654. *Adsorption of the Aliphatic Acids, Acetic to Octanoic, at the Nitromethane Solution–Air Interface.*

By D. C. Jones and L. Saunders.

A study of the surface layers, at the air–solution interface, of solutions of the aliphatic acids, acetic to octanoic, in nitromethane has been made. The surface tensions of solutions of various concentrations have been determined and also the partial vapour pressures of the solvent in equilibrium with these solutions. From these results surface-excess concentrations have been calculated, and, by use of the general form of Gibbs's equation together with different conventions, in particular the U convention of Guggenheim and Adam and the Z convention of Fu and Bartell, the absolute surface concentrations have been evaluated. The results show that the adsorption excess plays a much smaller role in determining the absolute surface concentrations in the adsorption of surface-active materials on solution in organic solvents of this kind than in adsorption on aqueous solution. The relations between the surface and the bulk mol.-fractions corresponding to the various conventions have been examined, and it appears that a reasonable explanation of these results would be that the adsorption layer is unimolecular and that the acid molecules arrange themselves intermediately between a horizontal orientation, with their long axes parallel in the surface, and a random arrangement.

THE basic method for determining concentrations of components in a reversibly adsorbed surface layer in equilibrium with a solution is still the Gibbs adsorption equation. This expresses the surface excess of solute in the layer in terms of the rate of change of surface tension of the solution with the chemical potential of solute in the bulk solution. The usual form of the equation

$$\Gamma_2 = -\frac{1}{RT} \cdot \frac{d\gamma}{d \ln a_2}$$

(Adam, " Physics and Chemistry of Surfaces," Oxford Univ. Press, 1946; $a_2 = f_2 N_2$, the activity of the solute in the bulk solution) is not applicable to more concentrated solutions. In these cases the general form of Gibbs's equation

$$\Gamma_2 - \frac{N_2}{1 - N_2} \Gamma_1 = -\frac{1}{RT} \cdot \frac{d\gamma}{d \ln a_2}$$

must be combined with another relation between Γ_1 and Γ_2, which cannot be derived thermodynamically, in order to evaluate Γ_1 and Γ_2 (Guggenheim, " Thermodynamics," Oxford Univ. Press, 1949). This second relation can only be obtained by making assumptions about the structure of the surface layer.

The work described in this paper consisted of a study of the adsorbed layer of some *n*-fatty acids at the interface between air and solutions of the acids in an organic solvent of moderately high surface tension (nitromethane). The experimental work consisted of measurements of the surface tensions and partial vapour pressures of solvent in equilibrium with solutions of various concentrations. From these results surface compositions have been evaluated, the general form of Gibbs's equation being used, together with two different conventions giving further relations between Γ_1 and Γ_2.

EXPERIMENTAL.

Materials.—The materials used were carefully purified and some physical properties were determined in each case. M. p.s were observed by using about 5 ml. of liquid contained in a double-jacketed tube; densities were measured by means of a single-bulb pyknometer of 5-ml. capacity; refractive indices were determined by means of a Pulfrich refractometer, and b. p.s were observed in an apparatus similar to that described by Jones and Betts (*J.*, 1928, 1177).

Water. Good distilled water was redistilled from a Bousfield still; γ^{20} 72·8 ergs cm.$^{-2}$ (cf. Harkins and Brown, *J. Amer. Chem. Soc.*, 1919, **41**, 499; 72·79); n_D^{20} 1·3330 (same as I.C.T.).

Benzene. Kahlbaum's purest benzene was fractionally frozen, dried over sodium, and distilled; it had m. p. 5·50°; d_4^{25} 0·8733.

Nitromethane. This was prepared from chloroacetic acid, sodium nitrite, and sodium carbonate; a quantity was also obtained from Kahlbaum. Both materials were dried ($MgSO_4$) and fractionally distilled, yielding products with identical physical constants: d_4^{25} 1·13130 (cf. Boyd and Copeland, *J. Amer. Chem. Soc.*, 1942, **64**, 2540; 1·13118); b. p. 101·0°; γ^{25} 36·23 ergs cm.$^{-2}$ (cf. Boyd and Copeland, *loc. cit.*, 35·78, by ring-pull method; I.C.T. value, 36·07).

Fatty acids. Kahlbaum's purest acids were fractionally frozen and the lower acids were fractionally distilled at low pressures.

TABLE I.

Properties of fatty acids.

