[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Microtome Measurements of the Adsorption of Hydrocinnamic Acid in the Surface of its Aqueous Solutions*

BY J. W. MCBAIN, T. F. FORD AND G. F. MILLS

It has been demonstrated that the composition of a *moving* surface bears little relation to monomolecular adsorption or to the Gibbs theorem.[1] The microtome method[1,2] was developed for measuring adsorption at *static* air–water interfaces. In principle this method fulfills the Gibbsian requirement of equilibrium, and therefore can, theoretically, be made definitive as well as accurate. Results obtained with this apparatus are here reported for solutions containing 1.5 g. of β-phenylpropionic acid in 1000 g. of water. Humphreys,[2] Swain,[1] and two of the present authors (T. F. F. and G. F. M.) have each independently obtained a final value for the absolute adsorption per square centimeter of between 5.2 and 5.6 $\times 10^{-8}$ g.

It is disturbing to find that time appears to be a factor and that these equilibrium values appear to develop only on solutions that have been aged for several hours. However, it has been well established[3] by many methods and in several laboratories that the lowering of surface tension of these solutions likewise requires long periods of time for development. The Gibbs equation involves only quantities measured under equilibrium conditions. Hence, although it may be interesting that the final values for adsorption agree with the initial non-equilibrium values of surface tension obtained by the drop weight method,[3] they must properly be compared with the somewhat higher values obtained from the later more static measurements of surface tension.

Experimental

Apparatus.—The apparatus differs in a number of details from that previously used.[1,2] In order further to eliminate evaporation, both the inner and outer enclosures were rebuilt. In the inner enclosure the independent suspension of the trough was discarded. Instead, a silver sub-trough one inch (2.5 cm.) deep was set between the rails so as to seal the entire space and so designed that the trough rested directly upon it. The surface of the solution itself came into contact only with pure silver, except at the ends of the trough where the edges were coated with dicetyl. The glass side walls of the outer enclosures were replaced by brass ones heavily plated with silver, and all that space lower than the rails themselves was hermetically shut off from the outside by means of silver-plated aprons; the small cracks where the parts of the enclosure were fitted together were sealed on the inside with paraffin wax, and the glass covers were fitted on the cases with apiezon wax. After thus eliminating all leaks, it was found that, in the saturated atmosphere existing in the enclosure, water condensed in the guides in which the inner doors operate, and that capillary forces prevented their opening. The automatic feature of the doors as constructed had then to be discarded, and in these experiments the inner doors were operated manually by an assistant.

The sample of solution collected by the car was removed to the interferometer cell for analysis by means of a suitably shaped pipet, thus obviating the necessity of lifting the car from the tracks and reducing the evaporation loss. Also the whole length of the tracks beyond the outer enclosure was covered by a tunnel constructed of glass and of cardboard coated with shellac to make it possible for the car to be started and stopped in contact with a vapor similar to that inside the enclosures.

The silver stirrer previously used was replaced by one made of thin glass rods welded in the shape of a ladder with many rungs. This stirrer lies flat on the bottom of the trough and is manipulated through the holes in the covers of the outer and inner enclosures by means of a bent glass rod.

The tracks were surveyed and levelled where necessary, using a 15-inch (38-cm.) Pratt and Whitney gage, with which differences of 0.00005 inch (0.00127 mm.) per foot (30.5 cm.) may be estimated. Surveys were made before the experiments were started and again afterward to detect possible changes in level. The tracks within the enclosure were of pure block silver six feet long and were scraped true and level; the twenty-six feet of tracks outside the enclosure were of steel.

The microtome barrel in which the liquid skimmed off was caught was, like the trough itself, made of pure silver, burned together by autogenous welding to avoid contamination from solder. All fresh surfaces of solution were cut off many times to remove contamination. They were then very thoroughly stirred for several minutes and time was counted from the completion of stirring.

Experimental Procedure.—All apparatus was thoroughly washed and dried under cover before the experiment was started. No parts were handled more than could possibly be avoided. To prevent contamination being carried into the enclosure on the runners of the car, they and the tracks were washed with distilled benzene before each experiment.

A blank run, from which an approximate value of otherwise indeterminable experimental errors could be esti-

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(*) Original manuscript received April 7, 1939.

