ADSORPTION AND SURFACE TENSION AT LIQUID-LIQUID INTERFACE

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The determination of the extent of surface is the chief difficulty confronted in adsorption problems. This has, to some extent, been solved for solid adsorbents by Fritz Paneth and Walter Vorwerk[1] but their method is limited to salts of metals which have radioactive isotopes. The extent of surface can more readily be determined for adsorption at liquid-gas and liquid-liquid interfaces. Langmuir[2] has taken advantage of this fact in his investigations on spreading of oils from which he developed, with the aid of material from other sources, his important theory of adsorption. Harkins and his co-workers[3] have done considerable work on the structure of the surface of liquids from the standpoint of surface energy obtained from surface tension and other similar data. Their results confirm the theory of Langmuir, as do the investigations of Adam[4] on "The Structure of Thin Films of Palmitic Acid on Water" and those of Iredale[5] on "Adsorption from the Gas Phase at a Liquid-Gas Interface."

The work described in this paper deals primarily with the application of the Gibbs adsorption equation, which gives the increase in moles per sq. cm. in the interface of a system.

$$\Gamma = -\frac{c}{RT}\frac{\partial\sigma}{\partial c} = -\frac{1}{RT}\frac{\partial\sigma}{\partial \ln c}$$

[1] Paneth and Vorwerk, Z. physik. Chem., 101, 445 (1922).

[2] Langmuir, THIS JOURNAL, (a) 37, 1154 (1915); (b) 38, 2221 (1916); (c) 39, 1848 (1917).

[3] Harkins and others, ibid., 39, 354, 541 (1917); 41, 970 (1919); 42, 700 (1920); 43, 51 (1921); 44, 2665 (1922).

[4] Adam, Proc. Roy. Soc., 99A, 336 (1921).

[5] Iredale, Phil. Mag., 45, 1088 (1923).

This equation has, since Gibbs' time, been derived in several different ways, and has been developed by Milner[6] without assuming that the perfect gas law holds in the surface layer. It is necessary only that it should hold for the osmotic pressures within the liquids.

The experimental verification of this relationship is very difficult and has been undertaken only by a few experimenters. Donnan and Baker[7] successfully confirmed the relationship for adsorption at a liquid-gas interface. W. C. McC. Lewis[8] attempted similar determinations for adsorption at the liquid-liquid interface of a hydrocarbon oil and water, with less success. The observed values were in almost all cases a great deal larger than the calculated. There are, however, a great many sources for discrepancies and difficulties connected with the determination which W. C. McC. Lewis recognized, and he himself does not consider the results as disproving the relationship.

Harkins and his co-workers[9] have developed the technique of surface-tension determinations by the drop-weight method and have applied it with success to the determination of interfacial tension. Morgan and his co-workers[10] have also done a great deal of work on the drop-weight method. Harkins' work is undoubtedly the most complete. He has determined the correction factor for the residual drop by careful experiments with the capillary-rise method. Further, he has shown that these corrections are equally applicable to interfacial tension, by measurements of capillary rise at liquid-liquid interface. The correction curve for residual drop was made from the tables of data of Harkins giving the relationship of $(r/V^{1/3})$ to $f\left(\dfrac{r}{V^{1/3}}\right)$ where r is the radius of tip and V the volume of the drop.

The equation for interfacial surface tension in dynes per cm. is $\sigma = \dfrac{V\partial(\rho_w - \rho_0)}{2\pi r N f\left(\dfrac{r}{V^{1/3}}\right)}$ where ρ_w and ρ_0 are the densities of water and the other liquid, respectively.

The apparatus devised for this work is shown in Fig. 1.

The pipet consists of a bulb of 25.74 cc. $\pm$ 0.005 capacity, joined by (0.5 cm. i. d.) tubing to the capillary tip (of 2 cm. i. d.). The inside bore was ground out to a distance of approximately 0.5 cm. from the end to a diameter of 0.351 cm. The inside diameter of the tip was determined by turning a brass rod to fit snugly into the bore of the tip. The diameter of the brass rod was measured with micrometer calipers, and the average of a number of readings taken. These did not differ by more than 0.002 cm. The

[6] Milner, *Phil. Mag.*, **13**, 96 (1907).

[7] Donnan and Baker, *Proc. Roy. Soc.*, **85A**, 557 (1911).

[8] Lewis, *Phil. Mag.*, **15**, 499 (1908); **17**, 466 (1909); *Z. physik. Chem.*, **73**, 129 (1910).

