Adsorption at the interface between two fluids, with special reference to the adsorption of certain dyes at liquid-liquid interfaces

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ADSORPTION AT THE INTERFACE BETWEEN TWO FLUIDS, WITH SPECIAL REFERENCE TO THE ADSORPTION OF CERTAIN DYES AT LIQUID-LIQUID INTERFACES.

THESIS

Presented in candidature for the degree of

Doctor of Philosophy

of the University of Durham

by

Cyril Clifford Addison
B.Sc., A.I.C.

entitled

Adsorption at the Interface between Two Fluids, with special reference to the adsorption of certain dyes at liquid-liquid interfaces.

Being an account of the work carried out during the Sessions 1934 - 35 - 36, at the Science Laboratories, Durham University, (Durham Division), under the direction of Dr. C.W.Gibby M.Sc., A.I.C.

* * *

CONTENTS.

ILLUSTRATIONS.

Publications.

The results described in this thesis have been published in the following form :-

1. An automatic device for recording drop numbers in interfacial tension measurements.

   by C.W.Gibby and C.C.Addison,

   Journal of Scientific Instruments, Vol.XII,No.6,June 1935.

2. Adsorption at the Interface between Two Fluids. Part 1. The adsorption of Methylene Blue, Methyl Orange, Congo Red and Orange II at benzene-water and chlorobenzene-water interfaces.

   by C.W.Gibby and C.C.Addison,

   Journal of the Chemical Society, Jan.1936 p.119.

   This paper was read at a meeting of the Chemical Society held at Burlington House on Dec.19th,1935.

   Reprints of these two papers are included here.

3. Adsorption at the Interface between Two Fluids. Part 2. The adsorption of five dyestuffs at a Paraffin-water and at an Air-water interface.

   by C.W.Gibby and C.C.Addison.

   This paper has been accepted for publication by the Chemical Society, and is expected to appear in the issue for September 1936.

ADSORPTION AT THE INTERFACE BETWEEN TWO FLUIDS. PART I. THE ADSORPTION OF METHYLENE-BLUE, METHYL-ORANGE, CONGO-RED, AND ORANGE-II AT BENZENE-WATER AND CHLOROBENZENE-WATER INTERFACES

BY

C. W. GIBBY

AND

C. C. ADDISON

Reprinted from the Journal of the Chemical Society,
January, 1936.

Reprinted from the Journal of the Chemical Society, 1936.

25. *Adsorption at the Interface between Two Fluids. Part I. The Adsorption of Methylene-blue, Methyl-orange, Congo-red, and Orange-II at Benzene–Water and Chlorobenzene–Water Interfaces.*

By C. W. GIBBY and C. C. ADDISON.

VERY few quantitative investigations of adsorption at liquid–liquid interfaces are on record. Lewis (*Phil. Mag.*, 1908, **15**, 499; 1909, **17**, 466) investigated the adsorption of a number of substances at the interfaces between their solutions and a hydrocarbon oil. In general, however, he records only one measurement for each substance, so that the magnitude of the experimental error is uncertain; moreover, a comparison of experimental results with Willard Gibbs's adsorption equation requires data over a considerable range of concentration. Patrick (*Z. physikal. Chem.*, 1914, **86**, 545) found the weights of various substances removed from solutions of various concentrations by a shower of small drops of mercury; only comparative results were obtained, no attempt being made to determine the area of the mercury surface, or to prove that it was saturated. Nonaka (*J. Soc. Chem. Ind. Japan*, 1928, **31**, 297) investigated the adsorption of soap at benzene–water and toluene–water interfaces, and suggested that the adsorbed layer is unimicellular.

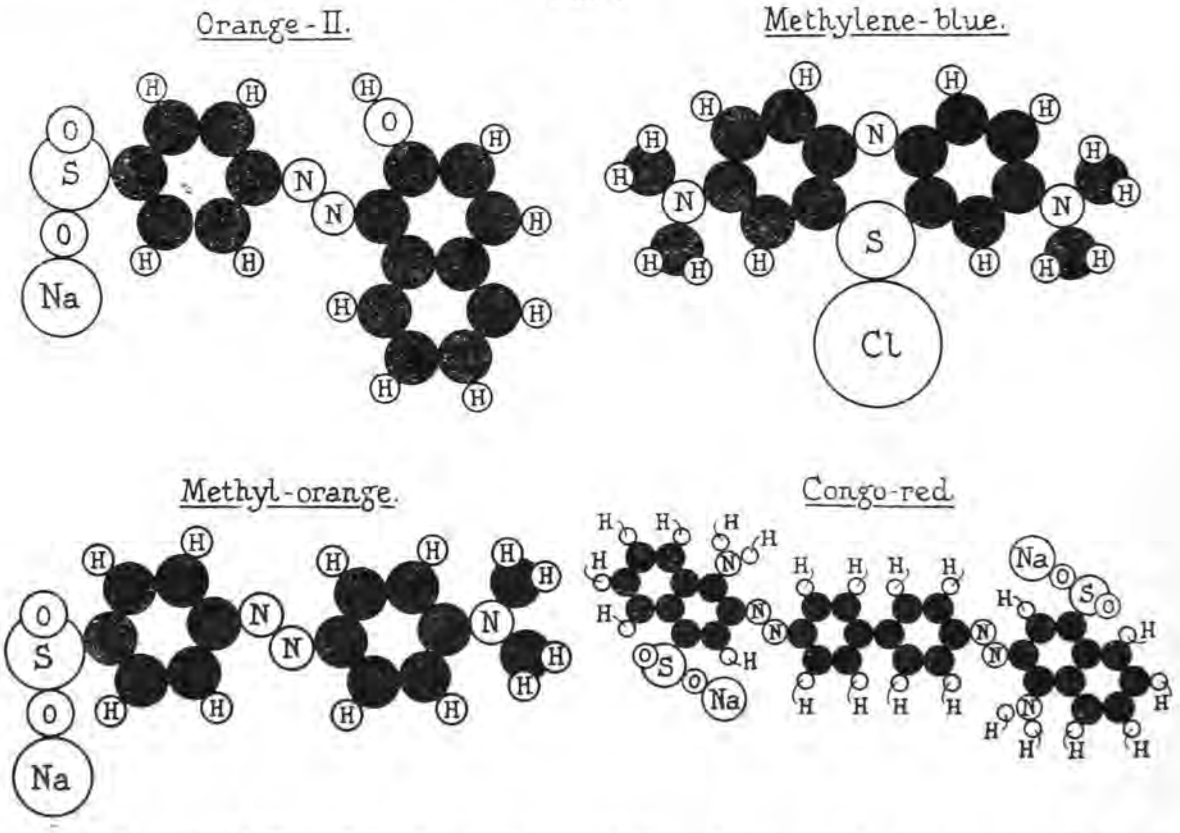
We have measured (i) the adsorptions of four dyes from various concentrations of each in water, at water–benzene and water–chlorobenzene interfaces, near 17°; (ii) the interfacial tensions of the systems. The four dyes mentioned in the title were specially purified. Benzene and chlorobenzene were chosen because of their ease of purification, the difference in their polar nature, and the insolubility of the dyes in them: Congo-red, methylene-blue, and methyl-orange were extremely insoluble; but orange-II dissolved very slightly when the solvents were in contact with concentrated solutions of it, but insufficiently to affect the results. The structures of these dyes, drawn to scale from data by Sidgwick and Bowen (*Ann. Reports*, 1931, **28**, 402), are shown in Fig. 1.

The equation first deduced by Gibbs ("Scientific Papers," I, 235), *viz.*, $\Gamma_{2,1} = -d\sigma/d\mu_2$, in which Γ is the surface excess of solute, σ the interfacial tension, and μ_2 the potential of the adsorbed component, leads to the expression $\Gamma = -c(d\sigma/dc)/RT$ in so far as the activity of the solute may be equated to its concentration (c). The quantity Γ, which must have the same dimensions as $c(d\sigma/dc)/RT$, *viz.*, those of mass per unit area, does not represent a concentration excess over that of the homogeneous part of the solution outside the range of surface forces, but the mass actually attached to unit area of the interface. The volume in which this adsorbed mass is contained is immaterial, for the surface layer was implied by Gibbs to extend to a thickness great enough to include all such adsorbed matter.

It is particularly to be observed that Gibbs's equation in this form is intended to apply only to the adsorption of a single component from a solution in which its behaviour is ideal with reference to concentration, and that in this, or in its original form, it applies only to interfaces unaffected by electrical charges. Any deviations, therefore, of the actual equilibria from those predicted by the equation will be due to interference with one or all of these conditions.

There is already evidence that one at least of our dyes does not behave as an ideal solute in pure water, even in the low concentrations in which it is used. This evidence is only indirect, as it refers to solutions containing excess of sodium chloride and at a few concentrations of dyestuff: whereas Valkó (Faraday Society Discussion on Colloidal Electrolytes, 1935, p. 230) found orange-II to be only very slightly aggregated, with a factor of 1·2, yet for Congo-red the factor found by him was 12, by Robinson 8·6 (*ibid.*, p. 245), and by Quesnel about 12 (*ibid.*, p. 259). Concerning the molecular state of the other two solutes, we know of no experimental evidence except that of Robinson (*loc. cit.*), who finds methylene-blue to be only slightly aggregated.

FIG. 1.



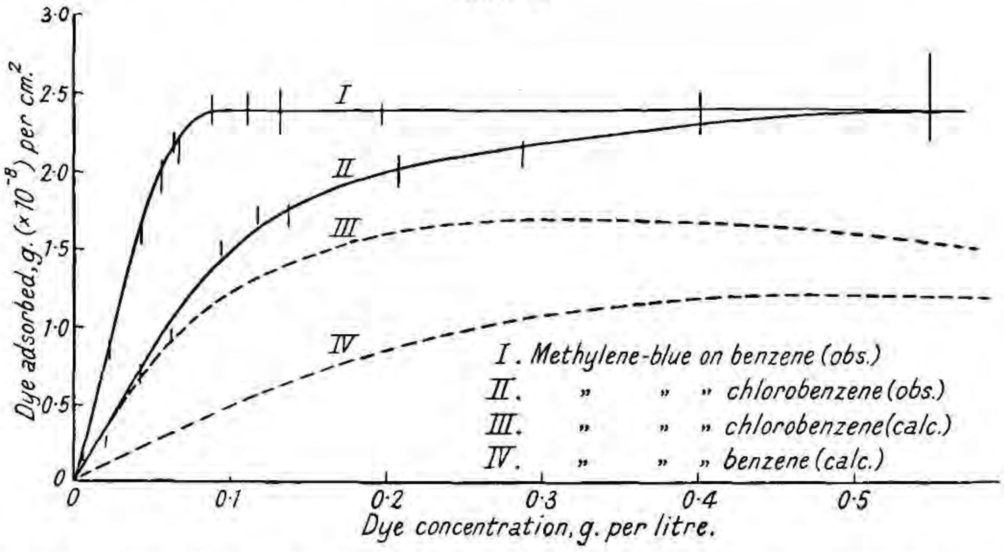
Orange-II. Methylene-blue. Methyl-orange. Congo-red.

As to the second disturbing factor, since all the solutes are electrolytes in which either the cation (methylene-blue) or the anion (the others) is complex, an electrical double layer is certain to be formed at the interface with benzene or chlorobenzene. It is permissible to doubt whether the interfacial adsorption in a polar liquid like water is ever free from the formation of electrical double layers. This factor cannot, as far as we are aware, be excluded from any practicable experiment. It has, *e.g.*, been shown by Alty (*Proc. Roy. Soc.*, 1924, **106**, 315) that bubbles of air passing through the purest obtainable water were sufficiently charged to move in an electric field. He noted that two bubbles of air repelled one another; we have observed similar phenomena with drops of benzene and of chlorobenzene passing through solutions of the dyestuffs.

Accordingly, it is not surprising that our results, which we have been able to make reproducible and regular, show marked quantitative deviations from the predictions of Gibbs's equation in each of the eight cases. No reconciliation can be made by expressing the solute concentrations in terms of a polymeric molecule, or by the assumption that only a fraction of the dye is available for adsorption, whether this fraction be constant or varying in accordance with the law of mass action, or whether single molecules or the aggregates constitute the available fraction. The equation gives values of approximately the right order of magnitude, and is in much closer agreement with our results than with Lewis's data, but there can be no doubt as to the influence of the factors referred to above.

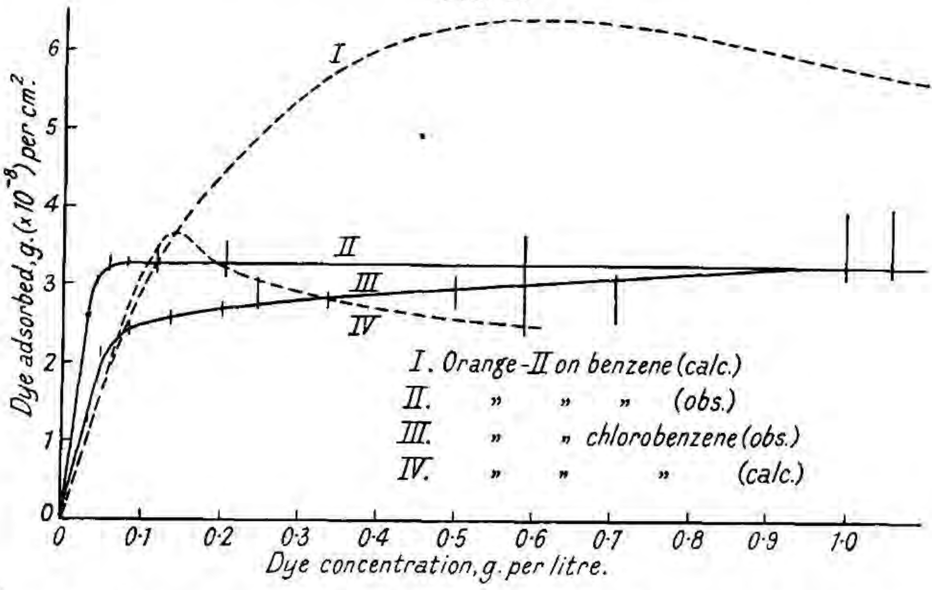
Two distinct types of concentration–adsorption curve are found here. The type differs according to the absorbate, but is independent of whether the interface is water-benzene or water–chlorobenzene.

FIG. 2.



In Type I, shown by methylene-blue and orange-II (see Figs. 2 and 3, and Table II, A, B, C, D), the curve rises fairly steeply to a maximum adsorption, and remains there even to the highest concentrations which we have been able to use. In Type II, shown by Congo-red and methyl-orange (see Figs. 4 and 5, and Table II, E, F, G, H), an initial rise to a sharp maximum is quickly followed by a fall towards, and even as far as, zero adsorption. Moreover, the numerical value of the adsorption reached in each of the first two cases is the same, whether benzene or chlorobenzene is used; in the last two cases, chlorobenzene is a much stronger adsorbent than benzene.

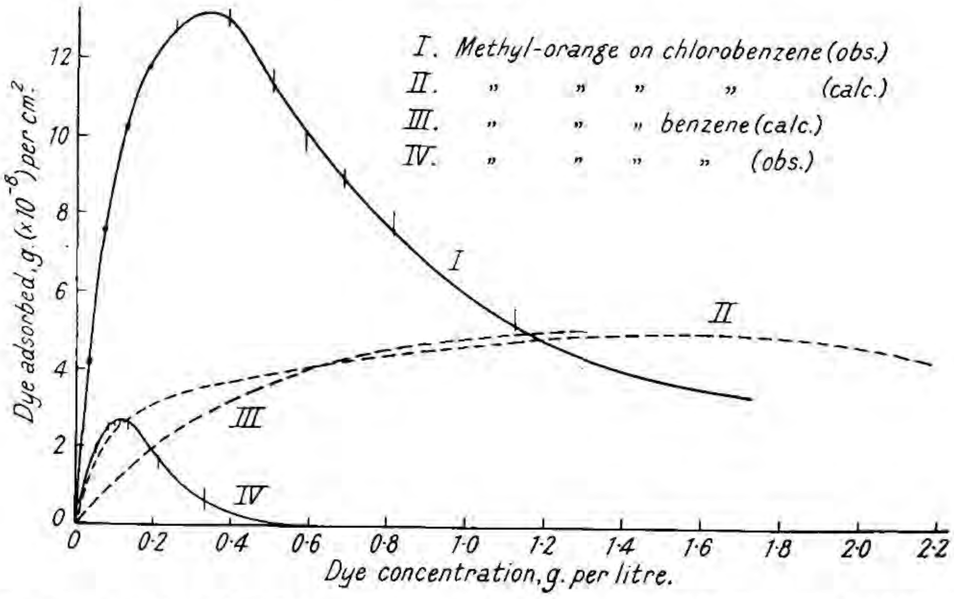
FIG. 3.



Having regard to the interfacial tensions concerned, Type II has the qualitative features of a Gibbs's curve; Type I has not. The form of an adsorption curve calculated from Gibbs's equation depends, of course, upon the manner in which the interfacial tension varies with the concentration. In the cases we have studied, as the concentration increases from zero, $d\sigma/dc$, which is large at low concentrations, either finally approaches zero asymptotically or diminishes rapidly. Consequently Γ passes through a maximum and approaches zero again in spite of increasing concentration.

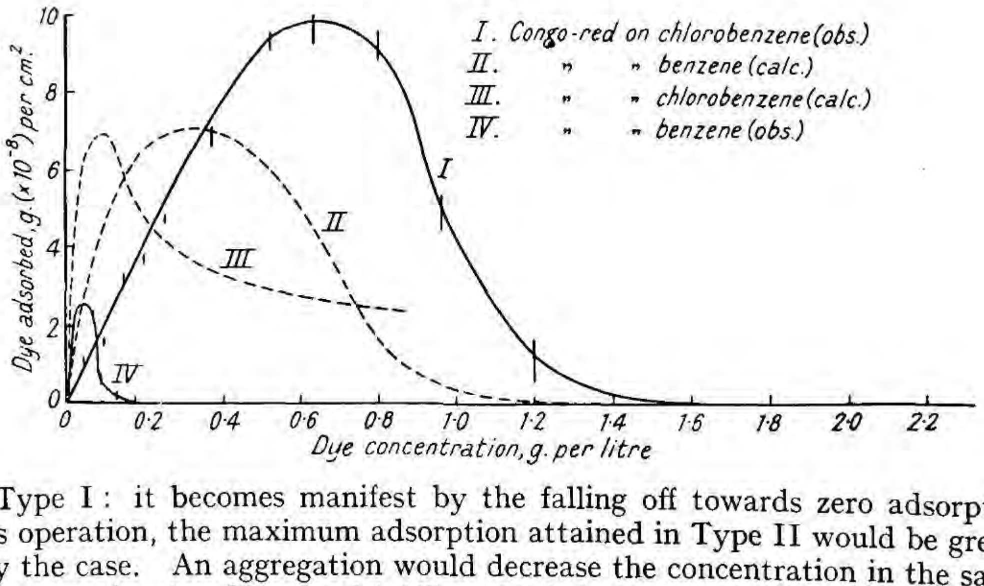
The shapes of the experimental curves for Congo-red and methyl-orange, although similar to those required by Gibbs's equation, could equally well be accounted for qualitatively on the assumption that only single molecules are adsorbed. Two opposing factors are then operating simultaneously: on the low-concentration side of the maximum, adsorption increases with rising concentration, but thereafter, this factor is outweighed by the shortage of single molecules caused by aggregation to form micelles.

FIG. 4.



We are not able clearly to correlate the contrast between these two types with any structural features of the respective simple molecules. There is obviously a change, increasing rapidly with concentration, which occurs to the solutes of Type II but not to those of Type I: it becomes manifest by the falling off towards zero adsorption, and, but for its operation, the maximum adsorption attained in Type II would be greater than is actually the case. An aggregation would decrease the concentration in the same sense, and it is noteworthy that Congo-red (of Type II) is known to be highly micellular, whereas orange-II and methylene-blue (of Type I) are mainly simple in solution. Further, in so far as adsorption is due to polar influences, it is to be expected that the monomeric form of a given polar solute will be more adsorbed than a coupled polymeric form of it,

FIG. 5.



because a dipole-association which constitutes a polymeride of the type $\begin{smallmatrix}\ominus & - & + \\ + & - & \oplus\end{smallmatrix}$ necessarily makes the residual field of force less than that of the unassociated molecule.

The area of the interface occupied by the adsorbed molecule, reckoned as monomeric, in the region of maximum adsorption can be calculated from our measurements. From plane projections of the four compounds (Fig. 1) the areas of their simple molecules can be approximately assessed in sq. Å. These two sets of values are compared in Table I.

TABLE I.

		On benzene.		On chlorobenzene.	
Dye.	Area, calc.	Area found.	Ratio.	Area found.	Ratio.
Methylene-blue	140	215	1·5	215	1·5
Orange-II	112	180	1·6	180	1·6
Methyl-orange	79	218	2·8	40	0·5
Congo-red	192	470	2·5	117	0·6

Even when all allowance is made for the necessarily inexact calculated area, it remains evident that in the first two cases the adsorbed layer, on either interface, is unimolecular, with possibly some slight lateral scattering, such as interionic repulsions between neighbouring molecules of these compounds might well produce. It is not clear why the two interfaces should act equally in this respect.

In the second pair of cases, the surface distribution on benzene is definitely more sparse than in a single layer of contiguous molecules, whereas on chlorobenzene it is roughly twice as thick as this standard. That benzene, the less polar fluid, should adsorb in these two cases less than chlorobenzene, or alternatively allow more lateral movement of adsorbed polar molecules, is understandable; while the doubled surface concentration in these two instances clearly means either that the adsorbed molecules are not lying flat (being attached, for instance, by the attraction between their sodium ions and the chlorine atoms of the chlorobenzene) or that they are lying flat on the surface, but in layers of an average thickness of about two molecules.

Attempts to extend Lewis's experiments with sodium glycocholate were abandoned on account of the difficulty of purifying this substance.

EXPERIMENTAL.

A. *Adsorption at the Benzene–Water Interface.*—Benzene stored in a reservoir *A* (Fig. 6) flowed through a constant-pressure head *B* down a long tube *C* past a mercury trap *D*. It issued through a jet *E*, and rose in drops through the solution of the dye in the tube *F*. The drops passed out through an inclined tube at the top of *F*, which was only slightly larger than themselves, and into a reservoir *G*. There they coalesced with a layer of benzene which overflowed through a side tube *H*. The adsorbed layer was shed in *G*, and experiments showed that no appreciable diffusion back into *F* took place during the time occupied by an experiment (see below). The apparatus was of glass throughout.

The average duration of an experiment was about 20 hours, during which about 4 l. of benzene passed through in drops of volume about 0·1 c.c. issuing at a frequency of about 40 per minute. The average area of interface exposed in one experiment was about 3·5 sq. m. The rate of flow was determined by weighing the benzene overflowing in a measured time, and was maintained substantially constant by the constant-pressure head. The number of drops of benzene passing in a measured time was counted at frequent intervals. In order to prove that the surface was saturated (see below), the apparatus was constructed in duplicate, with columns of different lengths having jets of diameters 0·58 and 1·26 mm.

At the termination of each experiment the solution from *G* was run out and weighed, and its concentration compared in a Duboscq tintometer with that of a sample of the original solution. In order to obtain reproducible results, it was found necessary to carry out all the comparisons in direct bright sunlight. The experimental error quoted in Tables I and II, A—H, is inversely proportional to the difference in heights of the two liquid columns in the tintometer, and this set an upper limit to the concentrations which could be used, on account of the difficulty of comparing deeply coloured solutions differing only slightly from one another.

B. *Adsorption at the Chlorobenzene–Water Interface.*—In the case of chlorobenzene, similar sets of apparatus were used, but here the liquid fell in drops from jets *C*, of diameters 0·4 and

0·32 mm. dipping into solutions *D* (Fig. 7). After passing through a constriction *E*, the drops coalesced with the chlorobenzene surface *G* at the bottom of the reservoir *F*, in which the adsorbed dyestuff collected. (The chlorobenzene passed through one tap in the constant-pressure head; this was lubricated once with a very small quantity of rubber grease.) The chlorobenzene overflowed through a syphon *H*, and by adjusting the variable syphon limb *K* the height of the interface *G* could be kept constant. The volumes, drop numbers, and interfacial areas were similar to those given above for benzene.

FIG. 6.

