117. *Adsorption at the Surface of Solutions. Part III. The Surface Structure of Solutions of the Lower Aliphatic Alcohols.*

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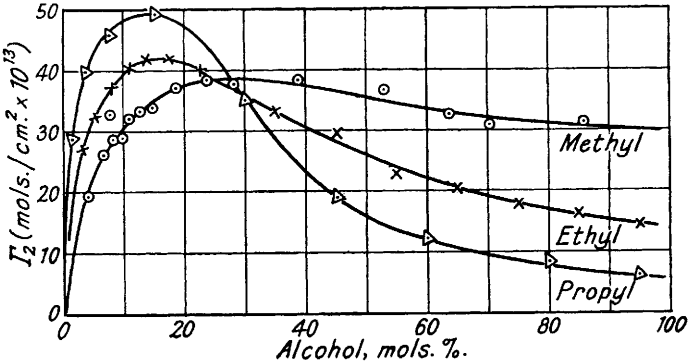
IN Part I (J., 1932, 2089) we described a redetermination of the surface tensions of aqueous ethyl alcohol solutions and discussed the interpretation of the values of the Gibbs adsorption derived therefrom. In no other case had both the surface tensions and the partial vapour pressures of the components been determined at the same temperature with sufficient accuracy for a reliable estimate of the Gibbs adsorption over the whole range of solutions. The partial vapour pressures at 25° of solutions of methyl and *n*-propyl alcohols have recently been determined in this laboratory by Butler, Thomson, and Maclennan (J., 1933, 674). In order to provide additional material for the discussion of the constitution of the surfaces of concentrated solutions, we have therefore determined the surface tensions of these solutions at the same temperature.

EXPERIMENTAL.

The alcohols were purified and the solutions prepared by the methods used in the determination of the vapour pressures (*loc. cit.*). The surface tensions of the propyl alcohol solutions were determined by the maximum bubble-pressure method, as described in Part I. With methyl alcohol solutions, it was very difficult to get reproducible readings by this method, particularly in the more dilute solutions, owing perhaps to the evaporation of alcohol at the surface of the bubbles; the whole series of these solutions was therefore determined by the capillary-rise method, the corrections described in Part II (J., 1932, 2098) being made. The experimental measurements, together with the corrected surface tensions derived therefrom, are given in Table I. The densities, of which approximate values are sufficient for the maximum bubble-pressure method, were obtained by interpolation from the data in I.C.T., Vol. III.

In order to determine the values of Γ_2, the measured surface tensions were plotted on a large scale against the molar fraction of alcohol, and where the points deviated appreciably from the best smooth curve a correction was made for the purpose of the calculation. The "smoothed" values so obtained, which only differ in a few cases from the observed values, are given in Table II.

The partial vapour pressures of the alcohols in the solutions were determined by $p_2 = p_2^0 N_2 f_2$, where p_2^0 is the vapour pressure of the pure alcohol, N_2 its molar fraction and f_2 its activity coefficient in the solution. The last was obtained from the curves of Butler, Thomson, and Maclennan (*loc. cit.*). The values of $\Gamma_2 = -1{\cdot}062 \times 10^{13}(-\Delta\sigma/\Delta\log_{10}p_2)$ were evaluated for the intervals between one solution and the next. In a few cases the variation of $\log_{10}p_2$ between the successive solutions of Table I was too small to be determined with sufficient accuracy, and in such cases Γ_2 has been evaluated for a larger interval. The values of Γ_2 for the three lowest alcohols are shown, plotted against the mean molar fraction of alcohol for the interval to which they refer, in the fig.



Adsorption at surface of water–alcohol solutions.

TABLE I.

Solutions of methyl alcohol. Capillary-rise method.

MeOH, mols. %.	$D^{25°}_{4°}$.	h_1.	σ.	MeOH, mols. %.	$D^{25°}_{4°}$.	h_1.	h_2.	σ.
0·00	0·9971	11·628	71·97	15·68	0·9576	7·307	—	43·49
2·24	0·9911	10·303	63·42	21·73	0·9442	6·698	11·495	39·34
2·74	0·9893	9·995	61·41	25·93	0·9348	—	10·917	37·15
5·51	0·9816	9·167	55·88	30·67	0·9243	—	10·449	35·16
7·73	0·9757	8·655	52·45	47·19	0·8884	—	9·428	30·49
8·13	0·9748	8·527	51·63	58·97	0·8630	—	8·956	28·14
8·95	0·9730	8·360	50·53	68·77	0·8442	—	8·614	26·48
10·13	0·9717	8·137	49·12	72·42	0·8377	—	8·500	25·93
11·87	0·9661	7·845	47·10	100·00	0·7864	—	7·679	21·99
13·74	0·9618	7·556	45·16					

Solutions of propyl alcohol. Maximum bubble-pressure method.

