

AGRICULTURAL EXPERIMENT STATION

KANSAS STATE AGRICULTURAL COLLEGE
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ADSORPTION AT LIQUID-VAPOR AND LIQUID-LIQUID INTERFACES AND SOME RELATED PHENOMENA



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SUMMARY

Freundlick's derivation of Gibbs equation for calculating adsorption at liquid-liquid and liquid-vapor interfaces is given.

The adsorption in the liquid-vapor interface in moles per square centimeter, and likewise the number of molecules, the area occupied by each, and their diameters for the first 10 acids of the aliphatic series are given in Table I.

The effect produced upon the surface tension of decylic acid by adding varying quantities of hydrochloric acid is shown in Table II.

A method of calculating adsorption by use of the Gibbs equation is described.

The adsorption of butyl, octyl, and cetyl alcohols is shown in Table III.

The weight of a hanging drop depends upon its time of formation.

The reason for this is to be found in the application of Fick's law. Figure 1 is a curve showing very clearly the relation between the time of formation and the weight.

Table IV and figure 5 give respectively the data and adsorption curves for allyl, propyl, and dipropyl amine.

Table V and figure 6 give respectively the data and adsorption curves for several esters.

On comparing the logarithmic curves of the acids and alcohols the alcohols are found to exhibit a greater adsorption than the acids, and also to possess a constant degree of adsorption through a greater range of concentration change. An explanation of this behavior may be found in the different electrolytic characters of the acids as compared with the alcohols.

The alcohols of four- and five-carbon atoms reach zero adsorption at the same concentrations as do the acids of the same number of carbon atoms. The alcohols of one-, two-, and three-carbon atoms show adsorption at a lower concentration than the corresponding acids.

The curves for the esters lie very nearly in the same position as those of the alcohols of the same number of carbon atoms. Taken as a whole the curves for the esters correspond closely to those of the acids. Ethyl propionate and propyl acetate, two esters having the same number of carbon atoms but differently arranged show an interesting relation. The former requires a higher concentration to produce the same adsorption. The more symmetrical the ester is the

smaller the adsorption after the adsorption has once become constant.

A method is shown whereby the solubility of a difficultly soluble substance may be ascertained.

At the interface water-benzene when the concentration in the aqueous solution was 0.04 moles per 1,000 grams of water, 1×10^{14} molecules were found to be present in one square centimeter of the film between water and benzene, while if the benzene were not present the concentration of the aqueous phase need be only one-third as great to be in equilibrium with the same number of molecules in the surface film.

The adsorption of substances of the type of organic acids, alcohols, and esters is always greater at the surface of water than at the interface between water and an organic solvent of the type of benzene or a paraffin.

An adsorption formula worked out by Dr. A. C. Lund of the University of Chicago is given in full.

The curves shown in figure 7 indicate single molecules of butyric acid are more soluble in water than in benzene, but that the double molecules are more soluble in benzene.

The presence of benzene as an upper layer does not change the number of butyric acid molecules in this monomolecular layer.

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ADSORPTION AT LIQUID-VAPOR AND LIQUID-LIQUID INTERFACES AND SOME RELATED PHENOMENA

H. H. KING²

OCCURRENCE OF ADSORPTION IN SOILS

Adsorption is a phenomenon which is finding an increasing application in the study of the chemistry of soil and soil solutions. Since adsorption is confined to surfaces, the enormous surface present in soil, together with the largely variant type of soil solutions, offers excellent opportunity for its manifestation. The colloidal character of some of the principal soil constituents certainly offers suitable conditions for adsorption. Among these may be mentioned humus and decayed material of an organic origin, aluminum and ferric hydroxides, decayed or weathered forms of silicates, and various types of bacteria.

Adsorption plays an important role in the retention of soil nutrients. The finely divided soil particles possess the power of withdrawing dissolved materials by surface concentration from the aqueous solution with which they are surrounded, thus preventing their washing out. Much material necessary for plant nutrition is undoubtedly held by this means. The products withheld in this manner are in excellent condition to be taken up by the plant rootlets penetrating into the region of the adsorbed substances. Such products as readily soluble fertilizers are thus prevented from being immediately leached out of the soil. Nitrates and soluble potash compounds are especially indebted to adsorption for their retention. Nitrates when added to a clay soil can only to a small measure be removed from the particles by washing with distilled water. The finer the soil particles the less the amount removable by use of a certain quantity of solvent.

Gases are also adsorbed when brought in contact with soil particles. No doubt oxidation within the soil is materially hastened by the adsorption of oxygen on the surface of the soil particles. Oxygen and hydrogen, though very stable when mixed together

¹ Contribution No. 94, from the Department of Chemistry.

² This work was done at the University of Chicago and the Kansas Agricultural Experiment Station under the direction of Dr. W. D. Harkins of the University of Chicago.

at ordinary temperatures, may explode if finely divided platinum is introduced into the containing vessel. In a similar manner oxidation within the soil should be enhanced by the surface condensation. The phenomena of nitrification are likewise affected by surface concentration forces.

Adsorption may become selective in character in that one kind of ion may be removed from solution to a greater extent than another.

It is well known that by shaking a sample of soil with a solution of potassium chloride the quantity of potassium will be diminished, having been supplanted by some of the bases of the soil. The resulting solution will have become much more acid in reaction. This phase of adsorption is very commonly met with in soil studies.

In the investigation described below much simpler solutions were employed than are found in the soil. In order to ascertain the general character and laws of operation of any physical or chemical phenomenon, the purest kind of products should be used and in the simplest fashion possible. From these simpler systems advance can more easily and accurately be made into the complex. This investigation is a part of the work originally planned to include a study of the adsorption of the normal paraffin acids and alcohols with chains from one to sixteen carbon chains in length both at the interface water-benzene and that of water-air, which was begun by Harkin and Humpherys (1916) in 1913.

DERIVATION OF THE GIBBS EQUATION

The general phenomena to be considered are those found at the interface where two phases meet. Willard Gibbs in his papers on "Equilibrium in Heterogeneous Systems," pointed out that in addition to the common variables, temperature, pressure, and concentration, we should also include the interface. He gave no experimental data in substantiation of his theory and for some time after his theoretical deductions were made no experimental work was undertaken to test the verity of these conclusions.

F. G. Donnan (1899) and W. C. McC. Lewis (1908) were the first to attempt an experimental verification of Gibbs' Law.

The deduction of Gibbs' Law has been put in simpler form by several authors. The one which is here given is that of Freundlick (1909).

Consider a dilute solution of volume, v , osmotic pressure, P , in contact with a vapor phase consisting only of the vapor of the solvent. The area of the separating surface between liquid and vapor is s ,

and the surface tension is γ . The solution is placed in a vessel fitted with a piston having a semipermeable membrane, the solution being on one side of the membrane, and on the other side an infinite reservoir of pure solvent in contact with it. The following cyclic process is carried out:

The surface area is increased by the amount ds , the work done being $-\gamma ds$. The volume of the solution is considered as having remained constant. At the same time the osmotic pressure, P , may have altered—its new value being given by the expression $(P + \frac{\partial P}{\partial s} ds)$.

By pulling out the piston the volume of the solution is now increased by dv , the work being $+(P + \frac{\partial P}{\partial s} ds) dv$. The surface area, s , is supposed to have remained constant in this last operation whilst the tension, γ , has changed to the value $(\gamma + \frac{\partial \gamma}{\partial v} dv)$. The surface area now contracts to its initial value, the work gained being $+(\gamma + \frac{\partial \gamma}{\partial v} dv) ds$. P has now returned to its initial value, and when the piston is pushed in, thereby doing the work $-Pdv$, the system has returned to its initial state. Since the process is isothermal and reversible, the total work is zero; that is,

$$\begin{aligned}
 &-\gamma ds + (P + \frac{\partial P}{\partial s} ds) dv + (\gamma + \frac{\partial \gamma}{\partial v} dv) ds - Pdv = 0 \\
 \text{or } &\frac{\partial \gamma}{\partial v} = -\frac{\partial P}{\partial s} \dots\dots\dots (1)
 \end{aligned}$$

This equation states that if the surface tension alters with the volume, that is with the concentration, then the osmotic pressure must alter with the surface area. The latter can be the case only if the concentration of the solute in the bulk of the solution depends on the surface area, and this can be so only if the concentration in the surface layer is greater or less than that in the bulk of the solution.

From the above it is seen that the concentration, c , of the solution is a function of v and also of s . If n moles are dissolved, then we cannot simply write $c = \frac{n}{v}$, but instead must allow for the fact that in the surface layer the solute is present to a greater or less

extent than in the bulk. Suppose we denote this positive or negative excess in the surface by u , where u is the mass of solute reckoned per unit area of surface. Then if the surface area is s , the quantity of solute in excess in the surface layer is us and hence the actual concentration in the bulk of the solution is given by

$c = \frac{n-us}{v}$. Note that the quantity, us , may be positive or negative. The above equation (1) may now be written in the form

$$\frac{\partial \gamma}{\partial c} \cdot \frac{\partial c}{\partial v} = - \frac{\partial P}{\partial c} \cdot \frac{\partial c}{\partial s} \dots \dots \dots (2)$$

$$\text{But } \frac{\partial c}{\partial v} = - \frac{(n-us)}{v}, \text{ and } \frac{\partial c}{\partial s} = - \frac{u}{v}.$$

So that equation (2) becomes $\frac{c \partial \gamma}{\partial c} = - u \frac{\partial P}{\partial c}$.

Since the solution is a dilute one, the gas law, $P = RTc$, may be applied, which finally gives, $u = - \frac{c}{RT} \cdot \frac{\partial \gamma}{\partial c}$.

This is the so-called Gibbs' Law. It was employed in the calculations of all the adsorption curves. This equation points out the fact that if the surface tension decreases as the concentration of the solute increases, the value of u will be positive, but if the reverse is the case, then u will be negative. This signifies that a positive adsorption means an accumulation of an excess of solute in the surface layer over that in the interior of the liquid.

No assumption is made concerning the nature of the boundary, and the formula should apply to all kinds of surfaces, such as solid-liquid, liquid-liquid, liquid-gas, etc. No correction is introduced for the dissociation of the solute, but may be so done by writing the osmotic pressure law as, $P = iRTc$, which gives, $u = - \frac{c}{iRT} \cdot \frac{\partial \gamma}{\partial c}$.