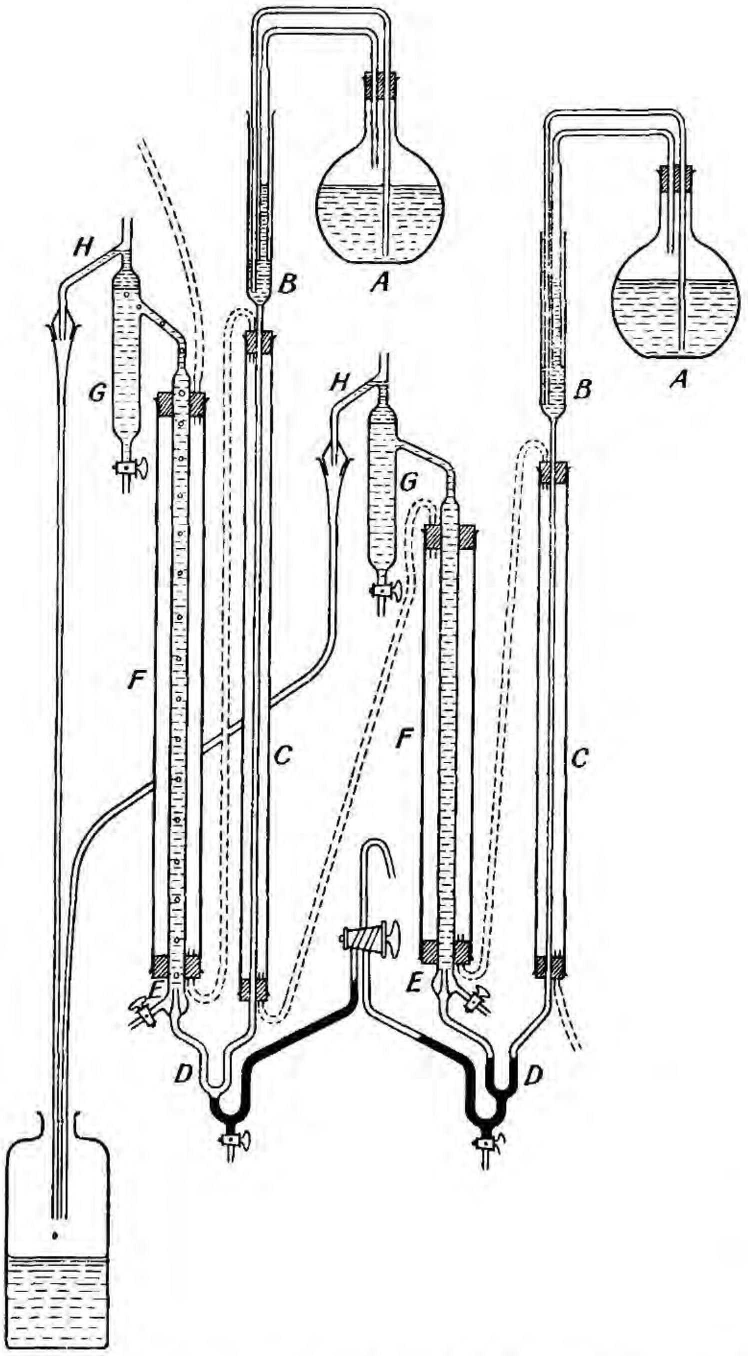
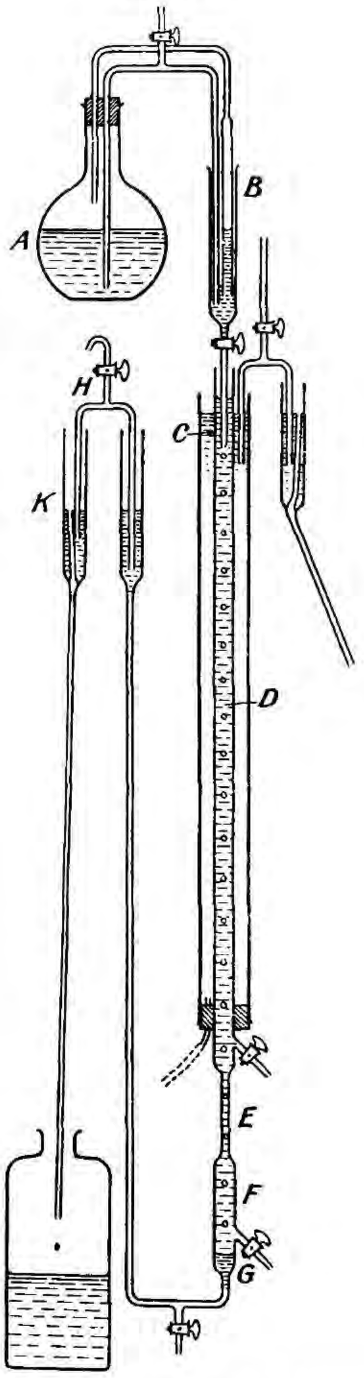


FIG. 7.



Absence of Diffusion.—In order to test the possibility of diffusion of solute from the reservoir in which the adsorbed material had collected, the reservoir was filled with 0·088*N*-sodium chloride solution, and the saturating column with distilled water. The sodium chloride solution lost only 3·5% in concentration in 20 hours, and this value was unaltered even if benzene drops were passing up. The greatest concentration difference of dye set up in any experiment was 0·000014 g.-mol./l., from which diffusion would be negligible.

The Interfacial Surface Area.—This was calculated from the total number of drops and the total mass of organic liquid passing, the drops being assumed spherical and of uniform size. The former assumption is justified by the slow rate of movement of the drops—about 6 cm./sec.—and the latter by the observed constancy of the rate of flow, of the drop rate, and of the distances between successive drops in the adsorption columns.

TABLE II.

(A) *Methylene-blue on benzene.*

Initial concn., g./l.	Time of flow, mins.	Surface area, cm.².	Adsorption coefficient, g./cm.² × 10⁸.
0·00436	1164	29,100	0·103 ± 0·007
0·0218	1035	29,070	0·85 ± 0·03
0·0436	900	41,800	1·6 ± 0·06
0·0550	1463	32,790	1·92 ± 0·07
0·0621	1862	50,240	2·18 ± 0·05
0·0653	810	27,580	2·11 ± 0·10
0·0872	1348	32,300	2·40 ± 0·10
0·1100	1250	40,880	2·41 ± 0·12
0·1310	818	37,920	2·40 ± 0·14
0·1960	1190	59,540	2·38 ± 0·06
0·4598	1292	32,680	2·6 ± 0·6
0·5475	1327	68,570	2·5 ± 0·3

(B) *Methylene-blue on chlorobenzene.*

Initial concn., g./l.	Time of flow, mins.	Surface area, cm.².	Adsorption coefficient, g./cm.² × 10⁸.
0·0210	1052	33,700	0·24 ± 0·01
0·0420	932	22,380	0·65 ± 0·03
0·0627	905	23,790	0·92 ± 0·04
0·0941	982	32,660	1·50 ± 0·05
0·1383	1148	28,910	1·74 ± 0·07
0·2074	893	32,320	2·0 ± 0·1
0·2879	1295	49,290	2·1 ± 0·1
0·4030	1292	34,290	2·4 ± 0·15
* 0·1177	1263	43,700	1·73 ± 0·05
0·1177	1397	33,130	1·71 ± 0·05

(C) *Orange-II on benzene.*

0·0191	1099	23,550	1·75 ± 0·03
0·0296	1506	30,020	2·61 ± 0·05
0·0411	1170	44,800	3·02 ± 0·04
0·0592	1405	33,160	3·25 ± 0·08
0·0823	1085	35,500	3·27 ± 0·04
0·0883	1383	38,560	3·38 ± 0·11
0·1183	975	26,370	3·25 ± 0·18
0·2006	847	29,200	3·37 ± 0·24
0·2057	3423	54,370	3·09 ± 0·11
0·3445	599	18,620	4·20 ± 0·67
0·4433	1394	33,500	3·21 ± 0·51
0·5890	1119	37,150	2·98 ± 0·74

(D) *Orange-II on chlorobenzene*

0·0298	1086	27,450	1·30 ± 0·02
0·0447	990	31,250	2·13 ± 0·03
0·0814	895	22,180	2·47 ± 0·06
0·1378	1077	26,800	2·55 ± 0·07
0·2444	861	21,230	2·90 ± 0·02
0·3353	1273	41,290	2·80 ± 0·10
0·5029	1142	36,440	2·9 ± 0·2
0·7071	1227	33,520	2·8 ± 0·3
1·0606	1098	35,490	3·6 ± 0·5
* 0·1995	1075	25,640	2·7 ± 0·1
0·1995	577	24,770	2·8 ± 0·1

* Of this pair of figures the upper was obtained at 22° and the lower at 17°.

(E) *Methyl-orange on benzene.*

0·01332	1120	19,940	0·5 ± 0·03
0·0305	830	38,610	0·96 ± 0·04
0·0333	1163	28,150	1·12 ± 0·05
0·0500	591	18,100	1·9 ± 0·10
0·0800	1135	23,770	2·47 ± 0·10
0·0828	1263	49,430	2·21 ± 0·06
0·1093	851	26,750	2·50 ± 0·20
0·1332	1240	60,780	2·50 ± 0·10
0·2120	1448	43,610	1·63 ± 0·20
0·3278	1368	41,530	0·68 ± 0·34
0·5337	1364	41,470	—
1·0673	973	28,340	—

(F) *Methyl-orange on chlorobenzene.*

0·0343	1243	46,020	4·16 ± 0·03
0·1308	1260	46,220	10·2 ± 0·1
0·2501	955	35,880	12·8 ± 0·1
0·3852	1073	39,900	13·0 ± 0·2
0·5022	930	23,410	11·5 ± 0·4
0·6816	1050	40,130	8·9 ± 0·2
1·1224	1300	54,500	5·3 ± 0·3
† 0·8155	1067	33,340	7·8 ± 0·3
0·5826	1320	40,960	9·8 ± 0·2

† These two values were obtained at 22°.

(G) *Congo-red on benzene.*

0·01196	1498	24,770	1·56 ± 0·02
0·0239	1141	44,320	2·58 ± 0·02
0·0283	836	32,150	2·29 ± 0·05
0·0329	1013	32,460	2·45 ± 0·05
0·0423	1156	29,560	2·46 ± 0·05
0·0425	520	24,470	2·28 ± 0·08
0·0486	837	30,040	2·50 ± 0·07
0·0624	1446	34,620	2·21 ± 0·08
0·0729	953	32,270	1·75 ± 0·1
0·0851	882	33,680	0·57 ± 0·09
0·1276	1180	42,310	0·20 ± 0·1
0·1822	1181	33,170	—
0·1881	1164	31,850	—
0·3300	1556	46,390	—

(H) *Congo-red on chlorobenzene.*

0·0205	1130	38,540	1·13 ± 0·01
0·0409	1130	36,140	1·08 ± 0·02
0·0629	1410	39,220	1·24 ± 0·03
0·0943	1230	42,640	1·59 ± 0·04
0·1425	912	24,610	3·18 ± 0·08
0·2503	1525	33,670	4·7 ± 0·1
0·3755	1380	38,880	6·8 ± 0·2
0·5247	1145	42,230	9·3 ± 0·2
0·6305	1047	24,110	9·6 ± 0·4
0·8000	965	25,150	9·2 ± 0·4
0·9608	876	30,210	4·9 ± 0·5
1·2000	913	31,800	1·1 ± 0·6
‡ 0·1981	1082	33,620	3·7 ± 0·1
0·1981	1152	27,340	3·7 ± 0·1

‡ Of this pair of data the upper was obtained at 22° and the lower at 17°.

Proof of Saturation of the Surface.—With all dyes, two adsorption columns of different heights were used—125 cm. and 88 cm. for benzene, and 145 cm. and 100 cm. for chlorobenzene. The results obtained with the duplicate columns were found to be interchangeable within the experimental error. The volume of the solution in the saturating column was at least eight times that of the reservoir, so the adsorption took place from a solution of virtually constant concentration.

Temperature Control.—Throughout the duration of the experiments the room temperature remained at 17° ± 1·5°. The apparatus was lagged with water jackets to minimise small fluctuations of temperature. With each dye, experiments with chlorobenzene were also carried out at 22°, and the results agreed, within the usual experimental error, with those of the same concentration at 17°.

Purity of Benzene and Chlorobenzene.—A. R. Benzene (Burgoyne, Burbidges, Ltd.) was used, but the results were unaffected by the substitution of benzene supplied as " Extra Pure." The chlorobenzene was B.D.H. " Purified."

Purification of the Dyes.—The test used as a criterion of the purity of all the dyes except methylene-blue was that the drop number of benzene against a solution of a particular concentration should be unaltered by further purification. Congo-red was salted out from aqueous solution four times with sodium acetate until free from chloride. It was then boiled with absolute alcohol, filtered off, and washed with alcohol until free from acetate as shown by the cacodyl test. Congo-red solutions faded on standing for several days, but not to any appreciable extent during the period of an experiment. All Congo-red solutions were made freshly for each experiment. Methyl-orange and orange-II were recrystallised from water respectively five and three times. Methylene-blue was free from zinc and sodium, the most probable impurities, and left no residue on ignition : it was therefore assumed to be pure.

FIG. 8.

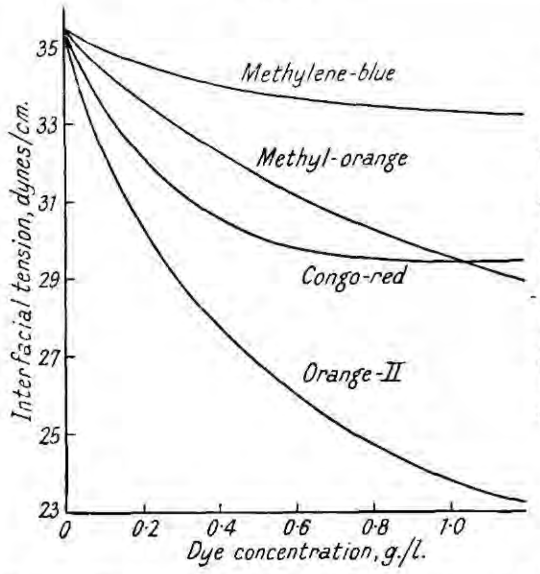
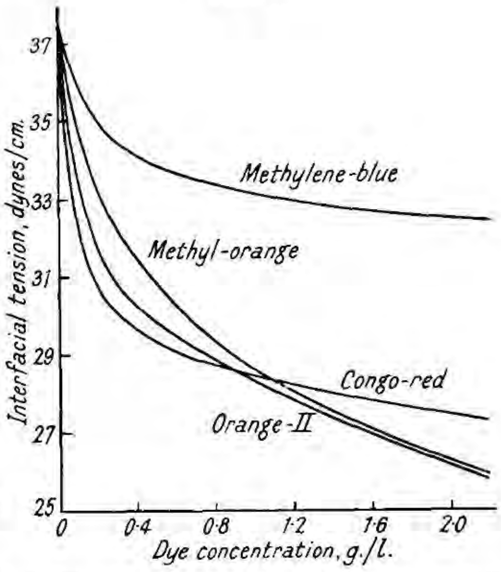


FIG. 9.



Interfacial Tension Measurements.—Interfacial tensions between dye solutions and benzene and chlorobenzene were determined by the drop-number method, in which a constant volume of the organic liquid, 29·328 c.c., issued in drops from a pipette, the tip of which dipped below the surface of the aqueous solution. Decrease in the interfacial tension resulted in a decrease in the drop size and a corresponding increase in the number of drops, from 188 for chlorobenzene against pure water to 283 for the most concentrated solutions tested, and from 228 to 354 for benzene. The tips were drawn to circular apertures of diameter 0·082 and 0·092 cm. (measured on a travelling microscope) in the cases of benzene and chlorobenzene respectively. For the latter liquid it was necessary that the tip should be ground to a knife edge.

The rate of flow was controlled by a fine air leak, and was never greater than 5 drops per minute. The numbers were recorded automatically by the device described by us (*J. Sci. Instr.*, **1935**, **12**, 198).

The interfacial tensions were calculated from the drop numbers according to Harkins and Brown (*J. Amer. Chem. Soc.*, **1919**, **41**, 499), the necessary densities being taken from the International Critical Tables. Values of $d\sigma/dc$ were read from the smoothed graph of σ against c (Figs. 8 and 9).

A drop number against pure water was determined frequently, and gave 35·4 dynes/cm. for benzene and 37·4 dynes/cm. for chlorobenzene, at 17° ± 0·5°. For the present purpose these compare satisfactorily with those recorded in the International Critical Tables (Vol. IV

436), *viz.* 35·2 (at 17°) and 37·41 dynes/cm. (at 20°) respectively, for the values of Γ are required only for comparison and do not affect the adsorption measurements. Furthermore, small errors in σ produce much smaller ones in $d\sigma/dc$.

These results, together with the values of the adsorption calculated from Gibbs's equation, are shown in Table III, and as broken curves in Figs. 2, 3, 4, and 5.

TABLE III.

Interfacial Tensions.

			Reading from σ–c curve.						Reading from σ–c curve.		
Concn., g./l.	Drop no.	σ, dynes/cm.	Concn., g./l.	$d\sigma/dc$.*	Adsorption, g./cm.^{2} × 10^8.	Concn., g./l.	Drop no.	σ, dynes/cm.	Concn., g./l.	$d\sigma/dc$.*	Adsorption, g./cm.^{2} × 10^8.
(A) *Methylene-blue–chlorobenzene.*						(B) *Orange-II–chlorobenzene.*					
0·0000	188	37·41	0·1	10·1	1·34	0·0000	188	37·41	0·08	21·8	2·53
0·0867	196	36·00	0·2	6·0	1·59	0·0532	205	34·55	0·1	21·5	3·12
0·2167	202	34·95	0·3	4·2	1·67	0·1064	213	33·35	0·12	20	3·48
0·4334	208	34·09	0·4	3·2	1·70	0·2128	225	31·70	0·14	18	3·66
0·5778	210	33·72	0·6	1·85	1·47	0·5319	240	29·86	0·16	14	3·48
1·0219	214	33·20	0·8	1·3	1·38	1·0638	255	28·21	0·18	12·5	3·3
2·0438	219	32·50	1·0	1·0	1·33	2·1275	283	25·58	0·2	11·1	3·22
			1·2	0·9	1·43				0·3	6·8	2·96
			1·4	0·75	1·39				0·4	4·7	2·73
			1·6	0·6	1·27				0·5	3·94	2·86
			1·8	0·5	1·19						
			2·0	0·42	1·11						
(C) *Methyl-orange–chlorobenzene.*						(D) *Congo-red–chlorobenzene.*					
0·0000	188	37·41	0·1	18·2	2·47	0·0000	188	37·41	0·02	43	2·49
0·1244	207	34·24	0·2	11·6	3·15	0·0495	210	33·79	0·04	43	5·02
0·3111	222	32·08	0·3	8·7	3·54	0·1503	228	31·32	0·06	37	6·34
0·6222	237	30·20	0·4	6·7	3·63	0·1981	232	30·82	0·08	29	6·62
0·9334	248	29·00	0·6	4·85	3·95	0·3962	241	29·73	0·10	23·5	6·71
1·2445	258	27·88	0·8	4·0	4·34	0·6604	246	29·17	0·15	13·6	5·83
1·8667	273	26·47	1·0	3·4	4·61	1·3208	256	28·10	0·20	8·1	4·63
			1·2	3·0	4·88	1·9812	263	27·38	0·30	4·45	3·81
			1·4	2·6	4·94				0·40	3·17	3·62
			1·6	2·3	4·99				0·50	2·30	3·29
			1·8	2·0	4·88						
			2·0	1·7	4·61						
(E) *Methylene-blue–benzene.*						(F) *Orange-II–benzene.*					
0·0000	228	35·4	0·1	3·875	0·519	0·0000	228	35·4	0·1	21·0	3·02
0·1340	232·5	34·7	0·2	3·19	0·837	0·1003	254	32·1	0·2	15·5	4·46
0·2681	236	34·4	0·3	2·65	1·056	0·2006	271	30·3	0·3	12·5	5·39
0·5475	241	33·7	0·4	2·2	1·156	0·3396	290	28·4	0·4	10·5	6·04
0·8580	244	33·4	0·5	1·81	1·190	0·5230	311	26·6	0·5	9·0	6·47
1·0725	246	33·2	0·6	1·5	1·182	0·6970	329	25·3	0·6	7·5	6·47
			0·7	1·25	1·149	1·0460	354	23·6	0·7	6·25	6·29
			0·8	1·025	1·077				0·8	5·25	6·04
			0·9	0·875	1·034				0·9	4·5	5·88
			1·0	0·75	0·985				1·0	4·0	5·75
(G) *Methyl-orange–benzene.*						(H) *Congo-red–benzene.*					
0·0000	228	35·42	0·1	8·8	1·184	0·0000	228	35·4	0·1	15·5	4·43
0·1334	237·5	34·01	0·2	7·5	2·013	0·0911	241	33·5	0·2	11·0	6·49
0·2669	245	33·13	0·3	6·63	2·67	0·1254	243	33·4	0·3	8·25	6·86
0·5337	259	31·5	0·4	6·0	3·22	0·1881	252	32·2	0·4	6·0	6·86
0·8518	273	30·0	0·5	5·4	3·64	0·2370	257	31·7	0·5	4·5	6·07
1·0673	281	29·2	0·6	4·95	3·99	0·3696	266	30·7	0·6	3·0	5·14
			0·7	4·55	4·25	0·4435	271	30·3	0·7	1·75	3·50
			0·8	4·15	4·48	0·6650	278	29·5	0·8	0·75	1·71
			0·9	3·90	4·71	0·8308	280	29·4	0·9	0·25	0·64
			1·0	3·75	4·97	1·0730	281	29·3	1·0	0·00	—

* Smoothed.

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THE DURHAM COLLEGES IN THE UNIVERSITY OF DURHAM.

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283. *Adsorption at the Interface between Two Fluids. Part II. The Adsorption of Five Dyestuffs at a Paraffin–Water and at an Air–Water Interface.*

By C. W. GIBBY and C. C. ADDISON.

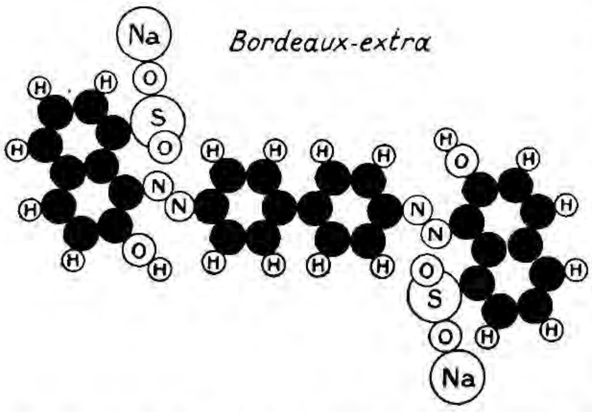
PART I (this vol., p. 119) described investigations of the adsorption of methylene-blue, methyl-orange, Congo-red, and orange-II at the surfaces of drops of benzene and chlorobenzene moving through aqueous solutions of those dyes. The investigations have now been extended to include two additional types of interface and a fifth dyestuff, Bordeaux-extra. Robinson (Faraday Society Discussion on Colloidal Electrolytes, 1935, p. 250) deduced from conductivity measurements that this dyestuff " exists in very dilute solutions in the form of single ions, or nearly so." It was therefore used because it should in this respect provide a substance having properties in the greatest possible contrast to those of micelle-forming dyestuffs such as Congo-red.

It was expected on general grounds that aromatic dyestuffs would be adsorbed from aqueous solution by aromatic liquids in which they were insoluble. Benzene and chlorobenzene were used in the hope of finding some correlation between the polar nature of an adsorbent and its adsorbing power. To provide a contrast to the action of these liquids, the adsorption at the interfaces between aqueous solutions and air, and aqueous solutions and a liquid aliphatic hydrocarbon (a light paraffin free from aromatic hydrocarbons), has been investigated. It was anticipated that adsorption at the air–water and paraffin–water interfaces would be much less than in the case of the aromatic liquids.

No adsorption of any of the five dyes at the air–water interface could be detected. This is consistent with the fact that the surface tension of the solutions, as determined by the capillary-rise method, at no concentration showed a lowering of more than 1 dyne/cm. The whole of the results obtained for liquid–liquid interfaces are summarised in the following table.

Dye.	Methylene-blue.	Orange-II.	Congo-red.	Methyl-orange.	Bordeaux-extra.
Nature in solution	Mainly simple	Mainly simple	Forms micelles	?	Simple
Anion	Chloride	Complex	Complex	Complex	Complex
Cation	Complex	Sodium	Sodium	Sodium	Sodium
Molecular area, A.^{2} (from scale drawing)	140	112	192	79	153
Adsorption curve on all three solvents	Stays at maximum	Stays at maximum	Returns to zero	Returns to zero	Returns to zero
	Actual area, A.^{2}, occupied per molecule, at max. adsorption.				
On C_6H_6	215	180	470	218	3840
On PhCl	215	180	117	40	5235
On paraffin	812	231	2300	674	1858

FIG. 1.



