AN EXPERIMENTAL TEST OF THE GIBBS ADSORPTION THEOREM: A STUDY OF THE STRUCTURE OF THE SURFACE OF ORDINARY SOLUTIONS[1]

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The object of this communication is to present a definite conception of the structure of the surface of ordinary solutions as deduced from several different kinds of evidence and confirmed rather directly by absolute measurements of adsorption in and near the surface of solutions.

A clear picture of the structure of films of insoluble materials resting upon a solvent such as water has been gained through Rayleigh, Hardy and Adam in England, Devaux and Bancelin in France and Langmuir and Harkins in America. For example, a film of the insoluble palmitic acid on water is a coherent momomolecular film, all the molecules being oriented perpendicular to the surface. Far less has been known about soluble materials and about the two fundamental questions as to whether in such cases momomolecular films are formed and as to how far beneath the surface the influence of surface forces such as adsorption and orientation extends.

Some of the conceptions resulting from the adsorption of a soluble substance in the surface of a solution are illustrated in Fig. 1. Langmuir, in 1917, suggested that the adsorbed layer of dissolved substance might well appear as a monomolecular layer upon the surface (Fig. 1a). The data which he obtained from calculation in the absence of any direct measurements corresponded, however, to a curiously incomplete, although constant, monomolecular layer (Fig. 1b). To explain this discrepancy Donnan, in 1923,[2] suggested that the molecules were partially submerged and, therefore, separated in the surface (Fig. 1c), whereas Langmuir suggested hydration of each molecule or alternatively that in some cases such as phenol and aniline the molecules lie flat instead of standing in their usual orientation.

The present communication affords for the first time accurate measurements of the absolute amount of adsorption and in each case the amount actually adsorbed is definitely greater than that which could be packed on the surface as a monomolecular film. Hence we suggest that there is probably a fairly complete monomolecular film upon the surface, but that in addition to this there is an excess concentration, or adsorption, within the solution in the immediate neighborhood of the surface, ex-

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[1] Read before the Mid-West Regional Meeting of the American Chemical Society at Madison, Wisconsin, May 28, 1926.

[2] Presidential address, Section B, British Association for the Advancement of Science, 1923; *Nature*, 112, 869 (1923).

tending inwards for many molecular diameters (Fig. 1d). This is shown in Fig. 1d as consisting of chains of oriented molecules extending inwards from the surface into the solution.

Previous Evidence that a Surface Layer Has Depth.—(1) The classical experiments of Hardy on lubrication have shown that a liquid between two metal surfaces can exhibit static friction even when the liquid layer is far deeper than the diameter of a molecule. This appears to be the first clear evidence that orientation of molecules may extend far below the actual surface. Of the two possible explanations of this undoubted effect, namely, either that the range of molecular attraction is great as compared with molecular diameter or, alternatively, that it is through a sort of chain effect that molecules are successively oriented through the depth of the liquid, of these we would prefer the second, although Hardy has favored the first.

(2) The studies of adhesion by McBain, Hopkins and Lee[3] have shown that a thin film of adhesive between two surfaces may yield a joint several times as strong as the adhesive substance itself. Furthermore, the thinner the layer of adhesive the stronger the joint, and this influence becomes especially great when the films are excessively thin. These results we would likewise interpret in terms of the chain effect of orientation of molecules in the neighborhood of the surface.

(3) Other evidence is provided by the study of the viscosity of liquids

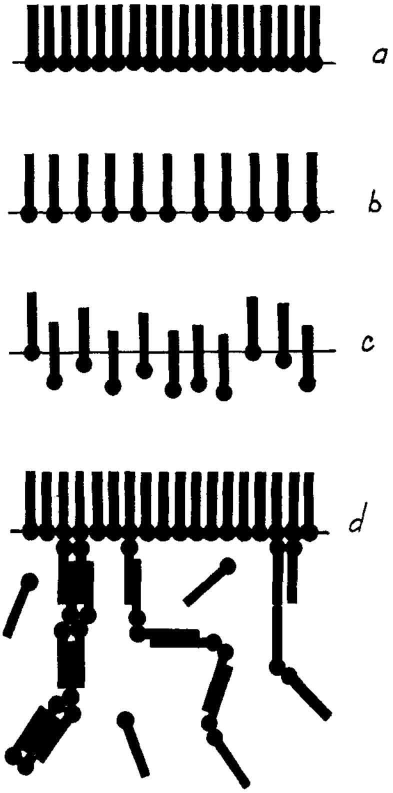

Fig. 1.—Diagrammatic representation of various conceptions of the structure of surfaces of ordinary solutions; (*a*) close-packed monomolecular layer of solute upon the surface, (*b*) curious incomplete monomolecular layer obtained by calculation using the simplified Gibbs' concentration adsorption formula, (*c*) Donnan's attempted explanation of (*b*) by assuming partial submergence, (*d*) the conception advanced in the present paper, a complete monomolecular film plus chains of oriented molecules of solute extending far below the surface.

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[3] (a) McBain and Hopkins, *J. Phys. Chem.*, **29**, 188–204 (1925); (b) Second Report of the Adhesive Research Committee, Appendix IV, 34–89 (1926); (c) *J. Phys. Chem.*, **30**, 114–25 (1926); (d) McBain and Lee, *Proc. Roy. Soc.* (London) **113A**, 605–20 (1927); (e) *J. Soc. Chem. Ind.*, **46** (1926); (f) *Ind. Eng. Chem.*, **19**, 1005 (1927).

in which solid particles are suspended. Hatschek[4] has proved that even in the simplest of such systems the viscosity coefficient alters with the rate of shear, a phenomenon for which he has been at a loss to account. It cannot be due to solvation or aggregation of particles in such a system as starch granules suspended in the indifferent liquid, toluene; but it is in obvious agreement with the conception that a chain effect extends into the liquid from any solid surface which has oriented any of the superficial molecules. Tests should be carried out with polar liquids where this effect would be expected to be greatest; likewise with solutions such as aqueous *p*-toluidine.

(4) The most direct method of studying the structure of surfaces is by measurement of the absolute amount of adsorption in and near the surface. Euler[5] has attempted absolute measurements of adsorption on gold and silver foils from solutions of silver nitrate, obtaining a result which is about double that for a monomolecular film of silver ions for this area of surface, assuming that the silver surface was smooth and continuous. This accords with our interpretation as illustrated in Fig. 1d, that is, a monomolecular layer in addition to the adsorption or excess concentration in the neighborhood of the solid surface. It should be borne in mind that adsorption in the surface of a liquid medium is very different from adsorption from a vapor or gas, because whereas in the liquid or solution the space below the surface is closely packed with contiguous molecules which merely have to be oriented, in the latter case the only molecules appreciably near the surface are those which are actually captured or adsorbed by the surface, and hence the surface effect cannot reach out from the actual surface into the gaseous space.

(5) In earlier experiments by W. C. M. Lewis[6] to determine the adsorption of various materials at a liquid-liquid interface, in nearly every case the approximate adsorption as determined was mostly much larger than expected, often 100 times larger. However, many of these substances were colloidal and the results are ambiguous.

(6) The only determinations of the absolute adsorption of a substance from true solution at the air interface are those of Donnan and Barker,[7] sixteen years ago, who employed an aqueous solution of nonylic acid. They blew a stream of air bubbles up through the solution which was placed in a simple still-head divided into a number of compartments

[4] (a) Hatschek, *Proc. Phys. Soc. London*, **28**, 274 (1916); (b) *Kolloid Z.*, **40**, 53 (1926); (c) *J. Phys. Chem.*, **31**, 383-392 (1927); (d) Friday Evening Discourse, Royal Institution, March 18, 1927.

[5] (a) Euler, *Arkiv. Chem., Mineral. Geol.*, **7**, No. 31, 16 pp. (1920); (b) *Z. Elektrochem.*, **28**, 2-6 (1922).