[1] For references, see McBain and Swain, *Proc. Roy. Soc. London*, **A154**, 608 (1936); McBain and Wood, *ibid.*, 286 (1940).

[2] McBain and Humphreys, *J. Phys. Chem.*, **36**, 300 (1932).

[3] *Cf.* McBain, Vinograd and Wilson, THIS JOURNAL, **62**, 244 (1940).

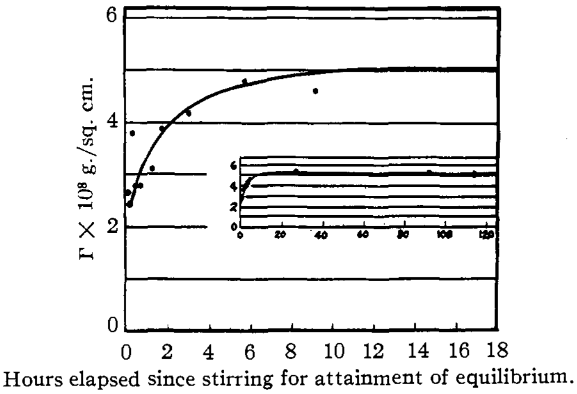

Fig. 1.—The measured adsorption of β-phenylpropionic acid in the surface of a solution containing 1.5 g./1000 g. water.

mated, was made by the usual procedure in which the sample placed in the microtome collecting chamber, or barrel, was of known original concentration. As a check the blank correction was divided into an evaporation and a dilution blank which were then added together. In the first, a known sample was poured into the barrel of the car after the car, wet with the same liquid, had been shot along the tracks; and this sample was then removed and analyzed. In the dilution blank the car was not shot at all, but a sample which differed by a known amount from the solution which had been used to rinse the barrel of the car was introduced into the barrel and removed again for analysis. The evaporation correction was −0.4, the dilution correction was +0.3, giving a composite blank correction −0.1 division of the interferometer dial for a 3-g. sample of 1.5 g./1000 g. hydrocinnamic acid. The corrections affect the final results by less than 4%. An 8-cm. Zeiss cell was used for analysis, reading to 0.1 division or 1.19×10^{-7} g. of hydrocinnamic acid to one gram of water.

A time schedule for a typical experiment was as follows. Three minutes after opening the inner doors only, the barrel of the car had been thoroughly rinsed with the stock solution. At 2, 3, 4 and 6 sec. later, respectively, the car was on the tracks, the outer doors opened, the car released, and the outer doors closed. At 21 and 51 sec., the sample had been placed in the interferometer cell and a sample of the liquid left in the trough had been removed and placed in the other compartment of the interferometer cell.

In the microtome measurements, the solutions were shielded from light or exposed during experiments only to the dimmest possible artificial light. Only dim indirect light was at any time permitted in the basement room in which the equipment was housed. This precaution was primarily to minimize temperature fluctuations, but it also guarantees the absence of light-induced polymerization of adsorbed solute. In the surface tension measurements in the same room, the solution was completely enclosed in an opaque box.

Results of Adsorption Measurements

The adsorption results for solutions containing 1.5 g./1000 g. water are collected in Table I and are shown graphically in Fig. 1. The table gives interferometer readings, Δ, for the surface liquid compared with that remaining in the trough from which the surface liquid had just been removed, and Γ the excess of solute found per square centimeter of the air-water surface over that corresponding to uniform concentration right up to the surface, where $\Gamma = \text{g./cm.}^2 = \Delta Vk/A$, where k is the interferometer constant, V is the volume of shaving, and A is the area of surface removed by the microtome, 288 sq. cm. in every case.

Table I

The Absolute Amount of Adsorption, Γ, per Sq. Cm. of Surface of Aqueous Solution

Concentration: 1.5 g. of hydrocinnamic acid per kg. of water. Temperature: maximum variation in 24 hr. 21.30–21.70°; during the 2 weeks represented by the experiments, 20.10°, 21.70°.