The adsorption curves for Bordeaux-extra at all three liquid–liquid interfaces are similar to those of Congo-red and methyl-orange, passing through a maximum and then falling again to, or towards, zero as concentration increases. The influence of the nature of the adsorbent is the reverse of that found in these two cases, the maximum adsorption on paraffin being twice that on benzene, and three times that on chlorobenzene. The latter order is, however, the same as that of the curves calculated from Gibbs's equation. The plane projection of the Bordeaux-extra molecule (Fig. 1, drawn to scale) has an approximate area of 153 sq. A., measured as a close, straight-sided polygon drawn round the figure. The quantity of this dyestuff adsorbed on all three interfaces constitutes at most only about one-twelfth of that necessary to form a close-packed unimolecular layer. This is in sharp contrast to the behaviour of Congo-red, although the structures of the two molecules differ only slightly. Furthermore, the discrepancies between the observed values for Bordeaux-extra, and those calculated from the approximate form of Gibbs's equation, are the largest of all those investigated (Fig. 2, and Tables I, E, F, G, and II, E, F, G).

FIG. 2.

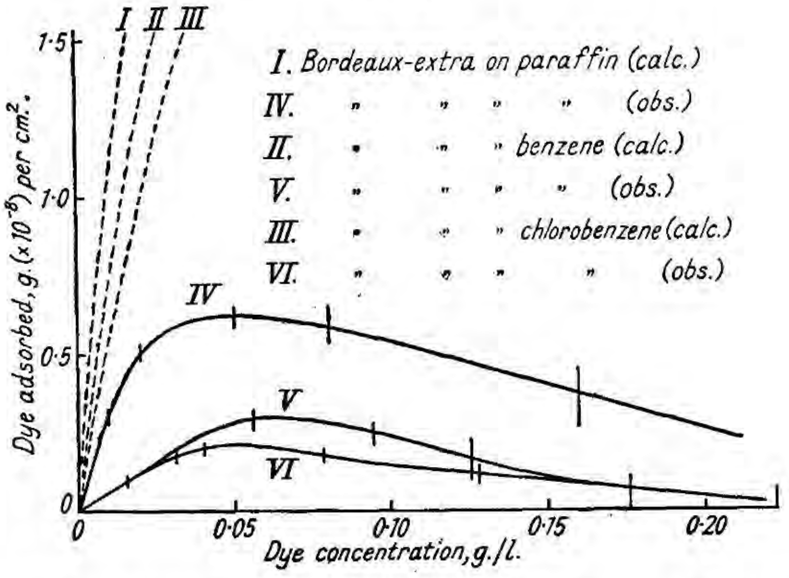


TABLE I.

(A) *Methylene-blue on paraffin.*

Initial concn., g./l.	Time of flow, mins.	Surface area, cm.².	Adsorption coefficient, g./cm.² × 10⁸.
0·0210	1420	59,330	0·10 ± 0·01
0·0421	1420	46,850	0·28 ± 0·03
0·1012	1103	47,570	0·60 ± 0·06
0·2023	1187	41,780	0·60 ± 0·15
0·3380	1200	60,710	0·6 ± 0·2
0·5400	1200	57,280	0·6 ± 0·3

(B) *Orange-II on paraffin.*

Initial concn., g./l.	Time of flow, mins.	Surface area, cm.².	Adsorption coefficient, g./cm.² × 10⁸.
0·0302	1185	40,520	1·09 ± 0·03
0·0678	1260	33,890	1·58 ± 0·06
0·1180	1054	39,950	1·9 ± 0·1
0·1715 *	1136	29,100	2·1 ± 0·2
0·2826	1395	45,600	2·0 ± 0·2
0·4340 *	1365	41,430	2·4 ± 0·3
0·6775	1100	37,150	2·3 ± 0·6
0·9801	3504	100,000	2·4 ± 0·3

(C) *Methyl-orange on paraffin.*

Initial concn., g./l.	Time of flow, mins.	Surface area, cm.².	Adsorption coefficient, g./cm.² × 10⁸.
0·0166	1176	35,530	0·14 ± 0·01
0·0554	930	31,210	0·55 ± 0·05
0·1108	1275	43,580	0·81 ± 0·08
0·1754	1200	36,560	0·6 ± 0·15
0·2338	900	34,100	0·4 ± 0·2
0·4962	1155	44,420	0·00 ± 0·35

(D) *Congo-red on paraffin.*

Initial concn., g./l.	Time of flow, mins.	Surface area, cm.².	Adsorption coefficient, g./cm.² × 10⁸.
0·00738	1370	69,720	0·14 ± 0·004
0·0203	1080	42,420	0·46 ± 0·02
0·0304	1260	44,860	0·47 ± 0·02
0·0407	1080	39,200	0·45 ± 0·03
0·0738	1330	58,660	0·23 ± 0·04
0·1215	1215	46,310	0·00 ± 0·08

(E) *Bordeaux-extra on paraffin.*

Initial concn., g./l.	Time of flow, mins.	Surface area, cm.².	Adsorption coefficient, g./cm.² × 10⁸.
0·0100	1580	61,120	0·300 ± 0·003
0·0200	1400	44,330	0·5 ± 0·15
0·0500	1200	43,050	0·62 ± 0·03
0·0800	1515	37,450	0·60 ± 0·06
0·1605	1200	49,230	0·36 ± 0·09

(F) *Bordeaux-extra on benzene.*

Initial concn., g./l.	Time of flow, mins.	Surface area, cm.².	Adsorption coefficient, g./cm.² × 10⁸.
0·0310	1357	51,710	0·17 ± 0·02
0·0558	1310	57,350	0·29 ± 0·03
0·0939	936	46,190	0·25 ± 0·06
0·1261	1260	44,020	0·16 ± 0·08
0·1765	1440	47,610	0·00 ± 0·1

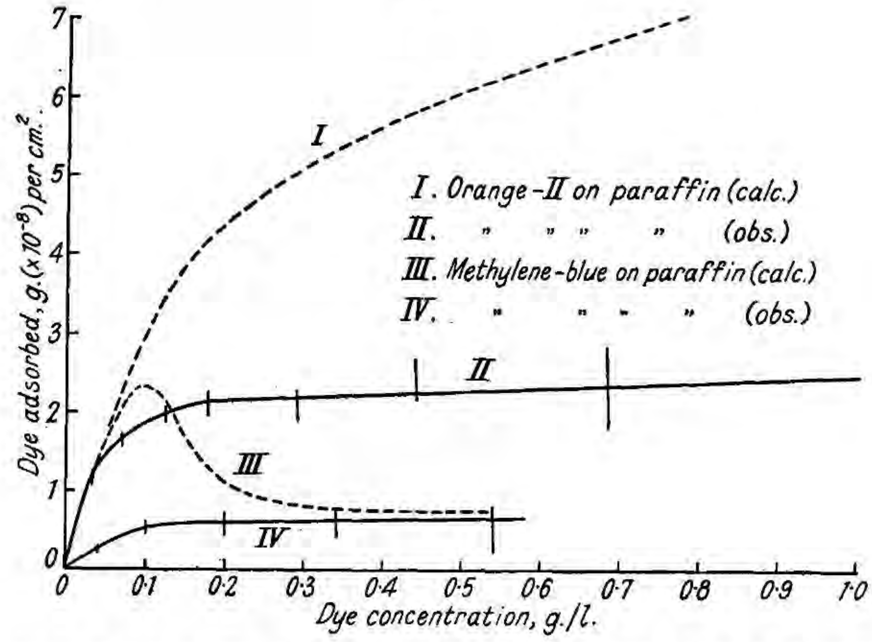
(G) *Bordeaux-extra on chlorobenzene.*

Initial concn., g./l.	Time of flow, mins.	Surface area, cm.².	Adsorption coefficient, g./cm.² × 10⁸.
0·0162	1353	43,480	0·100 ± 0·005
0·0408	1257	38,560	0·20 ± 0·015
0·0783	1327	47,080	0·18 ± 0·02
0·1280	1292	48,980	0·13 ± 0·03
0·2227	1325	47,820	0·00 ± 0·007

* " AnalaR " Petroleum ether.

The adsorption curves for the other four dyes on paraffin, though showing in each case a much smaller adsorption than on benzene or chlorobenzene, yet maintain the same form as on these two adsorbents.

FIG. 3.



The adsorption of methylene-blue on paraffin (Fig. 3 and Table I, A) rises with concentration to a maximum which represents only one-quarter of the corresponding surface density on benzene. Nevertheless, the adsorption maintains a maximum value which corresponds to an adsorbed layer containing only about one-sixth of the amount of dye necessary for a unimolecular layer. The adsorption curve for orange-II on paraffin (Fig. 3,

TABLE II.

			Reading from σ–C curve.						Reading from σ–C curve.		
Concn., g./l.	Drop no.	σ, dynes/ cm.	Concn., g./l.	$d\sigma/$* dc.	Adsorption, g./cm.^{2} $\times 10^8$.	Concn., g./l.	Drop no.	σ, dynes/ cm.	Concn., g./l.	$d\sigma/$* dc.	Adsorption, g./cm.^{2} $\times 10^8$.
(A) *Methylene-blue on paraffin.*						(B) *Orange-II on paraffin.*					
0·0000	228	51·35	0·05	24·0	1·58	0·0000	228	51·35	0·05	29·0	2·08
0·1038	243	48·36	0·10	18·0	2·36	0·1460	253	46·55	0·10	21·0	3·02
0·2000	248	47·43	0·15	8·9	1·75	0·2910	266	44·39	0·15	19·0	4·09
0·3460	250	47·07	0·20	3·8	1·00	0·5820	284	41·71	0·20	16·0	4·60
0·7200	252	46·72	0·25	2·8	0·92	1·0200	305	38·96	0·25	13·0	4·67
1·0380	255	46·21	0·30	2·4	0·95				0·40	9·6	5·52
			0·40	1·8	0·95				0·60	7·0	6·03
			0·50	1·15	0·76				0·80	6·3	7·24
			0·60	0·8	0·63				1·00	5·95	8·55
(C) *Methyl-orange on paraffin.*						(D) *Congo-red on paraffin.*					
0·0000	228	51·35	0·05	22·0	1·47	0·0000	228	51·35	0·02	76·0	4·34
0·1272	243	48·29	0·10	19·0	2·55	0·0357	245	47·98	0·05	45·0	6·43
0·2544	252	46·73	0·15	13·0	2·61	0·0520	249	47·25	0·08	25·0	5·71
0·4070	260	45·42	0·20	11·4	3·06	0·1070	258	45·69	0·10	18·5	5·29
0·6784	270	43·78	0·25	10·5	3·52	0·4000	269	43·92	0·15	8·3	3·56
1·0176	279	42·46	0·30	9·2	3·70	0·8000	273	43·32	0·20	6·3	3·60
			0·40	7·4	3·97	1·2094	280	42·29	0·25	5·3	3·70
			0·50	6·5	4·36				0·30	4·5	3·80
			0·60	5·5	4·42						
(E) *Bordeaux-extra on paraffin.*						(F) *Bordeaux-extra on benzene.*					
0·0000	228	51·35	0·04	26·0	2·9	0·0000	136	35·38	0·02	19·1	1·09
0·1000	241	48·67	0·06	24·0	4·1	0·1200	144	33·44	0·06	14·6	2·51
0·2000	248	47·38	0·10	16·8	4·8	0·2400	149	32·31	0·10	11·9	3·41
0·3650	256	45·94	0·20	10·2	5·8	0·3600	152	31·82	0·20	8·1	4·64
0·5520	264	44·63	0·30	8·0	6·9	0·5000	157	30·81	0·30	6·6	5·67
0·7360	268	44·03	0·40	6·6	7·6	0·6305	161	30·00	0·40	5·9	6·76
0·9210	272	43·46	0·50	5·2	7·4				0·50	5·5	7·88
(G) *Bordeaux-extra on chlorobenzene.*											
0·0000	188	37·41	0·02	16·2	0·93						
0·0820	194	36·33	0·06	12·0	2·06						
0·1640	198	35·60	0·10	9·3	2·66						
0·2907	202	35·08	0·20	6·1	3·50						
0·4100	206	34·46	0·30	4·8	4·13						
0·5200	208	34·07	0·40	3·8	4·35						
0·5726	209	33·90	0·50	3·1	4·44						
			0·60	2·5	4·30						

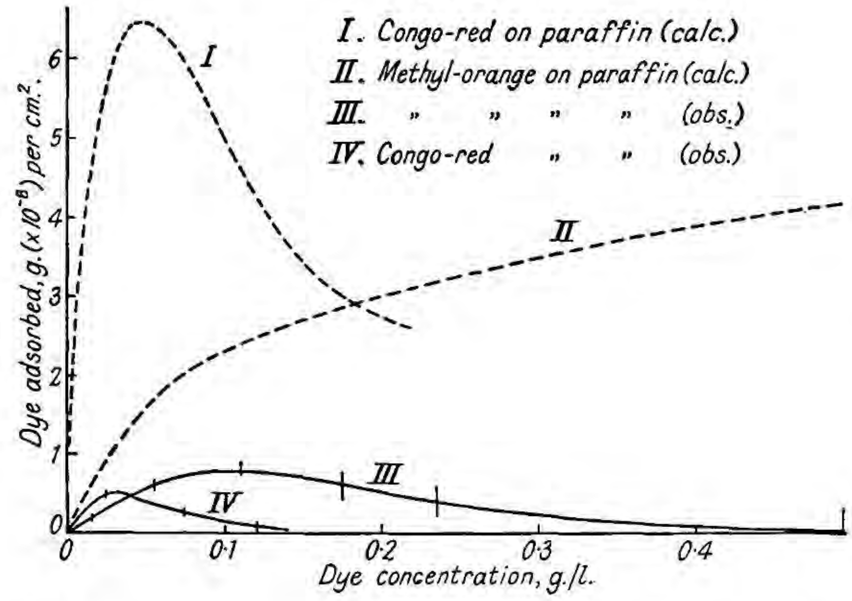
* Smoothed.

and Table I, B) is still rising at a concentration where investigation was abandoned for experimental reasons. It is therefore possible that at some higher concentration the adsorption will reach the same maximum value as it attains on both benzene and chlorobenzene. The curves showing the adsorption of Congo-red (Fig. 4, and Table I, D) and methyl-orange (Fig. 4, and Table I, C) on paraffin are of the same form as those for the two aromatic adsorbents, but the adsorption reaches a maximum value only one-third (for methyl-orange) and one-fifth (for Congo-red) of the corresponding maximum value on benzene.

The interfacial tensions of Bordeaux-extra solutions against benzene and chlorobenzene, and of all five dyes against paraffin, have been measured by the drop-weight method previously described. These results, together with the values of the adsorption calculated by means of the approximate form of Gibbs's equation, are given in Table II. They represent curves of similar shapes to those published for benzene and chlorobenzene.

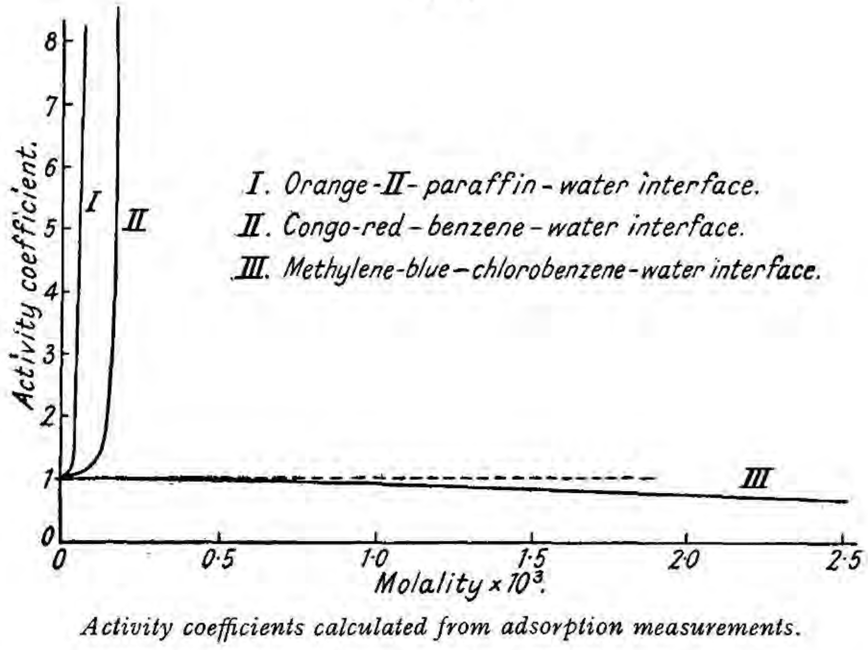
Calculation of Activity Coefficients.—Much emphasis is often, and rightly, laid upon the approximate nature of the equation $\Gamma = -c(d\sigma/dc)/RT$, and the desirability of replacing concentrations (c) by activities (a) as in the exact equation $\Gamma = -a(d\sigma/da)/RT$. Since, however, activity coefficients are defined as approaching unity at great dilutions, the values of Γ calculated from these two equations should approach one another as the concentration of the solution diminishes. If, therefore, the use of concentration instead of activity were the only cause of the discrepancy between experimental results and values of Γ calculated from the approximate equation, the experimental and the calculated curves should coincide at very low concentrations. Out of the 15 adsorption curves which have been obtained, we find this coincidence in only 3 cases, *viz.*, methylene-blue on chlorobenzene, Congo-red on benzene, and orange-II on paraffin. In all other cases the slopes of the curves as concentration approaches zero are markedly different.

FIG. 4.



We have determined for these three cases the values of activity coefficient necessary to bring the observed and the calculated curves into coincidence, as follows. Let Γ_o and Γ_c represent respectively the amounts of adsorption observed and calculated from the approximate equation. Then Γ_o should equal $-\,a(d\sigma/da)/RT$; therefore

FIG. 5.



Activity coefficients calculated from adsorption measurements.

$$\Gamma_o = -\,\{c(d\sigma/dc)/RT\}\{a(dc/da)/c\} = \Gamma_c\{a(dc/da)/c\}$$

and $a(dc/da)/c = \Gamma_o/\Gamma_c = f(c)$.

The values of this ratio can be read from the adsorption graphs.

Now $a\,.\,dc/da = c\,.\,f(c)$, therefore

$$\int_{c_1}^{c_2}[1/cf(c)]dc = \int_{c_1}^{c_2} da/a = [\log a]_{c_1}^{c_2}$$

$1/cf(c)$ can be plotted against c, and the value of the integral between the limits c_1 and c_2 can be obtained by measuring the area under the curve; c_1 is taken as the highest concentration at which Γ_o and Γ_c coincide. The activity coefficients, γ, so obtained are shown in Fig. 5 and Table III, from which it can be seen that in two out of the three cases the values are plainly impossible. Even in the third case, that of methylene-blue, the values are scarcely probable, in view of the low concentrations involved.

TABLE III.

Concn., g./l.	$\Gamma_c \times 10^8$.	$\Gamma_o \times 10^8$.	$f(c) = a(dc/da)/c$.	$\int_{c=c_1}^{c=c_2} dc/cf(c)$.	2·303 log a.	a.	γ.
(A) *Congo-red on benzene.*							
0·01	1·0	1·0	1·0	0·00	−4·606	0·01	1·0
0·06	3·3	2·3	0·69	1·88	−2·72	0·068	1·13
0·08	4·0	1·0	0·25	2·50	−2·10	0·12	1·5
0·10	4·6	0·3	0·065	4·02	−0·58	0·56	5·6
0·12	5·1	0·2	0·039	7·22	+2·62	13·8	115
0·14	5·6	0·12	0·021	12·42	7·82	251	1793
0·16	6·0	0·1	0·016	19·62	15·00	$2·8 \times 10^6$	$1·75 \times 10^7$
(B) *Methylene-blue on chlorobenzene.*							
0·08	1·15	1·15	1·0	0·00	−2·47	0·08	1·0
0·10	1·20	1·50	1·25	0·17	−2·30	0·10	1·0
0·20	1·60	1·95	1·22	0·82	−1·65	0·19	0·95
0·30	1·70	2·20	1·30	1·14	−1·33	0·26	0·87
0·40	1·67	2·57	1·42	1·35	−1·12	0·33	0·83
0·50	1·60	2·40	1·50	1·50	−0·97	0·38	0·76
0·60	1·50	2·40	1·60	1·61	−0·86	0·43	0·72
0·70	1·44	2·40	1·67	1·71	−0·76	0·47	0·67
·0·80	1·38	2·40	1·74	1·79	−0·68	0·51	0·64
(C) *Orange-II on paraffin.*							
0·03	1·1	1·1	1·0	0·0	−3·51	0·03	1·0
0·06	2·0	1·55	0·775	8·1	+4·59	100	
0·08	2·5	1·70	0·68	12·1	8·59	5,370	
0·10	3·0	1·80	0·60	15·5	12·03	16,600	very large
0·20	4·3	2·10	0·49	28·8	25·33		
0·30	5·0	2·13	0·426	38·0	34·53		
0·40	5·6	2·18	0·39	45·2	41·73		
0·50	6·0	2·20	0·367	51·0	47·53		

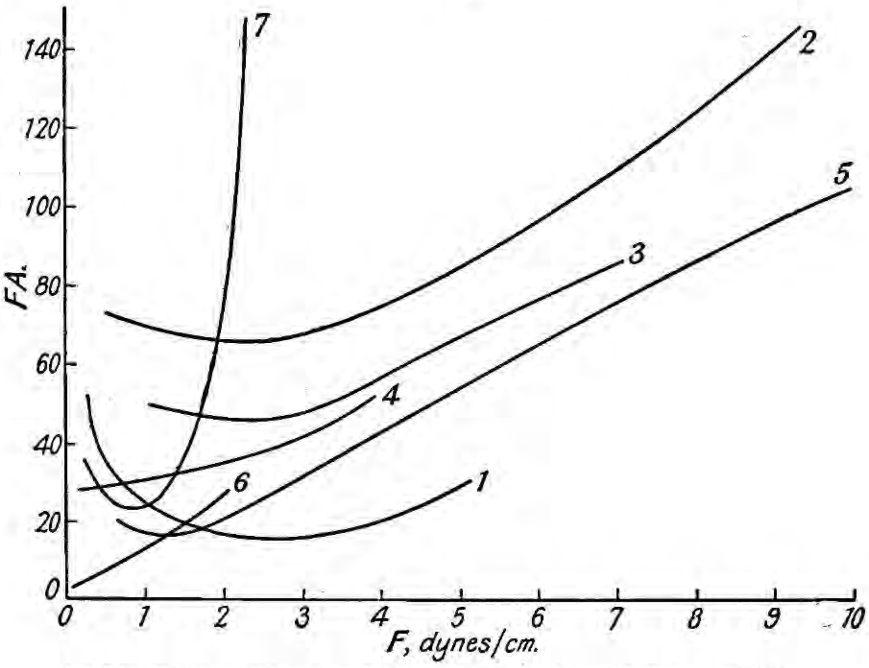
c_1 = (A) 0·01; (B) 0·08; (C) 0·03.

It seems clear, therefore, that the difference between the observed and the calculated values of Γ which we have obtained cannot be due entirely to the lack of data for the activities of the solutes. Hence, no further useful purpose can be served by endeavouring to apply Gibbs's equation in the absence of further information as to the influence of the electrical and other factors expressly excluded in its derivation.

Application of Gas Laws to Adsorbed Layers.—In those cases in which adsorption passes through a maximum and falls again to zero as concentration increases, there arises a paradox similar to that commented upon by McBain (*Nature*, 1936, **137**, 659), and of which he has suggested a possible explanation. The interfacial tension between the dye solution and the organic liquid is reduced, yet we can detect no adsorption at the interface. This is inexplicable unless it is assumed that at certain concentrations a solute may lower the interfacial tension of the solvent by some other mechanism than movement from the body of the solution to the interface. This anomaly is further emphasised and this conclusion strengthened if our results are treated in the manner introduced by Langmuir (*J. Amer. Chem. Soc.*, 1917, **39**, 1883) and since adopted by Rideal and others (*e.g.*, *Proc. Roy. Soc.*, 1925, *A*, **109**, 57; 1926, *A*, **110**, 167) for soluble substances. In this treatment the adsorbed material is regarded as existing in a layer of unimolecular thickness. An equation $FA = RT$ can then be deduced, to represent the connection between F (the surface pressure as measured by the diminution in interfacial tension) and A (the area of interface occupied per g.-mol.). This equation can be applied so long as the adsorbed material behaves like a gas whose molecular movements are restricted to two dimensions. It can therefore be used to discriminate between " gaseous " and " liquid " adsorbed layers, since in the latter case A will be constant over a wide range of pressures.