[6] (a) Lewis, *Phil. Mag.*, **15**, 499 (1908); (b) **17**, 466 (1909); (c) *Z. phys. Chem.*, **73**, 129 (1910).

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

vertically above each other. They considered (erroneously, see below) that the partitions would prevent mixing of the liquids in the several compartments. They took for analysis the whole of the liquid except that in the uppermost compartment and, after mixing it until homogeneous, determined the loss of nonylic acid. They do not record any measurement of a corresponding gain in the uppermost compartment, neither was there any test of the effect of altering the age of the bubble or time of contact between air and solution. From the number and dimensions of the bubbles which had passed through the solution they knew the total area involved and they estimated the surface tension by means of drop numbers, using this also as their means of analysis. They compared their results with those computed from the surface-tension curve by means of the so-called Gibbs theorem: Γ, the excess of nonylic acid in the interface $= -\frac{c}{RT} \cdot \frac{d\sigma}{dc}$, where c is the concentration and σ the surface tension. Some uncertainty attached to the degree of dissociation in these extremely dilute solutions; in the results collected in Table I, four calculated values are given for comparison with Donnan and Barker's observations taken from Donnan and Barker's curve and Forch's curve for surface tension, respectively, calculated in each case for "ι" alternately equal to 1 or equal to 2, that is, for no dissociation and for complete dissociation of nonylic acid.

TABLE I

THE OBSERVATIONS OF DONNAN AND BARKER ON THE ADSORPTION, Γ, OF NONYLIC ACID IN THE AIR-WATER INTERFACE COMPARED WITH THE VALUES PREDICTED FROM THE SO-CALLED GIBBS THEOREM

Concn. of soln., %	Γ obs., g. × 10^{-8}	Γ calcd. (g. × 10^{-8})			
		Forch's curve		Donnan's curve	
		"ι"[a] = 1	"ι" = 2	"ι" = 1	"ι" = 2
0.00243	9.5	5.8	2.9	5.5	2.6
.00500	15.2	12.3	6.1	11.4	5.7
.00759	10.9	15.8	7.9	12.6	6.3
.00806	9.15	16.3	8.1	...	...

[a] "ι" is the degree of dissociation of nonylic acid in these solutions.

Since these four numbers constitute the only careful test of the adsorption in the air-water interface hitherto published, it is necessary to scrutinize them closely. They can be considered as confirming the order of magnitude of the effect but they are subject to serious error, as will be shown. Since they must be regarded as only semi-quantitative, no stress need be laid on the fact that they do not conform to Langmuir's prediction that they should reach a constant maximum value with increase of concentration; neither need attention be paid to the fact that the result of 10 × 10^{-8} g./sq. cm. gives an area of 26 × 10^{-16} sq. cm. per molecule, which is distinctly less than monomolecular and corresponds to the state of affairs that is illustrated in Figs. 1b or 1c. Our reason for regarding the method as inherently erroneous is given in the following paragraph describing extensive series of careful determinations (about 100) carried out during several years in the Bristol Laboratory, and all discarded.

Rejection of All Results by the Donnan and Barker Method.—There is a close resemblance between the determination of transport numbers and a determination of adsorption by the stream of bubbles used in the Donnan and Barker method. In the first the transport is electrical, in the second the bodily movement is mechanical. In the first, a careful experiment requires a demonstration that the gain or loss in the anode compartment is equal to the loss or gain in the cathode compartment and that the middle portion is unchanged. In precision work it is customary to take a series of middle portions to avoid chance compensation. We had taken all these precautions, analyzing every portion separately by the accurate method of the Zeiss interferometer and testing the effects of concentration, time, total area, etc.

There is one fatal objection to all measurements by this method, that is, the pumping action that goes on throughout the apparatus every time a bubble is injected and passes through. Donnan and Barker were misled by a strange blank experiment in which they observed no mixing. Within each compartment the stream of bubbles necessarily causes rapid stirring, so that the liquid in each compartment is kept sensibly homogeneous. As each bubble is passed into the bottom of the apparatus its own volume of liquid is necessarily pumped into the next compartment above, and a similar volume of liquid is returned when the bubble leaves each of the compartments successively. Since there are perhaps 24,000 separate bubbles it is easy to compute the amount of mixing that is inevitable, given the size of bubble relative to a given compartment. Hence a stationary state is reached which is definitely illusory, giving much less than the true adsorption.

THE STOPPER METHOD.—We tried a method of circumventing the mixing between successive compartments by carefully arranging the diameter and rate of passage of the bubbles and the dimensions and form of the orifices between compartments so that no bubble should leave an orifice until the next bubble had just caught up to it and taken its place. With care a third bubble could be added so that two at a time acted as stoppers in each orifice. Great care is necessary to prevent the bubbles from actually touching the glass, through breakdown of the thin film of liquid between, and also the dimensions of orifices of the successive compartments have to be adjusted to the lessening hydrostatic pressure as the bubbles travel upwards. Hence this difficult technique was discarded in favor of the very easy experiments to be described later.

The Nature of the Findings of the Present Investigation.—The measurements to be described for solutions of *p*-toluidine, of camphor and of amyl alcohol give quantitative information as to the amount of adsorption per square centimeter of surface of their aqueous solutions. In the first place, the amount of adsorption which occurs is definitely much greater than the material which could be packed into a monomolecular layer according to the dimensions of molecules obtained from the study of insoluble films and from x-ray measurement of crystals. For example, there is one molecule of toluidine adsorbed for every 14×10^{-16} square centimeters of surface, whereas one molecule can cover 23×10^{-16} square centimeters of surface. One molecule of amyl alcohol is absorbed for each 9×10^{-16} square centimeters of surface, whereas it should cover 21×10^{-16} square centimeters. These and the similar results for camphor show that the measured adsorption is several times greater than the amount of material which can be accommodated in a monomolecular layer and we, therefore, deduce an arrangement such as that depicted in Fig. 1d, where adsorption occurs not only upon the surface but within it. This shows that surface forces and surface tension are conditioned not solely by the outermost layer of molecules but also by much deeper layers. The study of the surface tension of ordinary liquids by such investigators as Sugden[8] has pointed to the similar conclusion that the total surface energy of a liquid is not defined entirely by the nature and orientation of the surface layer of molecules. Fig. 1d goes further in that it suggests a mechanism for this effect.

A second important result following from our numerical data is that the so-called Gibbs theorem, in which adsorption is related to concentration and surface tension, is shown to give highly erroneous values differing by several fold from those actually observed. Hence, this commonly used concentration formula must be rejected as being of only qualitative significance. In the following pages our method of experiment and its numerical results will be presented and afterwards it will be shown that a more careful consideration of the requirements of the true Gibbs formula, which involves thermodynamic quantities and all the components of the system (such as the gas used in bubbling) is required for adequate treatment on this subject.

Other Relations That Follow from the Conception of Chains of Oriented Molecules Extending Inwards from the Surface.—If this conception is correct it should find manifold applications and one should seek information in very diverse fields. For example, it affords an explanation of the otherwise surprising effect of inert fillers upon the strength and resiliency of rubber, as in rubber tires. It explains why extremely fine subdivision produces the greatest effect; the whole of the very extensive surface has the role of orienting the molecules in immediate contact with it and the

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[8] Sugden, *Trans. Faraday Soc.*, **22**, 486 (1926).

chain effect extends with diminishing intensity into the surrounding rubber. Fine subdivision not only increases the surface but diminishes the distance between these orienting particles.