Expt.	Time since stirring	Vol. of shaving	Δ	$\Delta_{\text{cor.}}$	$\Gamma \times 10^8$
10	7 min.	0.75±0.04	9.1	8.7	2.7
8	13 min.	1.0 ± .04	6.4	6.1	2.5
5	25 min.	2.53± .08	2.8	2.7	2.8
3	45 min.	2.15± .08	3.3	3.15	2.8
11	1 hr. 15 min.	1.90± .12	4.1	3.95	3.1
14	1 hr. 45 min.	0.49± .04	[a]	[a]	3.9
2	3 hr.	1.75± .08	6.0	5.8	4.2
6	5 hr. 45 min.	2.05± .08	5.8	5.65	4.8
4	9 hr. 20 min.	0.85± .04	13.5	13.15	4.6
9	27 hr.	0.49± .04	[a]	[a]	5.4
12	93 hr.	4.50± .25	2.9	2.8	5.2
13	116 hr.	1.65± .10	7.6	7.4	5.0

[a] Analyzed mixture with equal volume of standard solution.

Survey of the tracks before and after each set of experiments disclosed differences in level of less than 0.001 cm. throughout the length of the trough, so that complete films were certainly collected.

Effect of Evaporation.—Extensive tests of the effect of evaporation upon the experimental results were carried out both with solutions of hydrocinnamic acid and with more concentrated solutions of phenol, the latter being volatile. It was shown that a correct result can be obtained only when the solution in the trough is kept in such an atmosphere that its composition undergoes no change over long periods of time. This is in accordance with the Gibbs requirement of true equilibrium. For the experiments recorded in Table I, for example, the change in concentration of the solution in the trough was less than 1 division, or 1×10^{-6} g./cc. or 0.0006% of the original concentration, in a month.

Twelve measurements also were made upon solutions containing 5.2 g./1000 g. water. These data are not displayed here because at the low temperatures they were too near saturation. With the exception of two low values (including 0.14 × 10^{-8} g./cm.^{2} at age one minute), they averaged 6.6 × 10^{-8} g./cm.^{2}. The last four values obtained at ages from twenty-three to fifty-three hours averaged 7.7 × 10^{-8} g./cm.^{2}, which is still distinctly below the Gibbs value predicted from surface tension of aged solutions (see Table IV).

When the solution of hydrocinnamic acid in the trough was exposed to the atmosphere of the room, approximately 4 g. of water evaporated per hour, corresponding to an increase in concentration of 0.25 g./liter, and the value of apparent Γ found during this period was increased fivefold over the equilibrium value.

Phenol.—With Kahlbaum phenol solution (36 g./1000 g. solution in boiled out distilled water) the average equilibrium value of Γ was 8.3 × 10^{-8} g./cm.^{2}; and determinations during evaporation and condensation at known rates for this phenol solution gave an interpolated value of $\Gamma = 10 \times 10^{-8}$ at the point where both evaporation and condensation were suppressed. The Gibbs equation gives for phenol at this concentration $\Gamma = 4.7 \times 10^{-8}$, as calculated by Goard and Rideal.[4]

Experiments were made by L. A. Wood with pure water, at one hour and after two days, but no difference whatsoever could be observed in the interferometer, showing complete absence of contamination.

Surface Tension Determinations on Aqueous Hydrocinnamic Acid Solutions. Drop Weight Method.—It is commonly supposed that the static or final surface tension of a crystalloidal solution is established within a small fraction of a second.[5] In many cases, and especially for hydrocinnamic acid solutions, this certainly is not true. Nevertheless, it is generally felt that the few seconds required for drop weight determinations[6] represent a close enough approach to a static condition, and consequently such measurements have been universally used for calculation of adsorption by the Gibbs equation. In the two previous papers on the microtome apparatus[1,2] drop weight surface tension measurements were utilized for calculating Γ. The measurements were made independently by C. R. Bacon and R. C. Swain in 1932 and 1933, Dr. Bacon using a tip kindly furnished by Professor Harkins.

The effective radii of the tips were calculated from the drop weight of conductivity water (σ = 72.11 dynes at 24.6°). The radii, and the technique, were checked with repeatedly distilled benzene (density 0.879) dried over calcium chloride, and also with a solution of resublimed Kahlbaum "zur Analyze" *p*-toluidine (density 0.9983), containing 2.0 g. per 1000 g. of water. The results of these preliminary experiments are given in Table II; upper row by C. B., lower row by R. C. S.