	γ^{20}, obs.	γ^{20}, I.C.T.	γ^{20}, calc.	n_D^{20}	n_D^{20}, I.C.T.	M. p.	d_4^{25}
Acetic	27·6	27·6	27·7	1·3718	1·3715 (22·9°)	16·5°	1·0443
Propionic	26·6	26·7	26·2	1·3868	1·3873 (19·9°)	−21·5	0·9877
Butyric	26·8	26·8	26·8	1·3979	1·3977 (20·3°)	−5·8	0·9527
Valeric	27·4	—	27·4	1·4082	—	<−30	0·9348
Hexanoic	28·1	—	28·0	1·4165	1·4145 (19·6°)	−4·6	0·9227
Heptanoic	28·7	28·3	28·4	1·4229	1·4216 (19·8°)	−8·8	0·9134
Octanoic	29·2	—	28·8	1·4282	1·4268 (21·0°)	16·2	0·9060

A number of the physical properties of the acids were determined. The results are given in Table I; the surface tensions at 20° were determined by the maximum bubble pressure method and are compared in the table with the values given in I.C.T. and the values calculated from Samygin's equation (*J. Phys. Chem. U.S.S.R.*, 1937, **10**, 455), viz.,

$$\gamma = \left[\frac{8 \cdot 49(n^2 - 1)}{n^2 + 2} + \frac{20 \cdot 9d}{M} \right]^4$$

where n is the refractive index for the sodium D line, d the density, and M the monomeric molecular weight of the acid. These physical properties are of two types—density and refractive index which vary regularly with molecular weight, and m. p. and surface tension which show minima in the middle of the series.

Measurements of Surface Tension.—All these measurements were carried out by using apparatus immersed in a copper water-tank of 50-l. capacity, fitted with plate-glass windows, whose temperature was controlled to within ±0·02° by a toluene–mercury regulator. The usual precautions were taken to eliminate grease from the glass apparatus.

The solutions of acids in nitromethane were made up by weight. Their contact angles on soda glass were examined by Bartell and Merrill's method (*J. Physical Chem.*, 1932, **36**, 1178). Nitromethane and solutions of acetic to valeric acids had zero contact angles for both advancing and receding menisci; surface tensions of these solutions were therefore determined by Ferguson's modification of the capillary-rise method, as used by Carter and Jones (*Trans. Faraday Soc.*, 1934, **30**, 1027). Some of these results were checked by Sugden's maximum bubble pressure method (*ibid.*) and excellent agreement was found. Solutions of hexanoic to octanoic acids had variable contact angles on soda glass for advancing menisci, and we could not obtain reliable surface tensions for these solutions by Ferguson's method owing to the insensitivity of the meniscus at the tip of the capillary to small changes of pressure; we therefore used Sugden's method for all the determinations of the surface tensions of these solutions.

Measurements of Partial Vapour Pressures.—The partial vapour pressures of the components in equilibrium with the solutions were determined by a modification of Shaw and Butler's apparatus (*Proc. Roy. Soc.*, 1930, *A*, **129**, 519). A known volume (707·2 ml.) of dry, carbon dioxide-free air at atmospheric pressure was slowly displaced by pure mercury and blown through about 10 ml. of the liquid under investigation, contained in inclined bubblers. The air and vapour passed through a U-tube, to allow any liquid spray to settle, and then through a weighed receiver cooled in solid carbon dioxide and ether. Apart from the receiver, the apparatus was completely immersed in a water thermostat. The short length of glass tubing leading to the receiver was kept slightly above the thermostat temperature (25°) by means of an electrically heated coil, to prevent condensation of vapour before it reached the receiver.

The receiver consisted of a U-tube with ground-glass joints on both limbs. One of these fitted on to the vapour-pressure apparatus and the other connected to a guard tube (against carbon dioxide and water) and a sulphuric acid pulsimeter. Before the receiver was attached, air was bubbled through the solution for a few minutes, the receiver was put on and then cooled, and the measured volume of air blown through the solution by slowly filling a glass globe with mercury, between two etched marks. When the mercury reached the upper mark, the receiver was removed, stoppered, and allowed to warm to room temperature. One stopper was eased for a few seconds, to adjust the contents to atmospheric pressure, and the receiver was hung in the case of a Sartorius balance, modified to act as a semimicro-balance, and weighed against a suitable counterpoise. The total weight of distillate was usually 50—90 mg. Blank experiments with completely dry apparatus gave no measurable increase in the weight of the receiver if this procedure was carefully followed.

A slight concentration change often occurred during the determination, owing to the small amount of the solution used; if this change was appreciable, the mean of initial and final mol.-fractions was taken as representing the mol.-fraction of the solution.

The distillate from the solutions of appreciably volatile acids was analysed after being weighed, by washing it out of the receiver with a measured volume of aqueous ethanol, into a flask in which it was titrated with N/100-alkali (in a carbon dioxide-free atmosphere). Blank titrations were carried out with an equal volume of aqueous ethanol, and the proportion of acid in the distillate was estimated from previously prepared titre–composition curves for solutions of the acids in nitromethane.