In a similar fashion inert fillers should increase the strength and elasticity of layers of adhesives, thus improving joint strength where the layers are not excessively thin (see Second Report of the Adhesives Research Committee, Appendix IV, 109–111 (1926)). Perhaps we have here the explanation of the effect of multiple gluing in increasing the strength of a joint, that is, the well-known great increase in strength of many joints when the adhesive is applied in successive thin coatings and each allowed to dry before the next is applied, and a final coat given just before the surfaces are brought together. Probably we fix successive chains before applying the next layer. All these suggestions should be accessible to direct experimental test.

Even the effect of oil upon troubled water, which Hardy has had to ascribe to the diminishing of its friction against the atmosphere may possibly be brought under this explanation, since the oil forms a stable film to which chains of stable molecules may be anchored. In other words, the conception assumes that a liquid is not always a liquid near its own surface but may become a semi-solid.

Even a pure liquid has been shown by H. B. Baker and others to consist of a mixture of simple and aggregated molecules and hence the composition and structure of the surface will be different from that of the bulk of the liquid. Several writers such as L. V. King and Ramden have shown that from physical and especially optical considerations, there is a tendency towards formation of minute protocrystalline aggregates of molecules throughout liquids, and this tendency must be greatly enhanced and given direction in the neighborhood of surfaces.

A New and Simple Method of Determining Absolute Adsorption in the Air-Water Interface

There are many possible ways of replacing the discarded Donnan and Barker method. The following is one of the simplest. It gives quantitative results accurate to a few per cent. and only a few hours are required for each determination. The principle is to use a long inclined tube of large diameter (1.6 meters long), so inclined that bubbles pass slowly along it, adsorbing to saturation value without appreciably altering the concentration of the liquid remaining in the tube, which thus acts as a reservoir. At the top of the incline the bubbles rise into a vertical tube so narrow that each bubble fills its diameter. Each bubble in the vertical tube rapidly overtakes the former ones and draining is so rapid that within a few inches there is a continuous column of cylindrical bubbles in contact with each other. At the height at which draining is found to be sufficiently complete the narrow tube is curved over and down. The films break in the downward portion of the tube, condensing to a liquid, which is caught and analyzed for comparison with the original solution. By changing the degree of inclination of the long, sloping reservoir the bubbles can be kept in contact with the solution for any desired period of time; but in the vertical tube the bubbles must not be allowed to burst before they have gone round the bend. In the case of the very unstable bubbles from aqueous *p*-toluidine the four seconds during which these films last is ample for this purpose. To forestall a possible source of criticism (see later) the films should be allowed to break within the narrow tube before they reach its exit.

The apparatus is shown in Fig. 2. Nitrogen from a cylinder fitted with a constant pressure regulator is purified by passing through aqueous sodium hydroxide and is then

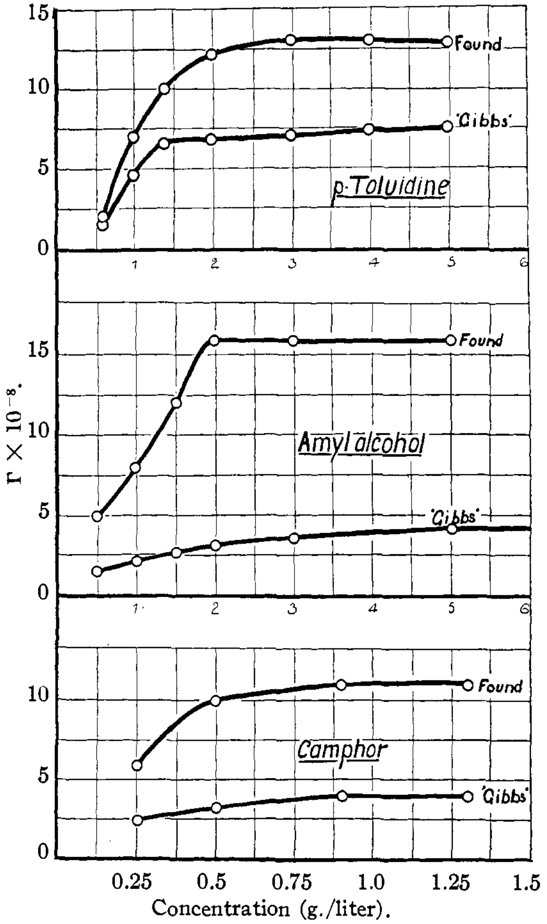

Fig. 2.—Comparison of absolute adsorption measured by the authors with that calculated from the so-called "Gibbs" (concentration) formula.

saturated with the vapors of the solution which is to be measured, first by bubbling it through a sample of that solution and then by passing it through a Washburn saturater filled with another sample of the same solution for final adjustment. The pressure is steadied by a capillary tube after which the gas bubbles into the apparatus through a suitably designed jet. The bubbles slowly pass up the long, inclined tube and rapidly up the narrower vertical tube, each pushing the previous ones out of the top of the liquid toward the vessel where the liquid from the collapsed films collects. From here the nitrogen, still saturated with the vapors from the solution, passes through a Parkinson and Gowan flow meter, previously calibrated by passing through it a known volume of air from a large gas holder. It was found that the volumes recorded by this instrument differed from the true values by less than one per cent.

It is essential that the narrow vertical tube be kept thoroughly wet so that bubbles do not break or come into real contact with the glass. For this purpose a further supply of original solution is provided in the supplementary reservoir and this is allowed to flow slowly into the apparatus until the orderly arrangement of bubbles and films has been fully attained. Thereafter, only such solution is supplied as is required to maintain the level of the liquid in the vertical tube constant at the optimum height. The experiment begins when this steady state has been set up; a fresh collecting vessel is put on and the first reading on the flow meter taken. When sufficient nitrogen is passed, that is, when a sufficient volume of liquid from collapsed film has been collected, the bubbling is stopped, the time taken, the flow meter read and disconnected and the collecting vessel stoppered and weighed. About 30 cc. of the solution is allowed to flow out through the narrow tube and collected in a separate vessel. The solution remaining in the inclined tube is all collected in the top reservoir, by applying gentle suction, and well mixed. The three solutions are then each analyzed in duplicate, using a Zeiss refractometer which determines the refractive index to about one division, which corresponds in the case of *p*-toluidine to about 1.49×10^{-6} g. of toluidine per cc. of solution. This is probably the most accurate method of analysis for such binary liquids.

Blank experiments were performed which showed that the method of cleaning and filling the apparatus was efficient, for the samples taken as in an experiment, but without any bubbling, were identical with the original solution. An essential blank experiment is one to show that saturation of the nitrogen is accurate, so that the nitrogen which escapes from the flow meter should neither impoverish nor enrich the solution under investigation as it passes through. For this purpose it was only necessary to allow the gas to pass through as usual but with the level of the liquid in the vertical tube sufficiently lowered so that no films escaped. Under these conditions we found that the concentration of the solution was completely unaffected by the passage of the previously saturated nitrogen. This is of great importance in the final considerations of the results which cannot be ascribed to this possible source of error.

If a thin surface film of toluidine solution of volume v and exposed area s be removed from the reservoir of liquid of original concentration c_0 to the collecting vessel, and if the actual surface contains its equilibrium amount of adsorbed toluidine Γ, then the weight of toluidine in the collecting vessel will be equal to $c_0v + \Gamma s$, and for n such films $c_0nv + \Gamma ns$. The volume of the solution in the collecting vessel V would be nv and its concentration c_1 will be $c_0 + \Gamma ns/v$; whence $\Gamma = [(c_1 - c_0)V]/ns$. In deriving this equation it is assumed that c_0, the concentration of the solution from which the films were taken, remains unchanged during the removal of the film, whereas in practice a relatively small but finite decrease will occur. If the final concentration of the remaining solution is c_f, then since $c_0 - c_f$ is very small compared with $c_1 - c_0$, then the increase in the concentration c_1 of the solution collected over that in the reservoir will be $c_1 - (c_0 + c_f)/2$ instead of $c_1 - c_0$. Hence $\Gamma = (V/ns)[c_1 - (c_0 + c_f)/2]$. The detail of the experimental procedure is best illustrated by giving the data of an actual experiment in full.