TABLE II

CALIBRATION OF DROP WEIGHT

Tip radius cm. (calcd.)	Water drop wt., g.	Benzene		*p*-Toluidine	
		Drop wt., g.	σ	Drop wt., g.	σ
0.2955	0.08377	0.03242	28.54	...	...
	at 24.6°	at 22.4°	28.56[a]		
0.2932	0.08325	0.03221	28.50	0.07300	63.76[b]
	at 24.7°	at 21.9°	28.63[a]	at 22.1°	

[a] Calculated for check from values in "International Critical Tables, Vol. IV, p. 454.

[b] 65.34 at 20° obtained by Gans and Harkins[6]; 64.89 at 16° (in tap water) by Ferguson and Kennedy, *Proc. Phys. Soc.*, 44, 517 (1932); and 65.6 at 16.6° by Brown, *Phil. Mag.*, [7] 11, 689 (1931).

Solutions were prepared by Bacon and Swain from recrystallized Eastman Kodak Co. hydrocinnamic acid. The experimental results are given in Table III. The values of Γ are calculated by the approximate formula

$$\Gamma = -\left(\frac{c}{RT}\right)\left(\frac{d\sigma}{dc}\right)$$

TABLE III

DROP WEIGHT OF SOLUTIONS OF HYDROCINNAMIC ACID

Concentration g./1000 h. H_2O	t°	Mean drop weight	σ, dynes/cm.	$\sigma_{21.5^{\circ}}$	$\Gamma \times 10^8$ g./cm.^{2}
0.5026[a]	22.7	0.07926	68.88	69.00	2.3
0.9617	22.2	.07673	66.39	66.49	3.8
1.5007	21.5	.07335	63.63	63.63	5.2
1.7506[a]	23.1	.06981	61.10	61.32	5.6
2.3515	21.9	.06801	59.20	59.25	6.2
3.0024[a]	22.1	.06375	56.06	56.14	6.7
4.1146	21.1	.05996	52.50	52.46	7.3
6.1291	21.5	.05380	47.24	47.24	8.5

[a] These done by R. C. S.; others by C. B.

Du Noüy Method.—In the ring apparatus of Harkins and Jordan[7] we have eliminated only the complicated device for bodily moving the bal-

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(4) Goard and Rideal, *J. Chem. Soc.*, **127**, 1668 (1925).

(5) Bond and Puls, *Phil. Mag.*, [7] **24**, 864 (1937).

(6) Harkins and Brown, THIS JOURNAL, **38**, 246 (1916); **41**, 499 (1919); Gans and Harkins, *ibid.*, **52**, 2289 (1930).

(7) Harkins and Jordan, *ibid.*, **52**, 1751 (1930).

ance, by floating the large platinum dish containing the solution on water whose level can be exactly and smoothly adjusted. Since both glass and paraffin tend to contaminate the surface of water after long periods, Bakelite lacquer was used, twenty coats being applied, each baked on at 140°. This coating is not only completely impermeable, but has no tendency whatsoever to contaminate water even after a day or so. Both platinum dishes and Bakelite coated metal were used.

The arrangement of the apparatus is shown in Fig. 2. Evaporation was prevented by surrounding the solution with a closed dish (also floating) draped inside with cloth dipping into a surrounding reservoir of solution several centimeters deep, and with a small hole in the top of the vessel for the connection to the balance. This opening was closed except during the moments required for a measurement. After forty-five days a 2.5 g./liter solution of hydrocinnamic acid was found to be 2.46 g./liter.

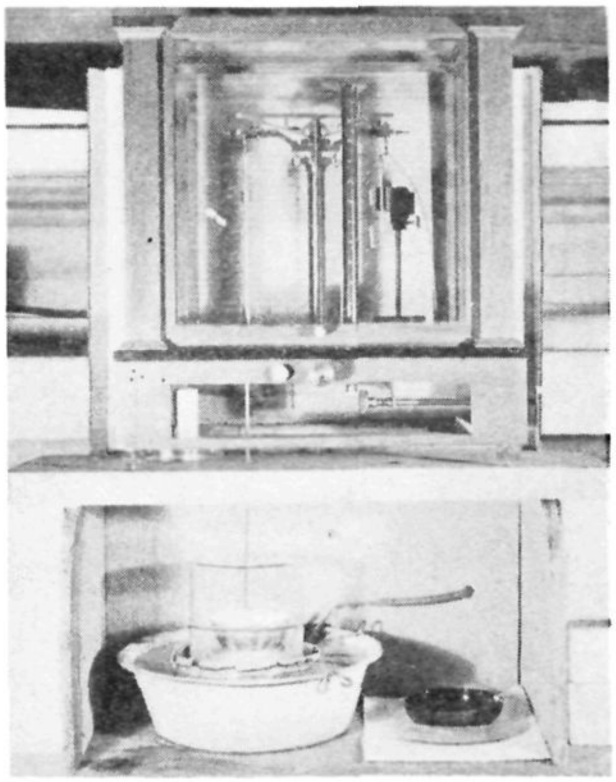

Fig. 2.—Modified ring method for measuring surface tension; outside container cut open to show interior, and wet draping also not shown.