Partial vapour pressures were calculated from the experimental results by the equation

$$\frac{1}{p_1} = \frac{M_1 V}{RT} \cdot \frac{1}{W_1} + \frac{1}{P}\left(1 + \frac{W_2 M_1}{W_1 M_2}\right)$$

a similar equation being used for p_2 in cases where this was measurable (M_1 and M_2 are molecular weights of nitromethane and acid, respectively; W_1 and W_2 are the weights in g. of distillate collected; V is the volume of air blown through the solution; P is the barometric pressure; R is the gas constant; p_1 is the partial vapour pressure of nitromethane).

The apparatus was first used to measure the vapour pressures of some pure liquids. Water gave a value 23·71 mm. at 25° (cf. 23·69 from I.C.T.); nitromethane gave 36·40 mm. at 25° which compares

FIG. 1.

p_1–N$_2$ *curves.*

Symbols used throughout for the different acids:
× Acetic.   + Hexanoic.
⊙ Propionic.   ⁄ Heptanoic.
⊡ Butyric.   ⟍ Octanoic.
△ Valeric.

FIG. 2.

Key.
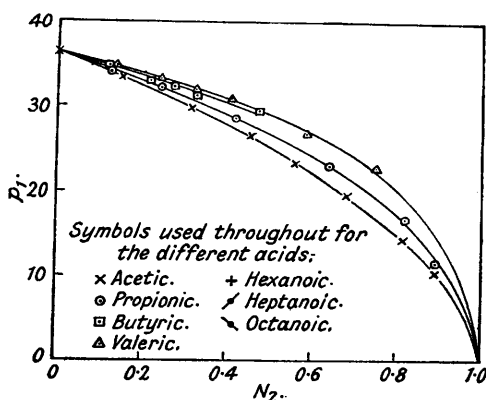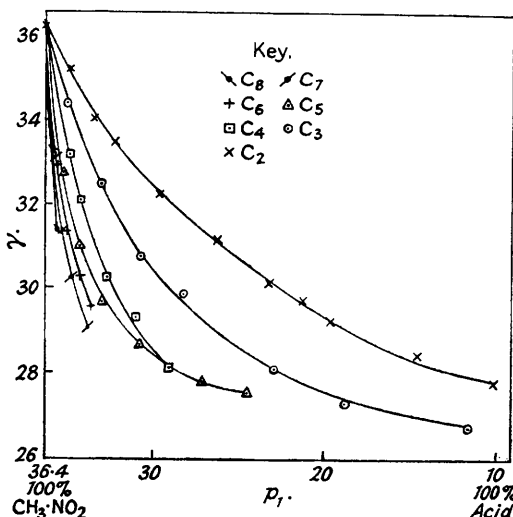⟍ C$_8$ ⁄ C$_7$
+ C$_6$ △ C$_5$
⊡ C$_4$ ⊙ C$_3$
× C$_2$

with the value 36·56 mm. calculated from an equation given by Williams (*J. Amer. Chem. Soc.*, 1925, **47**, 2644) based on direct pressure measurements. This agreement indicates that nitromethane vapour is not appreciably associated at 25°.

The results at 25° for pure acetic and propionic acids when compared with values obtained by direct pressure measurements (15·54 mm. for acetic acid, MacDougall, *J. Amer. Chem. Soc.*, 1936, **58**, 2585; 4·14 mm. for propionic acid, I.C.T.) indicated considerable association of the vapours of these acids at 25°. From the results, mean molecular weights of these two acids in the vapour phase were calculated to be 110·9 for acetic acid (corresponding to a degree of dissociation of double molecules of 0·082; cf. *idem, ibid.*, 0·081) and 91·0 for propionic acid. These mean molecular weights were used in the calculations of the partial vapour pressures of the solutions of acetic and propionic acids in nitromethane.

The partial vapour pressures of acetic acid and nitromethane in equilibrium with their solutions could be quite closely represented by the Margules integration of the Gibbs–Duhem equation :

$$p_1 = p_1°N_1 e^{\beta N_2{}^2}, \qquad p_2 = p_2°N_2 e^{\beta N_1{}^2}$$

where $p_1°$, $p_2°$ are the vapour pressures of pure nitromethane and acetic acid, respectively, N_1, N_2 are the mol.-fractions in the solutions, and β is a constant whose value was found to be 0·23 at 25°.

All the acid solutions in nitromethane showed positive deviations from Raoult's law (see Fig. 1).

Calculation of Surface Concentrations.—The experimental values of surface tensions and partial vapour pressures of nitromethane were plotted against solution mol.-fractions, and from these, surface tensions and partial vapour pressures at round-figure mol.-fractions were determined and these were used in the subsequent calculations (see Table II).