Experiment 4 of Section V.—Twenty-four minutes were required for this experiment during which the flow meter registered the passage of 0.05 cu. ft. = 1420 cc. The rate of formation of films (or bubbles) was 100 in 74 seconds at the beginning, at the end and throughout the experiment. The time of contact between bubble and solution in the reservoir was 14 seconds, many previous experiments having shown that no further adsorption occurred after 4 seconds, hence a threefold margin of time is always allowed.

The volume of solution collected from collapsed films (weighed) was 38 cc. A further sample of 38 cc. of liquid was allowed to flow out through the vertical tube and 350 cc. remained in the reservoir. The original solution contained 1.000 g. of toluidine per liter and when placed in a 4cm. cell in the interferometer and compared with water produced a change in reading of 640 divisions on the micrometer screw (this deflection being directly proportional to the difference in concentration, one division corresponding to 1.49×10^{-6} g. per cc.). The liquid collected from the collapsed films showed a gain over the original solution of 20 divisions, the sample of liquid taken from the vertical tube likewise showed a gain, although of only one division, showing that the transport of toluidine by the films is not quite complete. This increase was added to the other liquid collected. The final solution in the reservoir showed a loss of between 3 and 4 divisions. Hence, the total change in total concentration of the solutions collected relative to the mean concentration of the initial and final solution in the reservoir is 23 divisions. Hence, the total transport of toluidine $= V[c_1 - (c_0 + c_f)/2] = 38 \times 23 \times 1.49 \times 10^{-6} = 1.3 \times 10^{-3}$ g. The total number of bubbles, n, = 1950. Hence the volume of each bubble is 1420/1950 cc. Each bubble in its final form is a right cylinder of radius 0.65 and, therefore, of length 0.55 centimeters. The total area of these cylindrical bubbles is equal to $1950 \times 2\pi \times 0.65 \times 1.2 = 9550$ square centimeters. Hence Γ = total transport$/ns = 13.6 \times 10^{-8}$ g.

In this particular experiment there was a slight decrease in concentration in the residual solution due to evaporation and loss of toluidine. The total gain in the liquid from the collapsed films is, therefore, rather less than observed in the original solution. In better experiments the two were equal within the experimental error. This is very important because, as has been mentioned, the gain in toluidine is twice as great as that corresponding to a monomolecular film or to that calculated from the so-called Gibbs concentration formula.

The partial pressure of *p*-toluidine above its aqueous solution has been measured in the Bristol Laboratory by F. H. Pollard. From his results one may deduce that the partial pressure of *p*-toluidine of the solution used above was about 0.0078 mm. at 16°. The total volume of nitrogen passed through, namely, 1420 cc., exactly saturated with this vapor would, therefore, contain 6.6×10^{-5} g. of toluidine. Now the total amount of *p*-toluidine adsorbed and transported in the surface was 129.9×10^{-5} g. Hence, since the total amount of toluidine in the gaseous phase is only a few per cent. of the amount actually transported in the surface of the bubbles, any lack of adjustment in the saturation of the nitrogen with the vapors of the solution must leave the final experimental result of $\Gamma = 13.6 \times 10^{-8}$ g. per sq. cm. almost unaltered.

The Effect of Size of Bubble upon the Value Obtained.—If it is the true value of the adsorption Γ that is obtained by these measurements, they should be independent of the actual surface used. The following series of experiments shows the effect of keeping all other conditions constant and varying only the size of bubbles in the same tube. This appears as a variation in the length of the cylindrical bubbles or in the distance apart of the visible films when the bubbles have drained after coming into contact. The results are collected in Table II.

TABLE II

THE EFFECT OF VARYING THE LENGTH OF BUBBLE UPON THE APPARENT VALUE OF THE ADSORPTION[a]

Length of cylinder, cm.	Total surface area (sq. cm.)	Γ in g./sq. cm., obs.
5.5	43,000	4.5×10^{-8}
2.5	25,000	8.4×10^{-8}
1.5	19,300	12.7×10^{-8}
1.2	23,000	13.0×10^{-8}
1.1	24,000	14.5×10^{-8}
0.75	17,200	14.8×10^{-8}
.57	12,500	14.7×10^{-8}
.52	15,300	14.9×10^{-8}
.36	13,600	14.5×10^{-8}

[a] Solution 4 g. toluidine per liter. Internal diameter of the vertical tube 1.30 cm.

The results in Table II, properly interpreted, show the validity of this method of measuring Γ and likewise reveal under what conditions true values are obtained. It is seen that as soon as the cylindrical bubbles are appreciably shorter than their diameter the value of Γ observed is constant and independent of further alteration in the surface area. This is readily understood when we consider the propulsive and retarding forces which act upon a cylindrical bubble passing up a tube. If the bubble is short it will move as a whole. If the bubble is very long in comparison with its diameter the propulsive force is applied to its ends, whereas frictional retarding force is applied to its sides, and if the bubble is long enough the middle part of the cylindrical sides will not move, even although separated from the glass walls by a finite thickness of aqueous solution. In the extreme case there will be a succession of flat films representing the ends of the bubbles pressing up through a tube lined with a film of the same or slightly greater concentration. Hence, in such a case the method cannot be expected to give correct results since the surface taken for the calculation is the whole internal area of the bubble whereas only the ends are actually transporting toluidine. As a check upon this it can be seen that the values for Γ in the last column of Table II become almost constant if it is assumed that only 1.1 cm. of the length of each bubble can actually be moved. Of course there will always be a residual drag which will be reflected in a slightly greater transport if the liquid remaining in the vertical tube is collected and analyzed. In the experiment quoted above this represented 1 division out of 23 expressed in interferometer readings. The length of the bubble usually employed throughout the final measurements was about 0.5 cm. and never exceeded 1 cm. In every experiment it was found that the value for total transport, as calculated from the decrease in concentration of original solution was, within the limits of analytical error, equal to that obtained from the increased concentration of the solution produced from the collapsed films. This is important as proving that the final movements of the bubbles did not extract toluidine from the previously saturated stream of nitrogen passing through. This proves, too, that even though there must be a drag upon any bubble passing through any solution, and hence a tendency towards thinning out or renewal of the forward surface and a corresponding thickening or concentration at the rear surface, the error introduced in the particular substance we have investigated can be only very slight. It might be far otherwise with any substance whose adsorption is quick and desorption slow but if such a substance were volatile, as ours are, the effect would be at once detectable by impoverishment of the gaseous phase which we have shown not to occur in our experiments. This argument is vital to the acceptance of our numerical values. It so happens that the partial pressure of the toluidine above the solutions is such that there is just about as much toluidine in the gaseous phase within each bubble as is adsorbed upon the surface of the bubble. Hence, if the nitrogen were robbed of all its toluidine the observed transport would be doubled, but since this effect did not occur this source of error is measurably absent. In other words, our results can only be a few per cent. too great. For the reason stated no dynamic method can be perfect and the ideal method must be static.

Experimental Results for the Adsorption of *p*-Toluidine in the Nitrogen-Water Interface

Our numerical data are collected in Table III, which gives the results for solutions of *p*-toluidine ranging from 0.6 g. per liter up to saturation.