[9] Harkins and others, THIS JOURNAL, **38**, 228 (1916); **41**, 499 (1919).

[10] Morgan and others, *ibid.*, (a) **37**, 1461 (1915); (b) **38**, 844 (1916); (c) **39**, 2151, 2275 (1917).

upper part of this pipet was provided with two tubes closed by stopcocks, one for filling and the other with a fine orifice to control the displacement of liquid by air.

An automatic counter was devised to count the drops. In its final form it worked very well and proved dependable, as shown when checked by actual counting and by the reproducibility of results. The device consisted essentially of a platinum vane of thin foil balanced on a platinum pinion so that when a drop of the liquid on being released from the tip impinged on it, the pointer on the other end dipped into the cup of mercury thus making contact. The terminals were connected to the secondary of a relay, with a switch and three storage batteries in series. The primary of the relay was connected in series with the counter and the batteries. The contact points of the relay were interchanged so that instead of one side breaking as the other made contact, they both made contact and broke together. The counter consisted of an electromagnet which operated a Veeder ratchet counter. When a drop impinged on the platinum vane and lifted it slightly, the circuit was completed and the relay operated the electromagnet. The armature of the electromagnet operated the ratchet lever of the counter, causing the next number to be brought into position.

The benzene was purified according to the standard method, to remove thiophene. A final fraction boiling at 79.5–79.7° (750.7 mm.) was obtained.

The dimethylaniline used was purified by distillation, collection of the fraction between 190° and 191°, freezing it twice to remove methylaniline, and again distilling it. The fraction used distilled at 190.5–190.8° (740.4 mm.).

The heptane was secured through the kindness of Professor Kremers of the Pharmacy Department of the University of Wisconsin. The interesting study of its production and properties has

Fig. 1.

been covered by Professor Kremers in a paper on "Chemistry of Heptane and its Solution."[11] The sample used distilled between 98.25° and 98.40° at 751 mm.

The densities of the materials were determined with a Sprengel pycnometer at 25° and were referred to water at the same temperature. The densities of several mixtures were determined to see whether the substances followed the mixture law, with the following results.

TABLE I

DENSITIES AT 25° REFERRED TO WATER AT 25°

Benzene (c. p. but not purified as above)..................	0.8753	
Dimethylaniline.......................................	.9565	
Heptane..	.6824	
Benzene—dimethylaniline, 50–50 (by vol.) obs..............	.9162	
calc...............	.9159	
deviation.........		0.04%
Heptane—dimethylaniline, 50–50 (by vol.) obs..............	.8210	
calc.............	.8195	
deviation........		.18%

[11] J. Am. Pharm. Assoc., 9, No. 9, 857 (1920); 10, No. 11 (1921).

According to Brown[12] and Linebarger,[13] who made a number of determinations of densities of mixed liquids, the maximum deviation is near the mixture of equal proportions. As the above deviations are within the experimental error of the rest of the work, the calculated densities for mixtures have been used in this paper.

All of the surface-tension determinations were made in a thermostat held at 25° ± 0.02°. The pipet was placed in a glass cylinder 7.5 cm. in diameter and held in place with a specially cut cork. The cylinder was filled to a height of 11.5 cm. with distilled water, except when otherwise noted. The pipet was filled with the original liquid to a point a little above the upper line, placed in position in the thermostat and allowed to stand for 20 minutes to half an hour, in order to come to the temperature of the thermostat. In starting a run, the rate of dropping was brought to the desired point by the time the second drop was released. This could be held quite constant with about two adjustments of the stopcock during the run to compensate for loss in head. The tables of data show that different runs could be checked to one-half a drop, representing an accuracy of from 1% to less than 0.5%. Test runs were made by first

TABLE II

DIMETHYLANILINE–HEPTANE AGAINST WATER AT 25°

No.	% Dimethylaniline by vol.	d_{25}^{25}	Drop. no.	Surface tension (dynes per cm.)
1	0.00	0.6825	205.75	50.39
2	1.19	.6858	222.0	46.48
3	7.14	.7021	248.5	39.65
4	14.30	.7216	255.0	36.22
5	25.00	.7509	246.0	33.49
6	50.00	.8194	189.25	30.98
7	75.00	.8878	125.5	28.23
8	100.00	.9563	50.80	25.57