γ–p_1 curves were then constructed (Fig. 2) and from these the value of $\Gamma_2^{(N)}$ was calculated (see Adam, *op. cit.*) :

$$\Gamma_2^{(N)} = \frac{N_1}{RT} \cdot \frac{d\gamma}{d \ln a_2} = \frac{N_2}{RT} \cdot \frac{d\gamma}{d \ln a_1} = \frac{N_2}{RT} \cdot \frac{d\gamma}{d \ln p_1}$$

The values of $d\gamma/(d \ln p_1)$ were found from the $\gamma-p_1$ curves by measuring the slopes of these curves at values of p_1 corresponding to the round-figure values of N_2 and multiplying them by p_1. Some uncertainty arises in this process of graphical differentiation, and the values of $d\gamma/dp_1$ determined directly from the curves were checked by fitting empirical equations to these curves and differentiating them algebraically. Suitable equations were found to be of the rectangular hyperbola form $(\phi + b)(\pi + c) = bc$, where $\phi = \gamma_1 - \gamma$, the difference between the surface tensions of nitromethane and the acid solution; $\pi = p_1{}^0 - p_1$; b and c are constants; $\phi = 0$ when $\pi = 0$.

TABLE II.

N_2	γ	p_1	$10^{10} \times$ $\Gamma_2{}^{(N)}$	$\Gamma_2{}^{(V)}$	N_2	γ	p_1	$10^{10} \times$ $\Gamma_2{}^{(N)}$	$\Gamma_2{}^{(V)}$
				Acetic acid solutions.					
0·05	35·31	35·40	0·54	0·54	0·4	31·56	27·93	1·54	1·50
0·1	34·70	34·55	0·94	0·93	0·5	30·62	25·20	1·43	1·39
0·15	34·07	33·55	1·23	1·22	0·6	29·82	22·21	1·31	1·26
0·2	33·50	32·42	1·41	1·39	0·7	29·13	18·93	1·07	1·02
0·3	32·50	30·32	1·55	1·52	0·8	28·47	15·61	0·81	0·77
				Propionic acid solutions.					
0·05	34·81	35·52	0·96	0·94	0·4	29·78	28·75	2·01	1·74
0·1	33·87	34·66	1·41	1·36	0·5	28·91	26·41	1·78	1·49
0·15	33·07	33·82	1·74	1·64	0·6	28·20	23·91	1·43	1·16
0·2	32·26	32·83	1·93	1·79	0·7	27·69	21·10	0·99	0·78
0·3	30·84	30·88	2·08	1·86	0·8	27·21	17·50	0·55	0·42
				Butyric acid solutions.					
0·025	34·98	36·05	0·95	0·93	0·2	30·82	33·25	2·51	2·19
0·05	34·10	35·70	1·38	1·33	0·25	30·08	32·46	2·41	2·07
0·075	33·36	35·27	1·73	1·64	0·3	29·52	31·70	2·38	1·96
0·1	32·80	34·90	1·98	1·85	0·4	28·70	30·10	1·81	1·41
0·15	31·74	34·07	2·39	2·16					
				Valeric acid solutions.					
0·01	35·40	36·20	0·56	0·55	0·2	30·30	33·80	2·57	2·14
0·02	35·03	36·10	1·02	1·00	0·25	29·75	33·10	2·33	1·85
0·03	34·70	36·00	1·49	1·45	0·3	29·32	32·40	1·98	1·51
0·04	34·27	35·87	1·91	1·83	0·4	28·68	30·90	1·75	1·24
0·05	33·80	35·72	2·19	2·09	0·5	28·20	29·15	1·25	0·83
0·075	32·80	35·40	2·70	2·51	0·6	27·83	27·10	0·92	0·57
0·1	32·07	35·10	2·89	2·62	0·7	27·57	24·52	0·62	0·36
0·15	31·03	34·45	2·63	2·23					
				Hexanoic acid solutions.					
0·01	35·38	36·27	0·89	0·88	0·075	32·07	35·40	2·58	2·34
0·02	34·67	36·14	1·42	1·38	0·1	31·32	35·06	2·69	2·38
0·03	34·00	36·00	1·79	1·72	0·15	30·32	34·40	2·79	2·32
0·04	33·42	35·86	2·07	1·97	0·2	29·60	33·72	2·67	2·09
0·05	32·97	35·73	2·29	2·15					
				Heptanoic acid solutions.					
0·01	35·37	36·24	0·82	0·81	0·05	32·40	35·64	2·53	2·34
0·02	34·55	36·09	1·54	1·49	0·075	31·03	35·27	2·57	2·29
0·03	33·80	35·94	2·14	2·04	0·1	30·21	34·90	2·55	2·30
0·04	33·07	35·79	2·36	2·21	0·15	29·42	34·30	2·72	2·18
				Octanoic acid solutions.					
0·005	35·60	36·32	0·45	0·45	0·03	32·78	35·84	2·67	2·52
0·01	35·10	36·22	0·90	0·88	0·04	31·50	35·64	3·56	3·30
0·02	33·90	36·02	1·79	1·72					