It is to be observed that a small quantity of solute may produce a marked lowering of the surface tension, but can only produce a small increase in it.

In making the adsorption curves the following procedure was followed: The surface tension of a whole series of solutions containing the solute in different quantities was determined and plotted against the logarithm of the concentration. The logarithm of the concentra-

tion may be employed, since we may rewrite the adsorption equation as, $u = -\frac{1}{iRT} \cdot \frac{\partial \gamma}{\partial \log c}$.

To ascertain the value of u for any concentration, it is only necessary to find the slope, $\frac{\partial c}{\partial \log c}$, of the adsorption curve at that point and substitute the found value into the equation and solve for u .

EXPERIMENTAL DATA ON THE FATTY ACIDS

FORMIC ACID

All the results were obtained for this acid by the drop-weight method. The first result (drop weight=0.0293) was obtained by the Morgan tip having a radius of 0.29925 cm. This tip was so badly damaged by accident that a new Morgan tip was employed. All the rest of the surface tension data for this acid was calculated from results secured by use of the new tip. The radius of this new Morgan tip was 0.27650 centimeter.

ACETIC ACID

All the points for acetic acid were taken from the work of Drucker, Karl (1905). His results were put in a different form from that used in this investigation, so it was necessary to recalculate all his work. His results were obtained by the capillary height method.

PROPIONIC ACID

The C. P. Acid was redistilled three separate times. The middle fraction was selected and had a boiling point of 140 degrees C. This acid was used in making up the solutions for running the adsorption curve. The first Morgan tip was employed, having a radius of 0.29925 centimeter. On the most dilute solutions 30-minute drops were run, but these did not differ materially from the 5-minute drops.

BUTYRIC ACID

This acid was run partly by Doctor Clark and partly by the writer. All points up to the 0.1N solution are those obtained by Doctor Clark, but beginning with the 0.1N solutions the points plotted are those obtained by the writer. The time of formation was as long as 10 minutes for a drop, but these were practically the same as the drop weights obtained for a 5-minute drop.

VALERIC AND CAPROIC ACIDS

The points plotted for these acids were obtained by recalculating the results of Szyszkowski (1908). He made use of the capillary height method in obtaining these results.

HEPTYLIC ACID

A Morgan tip of radius 0.29925 centimeter and 30-minute drops were used. These 30-minute drops were practically the same as the 5-minute drops in weight. No difficulty was encountered in obtaining checks with this acid. The weights of the 30-minute drops seemed to be always slightly lighter than the 1-minute drops but the results were not always uniform; that is, the differences were not always of the same value.

NONYLIC ACID

A Morgan tip of radius 0.29925 centimeter was used. Time plays an important part in obtaining the drop weights. For the more concentrated solutions of this acid the time was much less than for those solutions which were more dilute. The points were plotted from the 30-minute drop weights for all except the first point. For this, 5-minute drops were used. The greatest error is very likely to be found in the most dilute solutions in that these drops from which the surface tensions were calculated may not have been allowed to hang until they had come to a state of equilibrium.

DECYLIC ACID

A Morgan tip of 0.29925 centimeter radius was used. This acid gave much difficulty, especially with the more dilute solutions, because of the time effect. The time effect, plotted in figure 1, deals with this acid and shows very clearly how important it is to take note of the time the drop hangs before dropping.

In these calculations 30-minute drops were used. An attempt was made to use a 60-minute drop, but the difficulties incurred in keeping a full-sized drop hanging for this time were too great.

The data obtained for the acids mentioned above will be found in Table I (pp. 14 to 16).

The first four columns of figures in Table 1 are self explanatory. The fifth column is the relation of the radius of the tube used to the capillary constant (Harkins and Humphery, 1916) and $f\left(\frac{r}{a}\right)$ represents a function of $\frac{r}{a}$; γ stands for the surface tension measured; a and \sqrt{a} represent respectively the space occupied by each molecule and its diameter.

ADSORPTION

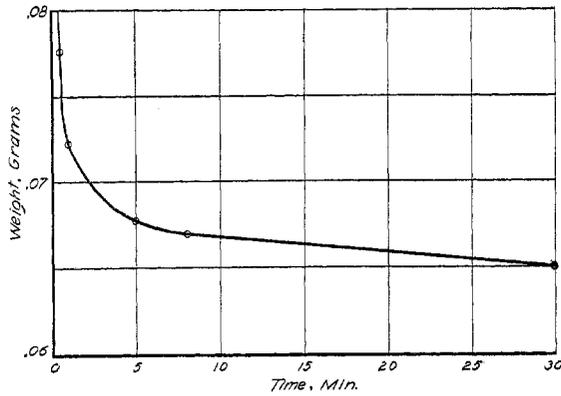


FIG. 1.—Effect of time on the drop weight of decylic acid, 0.0015 N

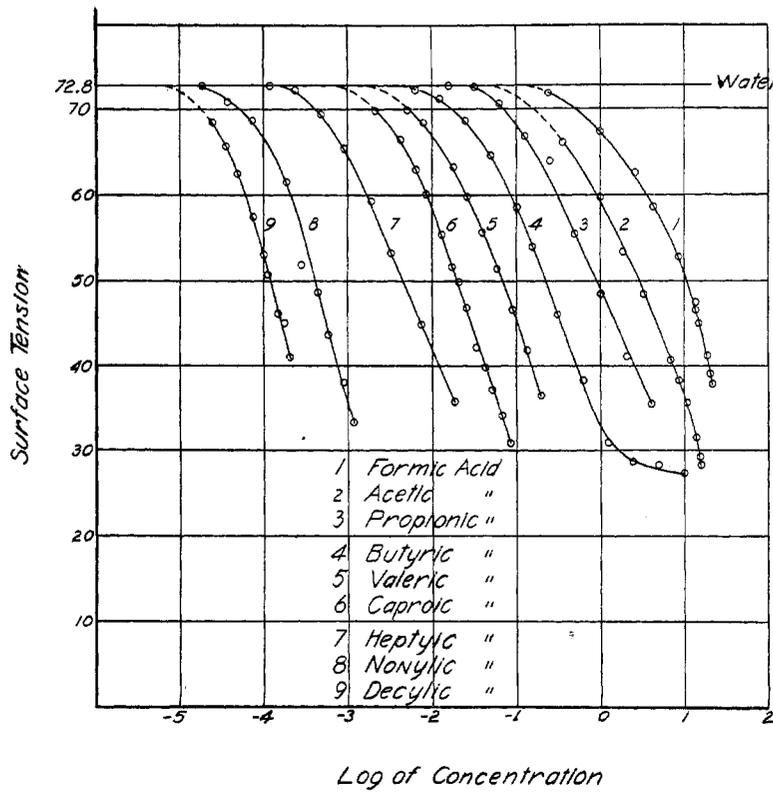


FIG. 2.—Adsorption curves for fatty acids

TABLE I.—ADSORPTION OF THE FATTY ACIDS FROM FORMIC TO DECYLIC

FATTY ACID (a)	Moles per liter	Moles per 1,000 gm. H ₂ O	Density	Degree of ionization	r/a	f (r/a)	γ	Moles per sq. cm.	Molecules	Area (a)	Diameter \sqrt{a}	
Formic	21.739	321.58	1.2067	0.07	(b) 1.143	0.5995	37.97					
	20.321	128.44	1.1900	.12	1.205	.5995	39.17					
	18.580	52.74	1.1807	.14	.960	.6010	41.22					
	14.889	39.07	1.1470	.22	.940	.6015	45.13					
	13.750	34.002	1.1372	.24	.930	.6020	46.74	2.898 x 10 ⁻¹⁰	1.7568 x 10 ¹⁴	58.92 x 10 ⁻¹⁶	7.545 x 10 ⁻⁸	
	13.261	14.211	1.1326	.245	.920	.6025	47.56	2.8977 x 10 ⁻¹⁰	1.755	56.98	7.545	
	8.591	5.259	1.0318	.61	.895	.6035	52.95	2.887	1.7503	57.135	7.559	
	4.239	2.885	1.0610	.82	.860	.6050	58.77	2.8878	1.7508	57.123	7.558	
	2.547	1.037	1.0400	1.37	.850	.6060	62.66	2.8655	1.7371	57.566	7.587	
	0.875	.2712	1.0380	2.68	.824	.6080	67.52	1.5895	.96356	103.78	10.187	
	.237	.0634	1.0000	5.50	.830		72.00	1.267	.7680	130.21	11.411	
	Acetic	15.580	238.955	1.054	0.02			28.25				
		15.220	175.345	1.061	.03			29.35				
		13.840	81.603	1.067	.03			31.60	1.550 x 10 ⁻¹⁰	0.9396 x 10 ¹⁴	106.43 x 10 ⁻¹⁶	10.310 x 10 ⁻⁸
10.870		31.253	1.068	.07			35.65	1.798	1.090	91.71	9.5766	
8.636		17.922	1.058	.10			38.35					
6.911		11.808	1.049	.12			40.75	3.293	1.9962	50.096	7.078	
3.207		3.971	1.026	.21			48.55	3.2675	1.999	50.026	7.072	
1.830		2.056	1.016	.29			53.50	3.2873	1.9928	50.18	7.084	
0.989		1.052	1.011	.41			59.85	3.2835	1.9905	50.24	7.088	
.362		0.369	1.006	.70			66.20	2.3537	1.4268	70.086	8.3716	
Propion c.	4.00	5.501	1.021	0.18	1.052	.5995	35.54	4.2338 x 10 ⁻¹⁰	2.5665 x 10 ¹⁴	38.96 x 10 ⁻¹⁶	6.242 x 10 ⁻⁸	
	2.00	2.551	1.011	.23	1.002	.5995	41.21	4.2316	2.5652	30.983	6.2436	
	1.00	1.080	1.0048	.37	0.970	.6000	48.52	4.2258	2.6517	39.033	6.248	
	0.50	0.5175	1.0010	.53	.940	.6010	55.62	3.329	2.0095	49.763	7.054	
	.25	.254	1.0001	.75	.920	.6020	64.01	2.4233	1.469	68.073	8.2507	
	1.125	.1261	0.9990	1.03	.9008	.6030	66.98	1.5341	.9300	107.53	10.357	
	0.0625	.0528	.9955	1.50	.8880	.6040	70.76					
	.0313	.0317	.9982	2.13	.8810	.6045	72.70					
.0157	.0157	.9982	3.01	.7660	.6140	72.80						