DIMETHYLANILINE–BENZENE AGAINST WATER

No.	% Dimethylaniline by vol.	d_{25}^{25}	Drop. no.	Surface tension (dynes per cm.)
1	0.00	0.8758	112.05	34.71
2	3.00	.8780	112.75	33.93
3	6.22	.8808	112.0	33.33
4	7.14	.8816	111.5	33.25
5	11.10	.8847	111.25	32.45
6	13.90	.8870	110.0	32.12
7	16.70	.8892	110.0	31.50
8	22.70	.8941	106.0	31.15
9	33.33	.9026	99.5	30.40
10	50.00	.9160	89.37	28.98
11	57.20	.9218	83.75	28.68
12	71.50	.9333	73.37	27.65
13	83.30	.9429	64.37	26.78
14	100.00	.9563	50.80	25.57

[12] Brown, *J. Chem. Soc.*, **39**, 202 (1881).
[13] Linebarger, *Am. Chem. J.*, **18**, 429 (1896).

saturating the water with the organic solvent, and without saturating it. The results checked in all cases within the experimental error; hence saturation of the water was not resorted to. A series of runs was made with benzene to determine the maximum rate of drop formation which
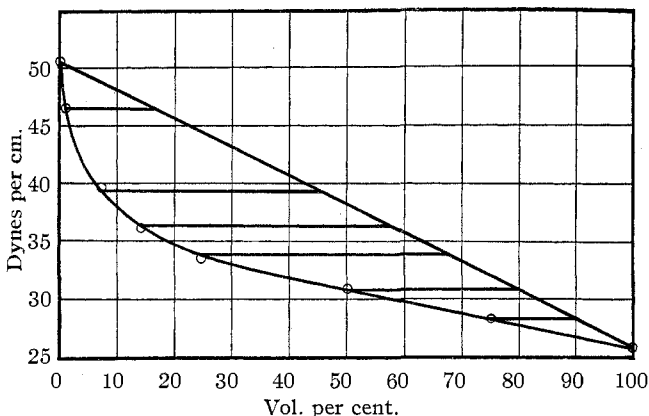
Dimethylaniline–heptane against water.

Fig. 2.

would give results comparable with static conditions. This was found to be six drops per minute. Varying the head in the cylinder by 2 cm. of water was found not to affect the results.

The surface tensions of mixtures of two pure organic liquids against water, which themselves have considerably different surface tensions

Dimethylaniline–benzene against water.
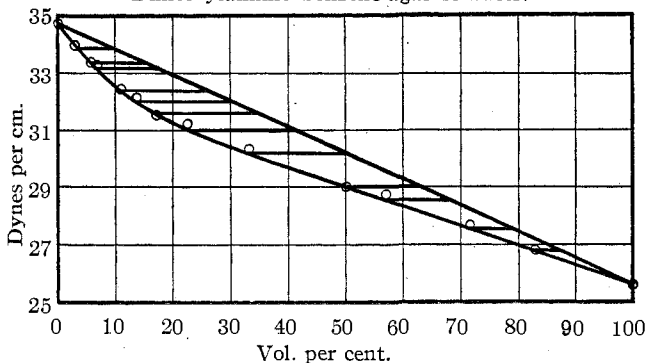
Fig. 3.

against water, were determined. The two systems, dimethylaniline–benzene against water, and dimethylaniline–heptane against water, were studied. The densities of these pairs follow the mixture law, showing that a solution of one in the other is not accompanied by association or

dissociation. The pairs are also miscible in all proportions. The data for these mixtures are given in Table II and the curves in Figs. 2 and 3.

The drop numbers and surface tensions are averages of several determinations. The rate of dropping in each case was less than six drops per minute.

The curves fall below the line joining the tensions of the pure constituents. The constituent of lower tension when added to the higher causes a considerable fall in surface tension, due evidently to the constituent

Log C.
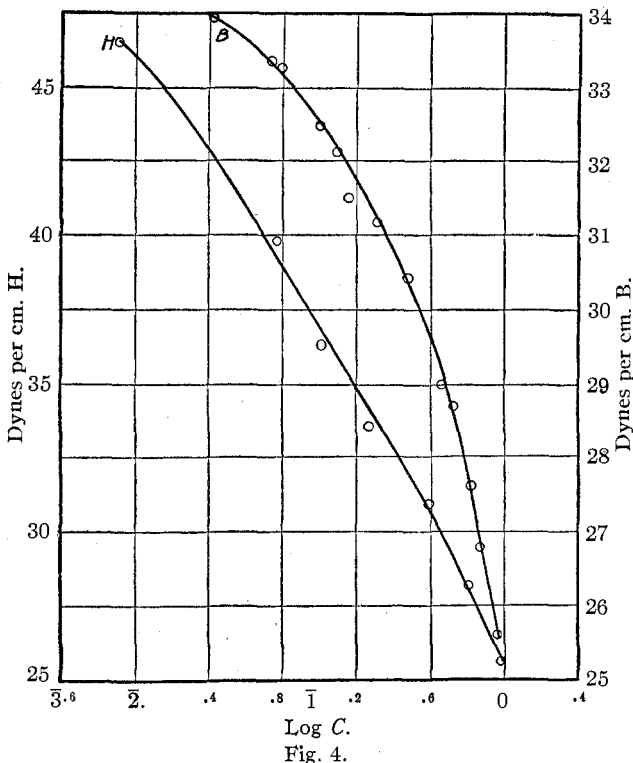
Fig. 4.