The FA–F curves for orange-II and methylene-blue at all three interfaces are, at any rate at low surface pressures, of forms similar to the PV–P curves for gases deviating somewhat from Boyle's law, and represent the behaviour of " gaseous " layers. Three of them (Fig. 6; curves 3, 4, and 5) involve constant values of A over considerable ranges of the higher values of F, indicating a transition from " gaseous " to " liquid " layers. Another type, shown by those dyes for which the adsorption curves pass through a maximum, *e.g.*, Bordeaux-extra on benzene, further illustrates the paradox, in that it involves at high surface pressures a simultaneous increase of pressure and of area occupied per molecule.

FIG. 6.



1. *Methylene-blue on paraffin.* $A = cm.^2$ *per g.-mol.* × 10^{10}.
2. *Orange-II on paraffin.*
3. *Orange-II on chlorobenzene.*
4. *Methylene-blue on chlorobenzene.* A = *cm.*² *per g.-mol.* × 10^9.
5. *Orange-II on benzene.*
6. *Methylene-blue on benzene.* A = *cm.*² *per g.-mol.* × 10^{11}.
7. *Bordeaux-extra on benzene.* A = *cm.*² *per g.-mol.* × 10^{10}.

Some further experiments were carried out with methyl-orange to confirm the fall in adsorption at high concentrations. A sample of this dye was treated successively with chloroform and paraffin in a Soxhlet extractor for several hours to remove organic impurities. It was then recrystallised four times from specially purified water of $\kappa = 8 \times 10^{-6}$ mho. This purification was additional to that described in Part I (*loc. cit.*), but the results fall on the curve previously obtained, chlorobenzene being used as adsorbent :

Concentration, g./l.	0·8568	0·9951	0·9280
Adsorption, g./cm². × 10^8	6·8 ± 0·2	6·0 ± 0·37	6·4 ± 0·3

EXPERIMENTAL.

The paraffin used in the majority of the experiments was the ordinary " petroleum ether," $d_{4^\circ}^{17^\circ}$ 0·716, distilling completely between 83° and 97° (74% below 90°) and containing 3% of aromatic hydrocarbons. Experiments upon " AnalaR " paraffin, free from aromatic hydrocarbons, gave results falling on the curves obtained with the commercial product. The interfacial tension between the paraffin and pure water was 51·35 dynes/cm. The drop pipette used with paraffin and benzene had a volume of 28·59 cm.^{3}, and a jet radius of 0·1435 cm. For chlorobenzene the pipette specified in Part I was used.

Bordeaux-extra (I.C.I.) was further purified by salting out four times from aqueous solution with 40% sodium acetate, followed by treatment with absolute alcohol until free from acetate (cacodyl test).

The adsorption apparatus and experimental methods used were precisely similar to those adopted for the experiments with benzene (*loc. cit.*). The experiments were carried out at 17° ± 1·5°.

In the attempts to measure the adsorption at the air–water interface, the method of McBain and Davies (*J. Amer. Chem. Soc.*, 1927, **49**, 2230), in which the bulk solution drains away from the bubbles which then pass over an inverted U-tube, was tested with apparatus of various dimensions, but was impracticable for the dyestuff solutions used: the bubbles collapsed before passing over the bend, since the surface tensions of the dye solutions were virtually the same as those of water. An apparatus based on similar principles to that of Donnan and Barker (*Proc. Roy. Soc.*, 1911, *A*, **85**, 557) was therefore used. Small bubbles of air were drawn into the apparatus through a jet of thermometer tubing, passed slowly up an inclined tube of relatively large diameter, and then through four large baffle chambers into a reservoir in which they collapsed. The solution from the inclined tube was compared in a tintometer with the original, after an interface of about 10 m.^{2} had been exposed. Experiments were carried out with each dye at three different concentrations. No adsorption was found, and blank experiments showed that the results were not invalidated by back diffusion.

We are indebted to Messrs. Imperial Chemical Industries, Ltd., for the gift of a sample of Bordeaux-extra. We thank the Chemical Society for a grant from the Research Fund. One of us (C. C. A.) is indebted to the Cumberland Education Authority for a grant from the Edward Seton Chance Fund.

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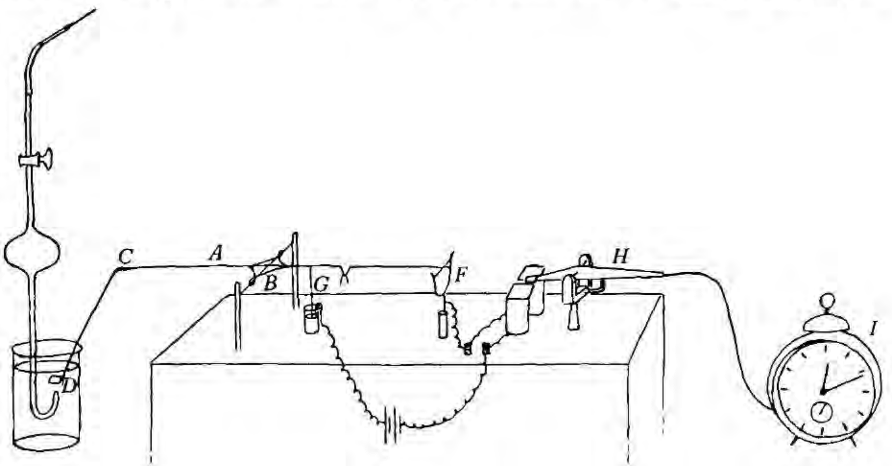
AN AUTOMATIC DEVICE FOR RECORDING DROP NUMBERS IN INTERFACIAL TENSION MEASUREMENTS.

BY C. W. GIBBY, M.SC., PH.D. AND C. C. ADDISON, B.SC., University of Durham

[*MS. received 22nd March*, 1935.]

IN the course of investigations involving measurements of the interfacial tension between benzene and dilute aqueous solutions by means of the drop pipette, it was necessary to count 600–700 drops of benzene. As the numbers were large and the rate of flow small, the mechanical device here described was constructed. Donnan and Barker* refer to the counting of drops of liquid falling through air by allowing them to strike a vane which actuated a Morse inker, but the motive power of drops of benzene is much less when rising through water.



Automatic device for recording drop numbers

A beam A, made of aluminium wire, is suspended at B by means of a cotton thread round which it is looped. At C it is fastened by shellac to a thin glass rod less than 1 mm. diameter to which is sealed a piece of microscope cover glass D. Drops of benzene rising from the pipette strike the under side of the inclined vane D, and deflect the beam (previously balanced by means of a rider), causing the platinum wire fastened to its other extremity to make contact with a transverse platinum wire held in an adjustable stirrup F. One permanent electrical connection is made by a platinum wire G, dipping into mercury. The closing of the circuit operates the relay arm H, the termination of which is a stiff wire passing through a small hole in the escapement lever of the clock I. The balance wheel of the clock has been removed, and the seconds dial replaced by one so divided that the seconds hand reads directly in bubbles and the minute hand in hundreds of bubbles. It is essential that C should be thin, or readjustment of the height of F is necessary on account of the increasing upthrust of the accumulating benzene.

* *Proc. Roy. Soc.* A, **85** 1911 (561).

Adsorption at the Interface between two Fluids.

Chapter 1.

Introduction.

This research was undertaken for the purpose of investigating that particular branch of surface chemistry which is concerned with the concentration of a solute at the interface between its aqueous solution and some other medium in which it is insoluble. Adsorption at the liquid-liquid interface has been given prominence, but some air-water experiments have been carried out for comparison.

Apart from a very few approximate determinations at liquid-liquid interfaces, which are discussed later, previous research on adsorption phenomena can conveniently be considered as being of two main types.

The one, which is especially important in industry, has been concerned with the adsorption on to a solid surface, from either gaseous or aqueous media. Owing to the essentially uneven nature of solid surfaces, and particularly of such common commercial adsorbents as carbon and cellulose, only an approximate estimation of the surface area can be made. The necessarily approximate nature of all results derived therefrom suggests that the translation of these results into terms of molecular thicknesses etc. at the interface is scarcely justifiable.

The other has been concerned chiefly with the adsorption, at a gas-liquid interface, of very large molecules, which remain in the surface either because they are only partly soluble in the liquid layer, or because they can produce there a layer so stable that it is capable of independent existence.

Adsorption work at liquid-liquid interfaces, however, though difficult to investigate experimentally, possesses some unique advantages. In such experiments it is possible to investigate the influence of the polar nature of the adsorbent on the extent of adsorption. The adsorption values for one and the same solute have been found to vary over a wide range as a result of changes in what is usually regarded as the "inert" medium. The liquid-liquid interface is as plane as is physically possible when due consideration is taken of the thermal agitation of the molecules; it will, therefore, offer no resistance to whatever orientating forces the molecular attractions may set up.

It is interesting to note that the concentration of any solute at the interface between two other media can be regarded as due to either a purely chemical, or a purely physical cause.

On the one hand, there is a natural tendency for some molecules to concentrate on the interface. Because of their similar polar nature, they may be attracted by the medium across the phase boundary, although not sufficiently so to be soluble in that medium. Again, as in the adsorption of long-chain fatty acid and hydrocarbon molecules on an air-water interface, the adsorbate may not be completely soluble in the aqueous layer. Only part of the molecule is attracted to the aqueous layer, and this tendency, together with the lateral cohesive forces between the hydrocarbon molecules themselves, causes the adsorbate to spread out on the surface in a film, which can behave as a two-dimensional gaseous or liquid film according to the lateral pressure exerted on it.

On the other hand, adsorption may be regarded as a mechanical movement towards the minimum potential energy of the system which its presence at the interface would produce. This lowering of surface tension is most readily pictured in terms of the molecular distribution caused by the various molecular attractions. If water molecules have a greater attraction for one another than for the solute, it is a natural consequence that the latter should go to the phase boundary. Since surface tension is determined by the attractions between the molecules in the actual surface, the smaller mutual attractions at the surface due to the concentration of the solute there must bring about a corresponding drop in the surface tension.

Although these chemical and physical influences are so closely interconnected that it might almost be argued that they are one and the same factor, the experiments described in this thesis have shown that a large adsorption resulting from the attraction of strongly polar groups in the adsorbent is not reflected to nearly the same degree in the drop in interfacial tension. Conversely, certain solutds whose tension-concentration curves are similar, are found to be adsorbed to widely differing extents.

Gibbs's Thermodynamic Conception of adsorption.

Willard Gibbs, in his mathematical studies of the influence of surfaces of discontinuity upon the equilibrium of heterogeneous masses, deduced a direct relationship between the quantity of any substance adsorbed in the region of an interface, and the change in potential brought about by its movement from the homogeneous phase to the boundary.

Since discontinuity between two phases is not mathematicall absolute, it is necessary in precise treatment to refer to some arbitrary geometrical surface, which is considered as being parallel to the surface of discontinuity, and reasonably coincident with it. This "dividing surface" is designated by the symbol S.

It is convenient to imagine a closed surface cutting S, and including part of the homogeneous mass on each side. This closed surface is limited in so far as that, while any lack of perfect homogeneity exists, the closed surface is such as may be generated by a moving normal to S.

The area of surface enclosed is denoted by s. The mass contained in the closed surface is divided into three parts by two further imaginary surfaces, one on each side of S, and very close to it. The part containing the surface is called M, and the two outer homogeneous phases M' and M''.

Accordingly, $e\ e'\ e''$, $n\ n'\ n''$, $m_1 m_1' m_1''$, $m_2 m_2' m_2''$, denote the energies and entropies contained in these masses, and the quantities of the various independent components which they contain. It is important to observe that Gibbs makes no exact stipulations regarding the thickness of the layer containing the adsorbed mass, but assumes that the arbitrary bounding surfaces are sufficiently far distant to be out of the range of whatever heterogeneity or discontinuity may be occasioned by the surface S.

Although the masses are separated only by imaginary surfaces which represent no break in the homogeneity, it is found convenient to represent the above energies and entropies as belonging to separate masses. This is permissible so long as the energy is distributed with uniform density, a condition which is implied in the original definition of the surfaces.

Since the boundaries of the mass M are considered to be constant, it may be treated as an isolated system, and reversible variations taking place within its boundaries will not effect the neighbouring masses;

The characters de,dn,dm etc. are used throughout to represent small changes in e,n,m etc.

For a reversible variation,

$$de = A_0 dn + A_1 dm_1 + A_2 dm_2 \text{ -------etc.} \qquad (1)$$

where $A_0 A_1 A_2$ etc. depend on the system.

From the definition of entropy, i.e. $t = \frac{de}{dn}$,

A_0 must equal t, the temperature of the surface of discontinuity.

Similarly $A_1 A_2$ etc. represent the potentials μ_1, μ_2 etc. of the masses at the same surface. Therefore :-

$$de = t\,dn + \mu_1 dm_1 + \mu_2 dm_2 \quad \text{------etc,} \qquad (2)$$

The volume occupied by the mass M is divided by the surface S into two parts, called v''' (next to M') and v'''' (next to M''). These volumes are considered as being filled by masses having throughout the same temperature, pressure, potentials, energy, entropy and components as the masses M' and M'', and also as containing the adsorbed material.

Considering the volumes to be constant, then from (2)

$$de''' = t'dn''' + \mu_1' dm_1''' + \mu_2' dm_2''' \quad \text{------etc. and}$$

$$de'''' = t''dn'''' + \mu_1'' dm_1'''' + \mu_2'' dm_2'''' \quad \text{---etc,}$$

But from (2) also,

$$d(e-e'''-e'''') = td(n-n'''-n'''') + \mu_1 d(m_1-m_1'''-m_1'''')$$
$$+\mu_2 d(m_2-m_2'''-m_2'''') \quad \text{-----etc.}$$

If, therefore, we define

$$\overset{s}{e} = e-e'''-e'''',$$

$$n^s = n-n'''-n'''',$$

$$m_1^s = m_1-m_1'''-m_1'''', \qquad \text{-----etc.}$$

then (2) becomes

$$d\overset{s}{e} = t\,d\overset{s}{n} + \mu_1 d\overset{s}{m}_1 + \mu_2 d\overset{s}{m}_2 \quad \text{---etc.} \qquad (3)$$

It should be emphasised here that the "superficial energy" $\overset{s}{e}$, represents the energy of the mass occupying the total volume, in excess of the energy it would have if the energy density of the homogeneous regions extended right up to the surface S, and corresponds to the energy of the mass adsorbed on the surface. Similar definitions apply for n^s, m^s etc.

It is evident that these terms will remain unaltered :-

a) whatever the positions of the arbitrary surfaces separating M , M' , and M'' , so long as these surfaces remain in the region of homogeneity, and

b) if the position of the surface S is varied by mere translation or rotation.

If, however, the form of S be altered, terms mustbe added to the right-hand side of equation (3) to allow for:-

1) variation ds in area of surface contained in closed space, and

2) variation in the principal curvatures dc_1 and dc_2.

Therefore from (3)

$$de^S = t\,dn^S + \mu_1 dm_1^S + \mu_2 dm_2^S \text{---etc}, + \sigma ds + C_1 dc_1 + C_2 dc_2 \quad , \qquad (4)$$

where σ = tension of the surface, and C_1 and C_2 depend on the system.

The position of the surface S can be so chosen that $C_1 + C_2$ will vanish, and Gibbs has shown that this position does in general coincide with the physical surface of discontinuity.

In a state of equilibrium, therefore, equation (4) becomes

$$de^S = t\,dn^S + \sigma ds + \mu_1 dm_1^S + \mu_2 dm_2^S \text{ ----etc.} \qquad (5)$$

This equation is regarded by Gibbs as a fundamental equation for plane surfaces of discontinuity between fluid masses.

On integrating this equation,

$$e^S = tn^S + \sigma s + \mu_1 m_1^S + \mu_2 m_2^S \text{ ----etc.} \qquad (6)$$

where t, μ_1, μ_2, and σ are invariable throughout the surface. When this equation is again differentiated, regarding all these quantities as variables, and the result compared with equation (5), it follows that

$$n^S dt + s\,d\sigma + m_1^S d\mu_1 + m_2^S d\mu_2 \text{ ----etc.} = 0 \qquad (7)$$

The superficial densities of energy, entropy, and the several components can be represented as :-

$$n_s = \frac{n^S}{s} \ , \quad e_s = \frac{e^S}{s} \ , \quad \Gamma_1 = \frac{m_1^S}{s} \ , \quad \Gamma_2 = \frac{m_2^S}{s} \ ,$$

in which case from (7)

$$d\sigma = -n_s dt - \Gamma_1 d\mu_1 - \Gamma_2 d\mu_2 \text{ ----etc.} \qquad (8)$$

The right-hand side of this equation may be extended according to the number of components.

When only a single component is concentrated at the interface, then μ_2 and μ_3 are zero, and t is constant. Therefore from (8)

$$d\sigma = -\Gamma_1 d\mu_1$$

Applying this generally to the adsorption of a single solute from a medium 1 on to the interface between two media 1 and 2, then

$$\Gamma_{1.2} = \frac{-d\sigma}{d\mu_1}$$

This is the form in which Gibbs stated the relationship, but it has been altered in the hands of other workers to a form more practically applicable.

For ideal solutions, the relation between concentration and chemical potential is given by :-

$$\mu = \mu_0 + RT \log_e C$$

Therefore,

$$\Gamma = -\frac{d\sigma}{RT.d\log_e c} = \frac{-c.\,d\sigma}{RT.\,dc}$$

This gives the form of the equation as it has been used throughout this work.

Since the quantity Γ has the same dimensions as $\frac{c\,.d\sigma}{RT\,.dc}$, viz. mass per unit area, it does not represent a concentration excess over that of the homogeneous part of the solution out of the range of surface forces, but the mass actually attached to unit area of the interface.

It has already been pointed out that the volume in which this adsorbed mass is contained is immaterial, since the surface layer was implied by Gibbs to extend to a thickness great enough to include all such adsorbed matter.

Because of the ideal nature of its derivation, the equation assumes certain conditions which can rarely be realised in actual practice.

It is particularly to be observed that Gibbs Equation in this form is intended to apply only to the adsorption of

a single component from a solution in which its behaviour is ideal with reference to concentration, and that in this, or in its original form, it applies only to interfaces which are not affected by electric charges.
For all solutions for which the dilution laws do not apply, the concentration factor may be replaced by the thermodynamic concentration, or activity, (a).
Therefore, $\Gamma = - \frac{a.d\sigma}{RT.da}$

The equation indicates that the adsorption may be either positive or negative, according to whether the solute lowers or raises the interfacial tension.

Gibbs's Equation, then, gives a value for adsorption depending directly upon the change of tension at the interface. It takes no account of any influences mentioned earlier, such as may be set up by direct chemical affinities. The investigations described in this thesis show clearly the great discrepancy existing between the observed values of adsorption and those predicted by Gibbs's Equation, and it is suggested that the deviations in actual equilibria from those predicted by the equation are due to the interference of one or all of these conditions. This matter is discussed fully in Chapter 4.

Chapter 2.

Historical.

This section deals generally with previous experimental work relevant to the present research, the substances and methods employed, the reasons and justification for their adoption, and the results obtained.

References are quoted in a bibliography.

Historical review of the actual details of apparatus, and the formulae used in the calculation of interfacial tensions etc., have been omitted from this outline, and are dealt with separately in their appropriate section.

It has already been mentioned that few practical investigations of adsorption on liquid-liquid interfaces have been undertaken. The significance of the work which has been done will be indicated from the point of view of its bearing on the present research.

The adsorption on solid surfaces from gaseous and aqueous media has hitherto received a great deal of attention because of industrial demands. Since, however, this type of work is scarcely relevant to the present investigation, it need receive no more than mention.

Adsorption on gas-liquid interfaces, however, has a closer connection, and is discussed in greater detail.

All conclusions put forward regarding surface orientation of molecules, layer thicknesses, the nature of gaseous and liquid adsorbed layers etc., depend on some original estimation of the mass of substance adsorbed on a known area of surface.

This information seems to have been obtained by employing either one of two very different methods. Some investigators have trusted in the validity of Gibbs's Equation for the conditions they employ, and have calculated adsorption values from the surface tension data usually available.

Since, however, only a few incomplete attempts have been made to prove the equation for either a gas-liquid or a liquid-liquid interface over any sufficient range of concentration, this procedure is unjustifiable. Others have measured this quantity experimentally, and their results may therefore be relied upon within the limits of their experimental error. Such results are treated in detail here.

The deviations of actual adsorption values from those predicted by Gibbs's Equation, so apparent in this research, emphasise that calculated values can have little practical significance. Work of this type is less relevant, and is discussed in no great detail.

Previous Experimental Determinations of Adsorption.

(1) Adsorption at Liquid-Liquid Interfaces.

Two chief experimental methods have been used; firstly, that involving the investigation of emulsions, and secondly the "moving bubble" method, in which a stream of single bubbles carry their adsorbed matter into a separate reservoir.

(a) The emulsion method has been developed during the research into the stabilising of emulsions by soap solutions. The quantity of emulsifying agent adsorbed is measured by examination of the continuous phase before and after the emulsification.

Considerable work has been done since first Langmuir (1) (2) and W.D.Harkins,E.C.H.Davies andG.L.Clark (3) suggested that emulsion stability was due to an orientated monomolecular layer of adsorbed matter.

E.L.Griffin (4) studied some emulsions of kerosene with solutions of sodium oleate and stearate, and found an approximately monomolecular layer at the interface.

Similar results were obtainedby P.A.Van der Meulen and W.Riemann (5) (6) , for toluene emulsified in sodium ricinoleate and oleate solutions.

W.D.Harkins and N.Beeman worked with finer emulsions than had previously been used, and found that the amount of various oleates adsorbed on very fine octane droplets was more than sufficient to form a monomolecular layer. (7) E.K.Fischer and W.D.Harkins (8) made further measurements of the adsorption of soaps at an oil-water interface. The total surface area was obtained by direct microscopic measurement of the oil particles, and the soap adsorbed by chemical means. They concluded that an emulsion is stabilised by either expanded or condensed monomolecular layers of the emulsifying agent.

(b) The moving bubble method for liquid-liquid adsorption was first used by

W.C.McLewis (9) who by this means investigated the adsorption of a range of solutes at the interface between their aqueous solutions and a hydrocarbon oil. Similar adsorption coefficients were obtained with large drops and emulsion droplets; it was assumed that the surface of even the emulsion droplets was sufficiently plane, when considered in molecular dimensions, to exhibit normal adsorption phenomena.

The adsorption of sodium glycocholate was measured by passing drops of hydrocarbon oil up a tower of its aqueous solution. The adsorbed material was collected in a reservoir at the top of the column. The drop-pipette method was used to measure the change of interfacial tension with concentration, and also to estimate the excess concentration in the reservoir due to adsorption. The results indicated an adsorption value of almost 100 times that calculated. Adsorption coefficients for Congo Red, Methyl Orange, and Caustic Soda were obtained by the emulsion method. The oil was emulsified in the solutions, and the fall in bulk concentration was measured by taking drop numbers through the emulsion. Experiments again indicated an actual adsorption of from 10 to 20 times the calculated quantity. Lewis attributes this discrepancy to the electrical double layer and other effects not taken into account in the derivation of Gibbs's Equation.

Attempts to repeat his experiments with glycocholate in this research were abandoned, because it was not possible to obtain a sample free from taurocholate.

Later (10) Lewis extended these experiments to the study of non-electrolytes and inorganic salts, the adsorbed material being estimated gravimetrically. For silver nitrate and potassium, barium,and copper chlorides, the actual adsorption was again from 10 to 20 times the calculated amount. A hydrocarbon oil was emulsified in a solution of the non-electrolyte, caffeine. This was the only substance used by Lewis which gave actual adsorption of the same magnitude as predicted by the equation.

These results of Lewis cannot, however, be taken as direct indication of the extent of divergence between actual and calculated adsorption values. In general he records only one measurement for each substance, so that the magnitude of the experimental error is uncertain. Moreover, a comparison of experimental results with the predictions of Gibbs's Equation requires data over a considerable range of concentration. The results given in this thesis have shown clearly that though at one concentration the two values may agree perfectly, at another concentration one may have many times the value of the other.

Patrick (11) measured the interfacial tensions of mercury against aqueous solutions of mercurous sulphate, neofuchsin, salicylic acid, morphine hydrochloride, picric acid and caffeine by the drop-weight method. He found that the mass of a mercury drop was independent of the rate of formation; a minimum time limit of one second for the formation of each drop was sufficient to ensure equilibrium.