	10.00	117.04	0.9726	0.038	0.9924	5994	27.40					
	5.00	10.971	.9984	.12	.9889	5998	28.29					
	2.50	3.219	1.0022	.27	.9853	.6000	28.65					
	1.25	1.409	1.0027	.30	.9485	.6010	30.95					
	0.625	0.663	1.0000	.50	.8508	.6060	38.31	4.566 x10 ⁻¹⁰	2.768 x10 ¹⁴	36.128x10 ⁻¹⁶	6.0109x10 ⁻⁸	
Butyric.....	.313	.322	0.9986	.58	.7508	.6150	46.17	4.5624 "	2.7658 "	36.156 "	6.013 "	
	.1563	.159	.9928	.69	.6930	.6210	54.04	4.553 "	2.760 "	36.232 "	6.0193 "	
	.1000	.101	.9992	1.03	.9000		58.63	4.648 "	2.8176 "	35.49 "	5.9574 "	
	.05	.050	.9983	1.30	.8770		64.69	3.9046 "	2.3674 "	42.24 "	6.499 "	
	.025	.024	.9982	1.84	.8700		68.72	2.870 "	1.7397 "	75.48 "	7.582 "	
	.0125	.013	.9982	2.60	.8600		71.22	1.7022 "	1.0318 "	96.91 "	9.844 "	
	.00625	.0066	.9982	4.03	.8500		72.29	1.0794 "	.6543 "	152.83 "	12.362 "	
	1.995	.2092	0.9995	0.87			36.52	5.1142x10 ⁻¹⁰	3.1006x10 ¹⁴	32.252x10 ⁻¹⁶	5.679 x10 ⁻⁸	
	1.333	.1356	.9990	1.07			41.82	5.1046 "	3.024 "	32.315 "	5.6847 "	
	.0884	.0893	.9985	1.32			46.74	5.092 "	3.0867 "	32.398 "	5.6266 "	
Valeric.....	.0589	.0593	.9982	1.75			51.47	5.0705 "	3.0737 "	32.534 "	5.704 "	
	.0393	.0395	.9982	1.98			55.76	4.264 "	2.5848 "	38.687 "	6.220 "	
	.0262	.0263	.9982	2.44			59.91	3.9318 "	2.3834 "	41.957 "	6.4774 "	
	.0175	.01756	.9982	2.94			63.48	2.8044 "	1.7001 "	58.82 "	7.6695 "	
	.0116	.0117	.9982	3.59			66.32	2.2215 "	1.3429 "	74.465 "	8.629 "	
	.0078	.00782	.9982	4.38			68.50	1.8264 "	1.1074 "	90.30 "	9.5025 "	
	.0052	.00522	.9982	5.33			69.96	1.573 "	.6541 "	104.82 "	10.238 "	
	.0840	.0845	0.9985	1.31			30.83	5.2244x10 ⁻¹⁰	3.167 x10 ¹⁴	31.575x10 ⁻¹⁶	5.619 x10 ⁻⁸	
	.0680	.0684	.9982	1.46			34.07	5.2166 "	3.1624 "	31.622 "	5.6321 "	
	.0510	.05125	.9982	1.68			37.17	5.2057 "	3.1554 "	31.69 "	5.6294 "	
	.0425	.04267	.9982	1.84			39.81	5.1971 "	3.1506 "	31.74 "	5.6339 "	
	.0340	.03410	.9982	2.05			42.28	5.1864 "	3.144 "	31.806 "	5.6396 "	
Caproic.....	.0256	.02566	.9982	2.42			46.82	5.168 "	3.1327 "	31.921 "	5.650 "	
	.0212	.02124	.9982	2.59			49.06	5.159 "	3.1275 "	31.974 "	5.6546 "	
	.0170	.01703	.9982	2.89			51.69	5.1452 "	3.119 "	32.06 "	5.662 "	
	.0128	.01281	.9982	3.32			55.47	5.123 "	3.1055 "	32.20 "	5.6745 "	
	.0085	.008507	.9982	4.06			60.13	4.2643 "	2.585 "	38.684 "	6.2196 "	
	.0064	.006402	.9982	4.63			63.04	3.3045 "	2.003 "	49.924 "	7.0657 "	
	.00425	.004252	.9982	5.69			66.46	2.3607 "	1.431 "	69.98 "	8.5393 "	
	.00212	.002124	.9982	7.96			69.82	1.3536 "	.8205 "	121.87 "	11.039 "	

TABLE No. I—CONCLUDED

FATTY ACID (a)	Moles per liter	Moles per 1,000 gm. H ₂ O	Density	Degree of ionization.	r/a	f (r/a)	γ	Moles per sq. cm.	Molecules	Area (a)	Diameter \sqrt{a}	
Heptylic.....	.0150	.01505	0.9982	3.08	1.12	.5995	35.75	4.875 x10 ⁻¹⁰	2.8821x10 ¹⁴	33.836x10 ⁻¹⁶	5.817 x10 ⁻⁸	
	.0075	.00753	.9982	4.32	0.964	.6000	44.87	4.8174 "	2.9204 "	34.242 "	5.8519 "	
	.00375	.003759	.9982	6.06	.841	.6040	53.36	4.738 "	2.8724 "	34.815 "	5.600 "	
	.001875	.001878	.9982	8.48	.8388	.6070	59.35	3.942 "	2.390 "	41.84 "	6.4683 "	
	.0009375	.000938	.9982	11.73	.7936	.6110	65.46	3.428 "	2.0788 "	48.103 "	6.9357 "	
	.00046875	.000469	.9982	16.14	.7849	.6115	69.45	3.161 "	1.9162 "	52.187 "	7.224 "	
	.00023437	.000235	.9982	19.87	.7830	.6118	72.37	2.230 "	1.3519 "	73.971 "	8.6006 "	
	.000117185	.0001173	.9982	29.54	.7750	.6120	72.80	1.2106 "	.7338 "	136.29 "	11.671 "	
	Monylic.....	.0012	.001203	0.9982	10.46	1.128	.5995	33.32	5.195 x10 ⁻¹⁰	3.1498x10 ¹⁴	31.754x10 ⁻¹⁶	5.635 x10 ⁻⁸
		.0009	.0009017	.9982	12.61	1.001	.6000	38.00	5.096 "	3.089 "	32.372 "	5.6896 "
.0006		.000601	.9982	14.41	1.001	.6000	43.70	5.0154 "	3.0405 "	32.89 "	5.735 "	
.00045		.0004509	.9982	17.34	0.8250	.6020	48.65	4.8903 "	2.9646 "	33.732 "	5.808 "	
.00030		.0003006	.9982	19.75	.9050	.6030	51.97	3.6162 "	2.1423 "	46.68 "	6.832 "	
.00015		.0001502	.9982	26.64	.8562	.6060	61.69	1.942 "	1.1969 "	84.948 "	9.2164 "	
.000075		.00007531	.9982	40.87	.7849	.6115	68.75	0.88554 "	.53683 "	191.02 "	13.807 "	
.0000373		.00003757	.9982	46.85	.7828	.6119	70.98					
.00001825		.00001828	.9982	65.07	.7750	.6120	72.80					
Decylic.....		.0002	.0002004	.9982	23.76	1.135	.5995	41.06	5.695 x10 ⁻¹⁰	3.4027x10 ¹⁴	28.965x10 ⁻¹⁶	5.382 x10 ⁻⁸
	.000175	.0001753	.9982	25.00	1.083	.5995	45.06	5.510 "	3.3403 "	30.006 "	5.4714 "	
	.000150	.0001503	.9982	26.64	0.995	.5995	46.13	5.439 "	3.297 "	31.036 "	5.571 "	
	.0001125	.0001127	.9962	30.79	.9039	.6035	51.84	5.266 "	3.1924 "	31.324 "	5.596 "	
	.00010	.0001002	.9982	40.87	.8900	.6040	53.02	4.149 "	2.5154 "	39.756 "	6.305 "	
	.000075	.00007514	.9982	41.67	.8550	.6060	57.66	3.424 "	2.0750 "	48.178 "	6.941 "	
	.000050	.00005009	.9982	46.85	.8199	.6080	62.44	2.220 "	1.3461 "	74.28 "	8.6186 "	
	.0000375	.000037509	.9982	55.89	.8026	.6095	65.77	1.326 "	.8039 "	124.40 "	11.153 "	
	.0000250	.00002505	.9982	65.07	.7900	.6110	68.46					
	.00001875	.000018715	.9982	85.59	.7750	.6120	72.80					

(a) No octylic acid was obtainable.
 (b) First drop made with different tip.

Figure 2 (page 13) represents the curves obtained by plotting the surface tension against the logarithm of the concentration.

From these curves the slopes may be determined and this value substituted in the Gibbs equation in calculating the adsorption.

CAPILLARY HEIGHT METHOD FOR DECYLIC ACID

Owing to the fact that it seemed likely sufficient time was not allowed for equilibrium to be established by the drop-weight method, an attempt was made to make these measurements by the capillary height method. Satisfactory results were not obtained by this process, as it seemed practically impossible to obtain checks. The capillary tube was thoroughly cleaned with chromic acid, rinsed with conductivity water, thoroughly steamed, and finally dried by a current of dry air. It was then filled completely with the decylic acid (saturated solution) and the column allowed to fall. It would not always come to the same level, however, and while in practically every instance there was a marked fall in the height of the liquid column, it was not uniform in different measurements. In some cases the column of liquid went through a maximum and then began to fall.

The reason for this behavior appeared to rest with the character of the surface film, This behaved as though it were partially solidified and had a tendency to stick, thus preventing the column of liquid sustained by it from moving freely.

EFFECT OF HCl UPON THE ADSORPTION OF SOME FATTY ACIDS AND ALCOHOLS

As it is commonly thought that only the un-ionized part of the molecule is effective in producing adsorption, it was thought advisable to learn what the effect would be of adding a strong mineral acid, like HCl, to some of the fatty acids. Decylic, which shows adsorption to the highest degree of those investigated, was chosen. The HCl itself, within the concentration employed, would have only very slight effect upon the surface tension.