PrOH, mols. %.	P_2, cm.	$D^{25°}_{4°}$.	σ.	PrOH, mols. %.	P_2, cm.	$D^{25°}_{4°}$.	σ.
0·00	39·32	0·997	71·97	12·11	14·11	0·943	26·04
1·00	27·45	0·911	49·98	20·00	13·91	0·915	25·60
2·00	23·21	0·987	42·58	29·96	13·73	0·887	25·27
5·00	16·86	0·976	31·01	39·94	13·57	0·866	24·97
5·76	15·70	0·972	28·89	50·53	13·42	0·849	24·69
8·02	14·77	0·962	27·19	69·63	13·13	0·826	24·16
10·00	14·25	0·954	26·23	100·00	12·68	0·780	23·32

DISCUSSION.

The decrease of Γ_2 in the more concentrated solutions might be accounted for in two ways. (1) Schofield and Rideal (*Proc. Roy. Soc.*, 1925, *A*, **109**, 57; *Phil. Mag.*, 1932, **13**, 806) have shown that if there is a complete surface layer of alcohol molecules at the surface

TABLE II.

Calculation of Γ_2 for solutions of methyl alcohol.

MeOH, mols. %.	σ.	$\log p_2$.	$\Gamma_2 \times 10^{-13}$.	MeOH, mols. %.	σ.	$\log p_2$.	$\Gamma_2 \times 10^{-13}$.	MeOH, mols. %.	σ.	$\log p_2$.	$\Gamma_2 \times 10^{-13}$.
2·74	61·41	0·717	—	11·87	47·10	1·347	32·0	47·19	30·49	1·828	38·1
5·51	55·88	1·020	19·4	13·74	45·24	1·407	32·9	58·97	28·14	1·896	36·7
7·73	52·28	1·166	26·2	15·68	43·49	1·462	33·8	68·77	26·48	1·950	32·6
8·13	51·63	1·187	32·9	21·73	39·34	1·581	37·1	72·42	25·93	1·969	30·8
8·95	50·53	1·228	28·5	25·93	37·15	1·642	38·1	100·00	21·99	2·103	31·2
10·13	49·12	1·280	28·8	30·67	35·16	1·698	37·7				

Calculation of Γ_2 for solutions of propyl alcohol.

PrOH, mols. %.	σ.	$\log p_2$.	$\Gamma_2 \times 10^{-13}$.	PrOH, mols. %.	σ.	$\log p_2$.	$\Gamma_2 \times 10^{-13}$.	PrOH, mols. %.	σ.	$\log p_2$.	$\Gamma_2 \times 10^{-13}$.
1·00	49·98	0·430	—	20·00	25·60	1·135	49·5	70·00	24·16	1·216	12·2
2·00	42·58	0·703	28·8	40·00	24·97	1·154	35·2	90·00	23·60	1·291	8·5
5·00	31·01	1·011	39·9	50·00	24·70	1·169	19·1	100·00	23·32	1·340	6·4
10·00	26·30	1·120	45·9								

of these solutions, it is necessary to assume an excess of water underneath the surface layer, the amount of which (Γ_1') is given by $\Gamma_2 = \nu_2^0 - N_2\Gamma_1'/N_1$, where ν_2^0 is the number of alcohol molecules in the surface layer and N_2/N_1 is the molar ratio of alcohol to water molecules in the bulk of the solution. (2) On the other hand, Butler and Wightman (*loc. cit.*) showed that a decrease of Γ_2 may also occur in the concentrated solutions when the surface layer alone differs in composition from the bulk of the solution, if this surface layer is not completely occupied by alcohol molecules. It was shown that the data for ethyl alcohol solutions are nearly, but not quite in accordance with this assumption. Guggenheim and Adam (*Proc. Roy. Soc.*, **1933**, *A*, **139**, 218) have also come to a similar conclusion with respect to ethyl alcohol solutions.