In conducting an experiment, the solution dish was filled to overflowing and the surface twice swept with clean paper toweling, more solution added, the vapor chamber placed in position and the solution allowed to age for some hours. The du Noüy platinum ring was heated to white heat, the surface swept four or five times, the ring heated again in a clear alcohol flame, and then kept submerged beneath the surface except during measurements. A contact angle is observed when the ring approaches the surface from above, but not when it has been kept below. Conductivity water from a Barnstead still ($<0.4 \times 10^{-6}$ mhos) and specimens of hydrocinnamic acid purified by different methods were employed. It was shown that excess carbon dioxide, where permitted, did not affect the results, which are given in Figs. 3 and 4. The temperature was 22.5 ± 0.5°. The surface tension of water measured in the same apparatus remained completely constant for twenty-four hours. This may be contrasted with the changes found by du Noüy and by Klopsteg not using our precautions.

It is evident that the thirty seconds usually allowed in drop weight experiments is inadequate for the attainment of the static surface tension of such solutions. Actually the surface tension seems to change for days or weeks. This persistent time change agrees with observations by Adam and Shute,[8] studying 0.01% solutions of cetyltrimethylammonium bromide. They find big changes in surface tension with time by the sessile drop method, and Tartar and Reed and Cadle[9] find similar results for alkyl sulfonate solutions using capillary tubes. All these authors report changes persisting for periods of a week or more.

It is evident that ordinary processes of diffusion are almost infinitely faster than these surface tension effects. Application of the film balance to these solutions by McBain and Perry and Spencer[10] has shown that quite complicated phenomena occur in their surfaces. Measurements[3] with the PLAWM trough and pendant drop methods (at Stanford and at Massachusetts Institute of Technology) confirm this slow establishment of surface tension.

Discussion

The figures which have been given show that adsorption measured by the microtome method does not attain its final value immediately, but that several hours may be required. For solutions containing 1.5 g. of hydrocinnamic acid per kg. of water, the final or asymptotic value $\times 10^8$

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[8] Adam and Shute, *Trans. Faraday Soc.*, **34**, 758 (1938).

[9] Tartar and Reed, This Journal, **58**, 322 (1936); Tartar and Cadle, *J. Phys. Chem.*, **43**, 1173 (1939).

[10] McBain and Perry, *Ind. Eng. Chem.*, **31**, 351 (1939); McBain and Spencer, This Journal, **62**, 239 (1940).

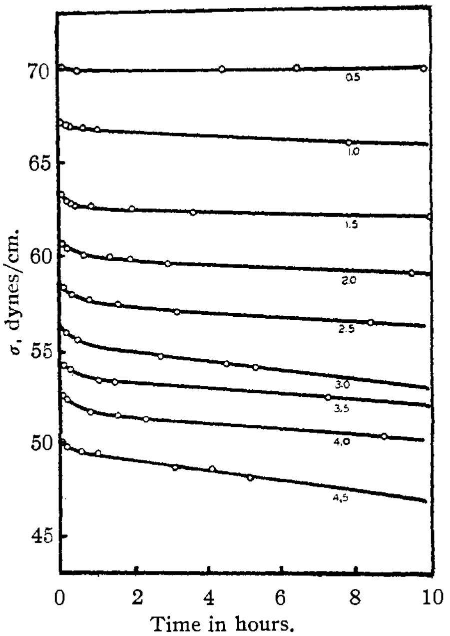

Fig. 3.—Change of surface tension of hydrocinnamic acid with time of solutions containing from 0.5 to 4.5 g. per liter.

appears to be 5.2 ± 0.4, as compared with previous average values 5.2[1] and 5.6,[2] in experiments where time effects were not studied, and the apparatus had not been refined. Similarly, experiments with the interferometer[11] (by G. F. M.) have yielded a final value 5.2 attained after some hours. For solutions of 5.2 g./liter the final result appears to be at least 7.7 × 10^{-8} by the microtome method.