Table II shows the results of one series of experiments, using 0.00005 N decylic acid with varying concentrations of HCl. (Ionization equals 46.85 percent.)

TABLE II.—EFFECT OF HCl UPON THE SURFACE TENSION OF 0.00005 N DECYLIC ACID

Concentration of HCl	Drop weight	Surface tension
0.000	0.0646	62.68
.804	.0638	59.65
.5315	.0632	59.13
.4550	.0625	58.48
.0910	.0575	53.81
.0671	.0595	55.72
.0455	.0906	56.66
.0227	.0615	57.50

According to these, it is to be seen that HCl of 0.091 N concentration has a maximum lowering effect upon 0.00005 N decylic acid. with concentrations of decylic acid, higher or lower than 0.00005 N, such noticeable effects were not observed, although a lowering was observed in practically all cases.

Butyl and actyl alcohols were selected from among the alcohol group for investigation. It is known that alcohols form oxonium salts with acids like HCl and it was thought that possibly they might produce some effect other than that produced by the pure alcohols, upon the surface tension. In the case of butyl alcohol a very slight lowering was obtained, but this was so small as to be almost within the limits of experimental error. No noticeable effect was observed in the case of octyl alcohol.

From these investigations it is apparent that if oxonium salts are produced when HCl is added to these alcohols they have practically the same effect upon surface tension as the alcohols themselves.

EFFECT OF TIME ON THE WEIGHT OF A HANGING DROP

Milner (1907) was the first to make quantitative measurements of the effect the time of hanging has upon the weight of a drop. He obtained some time effects of a considerable magnitude by using solutions of sodium oleate.

In experiments with the fatty acids and alcohols, it soon became evident that to produce consistent results, special precautions were necessary as regards time of formation. This effect is the more pronounced the higher the molecular weight of the acid or alcohol. While for the acids it is very little up to and including butyric, for acids and alcohols having a larger number of carbon atoms it becomes much more noticeable. In figure 1 are plotted the drop weights against the time of formation for 0.0015 N decylic acid.

This curve shows very plainly the effect produced by the time of formation.

With octyl alcohol a very noticeable difference in drop weight with time was observed, but the effect was the exact reverse of that of the acids, for an increase in time produced an increase in drop weight. In figure 3 are plotted the values of the surface tension against the logarithm of the concentrations.

The top curve contains the values of the surface tensions calculated from 30-minute drops, while the second contains the values of 1-minute drops made on the same solutions. Each curve pro-

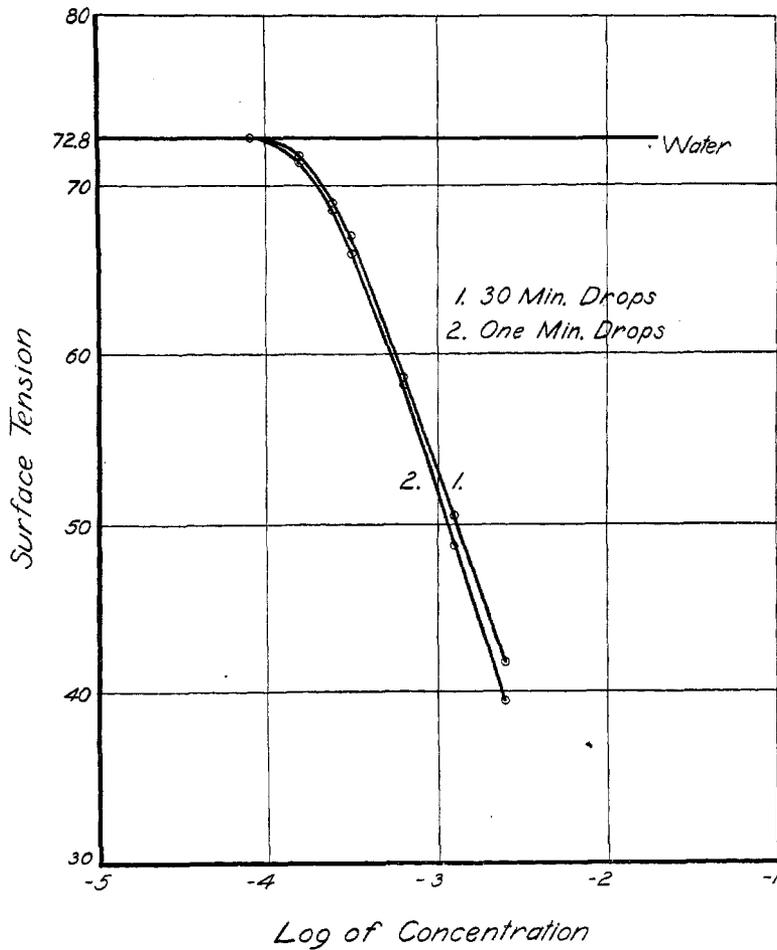


FIG. 3.—Effect of time on the drop weights of octyl alcohol

duces consistent results with itself, but differs very markedly from the other. Results were obtained only for a concentration of 0.0025 N for a one-half minute drop.

With cetyl alcohol containing 16-carbon atoms, time would be expected to play a still more noticeable effect, and such is indeed the case. Figure 4 contains the adsorption curves for three alcohols.

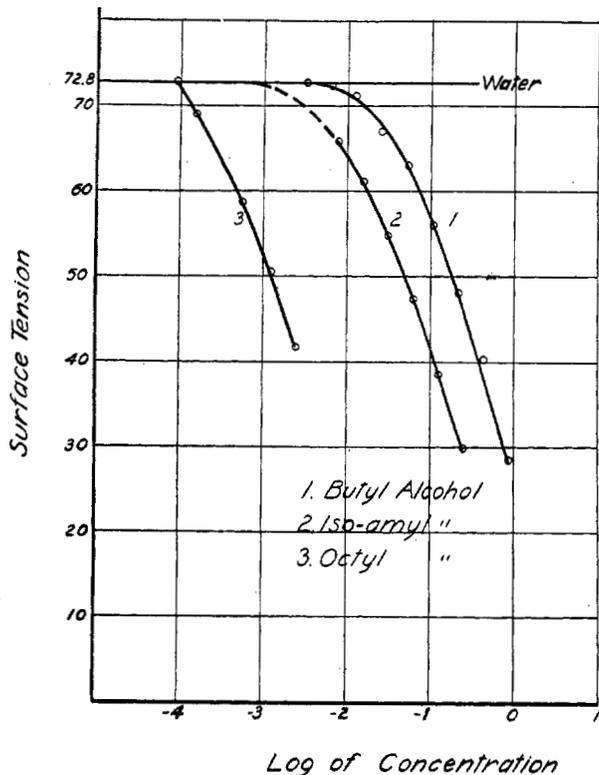


FIG. 4.—Adsorption curves for alcohols

Cetyl alcohol should have a greater slope than the alcohols of smaller carbon atom content while, as a matter of fact, its slope is much less than those next to it. With cetyl alcohol of one-eighth saturated solution, the drop weight for a one-fourth minute drop was 0.0845 grams; for a 5-minute drop it was 0.0840 grams; for a 30-minute drop it was 0.0825 grams; and for a drop hanging for one hour, it was 0.0779 grams. This indicates that it is impossible to obtain accurate results for this alcohol by the drop-weight

method, owing to length of time it takes the film to become saturated.

With butyl alcohol, the effect of time upon drop weight was very small, but the general indication was similar to the results obtained with octyl alcohol.

The cause of the decreases in the drop weight with the time is undoubtedly to be found in the speed of diffusion of the molecules themselves. In order that equilibrium may be established between the excess of molecules of solute in the surface film and those within the interior, time must be allowed for the molecules from the interior to migrate to the surface. In case the solution is fairly concentrated the time necessary to obtain equilibrium will be very short, but if the solution is very dilute, as is the case for the acids and alcohols of high molecular weight, the time effect will be more pronounced.

The first quantitative measurements on the migration of the particles of solute from one part of the solution to another, were made by Nernst (1889). He made use of Fick's Law (1855) that the quantity of salt which diffuses through a given volume is directly proportional to the concentration differences of two areas infinitely near each other. If the difference in concentration at these points is dc , and the difference in distance is dx , then the concentration gradient will be $\frac{dc}{dx}$. Fick's Law states that the amount, ds , which will cross the cross sectional area, a , in time, dt , is given by the expression, $ds = -Da \frac{\partial c}{\partial x} dt$. The rate of change may be expressed by $\frac{ds}{dt} = - \frac{\partial c}{\partial x}$.

This negative value indicates the motion is in the direction of decreasing concentration. D is the specific diffusion rate. In case of solutions where the value of the concentration differences is very small the speed of diffusion must also be correspondingly slow. Such is the case with the solutions of the higher acids and alcohols. Also the higher the molecular weight the slower the diffusion,

With the octyl alcohol which gives the reverse effect, an explanation has not as yet been deduced.

EXPERIMENTAL DATA ON THE ALCOHOLS

DIETHYL, ETHYL, PROPYL, AND ISOAMYL ALCOHOL

The points for these compounds were recalculated from the results found by Traube (1891). It was necessary to change his system of expressing the results into the one used in this investigation and also to change from volume molar to weight molar.

BUTYL ALCOHOL

Kahlbaum's best butyl alcohol was dried with metallic calcium and distilled under reduced pressure. A Morgan tip with 0.29925 centimeter radius was used. Thirty-minute drops were used in making the adsorption curve. These drops were heavier than those resulting from the one-fourth, 1-, and 5-minute drops, but not to the extent manifested by the octyl alcohol.

OCTYLALCOHOL

Octyl alcohol was purified in the same manner as butyl alcohol. A Morgan tip of 0.29925 centimeter radius was used. The adsorption curve given was calculated from 30-minute drops. The 30-minute drops were uniformly heavier than those of shorter times.

CETYL ALCOHOL

This curve was calculated from 30-minute drops. It is very evident that the time during which these drops hung was not long enough for equilibrium to be established. The slope of the curve for this alcohol should be steeper than for butyl alcohol, while it really is much less.

Table III contains the data for the alcohols studied.