Table III

Absolute Measurements of the Adsorption of *p*-Toluidine in the Surface of its Aqueous Solution

Concn. of soln., g./liter	Length of bubble, cm.	Total surface, sq. cm.	Increase in concn. of film (divs.)		Cc. of film soln.	$\Gamma \times 10^8$ obs. g./sq. cm.
			uncorr.	corr.		
0.6	0.62	8100	3	3		2.3
	.67	10000	4	4		2.3
	.66	10500	5	5		3.0
	.71	11700	3	3		2.0
	.73	13000	5	5		2.5
	.69	12000	4	4		2.1
					Mean =	2.4
1.0	0.55	7700	7	7	45	6.1
	.68	10200	9	10	45	6.6
	.79	9600	8	8	47	5.9
	.66	10500	9	10	44	6.3
	.70	7600	7	8	46	7.2
	.96	6600	7	8	42	7.6
					Mean =	6.5
1.40	0.60	9200	13	14	45	10.2
	.70	11000	15	17	53	12.1
	.55	7620	10	12	45	10.5
	.59	9200	13	14	45	10.2
	.59	9230	12	13	44	9.4
	.57	7500	11	12	42	10.0
					Mean =	10.4
2.0	0.62	10900	16	18	51	13.3
	.53	9800	14	16	52	12.7
	.58	11000	19	21	42	11.9
	.58	11200	19	21	46	12.9
	.63	8900	13	16	50	13.4
	.62	6250	11	12	42	12.1
					Mean =	12.7
3.0	0.61	10800	24	27	38	14.1
	.54	9600	15	18	47	12.9
	.67	10400	17	20	50	14.3
	.56	9500	20	23	38	13.6
	.60	10900	21	24	41	13.5
	.58	11200	21	23	40	12.4
	.56	7600	11	14	47	12.9
					Mean =	13.4
4.0	0.51	12000	30	33	34	13.9
	.49	10140	30	34	26	13.0
	.50	12130	24	27	42	13.9
	.49	13230	28	32	37	13.3
	.56	11300	28	32	32.5	13.7
	.53	11750	26	29	33	12.2
	.52	11860	26	30	33	12.4
					Mean =	13.2

Table III (*Concluded*)

Concn. of soln., g./liter	Length of bubble, cm.	Total surface, sq. cm.	Increase in concn. of film (divs.)		Cc. of film soln.	$\Gamma \times 10^8$ obs. g./sq. cm.
			uncorr.	corr.		
5.0	0.47	12500	31	34	31	12.0
	.54	11560	29	30	33	12.8
	.48	13300	28	29	34	11.3
	.53	12660	27	31	38	13.8
	.50	11500	23	32	34.5	14.2
	.48	12260	26	30	38.5	14.0
					Mean =	13.0
6.0(satd.)	0.41	11700	20	23	30.5	9
	.54	15300	25	27	33.5	8.5
	.43	10500	21	24	28.5	9.5
					Mean =	(9)

The two extreme concentrations yield only approximate results because in the most dilute solution the absolute change is small and in the saturated solution the liquid from the collapsed films was supersaturated and before analyses could be carried out a few small crystals of toluidine were observed to separate. Thus the true value must be greater than that actually recorded. Sufficient data are given to show the degree of reproducibility of the experiments and to estimate the approximate error in the results. The toluidine was obtained from Kahlbaum and well recrystallized, m. p. 45.6°. The solubility measured by Edwards was 0.654 g. in 100 cc. of water at 15°. Conductivity water was used as solvent. The temperature was 16°.

Comparison of the Adsorption Observed with the Amount Needed for a Monomolecular Film

It is of course impossible to measure directly the amount of a soluble substance which is required to form a true monomolecular film. There are, however, two other means of estimating the dimensions of the molecule. The first is by comparison with substances higher in the homologous series which are sufficiently insoluble and whose area has been directly measurable by the film method. For example, Adams has found the area covered by a single molecule of hexadecylaniline in a close-packed monomolecular film on water to be 24×10^{-16} sq. cm. and for hexadecylphenol 24×10^{-16} sq. cm., whereas we have found one molecule of toluidine for each 14×10^{-16} sq. cm. of available surface. Even if shorter molecules might be packed slightly more closely than longer ones and even if through competition there were a tendency for the monomolecular film of a soluble material to be rather more closely packed than an insoluble film, the discrepancy is undoubted and clearly points to the conclusion that there is not room on the surface for all of the adsorbed material.

The extent to which molecules in a monomolecular film can be compressed is limited by the dimensions of the molecules themselves and these are given by x-ray analysis of the solid crystals. The toluidine molecules occupy the minimum area when oriented perpendicular to the surface. The dimensions of molecules containing the benzene ring have been obtained by Bragg using naphthalene[9] and by Shearer using benzene.[10] From the data for naphthalene it has been concluded that the area of cross section of a benzene ring is 25×10^{-16} sq. cm., while Shearer obtained from the unit cell of benzene itself a cross-sectional area of 23.3×10^{-16} sq. cm. Both of these agree with the dimensions of a single molecule in a monomolecular film but show that if there is one molecule of toluidine for each 14×10^{-16} sq. cm. not much more than half can be upon the actual surface.

The Change of Surface Tension with Concentration

Our measurements have demonstrated that the adsorption is constant over a wide range of concentration and that nevertheless the surface tension continues to fall with increase of concentration even after this constant value has been attained. This requires explanation. At first sight it might have been expected that the surface tension should be constant once the monomolecular film on the surface had been formed and the adsorption was constant. The surface tension as measured experimentally may be regarded as being the sum of the surface tension of the exposed outer surface of the monomolecular film of *p*-toluidine plus the interfacial tension between the film and the solution. This is the expression used by Antonoff[11] for the surface tension of a complete film and verified by him for the benzene in water system. The surface tension of the film is taken as constant since the molecules therein have a constant orientation and resemble those in the surface of liquid toluidine in bulk. Hence in applying this conception to the present systems, namely, unsaturated solutions, which are more complicated than the saturated systems hitherto studied, it is necessary to ascribe any change in total surface tensions to change in the interfacial tension between the monomolecular film and the solution upon which it rests.

Morgan and Egloff[12] studied the partially miscible liquids phenol-water and found at saturation the surface tension of each of the two layers was the same as the surface tension of pure phenol. For regions in which only one layer could exist they found that the addition of phenol lowered the surface tension until at saturation it was that of pure phenol. Similar behavior was found with solutions of amyl alcohol and triethylamine. We, therefore, conclude that in our system, aqueous toluidine,

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[9] Bragg, *Proc. Roy. Soc.* (London), **35**, 167 (1923).

[10] Shearer, *Proc. Phys. Soc. London,* **35**, 81 (1922).

[11] Antonoff, *J. chim. phys.*, **5**, 392 (1907). See also Iredale, *Phil. Mag.*, **49**, 466 (1921), who verified this expression for a monomolecular film of water on mercury.

[12] Morgan and Egloff, THIS JOURNAL, **38**, 844 (1916).

the saturated solution should have approximately the same surface tension as liquid toluidine, that is, the surface tension of the outside layer of *p*-toluidine molecules. This assumes that in this saturated solution there is no interfacial tension between the film and the aqueous layer. The suggestion thus derived may be summed up in the statement that the more concentrated the solution, the less disparity will exist between it and the monomolecular film on its surface, and the less, therefore, will be its interfacial tension. The interfacial tension will, therefore, decrease with increasing concentration until it becomes vanishingly small for the saturated solution. This decrease in interfacial tension would explain why the experimentally measured surface tension of a solution continues to alter with increase of concentration even after a monomolecular film is formed on the surface, and predicts a definite value toward which surface tension should tend with approach to saturation.

Using the du Noüy tensimeter (inaccurate for such systems) for *p*-toluidine solutions near saturation it was found that within the experimental error the solutions attained a constant value of surface tension. Three solutions containing 5.6, 6.0 and 6.4 g. of toluidine per liter gave each a surface tension of 52.6 dynes. It is interesting to note that the so-called Gibbs theorem would predict zero adsorption for these solutions, whereas the actual adsorption is the same as for the more dilute solutions where the surface tension is changing rapidly with concentration.