Having established the experimental values, the unexpected difficulty lies in finding what are the theoretical values predicted by the Gibbs theorem, since the surface tension changes so much and so slowly with time. Actually, although the surface tension falls for long periods, the slope of the surface tension–concentration curve and hence the predicted adsorption may change very little, and with the stronger solutions the amount of adsorption predicted from the Gibbs formula may even diminish with time, in contrast to the falling surface tension.

In Table IV are given data for the adsorption predicted for solutions containing 1.5, 4.0, 4.5 and 5.2 g./kg. of water, respectively, by the drop weight and by the ring method.

It appears that the actual equilibrium adsorption agrees very well with the value predicted from the non-equilibrium drop weight surface tensions, but is somewhat less than the proper values predicted from equilibrium surface tension.

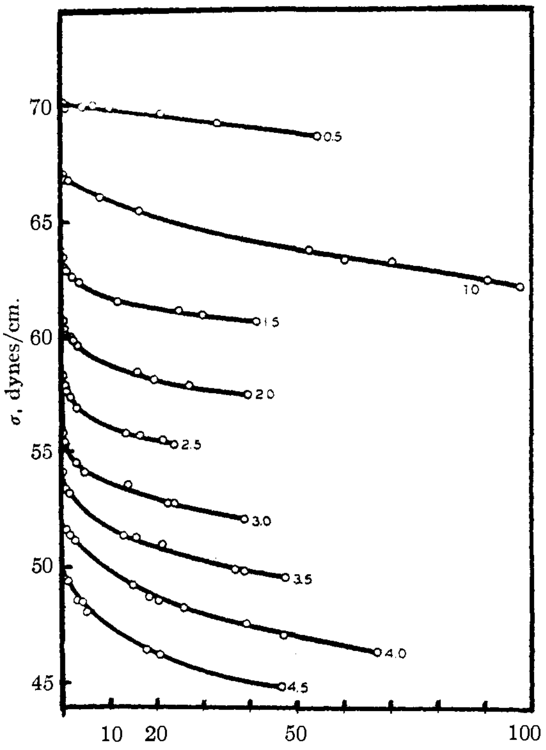

Fig. 4.—Change of surface tension of hydrocinnamic acid with time.

TABLE IV

ADSORPTION, Γ × 10^8 IN G./CM.^{2}, PREDICTED FROM GIBBS EQUATION, FOR SOLUTIONS OF HYDROCINNAMIC ACID OF DIFFERENT AGES OF SURFACES

Concentration g./1000 g. H_2O	Drop weight 30 sec.	5 min.	Du Noüy 1 hr.	9 hr.
1.5	5.2	5.9	5.9	6.3
4.0	7.3	9.0	8.8	8.8
4.5	7.7	10.2	9.1	9.1
5.2	7.6	..	..	..

In the adsorption experiments the solution was always thoroughly stirred before time was counted. The equations for ordinary diffusion are well known[5,12] and with the stirring employed the calculated time required for replenishment of the solution near the surface denuded by adsorption would be[12] about 10^{-1} second. The adsorption per square centimeter is 5 × 10^{-8} g., which comes from a solution which is 0.01 N and contains 1.5 g./liter. It therefore could deplete this to a depth of several Ångström units, and this would be restored to the extent of 90% in

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[11] Ford and McBain, THIS JOURNAL, **58**, 378 (1936).

[12] Langmuir and Schaefer, *ibid.*, **59**, 2407 (1937); **60**, 2805 (1938).

0.003 sec. and to the extent of 99% in 0.3 sec. In only three experiments did we attempt a measurement until at least twenty minutes after stirring. As Doss has emphasized,[10,13] here the adsorption is delayed and therefore the diffusion "activated."

It is clear from all the phenomena referred to that the surfaces of ordinary solutions are far from being the simple structures commonly taken for granted. As was recently pointed out[10] the Gibbs equation is sometimes incompatible with their being monomolecular; for solutions of the simpler soluble fatty acids the Gibbs predicted adsorption remains constant with increase in concentration while the surface tension continues to drop. Much remains to be discovered about the depth, electrification and organization of surfaces of solutions.