There are no strictly thermodynamical grounds for distinguishing between these and other possibilities, since a given value of Γ_2 might be produced by a number of different arrangements of molecules near the surface. It may, however, be argued that some of the possible structures of the surface are improbable either because they are unnecessarily complicated or on other grounds.

On the hypothesis that the only part of the surface region which differs in composition from the bulk of the solution is a surface layer characterised by

$$A_1\nu_1 + A_2\nu_2 = 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the following relation is obtained (Part I) between the surface composition and the Gibbs adsorption :

$$\Gamma_2 = \nu_2^0 - (A_1/A_2 + N_2/N_1)\nu_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where ν_1, ν_2 are the numbers of molecules of water and alcohol in unit area of the surface layer, A_1, A_2 the areas occupied by these molecules, and $\nu_2^0 = 1/A_2$ the number of alcohol molecules in a completed surface layer. In order to use these equations it is necessary to know A_1 and A_2. When these are known ν_1, ν_2 can be determined for any given value of Γ_2, but the values obtained will only be real if the initial assumption is correct.

In order to judge the validity of this assumption, the criterion that ν_2 must increase continuously as the proportion of alcohol in the solution is increased was employed. It was found that with ethyl alcohol solutions, this criterion is not *strictly* satisfied with any reasonable values of A_1 and A_2, and it was therefore concluded that, although the divergence is small, the assumption of a single unimolecular layer is not strictly true.*

The values of Γ_2 for methyl alcohol solutions are, however, compatible with a single adsorption layer which satisfies this criterion. Table III gives the values of ν_2 and ν_1, calculated by (1) and (2) on the assumptions that $\nu_2^0 = 48·6 \times 10^{13}$ mols./cm.^{2}, and

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* Guggenheim and Adam suggested that the difficulty might be overcome by assuming variable values of A_1 and A_2. We have satisfied ourselves that no reasonable variation of A_1 and A_2 would suffice to make ν_2 increase continuously with N_2.

(i) $A_1/A_2 = 0{\cdot}5$, (ii) $A_1/A_2 = 1$. In both cases we obtain values of ν_2 which increase steadily with the proportion of alcohol in the solution.

TABLE III.

Possible surface compositions of methyl alcohol solutions.

		$\nu_2^0 = 48{\cdot}6$; $A_1/A_2 = 1$.		$\nu_2^0 = 48{\cdot}6$; $A_1/A_2 = 0{\cdot}5$.	
N_2.	Γ_2.	ν_2.	ν_1.	ν_2.	ν_1.
0·05	21·6	22·8	25·8	23·1	51·1
0·10	30·8	32·6	16·0	34·0	29·1
0·20	37·3	39·6	9·0	41·0	15·1
0·30	38·6	41·9	6·7	43·6	10·0
0·40	37·5	42·0	6·6	43·8	9·5
0·50	35·7	42·2	6·4	44·3	8·6
0·60	34·2	42·8	5·8	45·0	7·2
0·70	32·8	43·9	4·7	45·8	5·6
0·80	31·6	45·2	3·4	46·7	3·8
1·00	—	48·6	0·0	48·6	0·0

On the other hand, it is impossible to reconcile the curve for propyl alcohol with this hypothesis, the divergence being much greater than in the case of ethyl alcohol. In general, the hypothesis of a single adsorption layer characterised by (1) is thus inadequate, and it is necessary to frame a wider theory which will take into account non-homogeneity below the surface layer.

Suppose that, as in Part I, a dividing surface is drawn in the solution in such a position that the solution is completely homogeneous below it. Let the numbers of molecules of water and alcohol in the region above this surface be n_1, n_2. Then it can easily be shown that

$$\Gamma_2 = n_2 - n_1 . N_2/N_1.$$

Now, let $n_2 = \nu_2 + \omega_2$ and $n_1 = \nu_1 + \omega_1$, where ν_1, ν_2 are the numbers of molecules in the surface layer of the solution, which are related by $A_1\nu_1 + A_2\nu_2 = 1$, and ω_1, ω_2 the numbers of molecules between this surface layer and the dividing surface. Then