Equations of this type are convenient, since on multiplication and rearrangement they can be written

$$\phi + (\phi/\pi)c + b = 0$$

so that if ϕ/π is plotted against ϕ, a straight line is obtained from which the values of the constants b and c can readily be determined. The differential coefficient is given by

$$d\phi/d\pi = -(\phi + b)/(\pi + c) = d\gamma/dp_1$$

and so by finding b and c from the straight-line plots, values of $d\gamma/dp_1$ can be calculated. The plot of ϕ/π against ϕ yielded quite good straight lines for all except the most dilute acid solutions (see Fig. 3). In general, the values of $d\gamma/dp_1$ found from these lines agreed fairly well with those obtained by measuring

directly the slopes of the γ–p_1 curves. Where any considerable divergence occurred, the values obtained from the empirical equations were preferred in the range where the ϕ/π–ϕ plots were linear.

Having determined $d\gamma/dp_1$ at various values of p_1 corresponding to the round figure values of N_2 we found the corresponding values of $\Gamma_2^{(N)}$. These were used as the starting points for subsequent calculations.

Table II shows the values of the surface tensions of the solutions in ergs/cm.^{2} at 25°, p_1 the partial vapour pressure in equilbrium with the solution at 25° in mm. of mercury, and $\Gamma_2^{(N)}$ and $\Gamma_2^{(V)}$ in g.-mols. cm.$^{-2}$, for the round-figure values of N_2 :

$$\Gamma_2^{(V)} = \frac{V_1}{V_1 N_1 + V_2 N_2} \cdot \Gamma_2^{(N)}$$

where V_1 and V_2 are the molar volumes of nitromethane and acid, respectively (Adam, *op. cit.*).

FIG. 3.
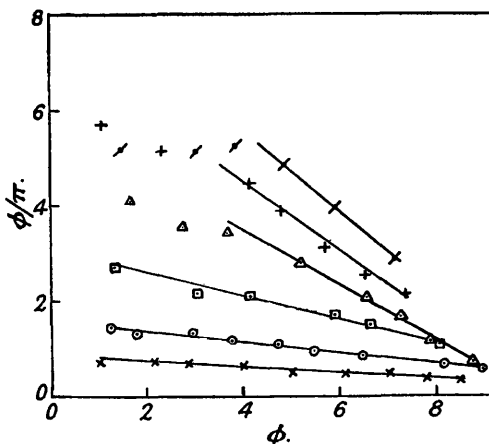
FIG. 4.

Adsorption of acetic acid.
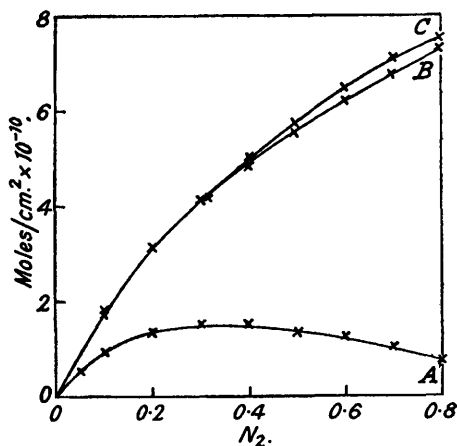
A. $\Gamma_2^{(V)}$.
B. Z_2, vertical orientation.
C. Z_2'', horizontal orientation.

DISCUSSION.

From the values of the surface-excess concentrations were calculated values of the absolute surface concentrations and mol.-fractions of acid in the surface layer, two conventions being used.

Convention I. This is Adam and Guggenheim's U-convention (*Proc. Roy. Soc.*, 1933, *A*, **139**, 218) which assumes that the areas per molecule of each component in the surface layer are independent of the bulk solution concentration and that

$$\Gamma_1 A_1 + \Gamma_2 A_2 = 1$$

where A_1 and A_2 are the areas per g.-mol. in the surface of the solvent and solute, respectively. This equation is solved simultaneously with the general Gibbs equation, giving

$$\Gamma_2^{(U)} = \frac{\Gamma_2^{(N)} + N_2/A_1}{1 + N_2[(A_2/A_1) - 1]}$$

The index (U) is used to indicate Γ values calculated by this convention. $\Gamma_2^{(U)}$, unlike $\Gamma_2^{(N)}$ and $\Gamma_2^{(V)}$, is an absolute surface concentration and not an excess concentration.