It is interesting to speculate as to the depth to which a surface really extends, that is, the depth to which it is different in properties or in concentration from the bulk of the liquid. One has to avoid the dilemma that on the one hand the range of molecular attraction extends only between molecules actually in contact and on the other that the composition of the layer immediately below the monomolecular film is different for each concentration of the solution as is shown by the change in surface tension with change in concentration. We have found that the total weight of excess toluidine associated with one square centimeter of surface is 14×10^{-8} g. Of this possibly 8×10^{-16} g. are in the monomolecular film of pure *p*-toluidine, leaving 6×10^{-8} g. in the adjacent submerged region. Since a saturated solution of *p*-toluidine contains only 6 g. per liter, 6×10^{-8} g. would in itself suffice to saturate a depth of 1×10^{-5} sq. cm., which is what was formerly regarded as within the range of direct molecular attraction. However, since the solution itself already contains anywhere from a few grams up to saturation amount of *p*-toluidine per liter, and this adsorption is additional and constant for all except the most dilute solutions, there is more toluidine concentrated below the surface than could be contained in a saturated solution. However, we do not conceive of these underlayers as supersaturated or even as uniform but explain them in accordance with Fig. 1d as due to the presence of the chains of *p*-toluidine reaching down deeply into the solution from various isolated points on the under side of the monomolecular layer.

Test of the So-Called Gibbs Theorem $\Gamma = \frac{-c\ d\sigma}{RT\ dc}$

All authors previous to 1925 did not use the true Gibbs theorem but substituted for it the simplified approximation formula given in the heading above in which adsorption is merely referred to as change of surface tension with concentration. Now that we have substantially accurate quantitative results, it is possible to show that this is inadmissible even for the simple crystalloidal substances we have used, namely, toluidine, amyl alcohol and camphor in aqueous solution.

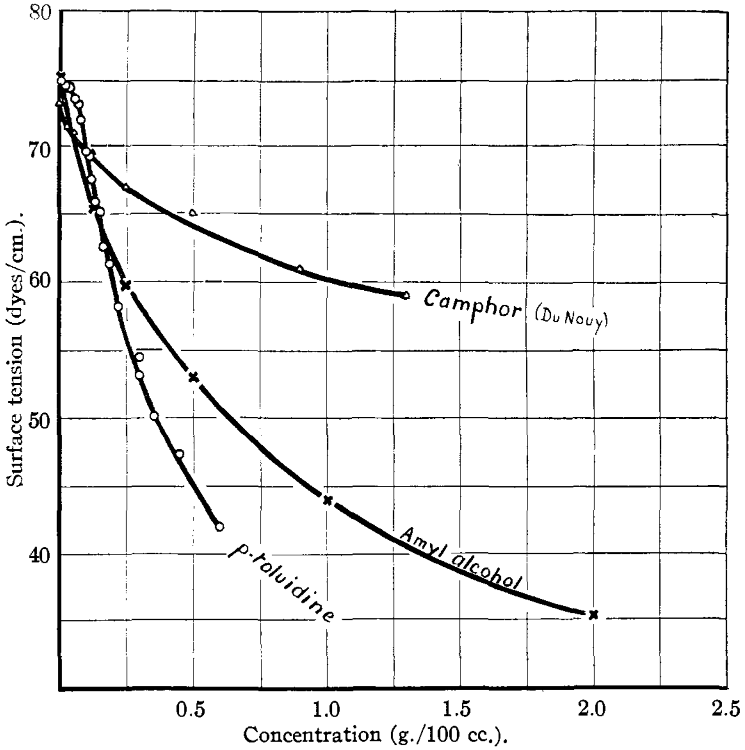

Fig. 3.—Surface tension of aqueous solutions of *p*-toluidine and amyl alcohol carefully measured by the Ferguson method and of camphor using du Noüy tensimeter.

Special care was devoted by P. R. Edwards to obtaining trustworthy values for the surface tension of aqueous solutions of *p*-toluidine. He employed the Ferguson method in which the pressure of air is measured which is required to blow down into a capillary tube inserted in the surface of a solution until the meniscus in the capillary is flat and exactly at the lower end of the capillary.[13] Fig. 3 gives the data obtained by Edwards for solutions of *p*-toluidine, each point being the mean of six readings. Fig. 3 shows also Edwards' values for aqueous amyl alcohol by the same method and our values for aqueous camphor[14] using the du Noüy tensimeter with the procedure suggested by Klopsteg.[15] Hence, the values for camphor can only be regarded as semi-quantitative, although consistent.

In calculating the slope of the surface-tension curves it has to be remembered that the slope is not obtained by direct measurement but by the difference in values of isolated measurements of the surface tension itself, that is, small differences between large numbers. However, this source of error is completely eliminated if the comparison of slope with observed adsorption is not confined to a single point but is spread out over a wider range of concentrations.

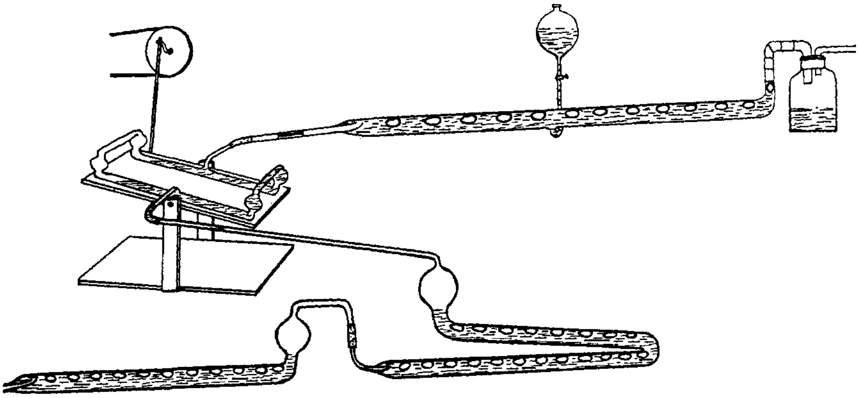

Fig. 4.—The apparatus employed for the measurement of absolute adsorption in the air-water interface.

In Table IV are given the values calculated by the concentration formula $\Gamma = \frac{-c}{RT}\frac{d\sigma}{dc}$ from the slope of the surface tension curve for comparison with the adsorptions actually observed, $R = 7.843 \times 10^{-8}$ ergs per g. The comparison is still more strikingly made in Fig. 4.

It is evident that although the predictions of the concentration formula are of the right order of magnitude it can only be regarded as being semi-quantitative. The same conclusion results from the fairly good experiments with amyl alcohol and the less exact experiments with solutions

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[13] (a) Edwards, *Trans. Faraday Soc.*, **16**, 384 (1921); (b) *J. Chem. Soc.*, **127**, 744 (1925).

[14] Although Edwards has published careful measurements of aqueous solutions of camphor his recorded concentrations should be divided by 10 and hence all his solutions are more dilute than those here used.

[15] Klopsteg, *Science*, **60**, 319 (1924).

TABLE IV

COMPARISON OF THE SO-CALLED GIBBS CONCENTRATION FORMULA WITH THE OBSERVED ADSORPTION OF *p*-TOLUIDINE

Concn.[a]	0.6	1.0	1.4	2.0	3.0	4.0	5.0
Slope[b]	55000	106000	106000	76810	51210	34000	32800
"Gibbs"	1.5	4.7	6.6	6.8	7.1	7.3	7.5
Observed	2.4	6.5	10.4	12.7	13.4	13.2	13.0

[a] Concn. in g. of *p*-toluidine per liter of solution.

[b] $d\sigma/dc$ in c.g.s. units.

of camphor now to be described. In all cases we are dealing with crystalloidal non-electrolytes. Hence, the concentration formula must be regarded as only a first approximation.