Adsorption experiments of a very approximate nature were also carried out on these substances. A fine shower of mercury droplets was sprayed down a tower, up which was passing a current of the solution. This spray was obtained by forcing the mercury, by head of pressure, through fine scratches in a ground glass connection. The adsorbed material was collected in a reservoir at the bottom of the tower, where the mercury droplets coalesced with a layer of mercury. In each experiment a constant mass of mercury was allowed to flow, and the solute removed from the tower was estimated colorimetrically. Results indicated that adsorption increased with concentration according to the relation found to hold for solid surfaces, except for morphine and caffeine, when no adsorption was found.

Since no attempts were made to estimate the size of the droplets, and thus the surface area, or to prove that the mercury surface was saturated, the results have only qualitative significance. A few experiments with mercury were carried out incidentally in the present investigation, and are mentioned in Appendix 1.

Nonaka (12) (13) has investigated the adsorption of soaps at the benzene-water and toluene-water interfaces, and found a greater adsorption value than that corresponding to a monomolecular layer. He suggests that the layer may be in unimicellular form.

K.M.Seymour,H.V.Tartar and K.H.Wright (14) also investigated adsorption of sodium oleate at the benzene-water interface. The oleate solution was prepared by saponifying pure oleic acid with a slight excess of caustic soda. The system is complicated by the fact that the oleic acid dissolves in the benzene. Aqueous and benzene solutions of oleic acid were therefore left in contact for about two weeks to reach equilibrium, and these media were used in the adsorption experiments. The moving bubble method was used; the drops passed up an inclined tube, over a bend at its upper extremity, down a narrower tube just large enough to accomodate the drops, and into a reservoir. This contained the coalesced benzene drops with the minimum of bulk soap solution. The adsorbed mass was found by estimation of the excess oleic acid in the benzene layer, and the excess sodium in the aqueous layer. The quantity adsorbed was more than 20 times that required for a monomolecular layer, when calculated from the oleic acid gain, but only 5 times the monomolecular quantity when calculated from the sodium gain. This indicates that considerable hydrolysis must have taken place in the solution. Furthermore, errors may have arisen from drainage of adsorbed material from the benzene drops, and from adsorption of oleic acid from the benzene side of the interface.

(2) Adsorption at a Gas-Liquid Interface.

Although reference should be made to the experiments of Zawidski (15) on foams produced by the addition of saponine to aqueous solutions of hydrochloric and acetic acids, Milner (16) may be regarded as the first to carry out experiments with the aim of measuring the excess surface concentration of solute at a gas-liquid interface. Bubbles of air were driven rapidly through a beaker of sodium oleate solution, and the foam produced was removed. The drop in oleate concentration in the beaker was measured by the change in electrical conductivity of the solution. The rather crude method, and the very approximate results thereby obtained were, however, sufficient to establish the order of magnitude of the adsorption. Gibbs's Equation was deduced, but the alteration of surface tension and adsorption of the soap solution with time rendered any comparison of actual and theoretical results unreliable.

Donnan and Barker (17) were the next to investigate gas-liquid adsorption. They passed a stream of gas bubbles up a vertical tower, baffled to prevent back diffusion, and the adsorbed material increased the concentration of the adsorbate in a reservoir at the top of the column. The excess reservoir concentration was estimated by the change in surface tension, as measured by drop weights from the Donnan pipette. The adsorption of nonylic acid and saponine was determined, and compared with theoretical values.

The experiments themselves are not reproducible to within several hundred percent. The observed and calculated values are compared for only one or two concentrations, and then agree only in order of magnitude. The results, then, cannot be taken as a test of the validity of Gibbs's Equation. J.W.McBain and G.P.Davies (18) contend that the experimental results of Donnan and Barker should be discarded, because the pumping action of the bubbles in passing into the reservoir would cause a remixing of the adsorbed material into the adsorption column.

Their alternative method is to pass bubbles of nitrogen along a tube inclined only slightly to the horizontal, so that the bubbles, in travelling slowly, have sufficiently long time to become saturated. At the top of the incline the bubbles pass into a vertical tube so narrow that each bubble fills its diameter. Drainage of bulk solution from these bubbles results finally in column of cylindrical bubbles in contact with one another, when only the surface layers are being carried over into the reservoir. This method is obviously only suitable for substances which can give a stable interfacial film. It is not understood here how the method was made to yield results for the negative adsorption of sodium chloride; it is to be expected that bubbles surrounded by a layer of water from which the salt was being expelled, would coalesce immediately on touching.

Adsorption values and surface tensions are determined for p-toluidine, amyl alcohol, and camphor. The excess concentration in the reservoir was detected by a Zeiss Refractometer. It was found possible to reproduce the experiments irrespective of bubble size, so long as the bubbles did not suffer elongation in passing up the vertical tube. Possible orientations of molecules at interfaces were discussed, and the adsorption values obtained were compared with the theoretical values. The agreement is not good, and in each case the amounts actually adsorbed are several times larger than either the calculated amount, or that required for the formation of a monomolecular layer.

These authors, also, suggest that Gibbs's Equation will only apply when account is taken of all factors whereby the actual surface differs from its actual conception.

This work was further developed by J.W.McBain and R.Dubois (19), who employed similar apparatus to measure the adsorption of acetic, butyric, caproic, and nonylic acids, isoamyl alcohol, phenol, resorcinol, thymol and sodium chloride. The bubbles were automatically counted by breaking a circuit between two platinum wires projecting into the adsorption tube. The area of interface occupied by a single molecule of the various compounds was deduced from X-ray literature; the quantity of solute adsorbed corresponded to 2-8 times that predicted by the equation, and 2-4 times the amount which could be accommodated in a vertically orientated monomolecular layer.

About the same time, M.E.Laing, J.W.McBain and E.W.Harrison (20) described experiments adsorbing sodium oleate on nitrogen bubbles, and found sufficient soap adsorbed to form a bimolecular layer.

Harkins and Gans (21) (22) found approximate agreement between observed and calculated values for nonylic acid at an air-water interface, but found a much higher value for amyl alcohol.

J.W.McBain and C.W.Humphreys (23) introduced the microtome method for measuring the adsorption at gas-liquid interfaces, and regard it as capable of giving sufficiently reliable results to serve as a crucial test for the applicability of Gibbs'sEquation. The solution in a trough is left stationary for as long as is necessary for equilibrium. A thin uniform layer is then cut from the surface by a rapidly moving microtome blade, and the concentrations compared in an interferometer.

J.W.McBain and R.C.Swain (24) apply this method to the adsorption of hydrocinnamic acid, phenol, and sodium chloride. They maintain that Gibbs postulated complete thermodynamic equilibrium, and that a stationary surface should be considered. They contend that the "moving bubble" method does not reach a "Gibbs" equilibrium, and that it therefore results in an adsorption value greater than the real value. It is not at all clear why this should be so, since it seems reasonable to expect that the surface friction experienced by a moving bubble would cause the adsorption to be lower, rather than higher, than that corresponding to equilibrium.

By this method, hydrocinnamic acid and phenol show positive adsorption, and sodium chloride negative adsorption. Comparisons are made between observed and calculated values, and are found to be in fairly close agreement. However, only three points are given for each substance, and the coincidence between observed and theoretical values for only three concentrations fairly close together can scarcely be taken as proof of the applicability of the equation over the whole range of concentration.

Although these authors were satisfied with the applicability of the equation, they did not think it was possible to reconcile it to systems where the surface tension has been found to go through a minimum.

In a recent communication, J.W.McBain and D.A.Wilson (25) refer to interesting results obtained with alkyl sulphuric acids; the surface tension curve reaches a minimum, and then rises again. Gibbs's Equation therefore implies that in concentrated solutions, where the surface tension is considerably lowered, there is actually negative adsorption at the interface. No such change in the sign of the slope of the tension-concentration curve has been observed in the present investigation.

These authors found that the time required for the surface to reach equilibrium was in some cases as much as 40 minutes. The matter was further considered by J.W.McBain and T.F.Ford (26) who found that b-phenyl propionic acid collected in the surface till the latter was as much as 12 hours old. This is understandable for soap-like substances, where the adsorbed molecules arrange themselves in a rigid orientation one with another. In the present work, however, where the adsorbed layers are mostly of an expanded nature, the adsorption is believed to be almost spontaneous.

(3) Adsorption of Dyes on Solid Surfaces.

W.D. and C.E.Barrett (27) adsorbed Methylene Blue on lead sulphate, and found that the position of the concentration-adsorption curve depended on the p_H of the solution.

Kolthoff and Rosenbaum (28) and Paneth (29) also investigated the adsorption of Methylene Blue on lead sulphate powder. The surface area was determined only approximately by the activity of adsorbed radioactive bodies.

N.Ando (30) adsorbed Methylene Blue on cellophane, and found that the adsorption varied with concentration according to Freundlich's Isotherm.

Adsorption Work involving Calculation from Gibbs's Equation.

Schofield and Rideal (31) (32) (33) studied the kinetic theory of surface films, and calculated adsorption values for various substances over a range of concentration. From this value, the area A occupied by a molecule on the surface was calculated. Following Langmuir's original method, the authors applied the gas laws $PV=RT$ to two dimensional layers, by substituting A for V, and F for P, where F, the lateral pressure experienced by the adsorbed molecules, is represented by the drop in surface tension. The factor FA/RT is graphed against F, for a range of long-chain fatty acids, and curves similar to those given by imperfect gases are obtained.

Wynne-Jones (34) points out that Schofield and Rideal's values for alcohol represent the total amount at the interface, not the excess. He recalculates the quantity, assuming a finite thickness for the surface layer, but his assumptions are regarded by the previous authors as being unsound thermodynamically.

These results are interesting in that they represent the extension of the Kinetic Theory to two-dimensional layers, but since the original values are calculated from Gibbs's Equation, the results can have no significance until proved by experiment.

R.Dubrisay (35) investigated the change in drop numbers of benzene in soap solutions, on the addition of electrolytes. The adsorption of soap on the benzene-solution interface is calculated, and it is suggested that the presence of electrolytes increases the amount of soap adsorbed.

Harkins and Wampler (36) measured the activity coefficients of n-butyl alcohol, and various other organic solvents in aqueous solution,by freezing point methods, and employed the results in the calculation of adsorption. The results indicated monomolecular adsorption.

Butler and Wightman (37) also investigated the surface tensions of water-alcohol systems, this time by a maximum bubble pressure method. The calculated adsorption corresponded to slightly more than a monomolecular layer of alcohol molecules.

J.L.Shereshefski (38) Applied Gibbs's Equation to the rather unusual case of a one component system. He suggested that the surface of a liquid in contact with its own vapour is neither a continuous transition nor an abrupt change, but that an adsorbed layer of vapour, denser than the vapour but less dense than the liqiud, provides the transition. By applying Gibbs's Equation to the change in surface tension and vapour density with temperature, he calculated that the thickness of this transitional adsorbed layer was rather less than one molecule.

J.W.Belton (39) (40) (41) carried out work of a different nature in measuring the surface tensions of binary liquid mixtures containing benzene. The surface tensions of the benzene-acetic acid, benzene-carbon disulphide, and benzene-carbon tetrachloride systems were found by the maximum bubble pressure method, and the adsorption of the various components calculated. It is interesting to note that for the benzene-acetic acid system, an adsorption-concentration curve with two maxima is obtained, with a point of zero adsorption between the two.

Chapter 3.

Particular Nature of this Investigation.

The previous chapter will have shown that little research on liquid-liquid interfaces has been carried out in comparison with that for other interfaces. Even where such work has been done, the "inert" medium has often been a chemically unknown quantity, and the adsorbates used have often been of doubtful stability. Not a few workers have assumed that Gibbs's Equation holds for all interfaces under all conditions. Considering the very approximate nature of the proof given for this equation, particularly for a liquid-liquid interface, this assumption seemed unjustified.

This research was therefore instigated with two purposes in mind :-

1) To measure the adsorption of chemically pure compounds at the interface between two immiscible liquids, over a range of concentration sufficiently large to represent the complete behaviour of the adsorbate, and

2) To ascertain how far Gibbs's Equation does hold for pure substances at a liquid-liquid interface.

Importance was consequently attached to the following factors :-

a) The adsorbates chosen should be soluble in only one of the two media at the interface.

b) These solutes should be capable of extreme purification, and should be stable in solution.

c) The two media should be as nearly as possible immiscible, so that the solubility of each in the other can be neglected, and the interface will be finite.

d) The adsorbent should be capable of extreme purification, and should be of known chemical constitution.

e) To minimise experimental error, solutes should be chosen which are adsorbed sufficiently to render detection easily possible by the ordinary methods available.

Choice of Adsorbents.

The interfaces employed were those between aqueous solutions of a range of dyestuffs, and

(1) Chlorobenzene.
(2) Benzene.
(3) Petroleum Ether.
(4) Air.

These media were chosen because they can be easily purified, and they represent a gradation in polar nature over a wide range.

As a general rule, simple aromatic substances are soluble in aromatic liquids, which indicates that some attraction must exist between all molecules of an aromatic nature. If, however, a more complex aromatic molecule is prevented from dissolving by other inorganic groups present, it is reasonable to anticipate that this substance will be adsorbed on to the surface of the aromatic liquid, since such an adsorbed condition would represent the closest possible approximation to solution in the adsorbent of the aromatic part of the adsorbed molecule.

Such "aromatic attractions" should therefore tend to raise the adsorption of the dyes on the two aromatis adsorbents above its value on air and petroleum ether.

Chlorobenzene has this "aromatic attraction" for an organic adsorbate, combined with the electrical attractions of its dipole, and that which its negative chlorine atom will provide for the positive sodium atom which in some cases is combined in the dyestuff molecule.

Benzene has no dipole moment, because of its symmetrical structure. The tendency of the aromatic part of the dye molecules to dissolve in the benzene will, however, be an aid to adsorption on its surface.

Petroleum Ether may be regarded for the purposes of this analogy as an almost inert medium. There can be little attraction between the aromatic dyestuff molecules and this mixture of aliphatic open-chain hydrocarbons. Any adsorption phenomena will therefore be due to simple surface tension effects.

Air. Since adsorption values have been found in general to depend on the polar strength of the adsorbent, it is reasonable to expect that adsorption on an air-water interface will correspond to that on a medium at the extreme lower end of this polar range.

A limited number of experiments on the mercury-water and nitrobenzene-water interfaces have been attempted incidentally during the course of this work, and are treated separately in Appendix 1.

Choice of Adsorbates.

Dyestuffs were chosen as adsorbates for the following reasons :-

a) They lower the interfacial tension between water and organic liquids considerably. It is probable, therefore, that they will concentrate on the interface. Accurate tension-concentration curves can be obtained, which permit calculation of adsorption values by Gibbs(s Equation.

b) Their molecules are of an aromatic nature. Consequently their adsorption might be expected to vary with the nature of the adsorbent.

c) The particular dyes chosen are readily soluble in water, but insoluble in the organic layers.

d) They are stable in solution, and do not hydrolyse to any appreciable extent.

e) They are readily purified. (see chapter 6)

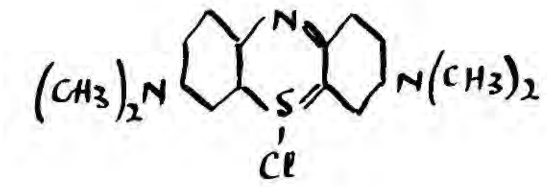
f) Small differences in the concentrations of their solutions may conveniently be detected and measured colorimetrically.

g) They exist in various states of aggregation in solution, either as single molecules or as colloidal micelles. An opportunity is thus afforded for investigating the influence on adsorption of the state of aggregation of the molecules.

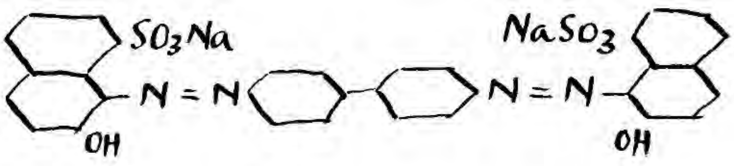
The dyes whose behaviour has been investigated are :-

Formula.

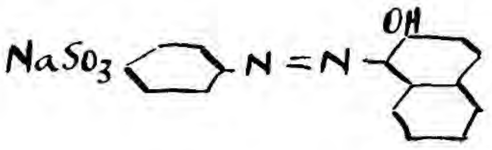
1) Methylene Blue.



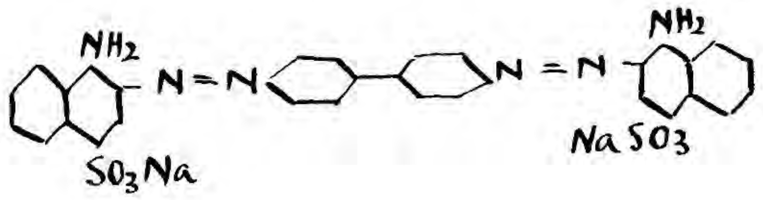
2) Bordeaux Extra.



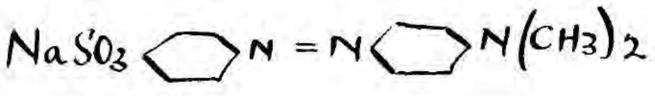
3) Orange II.



4) Congo Red.



5) Methyl Orange.



The structures of these dyes, drawn to scale from the data by Sidgwick and Bowen, (42) are shown in Figure 1.

Experiments attempted with other adsorbates are discussed in Appendix 2.

Practical Methods Employed.

a) Adsorption Measurements.

The moving bubble method was used to measure the adsorption between the dye solutions and the organic liquids. Drops of the liquid rose or fell, according to density, through a tower of the dye solution. The drops

Figure 1.

Structures of Dye Molecules.

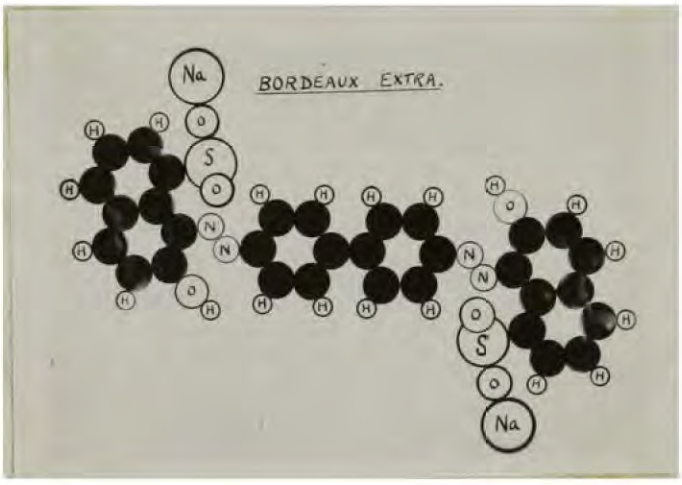
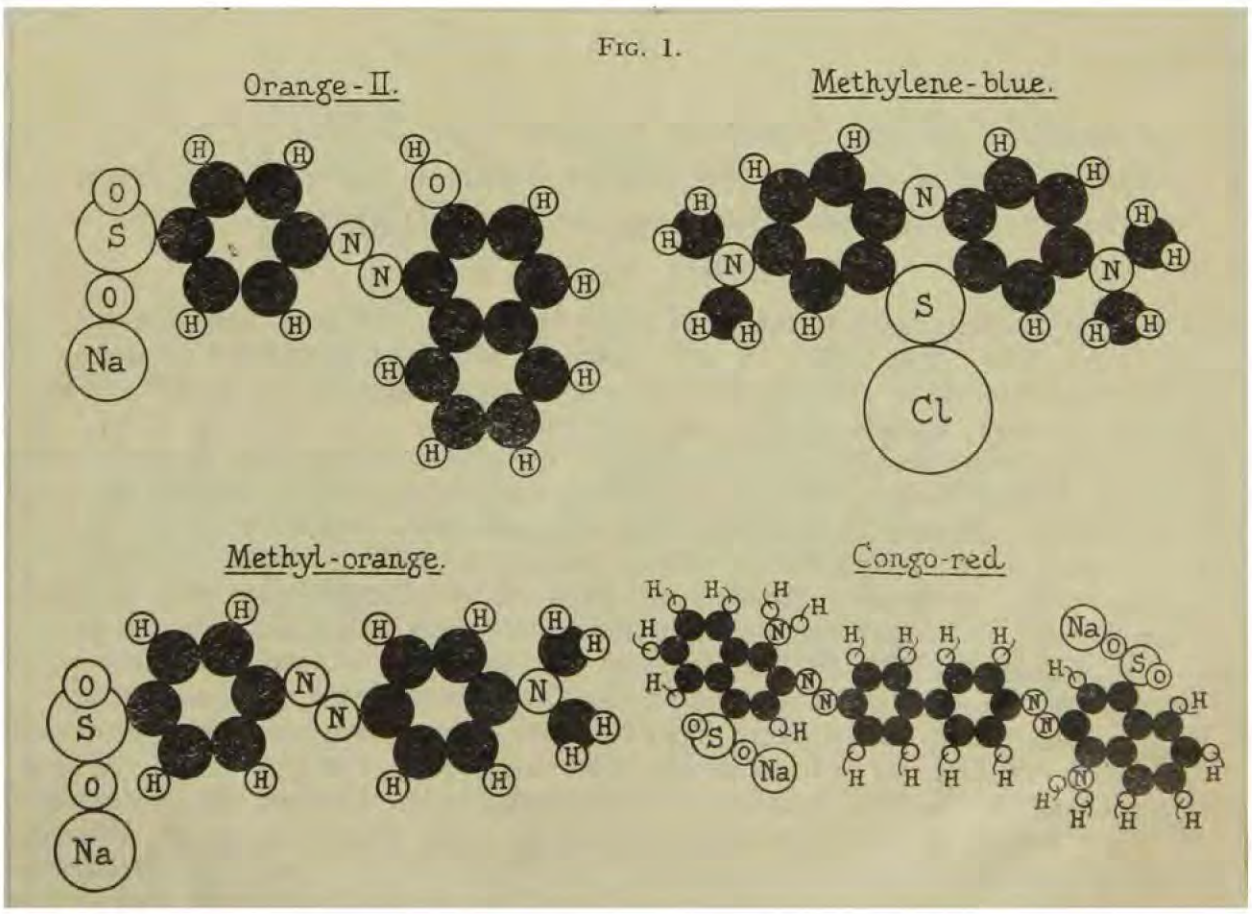


Fig. 1.



passed into a reservoir, and in coalescing with a layer of the organic liquid they cast off their skin of adsorbed dyestuff. This therefore concentrated in the reservoir, and was estimated tintometrically.

An essentially similar method was used for adsorption on an air-water interface. The bubbles passed along a tube inclined slightly to the horizontal, up a tower baffled to prevent back-diffusion, and into a reservoir. In this case, the solution from the tube from which adsorption would take place was compared tintometrically with the original solution.

b) Interfacial Tension Measurements.

The interfacial tensions of the same systems have been measured, and the adsorption calculated from Gibbs's Equation over the same range of concentration as in the actual experiments.

Tensions against the organic liquids were taken by the drop-weight method, and surface tensions were measured by the capillary rise method.

Experimental details are given fully in Chapter 6.

Chapter 4.

Theoretical Consideration of Results.

Each of the five dyes investigated is adsorbed to a greater or lesser extent on the interface between their solutions and the organic liquids. In no case was any adsorption observed on the air-water interface.

The results are arranged graphically in the following order :-

Figure 2. Adsorption of Methylene Blue.
" 3. Adsorption of Orange II.
" 4. A and B. Adsorption of Congo Red.
" 5. A and B. Adsorption of Methyl Orange.
" 6. A and B. Adsorption of Bordeaux Extra.

Each graph is composed of six curves, viz. the calculated and observed curves for adsorption on chlorobenzene, benzene, and petroleum ether.

A survey of the curves will make one feature immediately obvious. Two distinct types of concentration-adsorption curve have been found. The type differs according to the adsorbate, but is independent of whether the interface is benzene-water, chlorobenzene-water, or petroleum ether-water.

1) In Type I, as shown by Methylene Blue and Orange II, the adsorption increases with concentration to a maximum, and remains there up to the highest concentrations it has been possible to investigate.

2) In Type II, as shown by Congo Red, Methyl Orange, and to a lesser extent by Bordeaux Extra, the initial rise to a sharp maximum is quickly followed by a fall towards, and even as far as, zero adsorption.