To obtain numerical values of $\Gamma_2^{(U)}$, it is clearly necessary to assign values to A_1 and A_2. This can only be done by making some assumptions about the surface layer structure. We have assumed that the nitromethane has no definite orientation; *i.e.*, we have put $A_1 = 0.120 \times 10^{10}$ cm.^{2} per g.-mol., corresponding to an area per molecule of 20.0 sq. A., which is equal approximately to the two-thirds power of the volume of the nitromethane molecule at 25°, and that the acid molecule has (*a*) an upright orientation in the surface layer, giving a value of A_2 corresponding to an area per molecule of 20.5 sq. A., ($\Gamma_2^{(U)}$); (*b*) no definite orientation, in

which case values of A_2 are taken corresponding to an area per molecule equal to the two-thirds power of the volume per molecule (A_2' and $\Gamma_2^{(U')}$).

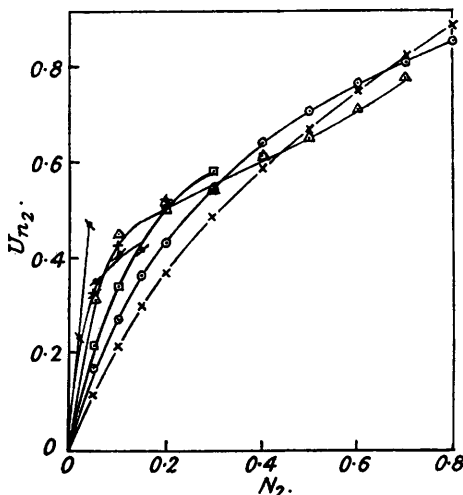The corresponding surface mol.-fractions $^U n_2$ and $^{U'} n_2$ were then calculated.

Convention II. This is the convention used by Fu and Bartell (*J. Phys. Colloid Chem.*, 1950, **54**, 537). The Adam and Guggenheim V-convention is used to calculate the surface-excess concentration of solute, and in order to obtain the absolute surface concentration Z_2, a quantity B, the concentration of solute which would have been present in the surface layer if no adsorption had occurred, is added to $\Gamma_2^{(V)}$. Values of B can only be obtained if assumptions are made about the thickness of the surface layer. We have investigated three different assumptions, all of which consider the surface layer as unimolecular with respect to acid : (a) The acid molecules are oriented perpendicularly to the surface, the surface layer thickness d being equal to the length of the acid molecule; this gives B and Z_2. (b) The acid molecules have no definite orientation, $d' =$ (volume per acid molecule)$^{1/3}$; this gives B' and Z_2'. (c) The acid molecules are oriented horizontally, *i.e.*, parallel to the surface, $d'' = \sqrt{20\cdot5}$; this gives B'' and Z_2''.

FIG. 5.

Adsorption of valeric acid.

FIG. 6.

Vertical acid orientation.
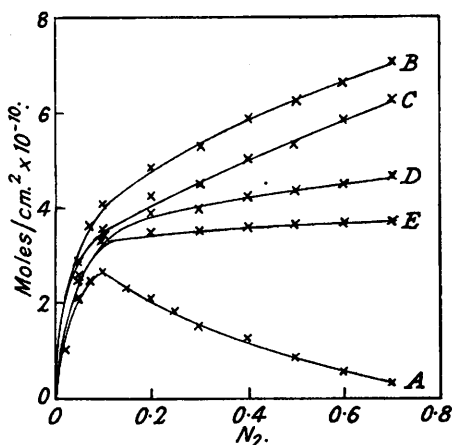
A. $\Gamma_2^{(V)}$
B. Z_2 } vertical orientation.
C. $\Gamma_2^{(U)}$
D. Z_2', random orientation.
E. Z_2'', horizontal orientation.

The calculations of the surface concentrations Z_2, and the corresponding Z_1 values were made following the method of Fu and Bartell; the Z_2'' and Z_1' values were calculated in a somewhat similar manner and from these the corresponding surface mol.-fractions of the acids ($^Z n_2$, $^{Z'} n_2$ and $^{Z''} n_2$) were then obtained.

TABLE III.