of lower tension concentrating in the interface. On the other hand, adding the constituent of higher tension to the lower has less effect, as it goes mostly into the interior of the drop.

The data as plotted in Fig. 4, surface tension against the log of concentration in g. per cc., make it possible to determine (Γ) moles per sq. cm. adsorbed on the interface. Where the slope of the curve becomes constant, $d\sigma/d$ log C, the effective amount adsorbed becomes constant due to complete covering of the surface. This was observed by Langmuir[14] and by King,[15] and used as a basis of calculating molecular cross sections. King found that butyric acid adsorbed at water–air and water–benzene inter-

[14] Ref. 2 c, p. 1895.
[15] King, *Kansas Exp. Sta. Tech. Bull.*, 9 (1922).

faces had the same molecular cross section, but that a greater concentration of butyric acid was required to give a complete interface layer in the former case. This can be explained on the basis of polarity. Butyric acid, which contains both a polar and a non-polar group, when dissolved in a polar liquid tends to go to the interface and become oriented so that the polar group remains in the polar solvent and the non-polar group, which is repelled, extends upwards into the indifferent air medium. When the interface, however, is water–benzene, in addition to the above forces there is the attractive force of the non-polar benzene for the non-polar group of the butyric acid. This increases the tendency of the butyric acid to go to the interface and lowers the concentration necessary to form a completely adsorbed layer. The fact that alcohol adsorbed at water–air interface forms a complete adsorption layer at a lower concentration than the corresponding fatty acid, can be similarly explained. Each contains a polar and a non-polar group. The acid contains the group COOH, which is more polar than OH, as is shown by the greater reactivity of organic acids than alcohols. It thus has a greater tendency to remain in the polar solvent which opposes the tendency to become oriented at the interface. According to the calculations of Langmuir on the data of Morgan and Egloff[16] triethylamine forms a complete surface layer at water–air interface at very low concentrations, whereas with phenol a considerably greater concentration is required. As the two hydrogens of the amine have been replaced by non-polar ethyl groups the compound is quite non-polar and tends to leave the polar solvent readily, whereas the phenol which has the polar hydroxyl group tends to remain in the polar solvent to a greater extent.

Applying this reasoning to the above data, the dimethylaniline, which is but slightly polar, tends to remain in the non-polar solvent, and hence a considerably higher concentration would be required to give a complete interfacial layer. This agrees entirely with the experimental results.

The molecular cross sections for dimethylaniline at heptane–water and benzene–water interfaces calculated on this basis are 0.695×10^{-14} cm.^{2} and 0.758×10^{-14} cm.^{2}, respectively.

By making two assumptions, the calculations can be made on an entirely different basis in which the thickness of adsorption is obtained directly and the area of cross section determined from this with the aid of Avogadro's number and the density. The first of these assumptions is that if there were no concentration in this interface, the surface tension of the mixtures would fall on the straight line joining the pure constituents against water, when plotted on a volume–percentage basis. Experiments have been made by Worley[17] to test the additivity law for surface tension on a

[16] Ref. 10 b, p. 848.

[17] Worley, *J. Chem. Soc.*, **105**, 276 (1914).

volume–percentage basis. For constituents of like polarity against air, which have no orienting effect, the relationship was fairly well followed, as would be expected when there was no concentrating in the interface. The assumption, hence, seems perfectly reasonable for liquids whose solutions show no such abnormalities as association or dissociation, since such other properties as density and refractive index are straight line functions. The other assumption is that it is justifiable to use concentration units down to thicknesses of molecular dimensions.