EXPERIMENTAL DATA ON THE AMINES

The adsorption curves for allyl and propyl amines were plotted from the results given by Traube. His results were in units different from those here employed and it was necessary to recalculate them. They were also changed to weight molar from volume molar.

The dipropyl amine adsorption curve was plotted from the results obtained in this investigation. The dipropyl amine was purified by fractional distillation, weighed quantities being added to weighed amounts of water in making up the solutions of different concentrations. The concentration was determined by titrating with standard hydrochloric acid from weight burettes. Time did not appear to play an important part in the drop weight. Five-minute drops were used in all cases.

These curves are shown in figure 5.

TABLE III.—ADSORPTION OF BUTYL, OCTYL, AND AMYL ALCOHOLS

ALCOHOL	Moles per liter	Moles per 1,000 gm. H ₂ O	Density	r/a	f (r/a)	γ	Moles per sq. cm.	Molecules	Area (a)	Dia. \sqrt{a}
Butyl	0.8401	0.8536	0.9997	1.185	0.6000	28.57	5.8631x10 ⁻¹⁰	3.5542x10 ¹⁴	28.135x10 ⁻¹⁶	5.3042x10 ⁻⁸
	.42045	.4334	.9982	1.0092	.5995	40.38	"	"	"	"
	.21022	.2110	.9961	0.911	.6030	48.08	"	"	"	"
	.10511	.1053	.9982			56.03				
	.05255	.05356	.9982			63.14				
	.02627	.0264	.9982			67.17	2.2333 "	1.372	72.887 "	8.5374 "
	.013139	.013239	.9982			71.26				
	.006569	.006580	.9982			72.36				
	.003234	.003290	.9982			72.80				
Octyl	.0025	.0025	.9982			41.79	4.8294x10 ⁻¹⁰	2.9277x10 ¹⁴	34.157x10 ⁻¹⁶	5.8444x10 ⁻⁸
	.00125	.00125	.9982			50.48	"	"	"	"
	.000625	.000625	.9982			58.64	"	"	"	"
	.0003125	.0003125	.9982			67.07	"	"	"	"
	.00015675	.0002347	.9982			68.00				
		.00015675	.9982			71.81	1.5505 "	.9399 "	106.4 "	10.315 "
	.000078375	.000078375	.9982			72.80				
		Saturated Solution	.9982			37.47				
Isoamyl	0.2500	0.2567	.09958			29.60	5.257 x10 ⁻¹⁰	3.187 x10 ¹⁴	3.1379x10 ⁻¹⁶	5.6016x10 ⁻⁸
	.1250	.1267	.9974			38.47	"	"	"	"
	.0325	.03296	.9982			47.29	"	"	"	"
	.03125	.03130	.9982			50.78				
	.015627	.01563	.9982			61.17				
	.0078135	.007820	.9982			65.87				

ADSORPTION

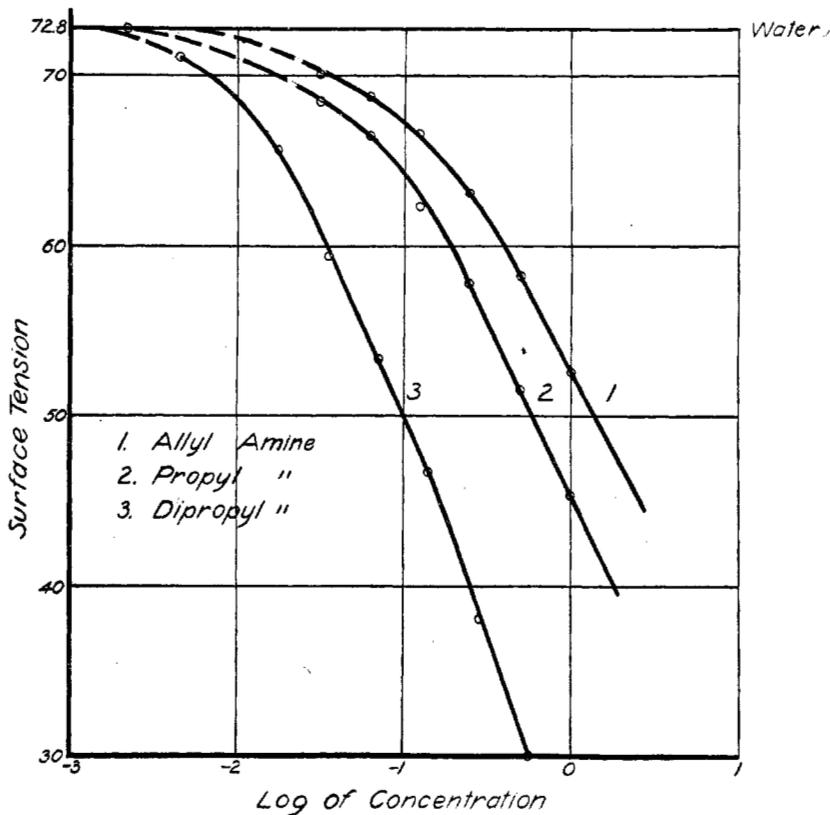


FIG. 5.—Adsorption curves for amines

The data for allyl, propyl, and dipropyl amines are given in Table IV.

COMPARISON OF THE LOGARITHMIC CURVES OF THE ALCOHOLS AND THE ACIDS

The slopes of the straight line portions of the alcohol curves are, in general, slightly steeper than those of the acids having an equal number of carbon atoms. Since the adsorption depends upon the slope, $\frac{dy}{d \log c}$, it is then evident that the alcohols exhibit a greater adsorption than do the acids of the same number of carbon atoms. In general, also the alcohols possess a constant degree of adsorption over a wider range of concentration; that is, the adsorption curve is a straight line through a greater concentration change.

As an explanation of this greater adsorption and of the fact of its being through a wider range may be mentioned, among other things, the difference in the electrolytic character of the acids and alcohols.

TABLE IV.--ADSORPTION OF ALLYL, PROPYL, AND DIPROPYL AMINES

AMINES	Moles per liter	Moles per 1,000 gm. H ₂ O	Density	r/a	f (r/a)	γ	Moles per sq. cm.	Molecules	Area (a)	Dia. \sqrt{a}
Allyl.....	1.0000	1.096	.9907			52.68				
	.50	.5177	.9849			58.26	3.172	1.923	52.00	7.211
	.25	.2544	.9969			63.14				
	.125	.1270	.9980			66.63				
	.0625	.06284	.9982			68.88				
	.03125	.03152	.9882			70.02				
Propyl.....	1.00000	1.075	.9871			45.39	3.725	2.258	44.29	6.655
	.50	.5171	.9930			51.56				
	.25	.2543	.9962			57.91				
	.125	.1270	.9977			62.32				
	.0625	.0628	.9982			66.53				
	.03125	.03152	.9982			68.44				
Dipropyl.....	0.5657		0.9912	1.111	0.5995	30.06	4.847	2.939	34.03	5.834
	½ Sat.	.2828		.9954	.8689	.600				
	4th "	.1414		.9971	.9132	.603				
	8th "	.0707		.9979		.5979				
	16th "	.03535		.9984	.7936	.6103				
	32nd "	.01767		.9982	.7535	.614				
	64th "	.08835		.9982	.7317	.617				
	128th "	.04417		.9982	.7174	.618				
	255th "	.022085		.9982	.6990	.620				

ADSORPTION

The alcohols show such a slight degree of ionization that no correction is used in the application of Gibbs' Law. The acids, for the more concentrated solutions, it is true are very weak electrolytes, but for the more dilute solutions the degree of electrolytic dissociation becomes of considerable magnitude as calculated from the Ostwald formula. This is especially true for the acids of high molecular weight which exhibit a marked effect upon surface tension even

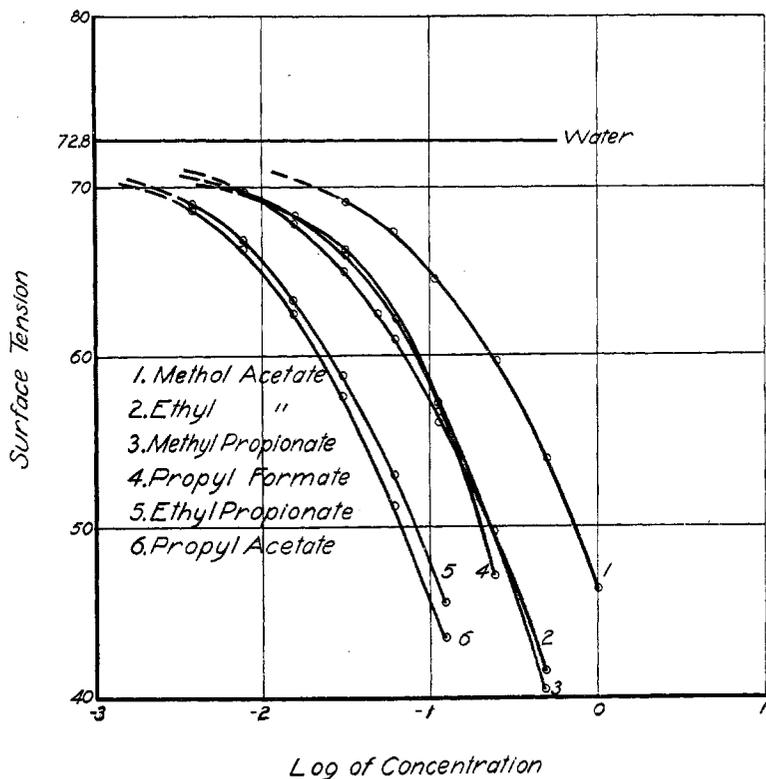


FIG. 6.—Adsorption curves for esters

when present in very small quantities. It is well known that the Ostwald formula is quite limited in its range of accuracy when applied to substances highly ionized. Furthermore, particularly for those acids producing solutions of high concentration, proper corrections for the degree of polymerization may not be made. In the case of formic and acetic acids over the most concentrated solutions used, this would be of considerable value, and it is not known exactly how the ordinary osmotic pressure equation may be ac-

curately used in each concentration. The solutions of the highly ionized acids are under a much different thermodynamic environment because of the presence of the electromagnetic forces arising from the electrically charged particles, than are the alcohols. It is quite well established that these electric forces affect the surface tension very materially.