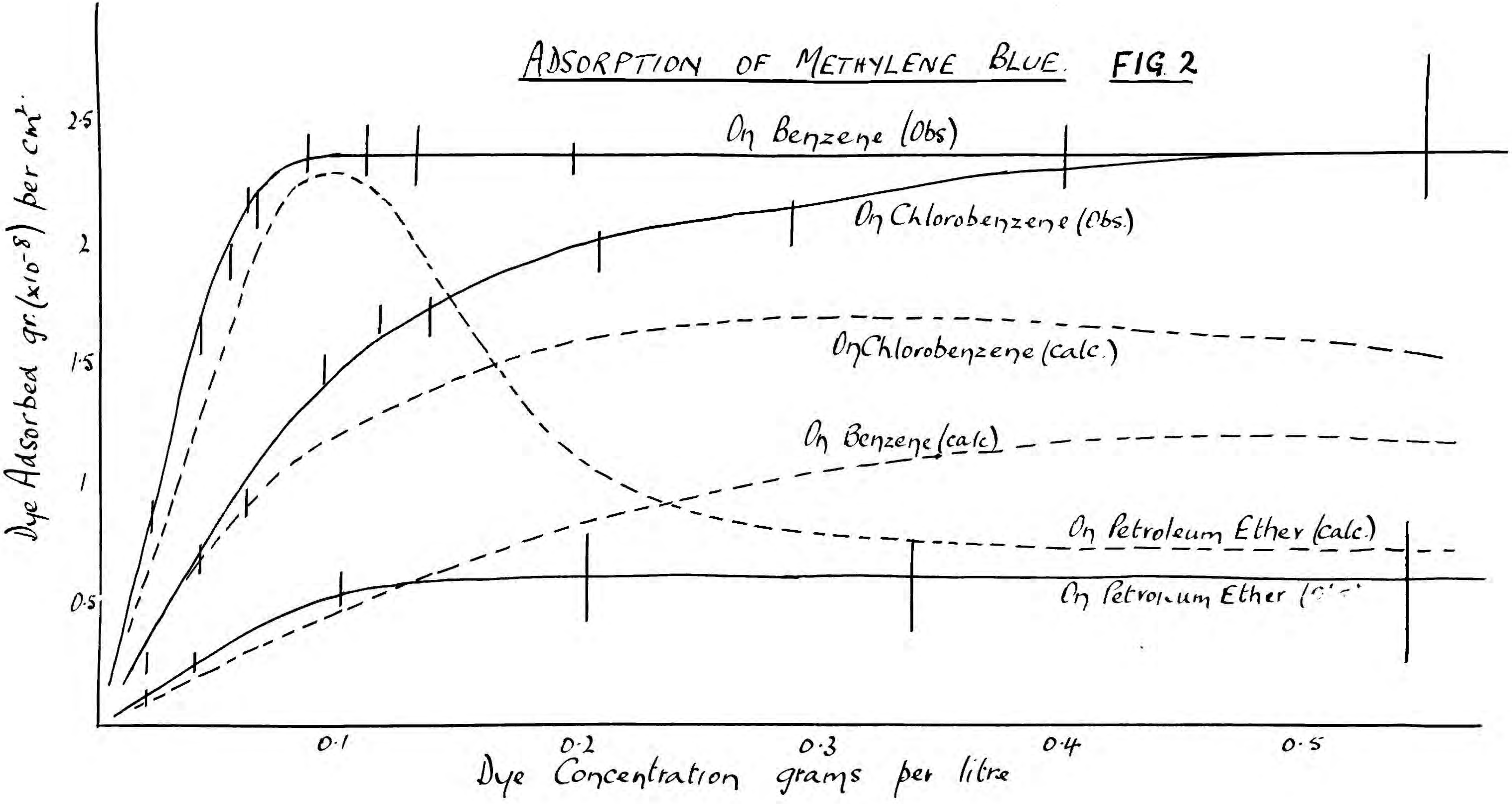
It is interesting at this point to connect this distinction in types with the nature of the respective dyes in solution. Valko (43) found Orange II to be only slightly aggregated, with a factor of 1.2, yet the factor for

Congo Red found by him was 12. This evidence is only indirect, as it refers to solutions containing excess of sodium chloride, and at a very few concentrations of dyestuff. The Congo Red factor was quoted by Robinson (44) as 8.6 , and by Quesnel (45) as being about 12. Robinson (loc.cit.) concludes from conductivity measurements that Methylene Blue is only very slightly aggregated, and that Bordeaux Extra behaves as though in solution it is composed entirely of single molecules. No published evidence regarding the state of aggregation of Methyl Orange in solution can be found.

The various sets of adsorption curves will be dealt with individually. The experimental error for each point is represented by a vertical line through that point covering the possible range of error.

The observed and calculated curves are shown respectively by continuous and dotted lines.

ADSORPTION OF METHYLENE BLUE. FIG. 2



Methylene Blue.

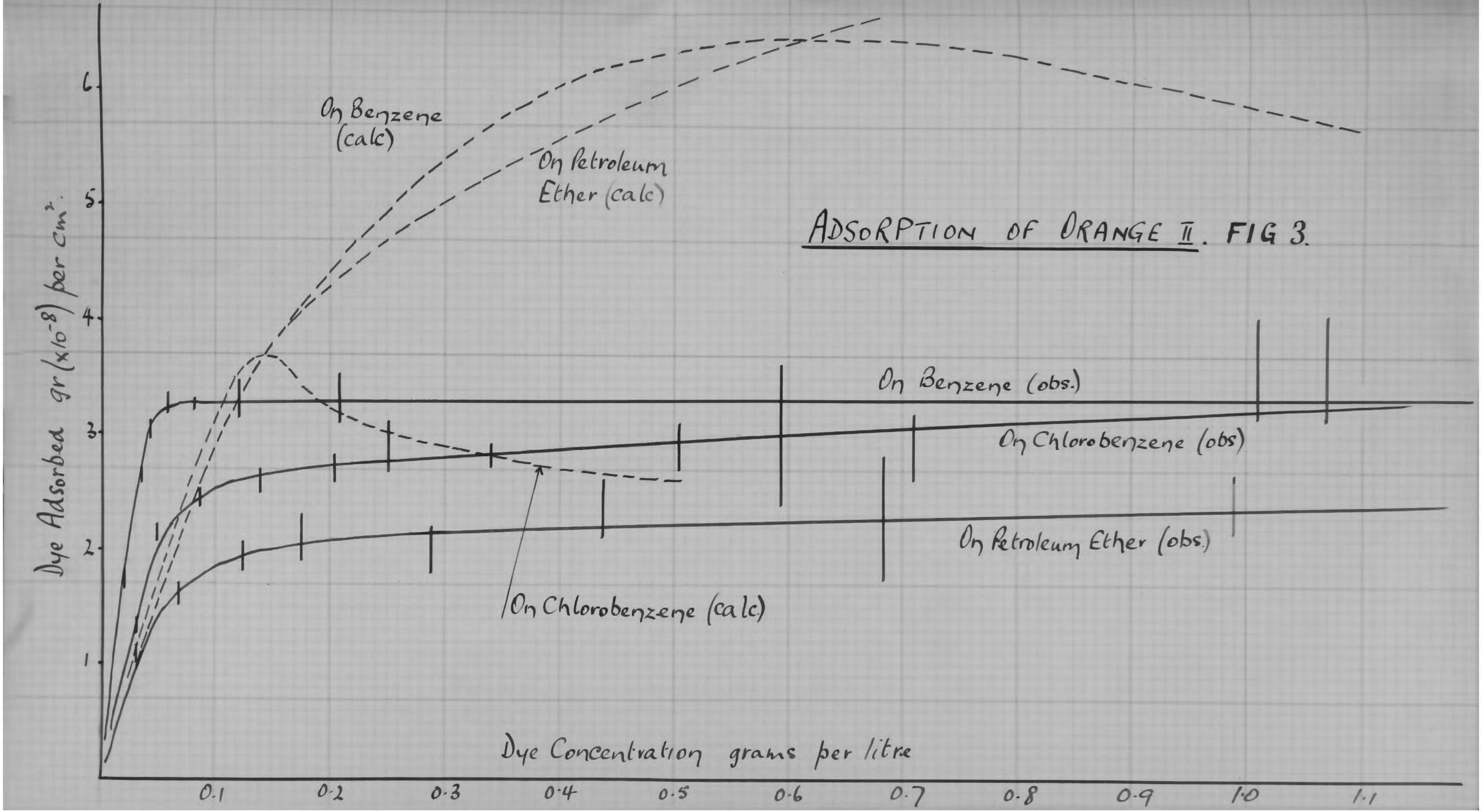
This dye is simple in solution , and shows adsorption curves of the first type. The adsorption on benzene rises fairly rapidly to a maximum value of 2.4×10^{-8} gr./cm^{2}, and remains there up to a concentration of 0.6 gr./litre. For experimental reasons explained later, it was not possible to investigate the adsorption to any higher concentration. Therefore, although the adsorption value may fall again at some higher concentration, the long flat maximum obtained in this curve indicates the presence of some influence which is not brought into play in the adsorption of solutes of Type II.

The adsorption coefficient on chlorobenzene rises eventually to the same maximum, but only reaches it at a much higher concentration. At first sight chlorobenzene, the more polar liquid, might be expected to adsorb more dye than would benzene. The reverse conditions found to hold can be explained in this case as due to the repulsive forces existing between the two negatively polar chlorine atoms in both Methylene Blue and chlorobenzene. A much higher bulk concentration, and therefore a higher local osmotic pressure, is necessary to maintain the maximum amount of dye on the chlorobenzene surface, than is necessary for the benzene surface.

The adsorption on petroleum ether is much less, and shows no sign of finally reaching the same maximum. The smaller adsorption value naturally incurs greater experimental errors, but even allowing for this, the adsorption shows little sign of falling towards zero. This small adsorption value is quite what might be expected as a result of the polar weakness ofcthe adsorbent.

The experimental and calculated curves on benzene and chlorobenzene show obvious discrepancies, and though in the case of petroleum ether the two curves agree within the limits of experimental error over a small range of fairly high concentration, for small concentrations the deviation is even more apparent than for the other two adsorbents. It is interesting to note that all three calculated curves go through a definite maximum.

No adsorption on the air-solution interface could be detected. If any such adsorption does exist, it has too small a value to be detectable by the means employed in this investigation.



ADSORPTION OF ORANGE II. FIG 3.

Orange II.

Like Methylene Blue, this dye is simple in solution, and gives similar adsorption curves. The adsorption on benzene rises rapidly to a maximum value of $3,25 \times 10^{-8}$ gr/cm^2, and again remains there up to the highest concentrations studied. The decreasing order of adsorbing power is again

benzene, chlorobenzene, petroleum ether.

The adsorption of Orange II on petroleum ether is relatively greater than that of Methylene Blue, and it is possible that at some higher concentration the adsorption on petroleum ether may reach the same maximum value that is reached on benzene and chlorobenzene.

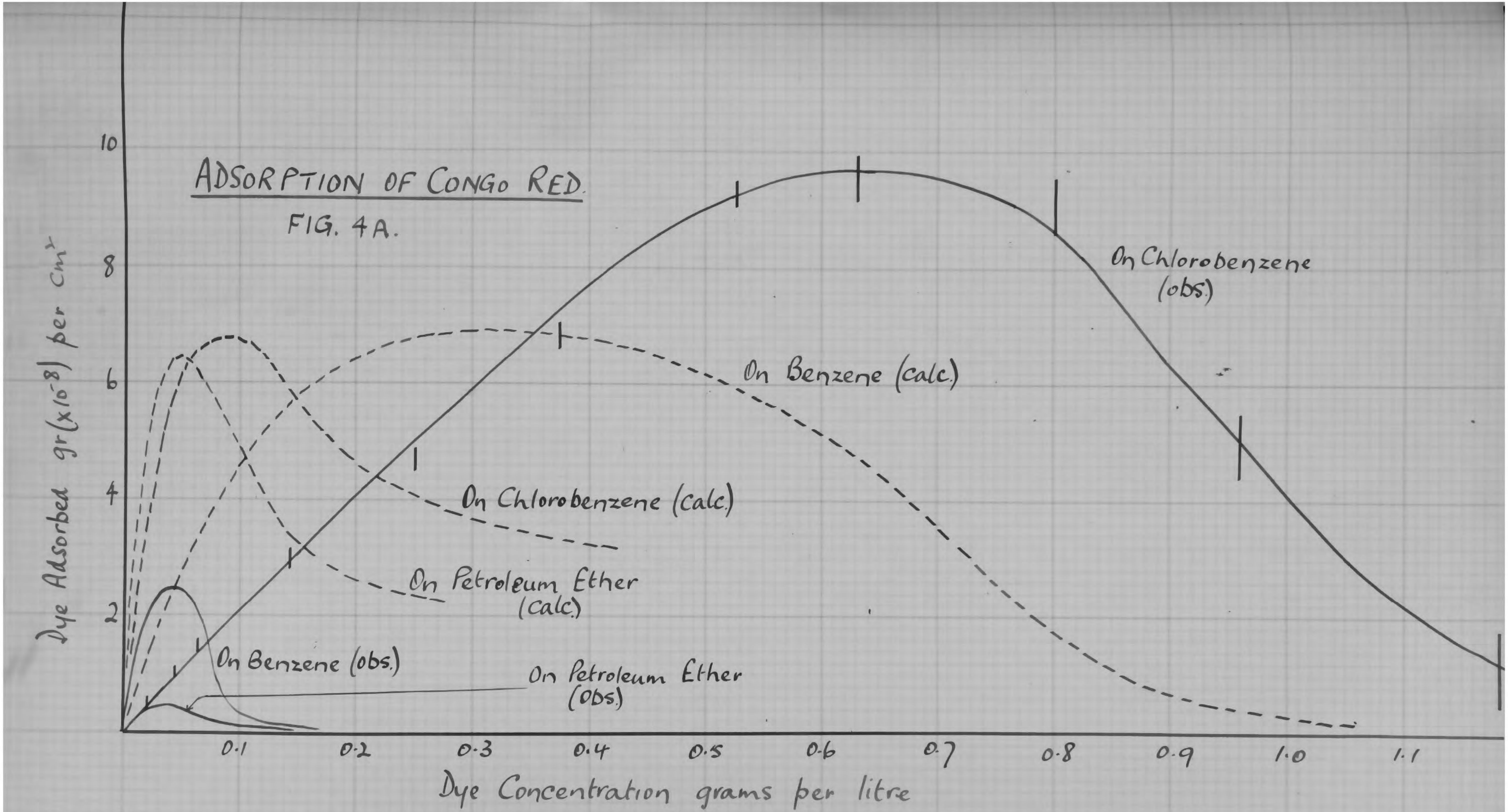
The adsorption on chlorobenzene does not reach the same maximum value as on benzene until a much higher concentration. It has not been possible to explain this behaviour on the basis of chemical affinities and repulsions, since the attraction between the Cl' atom of the chlorobenzene, and the Na^+ atom of the OrangeII , should on this theory result in a greater adsorption on chlorobenzene than on benzene.

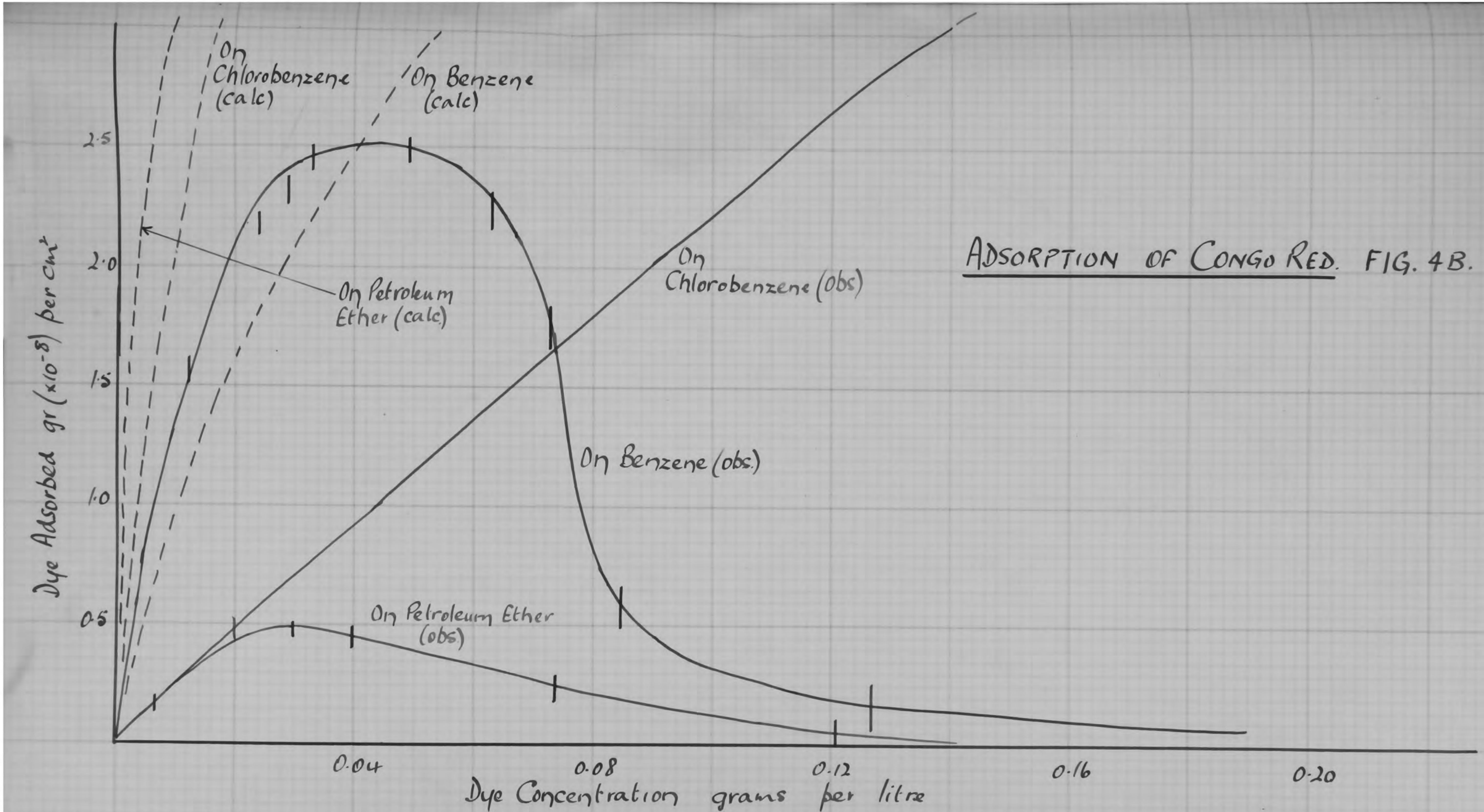
No connection can be observed between the calculated and observed curves for any one adsorbent.

No adsorption was detected on the air-solution interface.

ADSORPTION OF CONGO RED.

FIG. 4A.





ADSORPTION OF CONGO RED. FIG. 4B.

Congo Red.

Because of the large differences in magnitude of the adsorption values found for Congo Red, all the experimental points cannot be shown conveniently on one graph. Figure 4A shows the complete adsorption curves on one scale, and in Figure 4B, the scale has been magnified in order to show the experimental points on the benzene and petroleum ether curves. (The results for Bordeaux Extra and Methyl Orange are also given in this way).

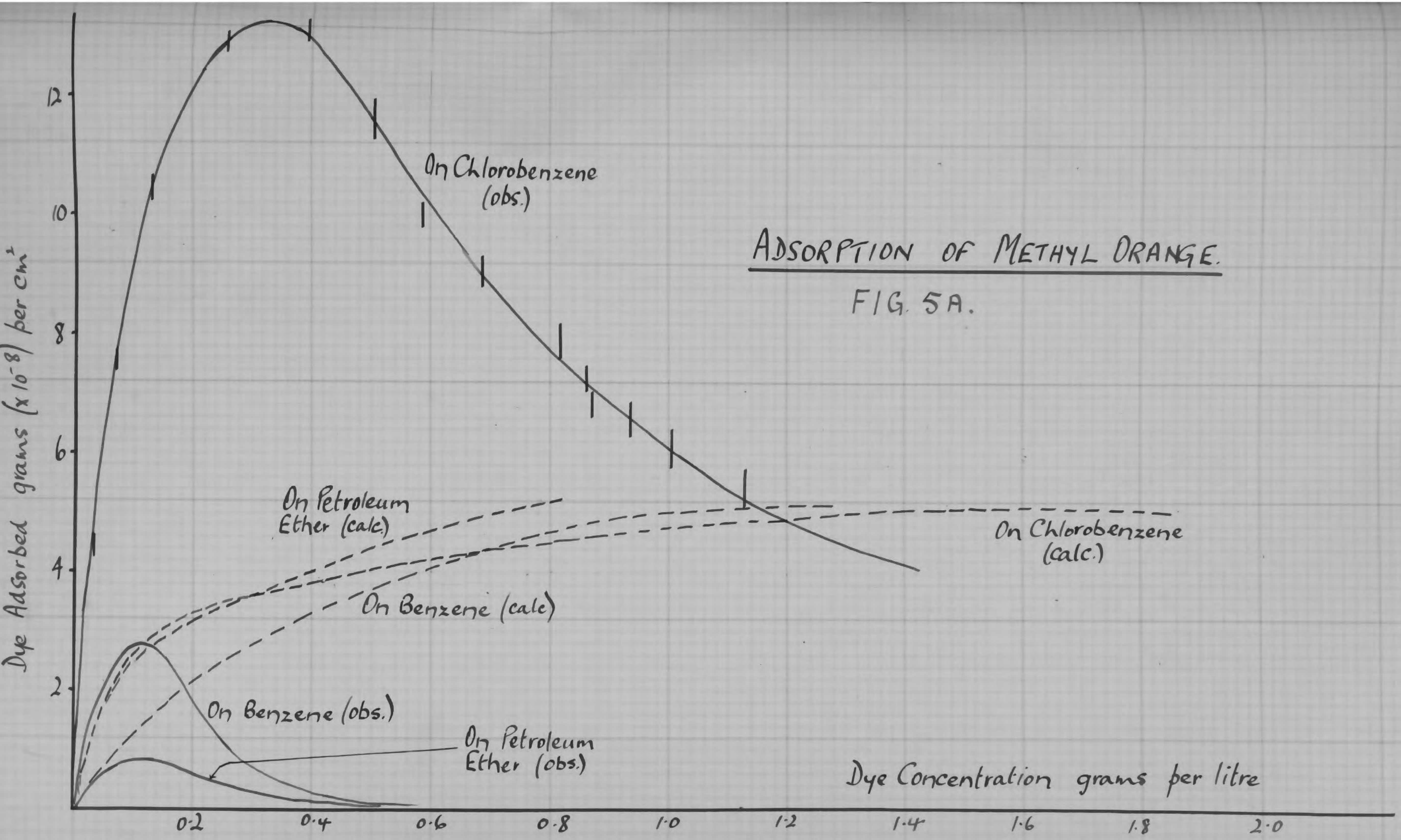
Congo Red shows adsorption curves of the second type. For each adsorbent, the adsorption rises to a maximum, which is followed in all cases by a fall, eventually to a zero value.

One of the most striking features of the Congo Red curves is the difference in magnitude between the adsorption values on chlorobenzene and petroleum ether. The influence of the polar strength of the adsorbent on the adsorption is very marked. The attraction which a strongly polar adsorbent like chlorobenzene can exert on Congo Red results in a maximum adsorption coefficient of 1.0×10^{-7} gr/cm^2, which is about 20 times the maximum value on petroleum ether.

Adsorption on benzene takes place to a much smaller extent than on chlorobenzene, and the adsorption on petroleum ether is almost negligible compared with the other two.