From the first assumption, the percentage composition in the interface corresponding to the percentage composition in the drop can be determined from Figs. 2 and 3 by drawing a horizontal line from the curve to the straight line joining the tensions of the pure constituents against water. By converting the interfacial concentration from percentage of dimethylaniline to moles of dimethylaniline per cc., the excess of dimethylaniline per cc. in the interface over that in the drop can be determined by difference, the change in concentration in the drop due to change in concentration in the interface being negligible. The thickness of the adsorbed layer can be calculated by dividing the value of (Γ), moles per cm.^{2}, by the

TABLE III

THICKNESS OF DIMETHYLANILINE MOLECULES CALCULATED FROM SURFACE-TENSION DATA

Heptane–Water Interface

No.	Dimethyl-aniline (by vol.) interface	d_{25}^{25} interface	Sol.	Moles of dimethyl-aniline per cc. × 10^3 (Interface)	(Excess)	$\dfrac{d\,\sigma}{d \log C}$	Moles. per cm.^{2} × 10^{10}	Thickness in cm. × 10^7 (mμ)	Cross sec-tion in sq. cm. × 10^{14} (mμ)
2	16.5	0.727	0.067	0.982	0.915	2.30	0.92	1.005^a	0.192^a
3	45.0	.803	.426	2.96	2.53	3.80	1.53	0.605	.318
4	57.0	.842	.843	3.93	3.09	4.25	1.72	.557	.345
5	67.0	.870	1.54	4.76	3.22	4.53	1.83	.568	.339
6	79.7	.901	3.35	5.88	2.53	5.02	2.02	.798	..
7	90.0	.929	5.46	6.85	1.39	5.87	2.37	1.70	..

Benzene–Water Interface

No.	Dimethyl-aniline (by vol.) interface	d_{25}^{25} interface	Sol.	Moles of dimethyl-aniline per cc. × 10^3 (Interface)	(Excess)	$\dfrac{d\,\sigma}{d \log C}$	Moles. per cm.^{2} × 10^{10}	Thickness in cm. × 10^7 (mμ)	Cross sec-tion in sq. cm. × 10^{14} (mμ)
2	9.0	.883	0.216	0.651	0.435	0.63	0.254	0.584	.333
3	15.5	.888	.448	1.13	.68	1.00	.403	.593	.325
4	18.0	.890	.515	1.31	.79	1.15	.464	.588	.327
5	26.5	.896	.802	1.94	1.14	1.61	.650	.571	.337
6	30.5	.900	1.01	2.25	1.24	1.74	.703	.567	.340
7	34.5	.903	1.18	2.55	1.37	1.94	.783	.572	.337
8	41.0	.909	1.66	3.05	1.39	1.97	.796	.573	.336
9	50.0	.916	2.45	3.75	1.30	2.39	.965	.742	..
10	63.0	.926	3.75	4.78	1.03	5.13	2.09	2.03	..
11	67.5	.930	4.32	5.14	0.82	5.39	2.18	2.66	..
12	78.5	.938	5.46	6.03	.57	5.39	2.18	3.83	..
13	87.0	.946	6.43	6.72	.29	5.39	2.18	7.52	..

^{a} This value is undoubtedly not exact as $d\sigma/d \log C$ for this point is uncertain, due to lack of points in this region.

excess of moles of dimethylaniline per cc. in the interface. The values obtained are given in Table III.

They agree very well with the values given by Langmuir for phenol and triethylamine adsorbed at a water–air interface. He obtained for phenol 0.43×10^{-7} cm. thickness and 0.34×10^{-14} sq. cm. cross section, and for triethylamine 0.56×10^{-7} cm. thickness and 0.11×10^{-14} sq. cm. cross section.

When a complete interfacial layer is formed the thicknesses start to increase, showing that the adsorption is more than one molecule thick.

Summary

1. The interfacial tensions of two binary mixtures against water were determined. The results show that an addition of the constituent of lower interfacial tension to the other causes a considerable change in interfacial tension, due to its going into the interface. On the other hand, an addition of the constituent of higher interfacial tension to that of lower has a less effect on the interfacial tension, as it goes mostly into the drop.

2. Gibbs' equation was applied to the data of this paper with the assumption that for non-associated or non-dissociated binary mixtures the surface tension would follow the mixture law, if it were not for the concentration effect in the interface. A second assumption is that concentration relationships can be used down to thicknesses of molecular dimensions. With these assumptions, adsorption results fully in accord with Langmuir's adsorption theory are obtained, as follows.

(a) Adsorption is one molecule thick up to concentrations where a complete surface layer is formed.

(b) The complete surface layer is formed only at high concentrations for the systems used, which fact can be accounted for on the basis of polarity.

(c) The molecular thicknesses and cross sections obtained agree with those of other investigators.

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