Molecular dimensions used in the calculations.

	d_4^{25}, g./cm.^{3}	V_1, cm.^{3}/g.-mol.	V_1, A.^{3}/mol.	$V_1^{2/3}$, A.^{2}/mol.	$V_1^{1/3}$, A./mol.	$10^{-10}A_1$, cm.^{2}/g.-mol.
Nitromethane	1·1313	53·9	89·5	20·0	4·47	0·120

Acid.	V_2, cm.^{3}/mol.	$10^{-10}A_2$, cm.^{2}/g.-mol.	$10^{-10}A_2'$, cm.^{2}/g.-mol.	$10^8 d$, cm.	$10^8 d'$, cm.	$10^8 d''$, cm.
Acetic	57·5	0·123	0·125	4·67	4·57	4·53
Propionic	75·0	,,	0·150	6·10	5·00	,,
Butyric	92·4	,,	0·175	7·48	5·35	,,
Valeric	109·1	,,	0·194	8·85	5·66	,,
Hexanoic	125·6	,,	0·212	10·18	5·93	,,
Heptanoic	142·4	,,	0·230	11·51	6·18	,,
Octanoic	159·0	,,	0·246	12·86	6·41	,,

The difference between conventions I and II is that if ordinary molecular dimensions are used, the U-convention assumes a film unimolecular with respect to both components, whereas convention II assumes a film unimolecular with respect to the " longer " component but multimolecular with respect to the " shorter " one.

In the case of horizontal acid orientation, the two conventions lead to about the same result owing to the molecular dimensions involved (see Table III). This case has therefore only been worked out for convention II.

FIG. 7.

Vertical acid orientation.
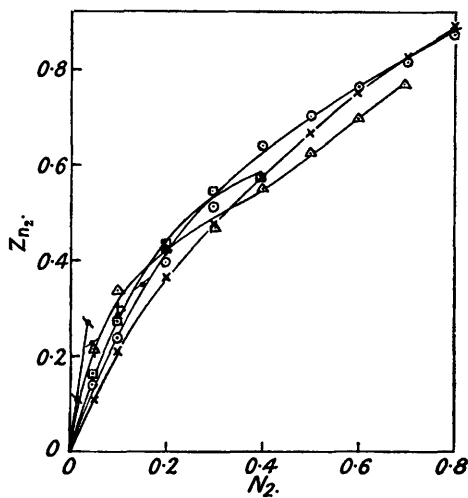
FIG. 8.

Random acid orientation.
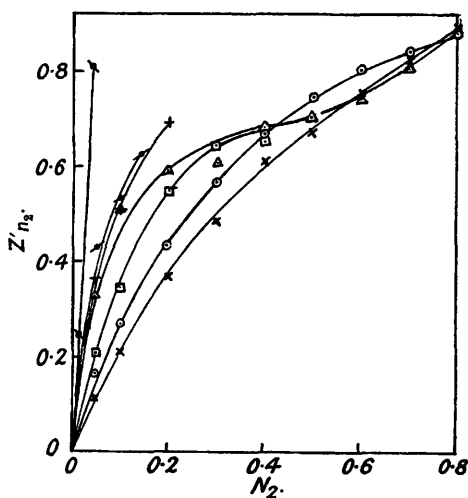
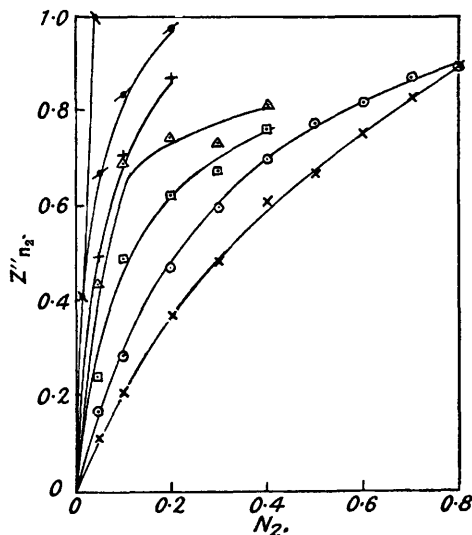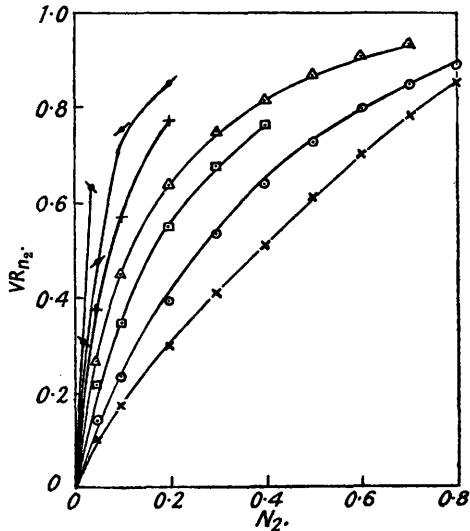FIG. 9.

Horizontal acid orientation.

FIG. 10.

Van Rysselberghe convention ; no orientation assumed.