The Adsorption of Amyl Alcohol and of Camphor in the Air-Water Interface

Iso-amyl alcohol supplied by Kahlbaum and distilling at 130° was employed. On account of its appreciable volatility great care was taken to have the nitrogen passed through the aqueous solution exactly saturated so that when no bubbles or films were allowed to leave the main reservoir the passage of the nitrogen caused no detectable alteration in the concentration of the solution. One division of the interferometer scale corresponded to 3.7×10^{-6} g. per cc. The results of the measurements have been collected in Table V. The values for the most dilute solutions are only approximate because of the small analytical change; amyl alcohol does not affect the refractive index nearly as much as toluidine. The same apparatus was used in all experiments.

TABLE V

ABSOLUTE MEASUREMENTS OF THE ADSORPTION OF AMYL ALCOHOL IN THE SURFACE OF ITS AQUEOUS SOLUTION[a]

Concn. of soln., g./liter	Length of bubble, cm.	Total surface, sq. cm.	Increase in concn. of film (divs.)		Cc. of film soln.	$\Gamma \times 10^{-8}$ obs. g./sq. cm.
			uncorr.	corr.		
0.5	0.98	11000	3	3	42	4
	1.14	11000	3	3	46	3
	0.82	9400	3	3	44	5
	0.89	9100	3	3	44	5
					Mean =	5
1.0	1.55	9900	4	5	44	8.2
	0.78	9660	4	5	48	9.2
	.72	9930	4	5	44	8.2
	.78	9600	4	5	44	8.5
					Mean =	8
1.5	0.86	9300	6	7	46	13
	.76	9800	7	8	38	12
	.96	11600	7	8	45	11
	.82	9400	6	7	44	12
					Mean =	12

TABLE V (*Concluded*)

Concn. of soln., g./liter	Length of bubble, cm.	Total surface, sq. cm.	Increase in concn. of film (divs.)		Cc. of film, soln.	$\Gamma \times 10^{-8}$ obs. g./sq. cm.
			uncorr.	corr.		
2.0	0.71	7600	7	8	40	15.6
	.86	10700	10	11	40	15.2
	.76	10600	9	10	44	15.4
	.97	7320	7	8	43	17
					Mean =	16
3.0	0.73	10000	9	11	41	17
	.79	10400	10	11	41	16
	.73	10000	10	11	39	16
	.65	10500	10	11	41	16
					Mean =	16
5.0	0.72	10900	10	12	42	17.1
	.57	11200	9	11	42	15.2
	.54	11600	13	15	34	16.2
	.56	11500	11	12	42	16.4
	.66	12000	9	11	45	15.2
	.48	12250	11	13	37	15
					Mean =	16

[a] Time of contact of nitrogen and solution varied between 12 and 15 seconds.

A constant value for the adsorption, namely, 16×10^{-8} g./sq. cm. is attained at and above the concentration of 2 g. per liter. This corresponds to one molecule of amyl alcohol for each 9×10^{-16} sq. cm. of surface. Langmuir found that the normal higher insoluble alcohol, hexadecyl alcohol, had an area in monomolecular film of 2×10^{-16} sq. cm. Hence, once more the observed adsorption is definitely greater than the amount which could be accommodated on the surface as a close-packed monomolecular film.

The experiments with camphor are more difficult because of the instability of the bubbles. Hence, a continuous flow of liquid was maintained over the bend at the top of the vertical tube. The camphor used was the best procurable natural Japanese, melting at 177°. One division of the interferometer reading corresponded to 2.7×10^{-6} g. per cc. The results are collected in Table VI.

It will be noted that for solutions whose concentration ranges from 0.5 to 1.3 g. per liter (saturated solution) the adsorption is approximately 10×10^{-8} g. per sq. cm., corresponding to an area of 23×10^{-16} sq. cm. per molecule of camphor.

Tables VII and VIII give the values predicted from the approximate Gibbs concentration theorem for comparison with the observed amounts of adsorption. The data are also given in Fig. 4 showing that the discrepancy is of the same order of magnitude, and in the same direction as in the case of toluidine.

TABLE VI

ABSOLUTE MEASUREMENTS OF THE ADSORPTION OF CAMPHOR IN THE SURFACE OF ITS AQUEOUS SOLUTION

Concn. of soln., g./liter	Length of bubble, cm.	Total surface, sq. cm.	Increase in concn. of film (divs.) uncorr.	corr.	Cc. of film soln.	$\Gamma \times 10^{-8}$ obs. g./sq. cm.
0.25	1.37	7800	3	4	43	6
	0.86	9300	3	5	42	6
	1.30	6600	2	3	41	5
	0.96	8800	3	4	40	5
					Mean =	6
0.50	1.12	8300	4	6	50	10
	1.92	7000	3	5	50	10
	0.91	8200	3	5	50	8
					Mean =	10
0.90	0.92	9000	5	8	43	10
	.86	9300	5	9	47	12
	1.00	8600	4	8	44	11
	0.82	9400	6	9	47	12
	.99	8700	5	9	43	12
					Mean =	11
1.3	0.73	10000	6	9	42	10
	.93	8900	5	8	43	11
	.97	8800	6	8	44	11
	.89	9100	6	8	40	10
	.82	9400	6	9	42	11
					Mean =	11

TABLE VII

COMPARISON OF THE SO-CALLED GIBBS CONCENTRATION FORMULA WITH THE OBSERVED ADSORPTION OF AMYL ALCOHOL

Concn.[a]	Slope[b]	"Gibbs"	Observed
0.5	7700	1.4	5
1.0	6299	2.3	8
1.5	4919	2.7	12
2.0	4249	3.1	16
3.0	3060	3.3	16
5.0	2250	4.1	16
10.0	1350	4.9	..

[a] Concentration in g. per liter.

[b] $d\sigma/dc$ in c.g.s. units.

TABLE VIII

COMPARISON OF THE SO-CALLED GIBBS CONCENTRATION FORMULA WITH THE OBSERVED ADSORPTION OF CAMPHOR

Concn.[a]	Slope[b]	"Gibbs"	Observed
0.25	12400	2	6
.50	9800	3	10
.90	7400	4	11
1.3	5000	4	11

[a] Concentration in g. per liter.

[b] $d\sigma/dc$ in c.g.s. units.

Since the error in the concentration formula is evidently several fold, this explains the results obtained by Langmuir and later workers who in lieu of actual experiment used this formula to obtain values for the adsorption of one molecule of a lower fatty acid for 31×10^{-16} sq. cm. of surface, whereas one molecule can only cover 22×10^{-16} sq. cm. in a complete monomolecular film and presumably the true adsorption is still greater. We hope to present experimental evidence in a further communication. The conclusion is that we must go back to the true equations as actually formulated by Gibbs.

Adsorption and Thermodynamics

The glaring discrepancy between adsorption as actually observed and the predictions of the simplified so-called Gibbs formula $\Gamma = (-c/RT)(d\sigma/dc)$ makes it necessary to examine the basis upon which the thermodynamic treatment of this subject rests.

The derivation given by Lewis and Randall[16] shows clearly the assumptions now usually made. These are that (1) only two components are present anywhere in the system, and that (2) the only free energy of a surface is its surface tension multiplied by its area. If so, necessarily $\Gamma = -(d\sigma/d\mu)$, where μ is the potential of Gibbs.[17] This may be written $\Gamma = -d\sigma/d\bar{F}$ or $\Gamma = (-a/RT)(d\sigma/da)$ where $\bar{F}$ and a are the partial molal free energy and activity of the solute in Lewis and Randall's nomenclature.

The formula is usually simplified by substituting concentration for activity, with the misleading results which we have previously discussed.