The alcohols of four- and five-carbon atoms reach zero adsorption at the same concentrations as the acids of the same carbon-atom content.

In case of the alcohols of one-, two-, and three-carbon atoms, the adsorption begins at a lower concentration than the corresponding acids. The curve for the three-carbon atom alcohol lies about two-tenths of a logarithmic unit to the left of the corresponding acid.

SOURCE OF DATA FOR ESTERS

All the data for the esters plotted was obtained by recalculation of the work published by Traube in the *Annalen* (1891).

These curves appear in figure 6. It was necessary to change all his values into the units employed in this investigation for expressing surface tensions and to change his concentrations from volume molar to weight molar. The data are shown in Table V.

COMPARISON OF THE LOGARITHMIC CURVES OF THE ALCOHOLS AND THE ESTERS

The curves for the esters lie very nearly in the same position as the curves for the alcohols of the same number of carbon atoms. As a rule, however, the curves for the esters lie at a higher concentration than the alcohols.

Ethyl propionate and propyl acetate, two esters having the same number of carbon atoms but differently arranged, show an interesting relation. The former requires a higher concentration to produce the same adsorption.

As a rule the adsorption of the esters begins at a lower concentration, takes place more gradually, and finally becomes constant at a higher concentration than the alcohols having the same number of atoms of carbon.

Taken as a whole the adsorption curves of the esters correspond somewhat more closely with the corresponding curves for the acids than they do for those for the alcohols.

A relation between symmetry of the ester and its adsorption curve is found in that the more symmetrical the ester is, the smaller the adsorption after the adsorption has once become constant.

TABLE V.—ADSORPTION OF ESTERS

Ester	Moles per liter	Moles per 1,000 gm. H ₂ O	Density	γ	Moles per sq. cm.	Molecules	Area (a)	Dia. = \sqrt{a}
Methyl acetate.....	1.0000	1.0777	1.0019	46.15	4.6512x10 ⁻¹⁰	3.0213x10 ¹⁴	33.099x10 ⁻¹⁶	5.753 x10 ⁻⁸
	0.50000	0.5190	1.0036	54.01	"	"	"	"
	.2500	.2548	0.9997	59.98	"	"	"	"
	.1250	.1261	.9995	64.26	"	"	"	"
	.0625	.06296	.9982	69.09	"	"	"	"
	.03125	.03138	.9982	69.09	"	"	"	"
Propyl formate.....	0.2500	0.2550	0.9990	47.12	6.059 x10 ⁻¹⁰	3.673 x10 ¹⁴	27.228x10 ⁻¹⁶	5.2178x10 ⁻⁸
	.1250	.1265	.9990	57.16	"	"	"	"
	.0625	.06296	.9982	62.46	"	"	"	"
	.03125	.03126	.9982	66.35	"	"	"	"
	.015627	.01563	.9982	68.31	"	"	"	"
	.0078135	.007820	.9982	69.70	"	"	"	"
Methyl propionate.....	0.50000	0.5232	0.9996	40.46	5.382 x10 ⁻¹⁰	3.2626x10 ¹⁴	30.65 x10 ⁻¹⁶	5.5363x10 ⁻⁸
	.2500	.2558	.9993	48.86	"	"	"	"
	.1250	.1265	.9991	56.79	"	"	"	"
	.0625	.06296	.9982	62.10	"	"	"	"
	.03125	.03125	.9982	65.88	"	"	"	"
	.015625	.015625	.9982	68.35	"	"	"	"
Ethyl acetate.....	.0078125	.007813	.9982	67.74	"	"	"	"
	.50000	.5222	.9993	41.45	4.5978x10 ⁻¹⁰	2.7871x10 ¹⁴	35.878x10 ⁻¹⁶	5.9899x10 ⁻⁸
	.2500	.2558	.9991	49.67	"	"	"	"
	.1250	.1263	.9991	56.17	"	"	"	"
	.0625	.06305	.9990	61.54	"	"	"	"
	.03125	.03129	.9982	65.09	"	"	"	"
	.015625	.015630	.9982	67.96	"	"	"	"
	.0078125	.007820	.9982	69.56	"	"	"	"

Propyl acetate.....	.1250	.1268	.9988	43.55	4.5087×10^{-10}	2.7332×10^{14}	36.589×10^{-16}	6.0487×10^{-8}
	.0625	.06302	.9982	51.27
	.03125	.03141	.9982	57.69				
	.015625	.0157	.9982	62.49				
	.0078125	.00783	.9982	66.32				
	.00390625	.0341	.9982	68.61				
Ethyl propionate.....	.1250	.1268	.9988	45.50	4.7047×10^{-10}	2.852×10^{14}	35.063×10^{-16}	5.9213×10^{-8}
	.0625	.0630	.9989	53.16
	.03125	.03130	.9982	58.85				
	.015625	.0157	.9982	63.38				
	.0078125	.00782	.9982	66.79				
	.00390625	.003960	.9982	68.92				

**MEASUREMENT OF SOLUBILITIES BY MEANS OF
SURFACE TENSION**

Surface tension measurements may be employed to ascertain the solubility of a substance, the solubility of which is very difficult to obtain by use of ordinary methods. Decylic and nonylic acids are so slightly soluble in water that by ordinary processes of measuring solubility the experimental error is almost as great as the solubility itself. Their solubilities in water were determined by use of the surface-tension method quite accurately and easily. To do this a saturated solution is produced and its surface tension measured. This value is plotted on the adsorption curve of the product, this curve having been produced by using solutions having known amounts of substance in solution. The value of the surface tension for the saturated solution is put upon the extended adsorption curve and the logarithm of the solubility read off on the abscissa.

**DESCRIPTION OF EXPERIMENTAL METHODS ON BENZENE-
WATER INTERFACE WITH BUTYRIC ACID DISTRIBUTED
BETWEEN BOTH SOLVENTS**

Purified materials were employed in each case. The water used for solvent was conductivity water and the benzene was some which had been especially well purified for a previous research and preserved in resistance glass bottles over metallic sodium. The butyric acid was fractionally distilled several times and the middle constant boiling point fraction selected.

Weighed quantities of both solvents and solute were taken in each case. The materials were then placed in a 500 c. c. glass-stoppered, resistance glass bottle and shaken at 20 degrees C by a special shaking apparatus in a water thermostat. The shaking was usually continued for 12 to 20 hours, after which the interfacial tension, the concentration of acid in each phase, and also the densities were determined. To insure that equilibrium of acid between the two liquids had actually been reached, the bottle was returned to the bath and the shaking again continued for three hours and the values given above once more ascertained. In no case was it found that equilibrium had failed to be set up after the material had been in the shaker for 12 hours.

The densities of the solutions, as in the case of all the other densities reported in this bulletin, were determined by use of the Harkins picnometer. This instrument is so made as to give exceedingly accurate results.

The concentrations of acid in the two phases were ascertained by titrating the solutions with approximately one-tenth normal sodium hydroxide from weight burettes, using phenolphthalein as indicator. No difficulty was encountered with the water solutions. With the benzene solutions considerable care was necessary. Water was added to the flask, well shaken with the benzene layer, and titrated as mentioned above. Prolonged shaking was required to insure complete removal of acid from the benzene layer.

The surface tensions for the points on the adsorption curve shown in figure 7 were obtained partly by the drop-weight method and partly by the capillary-height method. It was the original intention to use the former method only. However, it was soon discovered that it was practically impossible to use this method on solutions which were rather dilute. For such concentrations the capillary height proved to be better adapted. The capillary height apparatus was that employed by Harkins and Humphrey (1916). The height of the liquid column was determined by use of the cathetometer. All points having a concentration in the water layer greater than 0.3501 N were calculated from results obtained by the drop-weight process. All those having a concentration of acid less than this were obtained by the capillary-height method.

The bulb of the drop-weight interface pipette had a capacity of 1.618 c. c. with a tip radius of 0.27171 c. c.

TABLE VI.—DISTRIBUTION COEFFICIENT OF BUTYRIC ACID BETWEEN WATER AND BENZENE ON THE BASIS OF MOLES PER 1,000 G. OF SOLUTION

C_w Moles per 1,000 g. solution	Water layer density	C_b Moles per 1,000 g. solution	Benzene layer density	C_w/C_b	C_w^2/C_b	γ Surface tension at interface
1.494		7.572		0.1973	0.294	3.91
1.180	1.0041	5.788	0.9130	.2039	.240	4.84
1.123	1.0039	5.430	.9127	.2068	.232	4.96
.7199	1.0014	3.356	.9066	.2145	.154	7.399
.4804	1.0001	2.220	.8902	.2164	.099	11.00
.3689	.9997	1.429	.8914	.2611	.096	14.22
.3501	.99961	1.098	.8884	.3138	.111	15.41
.2088	.9996	.4705	.88104	.4438	.116	19.40
.1651	.9994	.3060	.8793	.5395	.088	21.80
.1351	.9988	.2127	.8797	.6351	.085	22.95
.09795	.9986	.1138	.8837	.8610	.054	25.00
.04824	.9985	.05821	.8804	1.2066	.070	28.00
.0353	.9982	.02305	.8787	1.5314	.054	30.10
.01996	.9982	.008072	.8787	2.4730	.049	32.20
.01372	.9982	.005100	.8782	2.6902	.036	33.00
.00382	.9982	.00130	.8779			33.49
.001087	.9982	.00040	.8779			34.60

TABLE VII.—DISTRIBUTION COEFFICIENT OF BUTYRIC ACID BETWEEN WATER AND BENZENE ON THE BASIS OF MOLES PER 1,000 G. OF SOLVENT

C_w Moles per 1,000 g. water	Water layer density	C_b Moles per 1,000 g. benzene	Benzene layer density	C_w/C_b	C_w^2/C_b	γ Surface tension at interface
1.710	1.0053	30.450	0.9148	0.056	0.006	3.91
1.310	1.0041	14.339	.9130	.091	.119	4.84
1.239	1.0039	12.487	.9127	.099	.122	4.96
.7674	1.0014	5.460	.9066	.139	.107	7.399
.5017	1.0001	3.195	.8902	.157	.078	11.00
.3747	.9997	1.866	.8914	.200	.075	14.22
.3614	.99961	1.387	.8884	.260	.094	15.41
.2116	.9996	.5603	.88104	.377	.079	19.40
.1676	.9994	.3590	.8793	.466	.078	21.80
.1369	.9988	.24704	.8767	.554	.075	22.95
.09009	.9986	.1302	.8837	.760	.075	25.00
.0485	.9985	.0665	.8804	.729	.035	28.00
.0355	.9982	.02629	.8787	1.35	.047	30.10
.02011	.9982	.009194	.8787	2.18	.043	32.20
.01376	.9982	.005797	.8782			33.00
.0039	.9982	.001481	.8779			33.40
.0011	.9982	.000457	.8779			34.60