Some of our results of the calculations of surface excess concentrations, Γ_2, and absolute surface concentrations are shown in Figs. 4 and 5. These bring out the major difference between the adsorption of surface-active materials on solutions in organic solvents and adsorption on aqueous solutions. The absolute surface concentration of acid, Z_2, in the former case is seen to be largely controlled by the bulk concentration, the adsorption excess playing a much smaller role in determining Z_2 than in aqueous adsorption.

Figs. 6—10 illustrate the relations between the surface mol.-fractions of acid, calculated

according to the various conventions, and the bulk mol.-fraction. It is seen that the various conventions that are considered all give a surface mol.-fraction which increases steadily with bulk mol.-fraction and, in this respect, all the conventions and assumptions of acid orientation considered yield reasonable results for any particular nitromethane–acid system.

The orientation assumptions are, however, sharply differentiated by the character of the plots obtained when the whole series of acid–nitromethane systems are considered together. It is seen that the assumption of vertical acid orientation ($^{U}n_2$ and $^{Z}n_2$, Figs. 6 and 7) leads to a set of curves which are brought very close together for the whole series of acids; in the case of the Z-convention (II), this effect is more pronounced than that in the U-convention (I), since in the former case the thickness of the surface layer is supposed to be determined by the long dimension of the oriented acid and this increases steadily with the length of the chain; the adsorption space is thus steadily increased and it is supposed that the nitromethane molecule can be adsorbed to a thickness of several molecules: *e.g.*, in the case of octanoic acid (see Table III) a surface layer nearly three molecules thick with respect to nitromethane is implied by the Z convention.

This grouping together of the n_2–N_2 curves seems unlikely to be correct. In solutions of the higher acids in which the surface tension is within a dyne of the value for the pure acid, the assumption of vertical orientation of acid leads to quite low values of n_2; *e.g.*, heptanoic acid, $N_2 = 0.15$, $\gamma = 29.42$, *i.e.*, is within 0.72 erg cm.$^{-2}$ of the value of the pure acid, and yet $^{U}n_2$ and $^{Z}n_2$ are only 0.42 and 0.35, respectively.

If no definite assumption is made about the acid orientation, *i.e.*, if it is considered completely random, the n_2–N_2 curves are spaced out more as would be expected, *i.e.*, the higher acids show a greater deviation from a straight-line relation than the lower ones (Fig. 8). In the case of heptanoic acid $N_2 = 0.15$, $^{U'}n_2$ and $^{Z'}n_2$ are 0.68 and 0.64, respectively.

If the acid molecule is assumed to be horizontally oriented in the surface layer, the U- and the Z-convention yield almost identical results with these systems and only the $^{Z''}n_2 - N_2$ results are shown (Fig. 9). Apart from some irregularities in the more concentrated valeric acid solutions (which have been left out of Fig. 9 for the sake of clarity), an even better separation of the curves for the different systems is obtained. For the heptanoic acid solution of $N_2 = 0.15$, $^{Z''}n_2$ is now 0.9, and for the octanoic acid solution of $N_2 = 0.04$, where the surface tension is 2 ergs cm.$^{-2}$ greater than that of the pure acid, $^{Z''}n_2 = ca.$ 1. The assumption of horizontal orientation therefore seems to exaggerate the separation of the curves.

The idea of a direct relation between surface concentration or mol.-fraction and surface-tension lowering was suggested by Matthews and Stamm (*J. Amer. Chem. Soc.*, 1924, **46**, 1071). Van Rysselberghe (*J. Physical Chem.*, 1938, **42**, 1021) suggested that, as a first approximation, the surface mol.-fraction of a solute could be taken as equal to the surface-tension lowering of the solution divided by the difference of surface tension between the two components: $^{VR}n_2 = (\gamma_1 - \gamma)/(\gamma_1 - \gamma_2)$ or $n_2\gamma_2 + n_1\gamma_1 = \gamma$ since $n_1 + n_2 = 1$.

We have plotted a set of values of $^{VR}n_2$ calculated by this method (Fig. 10); no assumptions need be made about orientations in the surface layer. It is seen that the $^{VR}n_2$–N_2 curves form a group which, as would be expected, show a regularly increasing deviation from the straight-line relation as the length of the hydrocarbon chain in the acid is increased. On comparing the $^{VR}n_2$–N_2 curves with the others, it is seen that they are situated intermediately between the random and horizontal orientation plots. If the validity of Van Rysselberghe's approximation can be accepted, then the acid molecules in the surface layer would appear to be oriented between a completely random and a horizontal arrangement (cf. Taubmann, *Acta Physicochem. U.S.S.R.*, 1936, **5**, 355).

It is interesting that this is also the conclusion reached from the preceding discussion of the various conventions based on the fundamental theory of Gibbs; the acid molecules on entering the surface layer encounter forces which tend to orient them so that their long axes are parallel to the surface, but which are inadequate to produce a completely ordered layer.

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