					
0·0	72·5	—	—	—	—
0·19	—	—	8	—	—
0·38	72·2	0·065	15	—	830
0·388	—	—	—	5	—
0·55	—	0·10	24	—	830
0·73	—	0·12	34	—	840
0·775	—	—	—	9	—
0·89	71·9	0·15	44	—	890
3·00	70·6	—	—	—	—
3·10	—	—	—	46	—
5·63	69·1	—	—	—	—
6·2	—	—	—	96	—
11·25	67·3	—	—	—	—
12·4	—	—	—	127	—

Concn., %	γ, dynes/ cm.	$10^{-14}\,\Gamma$, molecules/ cm.^{2}	ΔV_0	ΔV_0 †	μ, mD
*Butane-*1 : 3-*diol.*					
0·18	—	0·083	25	—	880
0·36	—	0·15	40	—	840
0·53	70·3	0·22	59	—	820
0·70	69·8	0·275	71	—	750
1·12	68·8	—	—	—	—
2·24	66·3	—	—	—	—
4·48	62·0	—	—	—	—
8·96	56·5	—	—	—	—

† Results of Frumkin, Donde, and Kulverskaya (*Z. physikal. Chem.*, 1926, **123**, 321).

The surface-tension values for ethylene glycol solutions agree closely with values reported by Frumkin, Donde, and Kulverskaya (*loc. cit.*) but the value of ΔV_0 determined in this work are greater than theirs. This may arise from the fluctuating nature of the potentials observed for these solutions. Although the air electrode was stationary, no truly steady state was reached with solutions of these two dihydric alcohols. The surface film behaved as though it was heterogeneous, and each of the ΔV_0 results given above is the mean of a series of fluctuating values. Nevertheless, the range of fluctuation was sufficiently narrow to indicate a real disagreement between the two sets of results. In no case was any significant disorientation potential observed on addition of the glycols to the trough, so the presence of a hydrophilic group at each end of the molecule serves to ensure its immediate orientation on arrival at the surface. The values of μ for each alcohol, determined directly from Helmholtz's equation, are given in Table 5. The close agreement indicates that the angle of tilt of the dipoles in these two glycols is not appreciably influenced by surface excess, or by alteration from 2 to 3 in the number of carbon atoms separating the polar groups; neither does it appear necessary for this constant angle of tilt that the polar groups should be in terminal positions in the chain. If the two dipoles are considered to make separate contributions to the surface potential, the value for each (about 424 mD) might be expected to lie between the minimum and maximum values observed for monohydric alcohols (Fig. 5), and this is in fact the case. However, it is inadvisable to employ this value in the calculation of angle of tilt of each dipole, in view of the possible influence of one dipole on the other which may result from their close proximity.

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