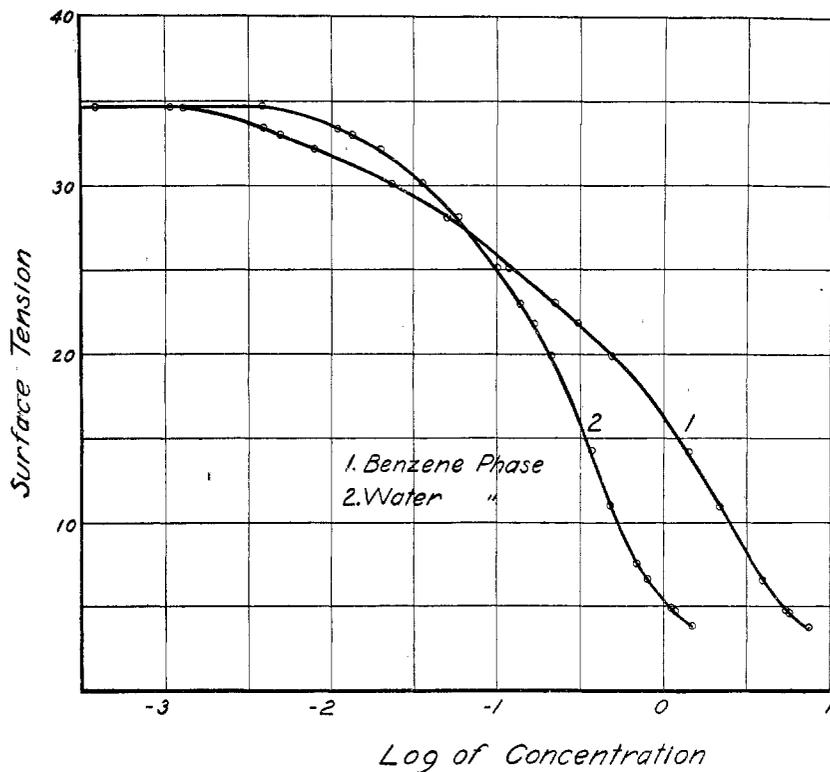


Fig. 7.—Adsorption curves of butyric acid at water-benzene interface

The solute represented by figure 7 (data in Tables VI and VII) is butyric acid, and the two systems are benzene-water and water-benzene. The first measurements on this system were made by Humphery (1916) in 1913 for use in developing the theory of orientation of molecules in surfaces and interfaces, and were made by the capillary-height method. These measurements were not considered precise enough, and the results given here are those obtained in this investigation by using the drop-weight method in the form developed by Harkins and Humphery, the most complete account of which will be found in a paper by Harkins and Brown (1916). The results on interfacial tension for the lower concentrations were obtained by the capillary-height method.

Using the equation given above the adsorption of butyric acid at both interfaces was calculated. When the concentration in the aqueous solution was 0.04 moles per 1,000 grams of water, 1×10^{14} molecules were found to be present in one square centimeter of the film between water and benzene, while if the benzene is not present the concentration of the aqueous phase needs to be only one-third as great to be in equilibrium with just the same number of molecules in the surface film. This shows that the molar activity or fugacity of the molecules in the interface between water and benzene is three times as high as on the surface of water, when both films have the same concentration of about 1×10^{14} molecules per square centimeter.

In order to give 1.5×10^{14} molecules per square centimeter in the interface between water and benzene, the concentration in the aqueous phase must be 0.1 moles per 1,000 grams of solution, while to give the same number of molecules on the surface of water the concentration needs to be only 0.02 mole, or the difference in activity is nearly the same as that described in the preceding paragraph.

As the number of molecules per square centimeter in the surface film increases the amount of solvent in the film becomes so small that the activity of the solute molecules in the film changes very rapidly when calculated on the basis of the concentration of solute in the film, so the number of solute molecules in the film remains practically constant over quite wide ranges of concentration of the adjacent liquid phases. A film of this kind has been designated by Langmuir as of one molecule in thickness. At the interface under discussion this constant film is obtained while the concentration in the aqueous phase varies from 0.2 to 0.5 of a mole¹

¹ Here the lower concentration only is significant for the present discussion, since at the higher concentration the film begins to thicken. This will be discussed later.

butyric acid to 1,000 grams of solution, while with the water phase alone and the same concentration in the surface, 2.77×10^{14} molecules per square centimeter is obtained at concentrations between 0.05 and 0.625 of a mole, showing for the lowest concentration at which this film is obtained, somewhat the same average ratio in the activity in the film; that is, the butyric acid in the interface has again an activity three or four times greater than that at the surface of water. These results indicate that, corresponding to the theory, the restraining force on the butyric acid molecules is much greater at the surface of the water than it is at the interface—water-benzene. This may be stated in the form that for equal concentrations in the aqueous phase the adsorption of substances of the type of the higher organic acids, alcohols, amines, etc., is always greater at the surface of water than it is at the interface between water and an organic solvent of the type of benzene or a paraffin.

CALCULATION OF THE ADSORPTION AT INTERFACES

In calculating the adsorption at interfaces the difficulty was met that none of the adsorption formulas which could be found took into consideration the presence of the solute in more than one phase. Since, even when water is the only solvent, the solute may be, and usually is in the vapor phase, the equations should take account of this fact. The adsorption formula presented here was worked out for use in this paper by Prof. A. C. Lunn of the Department of Mathematics, University of Chicago. It is based on the laws of thermodynamics and the equation for maximum work considered in connection with osmotic pressure.

Notation: λ = latent heat μ = adsorption α = area γ = surface tension	}	p, p' = osmotic pressures of film l, l' = latent heats v, v' = volumes r, r' = dilutions, or reciprocals of concentrations (c, c')	}	of vol- ume phases
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s = entropy

c = thermal capacity of system

M = total mass of solute

q = heat added to system

w = work done by system

ϕ = Helmholtz free energy

The first law of thermodynamics may be stated in the form

$$dq = c dt + l dr + l' dr + \lambda da \quad (1)$$

The equation for reversible work is

$$dw = p dv + p' dv' - \gamma da \quad (2)$$

The negative of the differential of the function of Gibbs, or of the Helmholtz free energy, is defined as

$$\begin{aligned} -d\psi &= d(st) - (dq - dw) \\ &= s dt + t ds - (dq - \gamma dw) \\ &= s dt + dw \end{aligned} \quad (3)$$

$$= s dt + p dv + p' dv' - \gamma da \quad (3b)$$

The total mass of salute (M) is given by the following equation:

$$\begin{aligned} M &= v c + v' c' + \mu a \\ \text{or } v/r + v'/r' &= M - \mu a \end{aligned} \quad (4)$$

Since r and r' are related at a given temperature, and also p and p' , the independent variables may be taken at t, r, v , and a . Then $p, p', l, l', \lambda, \mu$, and γ , will be functions of r and t .

The mass of substance in the phase represented by primed letters is given as follows:

$$\begin{aligned} m' &= v' c' = v'/r' = M - \mu a - v/r, \text{ so} \\ v' &= r' (M - \mu a - v/r) \end{aligned} \quad (5)$$

$$\begin{aligned} \text{so } dv' &= \left(\frac{\partial r'}{\partial r} dr + \frac{\partial r'}{\partial t} dt \right) (M - \mu a - \frac{v}{r}) \\ &\quad - r' \left(a \frac{\partial \mu}{\partial r} - \frac{v}{r^2} \right) dr - r' a \frac{\partial \mu}{\partial t} dt \\ &\quad - \frac{r'}{r} dv - r' \mu da \end{aligned} \quad (6)$$

$$\begin{aligned} &= \left[\frac{\partial r'}{\partial t} (M - \mu a - \frac{v}{r}) - r' a \frac{\partial \mu}{\partial t} \right] dt + \\ &\quad \left[\frac{\partial r'}{\partial r} (M - \mu a - \frac{v}{r}) - r' \left(a \frac{\partial \mu}{\partial r} - \frac{v}{r^2} \right) \right] dr \\ &\quad - \frac{r'}{r} dv - r' \mu da \end{aligned} \quad (7)$$

Substituting (7) in (3b):

$$\begin{aligned} \therefore -d\psi &= \left(s + p' \left[\frac{\partial r'}{\partial t} \left(M - \mu a - \frac{v}{r} \right) - r' a \frac{\partial \mu}{\partial t} \right] \right) dt \\ &+ p' \left\{ \frac{\partial r'}{\partial r} \left(M - \mu a - \frac{v}{r} \right) - r' \left(a \frac{\partial \mu}{\partial r} - \frac{v}{r^2} \right) \right\} dr \\ &+ \left(p - \frac{p' r'}{r} \right) dv - (\gamma + p' r' \mu) da \end{aligned} \quad (8)$$

In order that this may be an exact differential, the following conditions must be met (9, 10, 11, 12):

$$\begin{aligned} \frac{\partial}{\partial r} \left\{ s + p' \left[\frac{\partial r'}{\partial t} \left(M - \mu a - \frac{v}{r} \right) - r' a \frac{\partial \mu}{\partial t} \right] \right\} \\ = \frac{\partial}{\partial t} \left\{ p' \left[\frac{\partial r'}{\partial r} \left(M - \mu a - \frac{v}{r} \right) - r' \left(a \frac{\partial \mu}{\partial r} - \frac{v}{r^2} \right) \right] \right\} \end{aligned} \quad (9)$$

$$\begin{aligned} \frac{\partial}{\partial v} \left\{ s + p' \left[\frac{\partial r'}{\partial t} \left(M - \mu a - \frac{v}{r} \right) - r' a \frac{\partial \mu}{\partial t} \right] \right\} = \\ \frac{\partial}{\partial t} \left(p - \frac{p' r'}{r} \right) \end{aligned} \quad (10)$$

$$\begin{aligned} \frac{\partial}{\partial a} \left\{ s + p' \left[\frac{\partial r'}{\partial t} \left(M - \mu a - \frac{v}{r} \right) - r' a \frac{\partial \mu}{\partial t} \right] \right\} = \\ - \frac{\partial}{\partial t} (\gamma + p' r' \mu) \end{aligned} \quad (11)$$

$$\begin{aligned} \frac{\partial}{\partial v} \left\{ p' \left[\frac{\partial r'}{\partial r} \left(M - \mu a - \frac{v}{r} \right) - r' \left(a \frac{\partial \mu}{\partial r} - \frac{v}{r^2} \right) \right] \right\} \\ = \frac{\partial}{\partial r} \left(p - \frac{p' r'}{r} \right) \end{aligned} \quad (12)$$

$$\begin{aligned} \frac{\partial}{\partial a} \left\{ p' \left[\frac{\partial r'}{\partial r} \left(M - \mu a - \frac{v}{r} \right) - r' \left(a \frac{\partial \mu}{\partial r} - \frac{v}{r^2} \right) \right] \right\} \\ = - \frac{\partial}{\partial r} (\gamma + p' r' \mu) \end{aligned} \quad (13)$$

$$\frac{\partial}{\partial a} \left(p - \frac{p' r'}{r} \right) = - \frac{\partial}{\partial v} (\gamma + p' r' \mu) \quad (14)$$

(14) is identically satisfied as $0 = 0$.