One reason for the disagreement between the facts and the simplified formula is due to the nature of the materials usually chosen. Surface-active substances are usually far from ideal and often of limited solubility, with corresponding deviation from the ideal partial vapor pressure. It should be clearly understood that the potential or activity is that exhibited by the solute in the bulk of the solution and it is not affected by whatever complications occur at the surface; the whole behavior at the surface is governed by the potential within the ordinary homogeneous solution, and the potential of each component in the surface must equal this, no matter how complicated the actual surface may be. For example, a crystalloidal solute might be adsorbed in colloidal form, but its amount would still be that predicted from the properties of the bulk of the solution; however, a solute which was so readily brought into colloidal form would be expected to possess a potential or activity differing from that of an ideal solution.

Reverting to the thermodynamic formulation, the first consideration

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[16] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1923, p. 250.

[17] In the notation used by Lewis and Randall, $\nu_2 = (-d\gamma/d\bar{F}_2)_\sigma$.

that arises is that seldom or never have true, two component systems been actually under observation, although this is fundamental. Solutions of electrolytes or substances capable of hydrolysis, such as soap, cannot be treated as two component systems except in the rare event that the composition of the adsorbed material is identical with that of the solute remaining in the solution. For example, the foam from a neutral soap solution contains acid soap; thus the free alkali remaining in the solution is introduced as a new and important variable component. The numerical data for the adsorption of soap will be dealt with in a later paper; they present the most flagrant conflict with the prediction of the simplified formula, differing in order of magnitude and even in sign.

The component (or components) actually present, but hitherto ignored, is the gas (or air) in presence of which the surface tension is measured and bubbles are produced. For the more general treatment it is simplest to proceed from the original equation in this subject, number 508 of Gibbs (Scientific Papers, page 230). Gibbs' equation 508 is an application of the first law of thermodynamics, and reads $d\sigma = -\eta_s dt - \Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 - \Gamma_3 d\mu_3$, etc., where the subscripts refer to the respective components (for example, Γ_1 water, Γ_2 toluidine and Γ_3 the nitrogen); the first term on the right vanishes for constant temperature. The equation implicitly excludes electrical, etc., effects. It makes the same assumption that the free energy of the surface is given by its surface tension multiplied by its area, but it explicitly mentions each component present in the system. The adsorptions Γ, here referred to by Gibbs are the absolute values, defined as the excess or deficiency of the amount of each component as compared with that which would have been present if the two homogeneous phases (solution and vapor) had extended without alteration up to an arbitrary mathematical dividing surface. This ingenious definition affords a definite value for the adsorption, no matter how deep, stratified or complicated the actual physical surface may be.

The value of Γ for any one component (preferably the solvent) may be set equal to zero by suitably placing the arbitrary mathematical surface. This may be done even if the solvent is actually absent from a layer of the physical surface, as is the case where we have a monomolecular film of solute upon the surface, with solution below and vapor above it. Having set $\Gamma_2 = 0$, the values of Γ_2 and Γ_3 are defined with reference to the solvent. The experiments described correspond with this definition, because they are so carried out that the vapor phase is kept unaltered as the surface is destroyed, and hence the whole of the material in the physical surface goes into the final liquid which is then analyzed for change in concentration relative to the solvent. Lewis and Randall's definition is the same, for they keep the total amount of solvent in the system constant and define Γ_2 as the amount of the second component it is necessary to add when the surface is increased if the bulk of each phase is to be kept unaltered in properties, such as partial molal free energies, and hence in concentration.

Where there are second and third components (such as *p*-toluidine and nitrogen) their adsorption is $\Gamma_2 = —(\mathrm{d}\sigma/\mathrm{d}\mu_2)_{\mu_3}$ and $\Gamma = —(\mathrm{d}\sigma/\mathrm{d}\mu_3)_{\mu_2}$, each of which is readily measured, although this has never been done. It is obvious that the two adsorptions will mutually interfere. The gas cannot be quite ignored. For example, it has been stated that the surface tension of mercury is 10% lower in the presence of one atmosphere of nitrogen than *in vacuo;* similarly, nitrogen lowers the surface tension of water by about 1%, which would correspond to the adsorption of about 3% as many molecules of nitrogen as of *p*-toluidine. However, such mutual interference cannot explain the high values of the observed adsorptions.

Several authors such as Donnan[7] have suggested that the Gibbs theorem applies only to a layer of the surface one or two molecules deep, and that other changes may occur in deeper layers which are not included in the Gibbs equation. This is to forget the strict definitions of Gibbs who in introducing his thermodynamic formula found it essential to include with the surface a layer of the adjacent phases so deep that the boundaries reached into the truly homogeneous phases on both sides. The Gibbs effect is, therefore, the sum total of all concentration changes whether one or very many molecules in depth from the surface.

In the Gibbs equation all electrical effects are expressly excluded. Nevertheless, all surfaces are electrified in that they exhibit electrophoresis, and this is just as prominent in the gas-liquid interface as in any other. Hence, it is necessary to add at least one term (namely, $—e\mathrm{d}V$, where e is charge and V is electrical potential) to Gibbs' equation even for dealing with surfaces of non-electrolytes. If ions in solution (such as $\mathrm{H}^{\cdot}$ and OH') are not adsorbed in absolutely identical amounts, this in itself adds one more component to the system. The term $—e\mathrm{d}V$ produces the equation $\mathrm{d}\sigma = —e\mathrm{d}V$ used by Lippmann[18] before Gibbs, when the temperature and the chemical potential are held constant, which is easily done if the composition and electrical potential of the vapor phases are kept constant.

The exact formulation is not quite simple because of the depth and complex structure of the surface layers. For example, Freundlich has demonstrated that the layer in which movement takes place exhibits an electrokinetic potential which bears little or no relation to the total difference in potential of the two homogeneous phases. Hence, the surface is far from behaving as a simple electrical condenser as envisaged by the earlier investigators. This, however, accords with the recent recognition of the fact that the total surface energy of a liquid is not defined entirely by the nature and orientation of the outermost monomolecular layer of

[18] Lippmann, *Ann. chim. phys.*, (V) **5**, 494 (1875).

molecules or ions. Great uncertainty exists as to the value or values of the potential difference between phases involving non-electrolytes. It is chiefly a matter of convention[19] that they are usually taken to be between 20 and 50 millivolts, and such experiments as those of Frumkin give values over ten times greater. Even the absolute charges may not be entirely negligible, as is shown by the behavior of thunder clouds in which mere coalescence of drops and diminution of air-water surface produces discharges of the order of one hundred million volts.

A further communication will deal with thermodynamic data for solutions of *p*-toluidine. The experiments here recorded were completed at Bristol University, England, in 1925.

Summary

1. A simple method has been devised for accurately measuring the absolute adsorption at an air-liquid interface and for the first time trustworthy quantitative data have been obtained. Aqueous solutions of *p*-toluidine, amyl alcohol and camphor have been studied.

2. In every case the amounts actually adsorbed are several times greater than that corresponding to a monomolecular film and it is, therefore, concluded that for these solutions of ordinary non-electrolytes over a wide range of concentration of solutions the surface consists of a saturated monomolecular film of solute resting upon a comparatively thick layer of concentrated solution, gradually falling off with depth to the bulk concentration of the solution.

3. The mechanical explanation of this structure is that chains of oriented molecules extend downwards into the solution from the outermost monomolecular film. It is not assumed that there is a wide range of molecular attraction but rather that in effect the same result is produced by chains of contiguous molecules. It was found that many lines of evidence are in agreement with this hypothesis.

4. The so-called concentration formula of Gibbs, as usually quoted, is shown to give erroneous values for adsorption. It is necessary to use the true thermodynamic formula of Gibbs and not only to take into account all the components (usually much more numerous than anticipated) but also to include the electrical effects which universally occur at surfaces but which were not included in the Gibbs equation. Hence, the numerous data which have been calculated by means of the Gibbs concentration formula are shown to be in error.

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[19] See *J. Phys. Chem.*, **28**, 706 (1924).