$$\Gamma_2 = \nu_2^0 - (A_1/A_2 + N_2/N_1)\nu_1 + \omega_2 - \omega_1 N_2/N_1,$$

and $(\omega_2 - \omega_1 N_2/N_1)$ is evidently the *excess* of alcohol in the region below the surface layer. If this quantity is negative, it may more conveniently be expressed as $-(\omega_1 - \omega_2 N_1/N_2)N_2/N_1 = -\Gamma_1' N_2/N_1$. $(\omega_1 - \omega_2 N_1/N_2) = \Gamma_1'$ is to be regarded as the *excess* of water below the actual surface layer, for ω_1 is the actual number of water molecules in this region, and $\omega_2 N_1/N_2$ the number which would be present if the ω_2 alcohol molecules were accompanied by water in the same proportion as in the bulk of the solution. We thus have

$$\Gamma_2 = \nu_2^0 - (A_1/A_2 + N_2/N_1)\nu_1 - \Gamma_1' N_2/N_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

It is, of course, impossible to determine both ν_1 and Γ_1' from this equation, but a consideration of the values of Γ_2 leads to the following observations. (1) In the case of methyl alcohol, not improbable values of the surface composition are obtained when Γ_1' is assumed to be zero. (2) In the case of propyl alcohol, unless ν_2^0 differs considerably from the value found for insoluble films of the higher fatty acids, Γ_2 is practically equal to ν_2^0 at the maximum of the adsorption curve ($N_2 = 0{\cdot}15$). At greater concentrations of alcohol, it is thus probable that ν_1 is approximately zero and therefore $\Gamma_2 = \nu_2^0 - \Gamma_1' N_2/N_1$. (This is the expression used by Schofield and Rideal for ethyl alcohol solutions.) The values of Γ_1' obtained on this assumption are given in Table IV. (3) The case of ethyl alcohol comes somewhere between these two extremes. If Γ_1' is taken as zero, the values of ν_2 do not increase continuously with N_2.* Since the maximum value of Γ_2 is about 42×10^{13} mols./cm.^{2}, it is improbable that ν_1 is zero at or near this maximum, consequently the values of Γ_1' obtained by putting $\nu_1 = 0$ are almost certainly too high.

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* For this reason we suggested in Part I that there was a small excess of alcohol under the surface layer of certain solutions near the maximum adsorption. This assumption is not adequate in the case of propyl alcohol solutions, and we therefore now think it more probable that in the case of ethyl alcohol solutions also, the divergence from the single layer requirements is due to an excess of water under the surface layer of the more concentrated solutions.

TABLE IV.

N_2	0·9	0·8	0·7	0·6	0·5	0·4	0·3	0·25
Γ_2	7	8	10	12	17	23	35	43
Γ_1'	4·7	10	17	25	32	39	33	18
$\nu_2{}^0N_1/N_2$	5·5	12	21	32	49	73	—	—

In conclusion we may observe that the conception of a complete or nearly complete surface layer of alcohol molecules, with an excess of water underneath, is misleading in the sense that it suggests a greater segregation of water and alcohol than actually occurs. The last line of Table IV gives the number of water molecules which would accompany the alcohol molecules of a complete surface layer, if their proportions were the same as in the bulk of the solutions. The values of Γ_1' for the more concentrated propyl alcohol solutions are only a little smaller. [If Γ_1' were equal to $\nu_2{}^0N_1/N_2$, the adsorption (Γ_2) of propyl alcohol would of course be zero.] Thus, assuming that at the surface of these solutions there is a complete layer of orientated alcohol molecules, it is necessary to suppose that they are accompanied, underneath, by water molecules in nearly the same proportion as in the bulk of the liquid. This may be explained by the tendency of water molecules, when present in small proportion in alcoholic solution, to be associated or co-ordinated with the hydroxyl groups. This tendency will be the greater the longer the hydrocarbon chain. It is thus possible to have at the surface of these solutions a complete layer of alcohol molecules, which are at the same time associated with water molecules in nearly the same proportion and in the same way as in the bulk of the solution.

SUMMARY.

1. The surface tensions of aqueous solutions of methyl and *n*-propyl alcohols have been determined at 25°, and the values of the Gibbs adsorption calculated.

2. The probable structures of the surfaces which are compatible with these observations are discussed.

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