(10) and (11) give

$$-\frac{p' \partial r' / \partial r}{r} + \frac{p' r'}{r^2} = \frac{\partial p}{\partial r} - \frac{p' \partial r' / \partial r}{r} - \frac{\partial p' / \partial r r'}{r} + \frac{p' r'}{r^2} \quad (15)$$

$$-p' \mu' \frac{\partial r'}{\partial r} - p' r' \frac{\partial \mu}{\partial r} = -\frac{\partial \gamma}{\partial r} - p' r' \frac{\partial \mu}{\partial r} - \frac{\partial p'}{\partial r} r' \mu - p' \mu \frac{\partial r'}{\partial r} \quad (16)$$

$$\text{or} \quad \frac{\partial p}{\partial r} - \frac{r' \partial p' / \partial r}{r} = 0 \quad (15)$$

$$\frac{\partial \gamma}{\partial r} - r' \mu \frac{\partial p'}{\partial r} = 0 \quad (16)$$

$$\therefore r' \partial p' / \partial r = r \partial p / \partial r \quad (17)$$

$$\text{and} \quad \mu = -\frac{\partial \gamma / \partial r}{r' \partial p' / \partial r} = -\frac{\partial \gamma / \partial r}{r \partial p / \partial r} \quad (18)$$

or the adsorption in moles is equal to the concentration of the solution times the rate of increase of the surface tension with the dilution divided by the rate of decrease of the osmotic pressure with the dilution.

$$(17) \text{ gives} \quad r' / r = (\partial p / \partial p') dt = 0 \quad (19)$$

Equation 19 may be written in the form:

$$c / c' = (\partial p / \partial p') dt = 0$$

or the rate of change of the osmotic pressure in one phase with respect to that in the other, at constant temperature, is equal to the ratio of the respective concentrations.

In the special case where the Van't Hoff formula holds

$$pr = RT \quad p' r' = RT \\ \therefore r' / r = p / p'; \quad \therefore dp / dp' = p / p' \quad (20)$$

isothermally, and p' / p is a function of t ; $\therefore r' / r$ is a function of t , which, changing r to l / c gives

$$\mu = -\frac{1}{RT} \frac{cd\gamma}{dc} = -\frac{1}{RT} \frac{c'd\gamma}{dc'} = -\frac{1}{RT} \frac{d\gamma}{d \ln c'} = -\frac{1}{RT} \frac{d\gamma}{d \ln c} \quad (21)$$

MOLAR ACTIVITY AND THE ASSOCIATION OF BUTYRIC ACID
 IN THE VOLUME PHASES

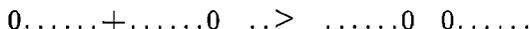
Since there is only one film between the two phases, the adsorption as calculated from one phase should be the same as that calculated from the other. Now Equation (19), in so far as it holds, signifies that the adsorption is a constant times the slope $(\partial \gamma / \partial x) dt = 0$ at any point of the curves which give surface tension plotted on the Y -axis, and the logarithm of the molar concentration on the X -axis (fig. 7). Whenever γ on the curve for the aqueous phase is equal to γ on that for the benzene curve, the two phases are in equilibrium and thus equation (19) indicates that for such points the slopes of the two curves must be equal, or

$$(\partial \gamma / \partial x) dt = 0 = (\partial \gamma' / \partial x') dt = 0$$

Now, the figure shows that this is very far from being true, which indicates that the osmotic pressure in one of the two phases, or possibly in both, deviates widely from the gas law. Previous work, however, indicates that weak electrolytes in aqueous solution, when allowance is made for the degree of ionization, give osmotic pressures which are nearly normal at concentrations of 0.5 M or less, such as are involved in this discussion. The large deviation must, therefore, occur in the benzene phase, but in this phase, below one molar, such extremely abnormal osmotic pressures as are required by the slope of the curve, are improbable. This leads to the idea that the concentrations which are plotted on the X -axis for the benzene phase are not molar, but only formula weight concentrations. Only in case the concentrations are actually molar should the curves have equal slopes for all points at which γ is the same on both. That the formal concentration in the benzene phase is thus much larger than the molar concentration, especially in the more concentrated solutions, seems the most probable hypothesis, and this means that the association of single into double or triple or even more highly associated butyric molecules increases rapidly with the concentration. If it were not for this association, the curve for the benzene phase would be of the same form as that for the water phase, and would lie entirely to the left of the latter. The two curves would not then cross each other. This crossing of the curves indicates that the formal solubility of the butyric acid in the benzene at all points to the left of the point of crossing, is less than that in the water, while at all points to the right, it is greater. The term solubility has been used here in a new and wholly comparative

sense, and indicates that the solute in both phases is in equilibrium with the solute in the interfacial film.

The curves may be interpreted as indicating that single molecules of butyric acid are more soluble in water than in benzene, when the solubility is calculated on the basis of either 1,000 grams of solvent or of solution,¹ but that the associated molecules are more soluble in benzene. That the association of such molecules decrease their solubility in water, and increase their solubility in benzene, is entirely in accord with the theory presented in this bulletin. Thus the union of single into double molecules, as is seen by the following equation,



decreases the free field due to the polar groups, and thus decreases the average intensity of the forces of the electromagnetic stray field.² This makes the molecules more like the benzene and less like the water. The association of two or more butyric acid molecules, by the union of their oxygen atoms, also lessens the extent of their union with the oxygen of the water, not only by the lessening of the stray field, but also by what may be called steric hindrance, that is, by occupying the adjacent space.

ASSOCIATION AS RELATED TO PARTITION COEFFICIENTS

While the relation of association to the slopes of the surface-tension curves, as pointed out in the last section, is new, the determination of the association of acetic acid in benzene by partition experiments, was the subject of a research by Nernst. The data of Table VI give similar partition values for butyric acid. The fifth and sixth columns of the table list the values of C_w/C_b and C_w^2/C_b , where C_w and C_b are the formal concentrations of butyric acid in the aqueous and the benzene phases, respectively. It is apparent that neither C_w/C_b nor C_w^2/C_b is constant, since the first decreases and the second increases with increase of concentration. The values at the lower concentration are somewhat affected by the ionization, while those at the higher concentrations may be affected by deviations from Raoulr's law, but as the intermediate values the table shows a much greater constancy for C_w^2/C_b . In this work the analyses of the aqueous phase were made with great care, and any irregularities which occur in the constants are due to the errors in the determination of the concentrations in the benzene phase. The

¹ However, on the basis of the mole fraction, the single molecules as well as the double may be more soluble in benzene than in water.

² Thus the double molecules have two paraffin chains instead of one, and only one polar group, and that in the middle of the molecule.

association will be determined later by a more direct method. The quantitative calculations will therefore be left for a subsequent publication.

ADSORPTION AT THE INTERFACE WATER-BENZENE AS COMPARED WITH THAT ON THE SURFACE

Tables VIII and IX give values for the adsorption of butyric acid at the interface water-air, and similar values for the interface between water and benzene.

TABLE VIII.—ADSORPTION AT THE INTERFACE WATER-AIR

Formula weights per 1,000 grams water	Moles per sq. cm. $\times 10^{10}$	Molecules per sq. cm. $\times 10^{14}$	a. Area per molecule in sq. cm. $\times 10^{16}$	a. Horizontal diameter of space in cm. $\times 10^8$
0.0066	1.078	0.654	153.	12.3
.013	1.70	1.03	96.	9.8
.024	2.87	1.99	59.	7.6
.050	4.50	(a) 2.82	36.6	6.05
.101	4.52	(a) 2.753	36.3	6.03
.159	4.558	(a) 2.763	36.2	6.02
.322	4.562	(a) 2.765	36.2	6.02
.663	4.566	(a) 2.767	36.1	6.01

(a) This number represents the constant or monomolecular film.

TABLE IX.—ADSORPTION AT THE INTERFACE WATER-BENZENE

Formula weights per 1,000 grams water	Moles per sq. cm. $\times 10^{10}$	Molecules per sq. cm. $\times 10^{14}$	a. Area per molecule in sq. cm. $\times 10^{16}$	a. Horizontal diameter of space in cm. $\times 10^8$
0.035	1.631	0.99	101.0	10.0
.1	2.45	1.48	67.6	8.3
.2	4.60	2.79	35.9	6.0

NUMBER OF MOLECULES IN THE CONSTANT OR MONOMOLECULAR FILM

One of the interesting and important points brought out by this work as shown by these tables is that the monomolecular film of butyric acid between water and benzene contains 2.79×10^{14} molecules per square centimeter, while that between water and air (plus vapor) contains 2.77×10^{14} , or, within the limits of error, both films contain the same number of molecules. Thus the presence of benzene as an upper phase does not change the number of butyric acid molecules in this constant or monomolecular layer.

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