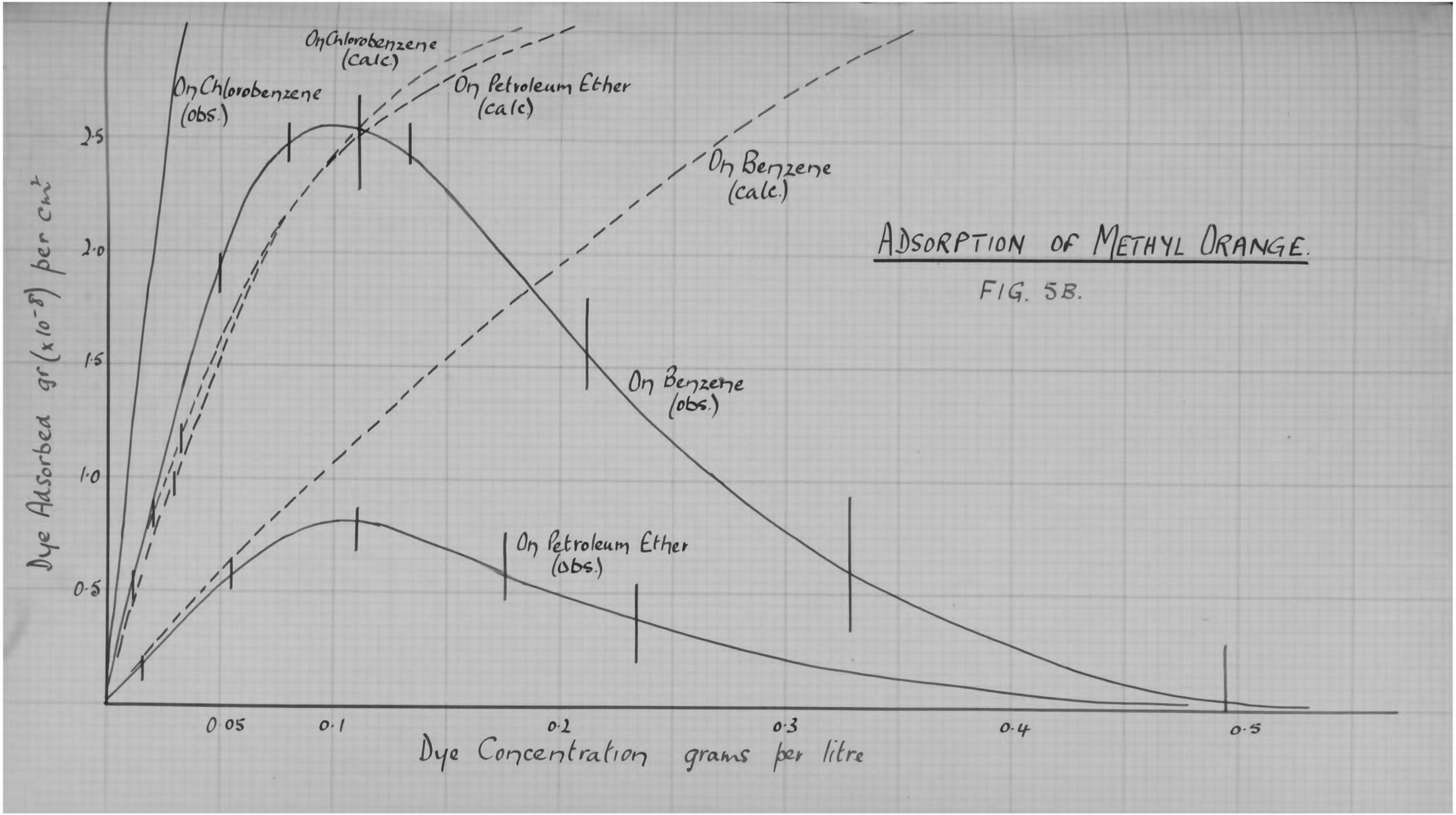
No correspondence whatever exists between the calculated and experimental curves.

No adsorption was found on the air-solution interface.



ADSORPTION OF METHYL ORANGE.

FIG. 5A.



ADSORPTION OF METHYL ORANGE.

FIG. 5B.

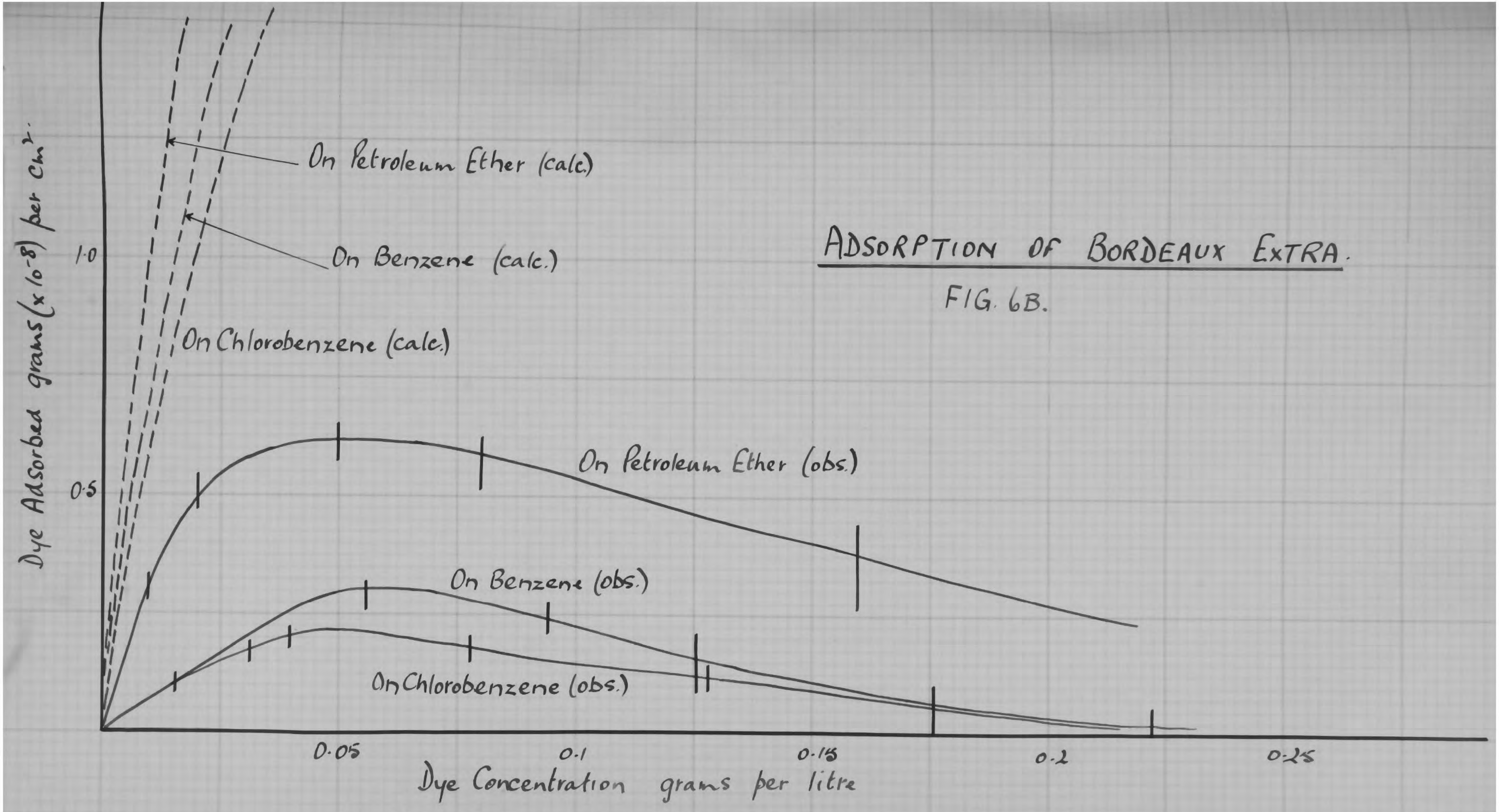
Methyl Orange.

This dye gives adsorption curves very similar to those of Congo Red, and again shows the influence which the adsorbent can have on the extent of adsorption.

The adsorption coefficient on chlorobenzene reaches the greatest value observed throughout this investigation, viz. 1.3×10^{-7} gr/cm^2, which is approximately 5 times that on benzene, and 15 times that on petroleum ether.

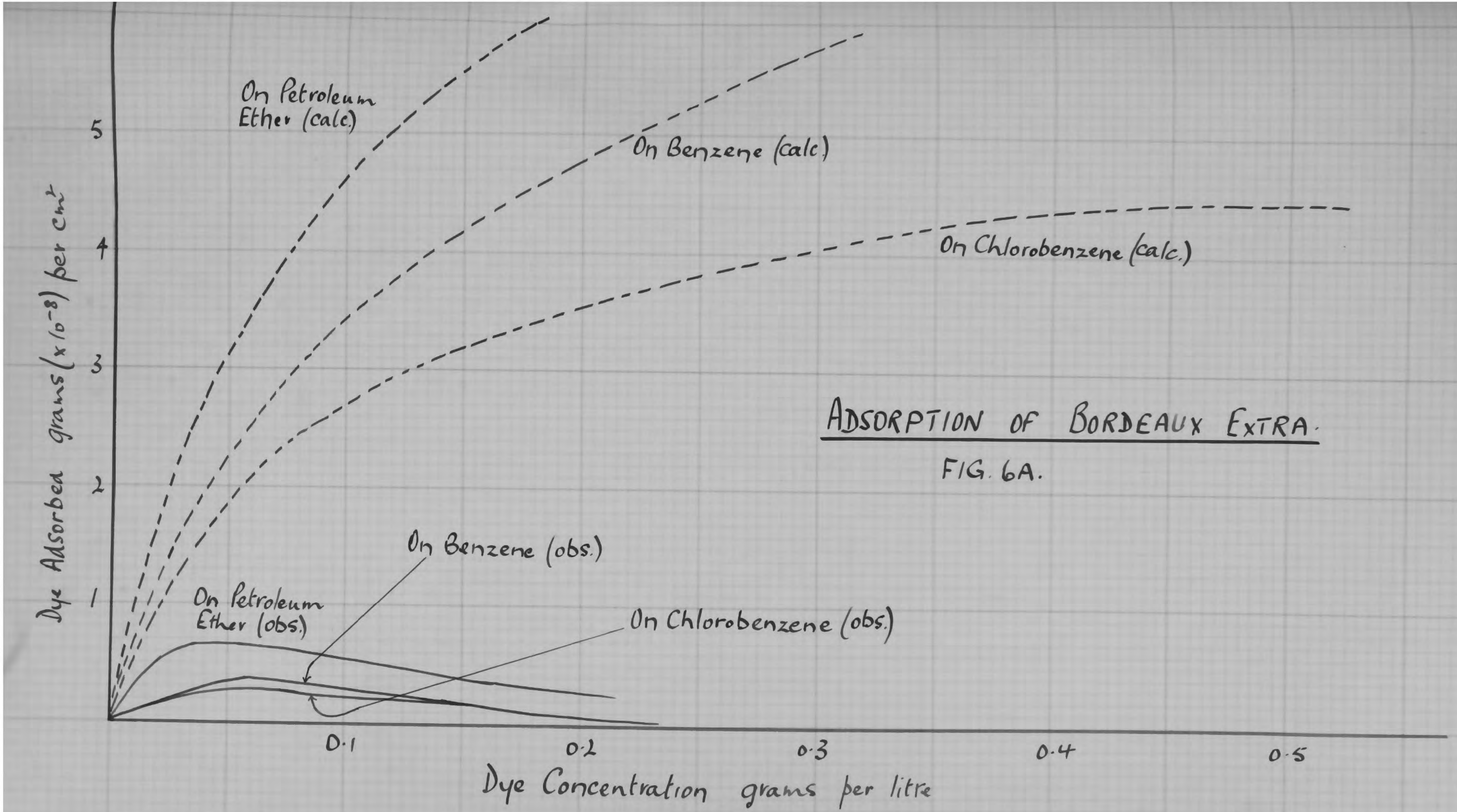
The observed and calculated curves are again completely different.

No adsorption was observed on the air-solution interface.



ADSORPTION OF BORDEAUX EXTRA.

FIG. 6B.



ADSORPTION OF BORDEAUX EXTRA.

FIG. 6A.

Bordeaux Extra.

The results with this dye are not in accordance with the general priciples which lead to the classification of the other four dyes into two types. It has been found impossible to explain the adsorption curves on any basis whatsoever.

The dye is simple in solution. Therefore it might be expected to show adsorption curves similar to those of Methylene Blue and Orange II. Actually, the adsorption is extremely small. It does not maintain its maximum value, but falls away towards zero adsorption like the dyes of Type II , and reaches a negligible adsorption when the dye solution is still very dilute.

However, unlike Congo Red and Methyl Orange, the effect on adsorption of change in the polar nature of the adsorbent is the exact reverse of that found for these two dyes. Petroleum ether adsorbs most, benzene less, and chlorobenzene least, dyestuff.

Again, the discrepancies between calculated and observed adsorption values for this dye are the most outstanding of all. Throughout the greater range of concentration, the two values are not even of the same order.

Again no adsorption could be detected on an air-solution interface.

General Observations.

The curves given by dyes of Type II possess the qualitative features of a "Gibbs" curve. The form of an adsorption curve calculated from Gibbs's Equation depends, of course, on the manner in which the interfacial tension varies with the concentration. In all the cases which have been studied, as the concentration increasesfrom zero, $\frac{d\sigma}{dc}$, which is large at low concentrations, either finally approaches zero asymptotically, or else is diminishing rapidly. Consequently, the calculated adsorption rises from zero, passes through a maximum, and must finally approach zero again, in spite of an increasing concentration term.

However, the shapes of the experimental curves for Congo Red and Methyl Orange, though similar to those required by Gibbs's Equation, could equally well be accounted for assuming that only single molecules are adsorbed.

It may be assumed that in a solution of Congo Red the equilibrium

$$nC \rightleftharpoons C_n$$

exists, where n is the number of single molecules C which must aggregate to form a micelle C_n. Increase in concentration will move the equilibrium conditions from the left-hand side,(representing single molecules of dye in dilute solution), to that of the aggregated state of the dye in stronger solutions. Two opposing factors then operate simultaneously to influence adsorption. On the low concentration side of the maximum, adsorption of single molecules increases with rising concentration, but thereafter, this factor is outweighed by the shortage of single molecules caused by the aggregation in solution to form micelles.

It has not been possible to correlate clearly the contrast between the two types with any structural features in the respective simple molecules. There is obviously a change, increasing rapidly with concentration, which occurs to the solutes of the second type, but not to those of the first. It becomes manifest by the falling off towards zero adsorption, and but for its operation, the maximum adsorption attained in the second type would be greater than is actually the case. However, an aggregation would decrease the concentration in the same sense, and it is noteworthy that Congo Red is known to be highly micellular, while Orange II and Methylene Blue are mainly simple in solution. Further, in so far as adsorption is due to polar influences, it is to be expected that the monomeric form of a given polar solute will be more adsorbed than a coupled polymeric form of it, because a dipole association which constitutes a polymeride of the form $\begin{matrix}\ominus & - & + \\ + & - & \ominus\end{matrix}$ necessarily makes the residual field of force less than that of the unassociated molecule.

Discrepancies between calculated and experimental curves.

It has already been observed that Gibbs's Equation is intended to apply only to the adsorption of a single component from a solution in which its behaviour is ideal with reference to concentration, and that it applies only to interfaces unaffected by electric charges.

In actual working, however, it is not possible to realise these ideal conditions, and the deviations of the predicted values from the actual equilibria must be due to the influence of the non-ideal conditions unavoidably present in any practical experiment. The equation gives values of approximately the right order of magnitude, and is in much closer agreement with the results given here than with those of previous liquid-liquid adsorption work, but there can be no doubt as to the influence of the factors here discussed.

These disturbing factors can be classified under convenient headings :-

1) Electrical Effects.
2) Nature of dyes in solution.
3) Polar influences of adsorbent.
4) Adsorption of other components.

1) Electrical Effects.

All the solutes are electrolytes, in which either the cation (Methylene Blue) or the anion (the others) is complex. The dye molecules will constitute a dipole, the action of whose field of force will be to orientate the molecules adsorbed on the interface, where an electrical double layer must therefore be formed. It is permissible to doubt whether the interfacial adsorption in a polar liquid like water is ever free from the formation of electrical double layers, since even at the interface between pure water and some other medium, the fields of force which surround the water dipole must result in the partial orientation of the layer of water molecules at the interface.

This is in accord with the present views on the structure of liquid surfaces, due originally to Langmuir (2) and Harkins, et alia (3). The chief factor determining the surface tension of a liquid in contact with air is the structure of the surface layer of atoms. Because of its residual valency, the more active part of the molecule is orientated inwards towards the liquid, with the result that the surface tension is largely dependent on the least active part of the molecule. If, however, an organic acid and water are in contact, the polar carboxyl group will be attracted towards the water, and the remaining organic radical will consequently be orientated towards the organic liquid. In view of such evidence, Harkins has pointed out that when two liquids are in contact, their like parts orientate towards one another at the interface in such a way as to make the transition to the adjacent phase less abrupt.

The interface therefore possesses a definite molecular structure, and cannot be regarded as being mathematically plane. The existence of surface structure introduces a factor which must nesessarily be included in any formula representing the behaviour of a polar adsorbate. It is probable that at the interface between chlorobenzene and water, the chlorine atoms are orientated towards the aqueous layer. The double bonds in the benzene ring are considered from this point of view to be slightly polar, and therefore at the benzene-water boundary the benzene molecules are probably lying flat on the interface.

This orientation occurs to perhaps a rather less marked extent on the aqueous side of the interface. It is interesting to recall here that Alty (46) found that bubbles of air passing through the purest water obtainable were still sufficiently charged to move in an electric field. This negative electric charge, whose origin is in the electrical double layer caused by orientation of the H atoms of the surface water molecules towards the water, should be correspondingly greater for an interface which is at least partly taken up by more complex and more strongly polar dye molecules. Alty noted that two bubbles of air repelled one another; the same phemomenon has been observed in these experiments, for drops of organic liquid passing through dyestuff solutions. When two approaching drops reached a certain minimum distance apart, they revolved rapidly round one another, and then flew apart.

It is generally agreed that the presence at the interface of this potential difference must invalidate the applicability of Gibbs's Equation. Lewis (47) suggested a modified form of Gibb's Equation which included a term depending on the potential difference across the interface, but the equation has received little experimental support. That adsorbed polar molecules should move or orientate in the potential field due to the interface is understandable, but no satisfactory mechanism has so far been suggested to explain precisely what influence this potential difference has on the adsorbed molecules.

2) Nature of dyes in solution.

Evidence has already been given (page 27) that one at least of these dyes does not behave in solution as an ideal solute, even in the dilute solutions in which it is used. Thus the behaviour of Congo Red, with an aggregation factor of 12, must be very different from that of an ideal solute, and though Methylene Blue, Orange II, and Bordeaux Extra have aggregation factors only slightly larger than one, it is conceivable that the activity of their solutions, even for the low concentrations used, may be appreciably different from their actual concentration. This point is treated more fully later.

3) Polar influences of the adsorbent.

From the derivation of Gibbs's Equation it follows that if a certain concentration of dye lowers the interfacial tension between its solution and two liquids respectively, at the same rate, then the adsorption of dye on each of the two interfaces should be the same. This research has shown that another influence, the polar attraction exerted by the adsorbent, can influence the adsorption to an even greater extent than does the change in interfacial tension.

Only one example of this need be given. A solution of Methyl Orange, of concentration 0.1gr/litre, lowers the interfacial tension of water against chlorobenzene and petroleum ether by the same amount, viz. 8.8 dynes/cm. The shapes of the tension-concentration curves between these limits are approximately the same, from which facts Gibbs's Equation predicts similar adsorption curves on the two media. Actually, the adsorption on chlorobenzene reaches a value approximately 15 times that on petroleum ether. This difference is attributed tovthe polar attractions exerted by the chlorobenzene.

The influence of this factor on the adsorption can similarly be traced throughout the whole investigation. Accordingly, it is not surprising that the results , which it has been possible to make reproducible and regular, show marked quantitative deviations from the predictions of Gibbs's Equation in all cases studied.

4) Adsorption of other components.

Gibbs's Equation applies to the adsorption of a single component, and the presence of any other adsorbate requires the introduction into the equation of a further term involving the chemical potential of that component. The dyes have been purified to such an extent that the presence of even the slightest trace of any other adsorbable impurity is very improbable.

There are various other factors, however, whose influence may be appreciable :-

a) No two liquids are completely insoluble in one another. Therefore in the case of (say) benzene and water, the actual boundary may be confused by the adsorption on to the interface of benzene from the aqueous layer, and water from the benzene layer.

b) Gortner, (Outlines of Biochemistry) has found that water is itself adsorbed on to surfaces, and that in this "bound" state it can exhibit entirely different properties from water in bulk. The molecular close-packing of such "bound" water results in a density greater than one. Though it is not desirable to draw too close a comparison between the surfaces of living organisms used by Gortner, and those employed here, it is nevertheless possible that in these experiments adsorbed water molecules may increase the density of the aqueous phase in the neighbourhood of the boundary, and so give rise to conditions there quite different from those assumed by Gibbs.

Qualitative agreement between the results.

If the adsorption curves obtained by theoretical and practical means be compared, there seems to be little agreement of any kind. If, however, the lowering of interfacial tension caused by the dye be taken as a measure of thepredicted extent of adsorption, a certain qualitative agreement can be noticed. The interfacial tension curves are included here for this purpose. Ignoring for the present the shapes of the adsorption curves, some slight agreement seems to exist between the extent of lowering of surface tension, and the magnitude of the adsorption observed experimentally.

a) Petroleum Ether curves.

Bordeaux Extra and Methyl Orange show very similar surface tension curves, and their adsorption curves are almost identical. At small concentrations, the tension curve for Methylene Blue is also similar to these two, and its adsorption curve rises to a similar maximum. Orange II causes the greatest lowering of tension, and it is the only dye whose adsorption on petroleum ether reaches any appreciable magnitude.

b) Chlorobenzene curves.

Bordeaux Extra has the least effect on the tension, and its adsorption has the least value for any dye on chlorobenzene. Methylene Blue has the next least effect,

FIG. 7.

INTERFACIAL TENSIONS OF DYE SOLUTIONS AGAINST PETROLEUM ETHER.

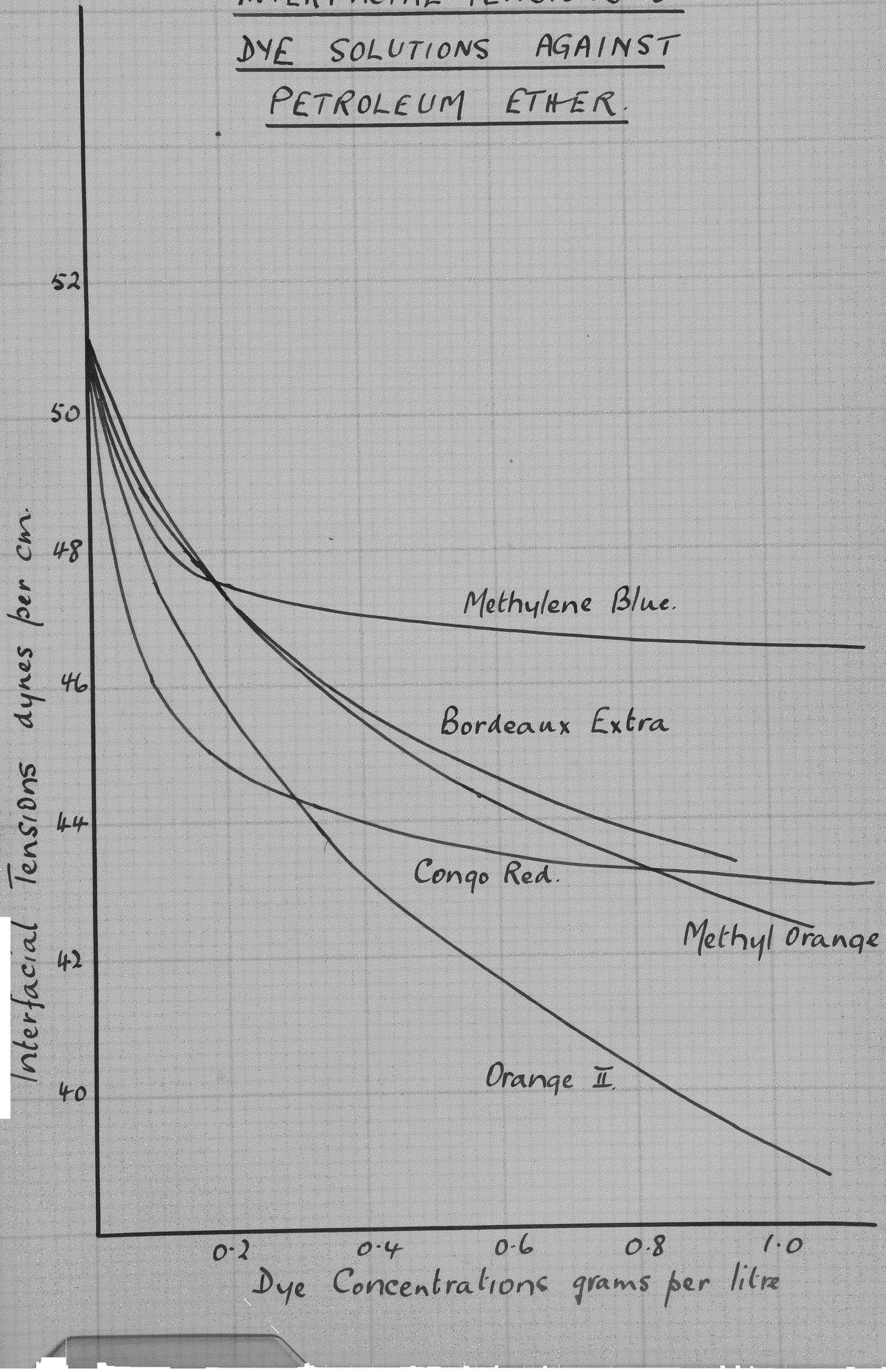


FIG. 8.