Summary

1. Even after efficient stirring, the experimentally determined adsorption of β-phenylpropionic acid in the surface of its aqueous solution as measured by the microtome method is not completed immediately, but may require several hours, whereas diffusion processes would require only about a tenth of a second.

2. The surface tension is not finally established until after much longer periods of time.

3. The final measured absolute adsorption seems to be slightly less than that calculated by the Gibbs theorem from surface tensions of comparable age and closest approach to equilibrium.

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[13] Doss, *Kolloid-Z.*, **86**, 205 (1939).

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

The Effects of Pressure, Temperature and Chemical Composition on the Absorption of Light by Mixtures of Aromatic Amines and Nitro Compounds

BY R. E. GIBSON AND O. H. LOEFFLER

Introduction

It has been known for a long time that, when pure aniline and pure nitrobenzene are mixed, the solution immediately develops a deep orange color.[1] This is an example of a very general phenomenon, similar color changes being observed whenever primary, secondary or tertiary aromatic amines are mixed with aromatic nitro compounds,[2] aliphatic nitro compounds such as tetranitromethane,[2,3] nitroso compounds, quinones[4] or liquid sulfur dioxide,[5] etc. These color changes are due neither to adventitious impurities nor to irreversible reactions; addition of dilute hydrochloric acid to aniline–nitrobenzene mixtures discharges the color immediately, and the deep orange or red solutions of aniline or dimethylaniline in nitrobenzene freeze to very pale yellow solids which are immediately stained red when melting begins.[6] Furthermore, in the solutions we have studied, phototropic effects are not obvious although the mixtures do not differ greatly from some phototropic compounds.[7]

A satisfactory discussion of the changes in light absorption which occur when amines are mixed with *mono-nitro* compounds does not seem to have been given. It has been assumed that the colors observed are due to the formation of small amounts of intermolecular compounds in the solutions[8] and this has received some support from the known existence of a wide variety of stable, colored, solid intermolecular complexes between polynitro compounds and amines or hydrocarbons, substances which have been studied extensively.[9]

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[1] I. Ostromisslensky, *Ber.*, **44**, 268 (1911). The phenomenon must have been noticed much earlier than this by such workers as Hepp (1882) or Kremann, but we have not been able to find any specific discussion of it in the literature.

[2] C. K. Tinkler, *J. Chem. Soc.*, **103**, 2171 (1913).

[3] D. L. Hammick and R. P. Young, *ibid.*, 1463 (1936).

[4] P. Pfeiffer, "Organische Molekulverbindungen," F. Enke, Stuttgart, 1927, p. 283.

[5] H. W. Foote and J. Fleischer, THIS JOURNAL, **56**, 870 (1934).

[6] For other examples see ref. 2.

[7] L. Chalkley, *Chem. Rev.*, **6**, 217 (1929).

[8] See P. Pfeiffer, ref. 4, pp. 358 and 384; G. M. Bennett and R. L. Wain, *J. Chem. Soc.*, 1108 (1936). Further references to articles supporting this view are given by D. L. Hammick and G. Sixsmith, *ibid.*, 972 (1939). In this paper we shall follow the customary practice and use the term "compound formation in solution" to mean the formation of covalent bonds between atoms in unlike molecules of the original components, as contrasted with general intermolecular attractions that result from dipole interaction or other polarization effects. A definite criterion, *viz.*, a measurable reaction velocity, has been proposed for this type of "compound formation" by D. L. Hammick and G. Sixsmith, *ibid.*, 580 (1935). Unless such a restriction is placed on the term "compound formation," it becomes too broad to be useful in the present state of our knowledge.

[9] (a) See P. Pfeiffer, ref. 4; (b) P. Pfeiffer, *Chem. Ztg.*, **59**, 205 (1935); (c) J. W. Baker and G. M. Bennett, *Ann. Rept. Chem. Soc., London*, **28**, 128 (1931); (d) D. L. Hammick and colleagues, papers in *J. Chem. Soc.* from 1935 to date; (e) G. Briegleb, *Z. physik. Chem.*, **B31**, 58 (1935); G. Briegleb and J. Kambeitz, *ibid.*, **B32**, 305 (1936); G. Briegleb, "Zwischenmolekulare Krafte und Molekulstruktur," F. Enke, Stuttgart, 1937.