INTERFACIAL TENSIONS OF DYE SOLUTIONS AGAINST CHLOROBENZENE.

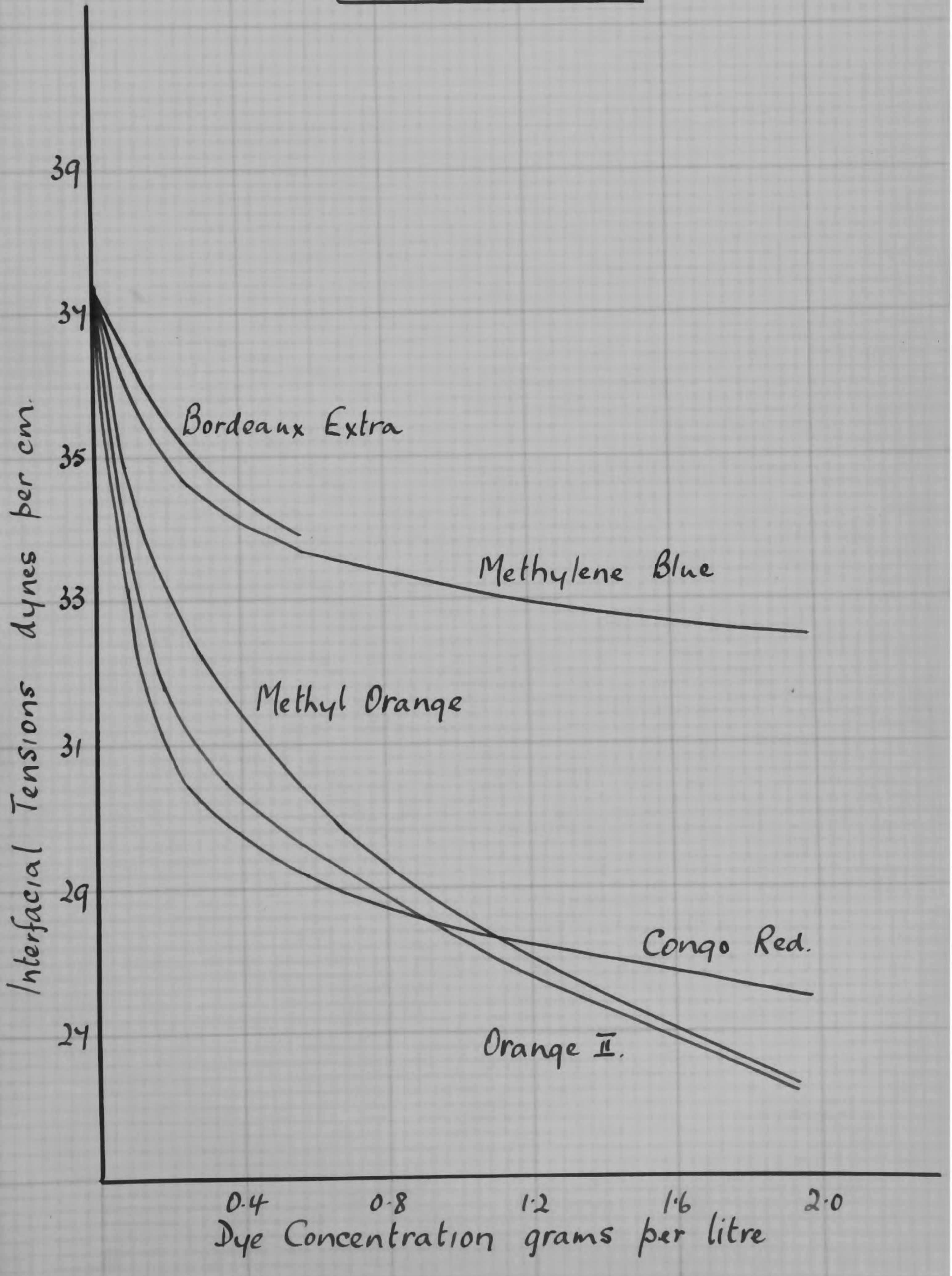
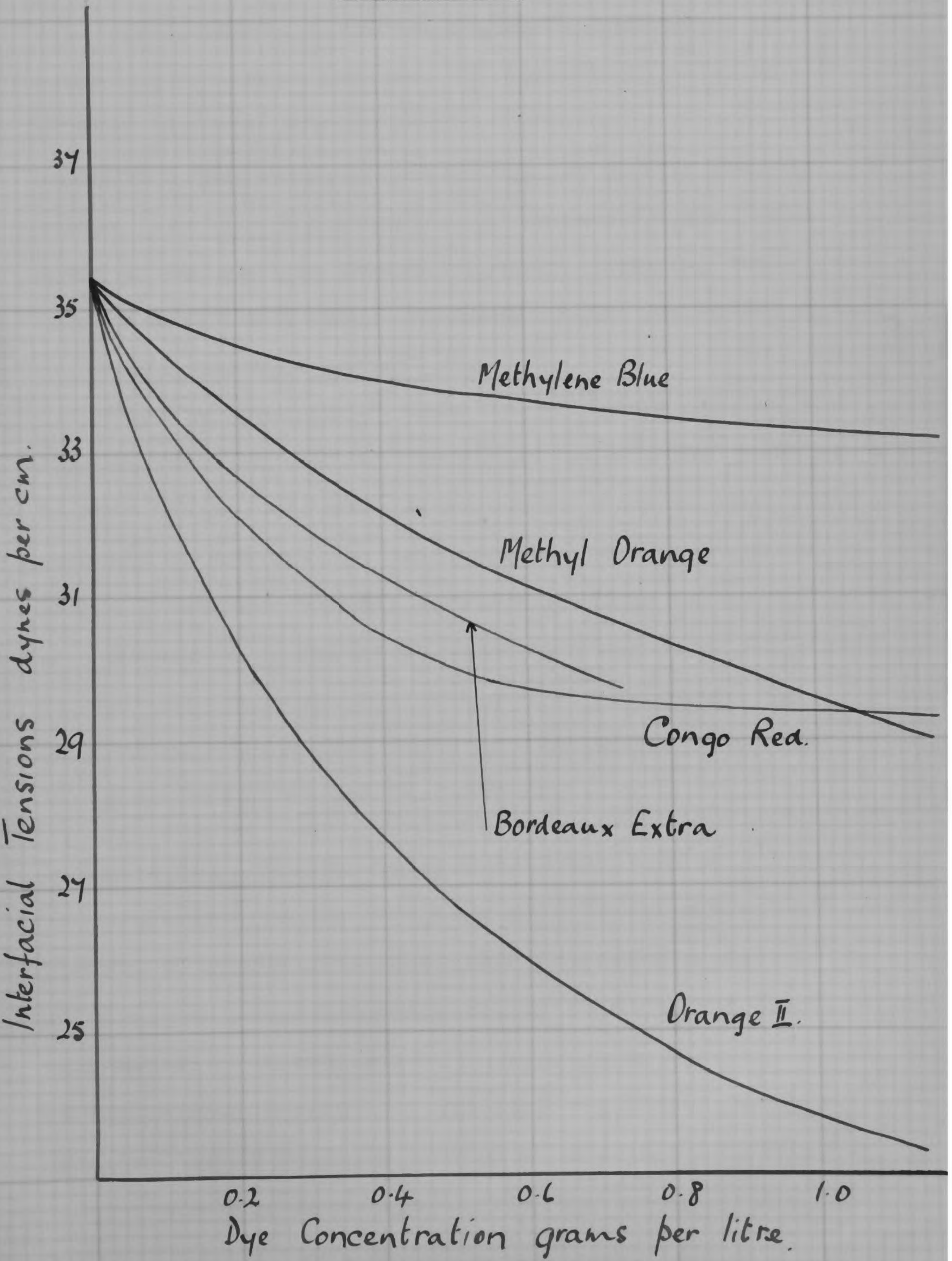


FIG. 9.

INTERFACIAL TENSIONS OF DYE SOLUTIONS AGAINST BENZENE.



and next to Bordeaux Extra, it has the least adsorption value. Methyl Orange, Orange II and Congo Red all show a much greater lowering of tension, and have all a much greater adsorption value. The very large adsorption values for Congo Red and Methyl Orange are not reflected, however, in the interfacial tension curves.

c) Benzene curves.

Especially at higher concentrations, OrangeII has a greater lowering effect on the tension than have the other dyes, and it maintains a greater adsorption a~~f~~t these higher concentrations. The increasing order of ability to lower tension is :-
Bordeaux Extra,Methylene Blue,Congo Red,Methyl Orange, Orange II. With the exception of Bordeaux Extra, this order is the same as that obtained by comparing the maximum adsorption values attained by the respective dyes.

d) Surface tensions against air.

Surface tensions of these dye solutions against air were measured by the capillary rise method. The lowering is very slight, and methods much more accurate than those commonly in use will be necessary before actual curves can be obtained. Gibbs's Equation predicts zero adsorption of a solute on an interface whose tension is not influenced by its presence, and this prediction is confirmed by experiment. In no case could any adsorption of dye on the air-water interface be detected.

Attempts to reconcile curves.

Various attempts have been made to reconcile the calculated curves with those obtained experimentally, by allowing for each disturbing factor in turn, but they have met with no success.

1) The molecular weight of the single molecule has been used in Gibbs's Equation throughout the calculations. The solute concentrations were alternatively expressed in

terms of a polymeric molecule, and a range of aggregation factors introduced. No closer agreement was observed.

2) The shapes of the adsorption curves for solutes of Type II can be explained qualitatively by assuming that only single molecules are adsorbed. No reconciliation could, however, be made by assuming only a fraction of the dye to be available for adsorption, whether this fraction be constant or varying with the Law of Mass Action, or whether single molecules or aggregates constitute the available fraction.

3) <u>Substitution of Activity for Concentration</u>.

Much emphasis is often rightly laid upon the approximate nature of the equation $\Gamma = -\frac{c}{RT} \cdot \frac{d\sigma}{dc}$

and the desirability of using instead the exact relation

$$\Gamma = -\frac{a}{RT} \cdot \frac{d\sigma}{da}$$

Since, however, activity coefficients are defined as approaching unity at great dilutions, the values of Γ calculated from these two equations should approach one another as the concentration of the solution diminishes. If, therefore, the use of activity instead of concentration was the only cause of the discrepancy between experimental results and values of Γ calculated from the approximate equation, the experimental and calculated curves should coincide at very low concentrations. Out of the 15 adsorption curves which have been obtained, this coincidence has been found in only three cases, viz.

Methylene Blue on chlorobenzene,

Congo Red on Benzene, and

Orange II on petroleum ether.

In all other cases, the slopes of the curves as concentration approaches zero are markedly different.

The values of activity coefficient necessary to bring the observed and calculated curves into coincidence have been determined as follows :-

With the usual notation, let Γ_o and Γ_c represent the amounts of adsorption observed, and calculated from the approximate equation, respectively.

Then
$$\Gamma_c = -\frac{c}{RT}\cdot\frac{d\sigma}{dc}$$

Therefore
$$\left(\frac{a}{c}\cdot\frac{dc}{da}\right)\Gamma_c = -\frac{a}{RT}\cdot\frac{d\sigma}{da}$$

Now if the activity equation is capable of giving results in agreement with experiment, Γ_o should equal $-\frac{a}{RT}\cdot\frac{d\sigma}{da}$

Hence,
$$\left(\frac{a}{c}\cdot\frac{dc}{da}\right) = \frac{\Gamma_o}{\Gamma_c} = f(c) = \text{a function of } c.$$

The values of Γ_o and Γ_c may be read off from the curves, and thus f(c) evaluated.

Further,
$$a\cdot\frac{dc}{da} = c.f(c)$$

Hence
$$\int_{c_1}^{c_2}\frac{dc}{c.f(c)} = \int\frac{da}{a} = \Big[\log_e a\Big]_{c_1}^{c_2}$$

The term a may now be evaluated for any desired value of the concentration c.

The factor $\frac{1}{cf(c)}$ is plotted against c, and the value of the integral between any limits c_1 and c_2 may be read off by measuring the area under the curve between these limits ; the smaller limit c_1 is chosen as that point where the observed and calculated curves begin to separate, since it is only at concentrations above this value that activity considerations come into play.

The value of $\log_e a$ corresponding to this zero value of $\int\frac{dc}{cf(c)}$ is obtained by direct calculation, as the following example from the adsorption of Congo Red on benzene shows.

Example

The curves separate at concentration = 0.01 gr/litre

Therefore c_1 = a = 0.01 gr/litre

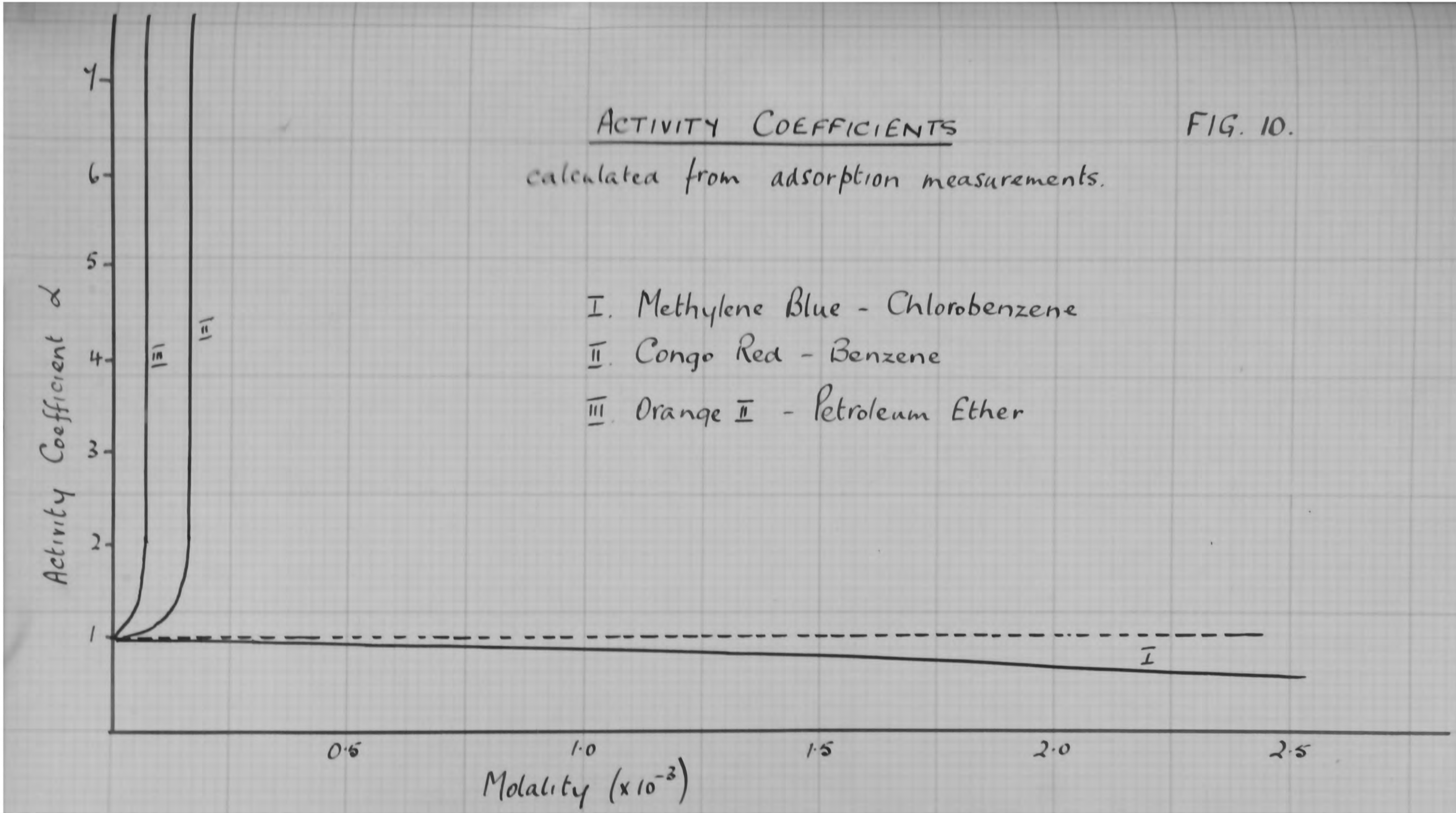
so $\log_{10} a = -2.0000$

and $\log_e a = -4.6$

FIG. 10.

ACTIVITY COEFFICIENTS

calculated from adsorption measurements.



This zero difference must be taken into account in calculating $\log_e a$ from the integral over the whole range of concentration.

<u>Example of calculation of a.</u>

Concentration of Congo Red $= 0.06$ gr/litre

and $\Gamma_0 = 2.3 \times 10^{-8}$ gr/cm^2

$\Gamma_c = 3.3 \times 10^{-8}$ "

Therefore $f(c) = \frac{\Gamma_0}{\Gamma_c} = \frac{a}{c} \cdot \frac{dc}{da} = 0.69$

So $cf(c) = 0.041$, and $\frac{1}{cf(c)} = 24.3$

$$\int_{c=0.01}^{c=0.06} \frac{dc}{cf(c)} = 1.88 \text{ (area read from graph)}$$

$\log_e a = -4.6 + 1.88 = -2.72$

Hence $\log_{10} a = -\frac{2.72}{2.303} = -1.17$

and $a = 0.068$

Therefore <u>Activity Coefficient</u> $= \frac{0.068}{0.060} = \underline{1.13}$

The variation in calculated activity with concentration is shown graphically in Figure 10. The integral graphs, and the readings from which they were drawn, are given in Appendix 6 and Figure 21.

It can be seen that in two out of the three cases, viz, Congo Red and Orange II, the values are plainly impossible. Even in the third case , that of Methylene Blue, the values are scarcely probable. The activity falls to 0.5 for a solution of concentration, 2.5×10^{-3} molar. It is very improbable that activity would have a value half that of the concentration in so dilute a solution.

It seems clear, therefore, that the difference between the observed and calculated values of Γ which have been obtained cannot be due entirely to the lack of data for the activities of the solutes. No further useful purpose can therefore be served by endeavouring to apply Gibbs's Equation in the absence of further information as to the influence of electrical and other factors expressly excluded in its derivation.

Chapter 5.

Nature of Adsorbed Layers.

From the plane projections of the five dyes shown in Figure 1, the area of interface occupied by their simple molecules can be approximately assessed in sq. Å. For this purpose the area was taken as that of a straight-sided polygon drawn closely round the projection. This area will enclose certain spaces between the various groups, not actually utilised by the molecule itself. It is improbable, however, that anybsystem of close-packing of the molecules on a surface could use up all the available space. Furthermore, atomic agitation within the molecule itself would probably forbid such intimate contact between neighbouring molecules.

The actual area of interface occupied by the adsorbed molecule, reckoned as monomeric, in the region of maximum adsorption, can be calculated from the adsorption measurements.

Example.

Maximum adsorption coefficient of Methylene Blue $= 2.45 \times 10^{-8}$ gr/cm^2

Molecular weight of dye $= 320$

Therefore, $\frac{2.45 \times 10^{-8}}{320}$ gram mols. of dye occupy 1 sq.cm. and therefore occupy 10^{16} sq. Å

Hence one molecule of dye occupies

$$\frac{320 \times 10^{16}}{2.45 \times 10^{-8} \times 6.061 \times 10^{23}}$$

$$= \underline{215 \text{ sq. Å.}}$$

Similar calculations have been made for all dyes.

The values obtained are collected in the following table.

(over)

			Area found on :-					
Dye	Molec wt.	Area calcd.	Benzene	Ratio	Chloro benzene	Ratio	Pet. Ether	Ratio
M.Blue	320	140	215	0.64	215	0.64	812	0.17
OrangeII	350	112	180	0.63	180	0.63	231	0.48
M.Orange	327	79	218	0.36	40	2.0	674	0.12
C.Red	696	192	470	0.40	117	1.64	2300	0.08
B.Extra	698	153	3840	0.04	5235	0.03	1858	0.08

The ratio refers to $\frac{\text{area calculated}}{\text{area observed}}$, and therefore provides a direct measure of the average thickness in molecules of the adsorbed layer.

When allowance is made for the necessarily inexact calculated areas, it is evident that the adsorbed layers of Methylene Blue and Orange II, on both benzene and chlorobenzene interfaces, may be unimolecular, with possibly some slight lateral scattering such as ionic repulsions between neighbouring molecules of these compounds might well produce. It is not clear why the two interfaces should act equally in this respect. The adsorption curve for Orange II on petroleum ether may at higher concentrations reach the same unimolecular adsorbed layer as on benzene and chlorobenzene. The adsorption of Methylene Blue on petroleum ether is, however, very slight, and, as shown later, the molecules are sufficiently far removed from each other's influence to behave as a perfectly gaseous layer.

In the cases of Congo Red and Methyl Orange, the surface distribution on benzene is definitely more sparse than in a single layer of contiguous molecules, whereas on chlorobenzene it is approximately twice as thick as this standard. That benzene, the less polar liquid, should adsorb in these two cases less than chlorobenzene, or alternatively allow more lateral movement of the adsorbed polar molecules, is understandable.

The surface concentration of these two dyes equivalent to a bimolecular layer, implies that the layer must be in one of three conditions :-

a) The molecules may be lying flat on the interface in layers of an average thickness of two molecules. Since Congo Red has at each end of its molecule a sodium atom which may be attracted by the chlorineatom of the chlorobenzene, this conception is quite feasible.

b) The molecules may form a monomolecular layer, but may not be lying flat. Since both are sodium salts, they may be attached to the surface by only one end of the molecule.

c) The dyes may be adsorbed in the form of micelles.

The adsorption of Bordeaux Extra constitutes on all three interfaces,at most, only about one twelfth of the amount necessary for a close-packed monomolecular layer. This is in sharp contrast to the behaviour of Congo Red, though the structures of the two molecules differ only slightly, and there must be some strong repulsive influences due to some property peculiar to its molecule, acting to prevent adsorption on the interface.

Application of Gas Laws to the Adsorbed Layers.

Following on Langmuir's original suggestion (2) Adam, and later Rideal and others (31) (32) (33) succeeded in applying the gas laws , in a modified form, to two-dimensional monomolecular layers of insoluble and soluble substances respectively.

An ideal gaseous film, to which the gas laws might be expected to apply, is one in which the molecules have a size negligible in comparison with the free space available and in which the molecules are so far removed from one another, that no intermolecular attractions or repulsions exist. It can be shown by the ordinary mathematics of the Kinetic Theory, that for such a layer, the equation

$$FA = kT$$

should hold, where F = surface pressure exerted on the molecules, measured by $\sigma_{water} - \sigma_{solution}$, and A is the surface area occupied by a molecule.

If F is expressed in dynes per cm., and A in cm^2 per gram mol., then k has the value of the gas constant R for these units, viz. $2 \times 4.2 \times 10^7$. Further, the product FA has the same dimensions as PV, since

$$PV = \frac{dynes}{cm^2} \cdot cm^3 = \frac{dynes}{cm} \cdot cm^2 = FA$$

Therefore the equation FA = RT applies to perfect gaseous layers, just as does PV = RT for perfect gases, so long as the adsorbed material behaves like a gas whose molecular movements are restricted to two dimensions.

Adam applied this equation to insoluble layers of esters of insoluble dibasic acids, and by plotting FA against F, found deviations from ideal behaviour similar to those obtained for gases. Schofield and Rideal (31) (32) who evaluated A from adsorption values calculated from Gibbs's Equation, found similar behaviour for a series of soluble acids.

Other insoluble substances have been found to form condensed films, in which case a large increase in F is necessary to bring about a small increase in A.

The results obtained in this investigation have been interpreted in the form of graphs, in which F and A have been plotted against one another. F, the lowering in tension, has been measured directly from the interfacial tension curves shown in Figures 7,8, and 9. The area A, in cm^2. per gram mol., has been calculated directly from the experimental adsorption coefficients.

The relation between F and A for a perfectly gaseous layer is shown by a hyperbola, while any change to a condensed layer will be represented by a straight line, in which A remains constant.

The curves obtained are shown in Figures 11,12,13 and 14, and appear to be of three types:-

1) Methylene Blue and Orange II on chlorobenzene and petroleum ether interfaces behave as gaseous layers, giving as the relation between F and A , curves which have the form of hyperbolae, (Figure 11). Since, however, the deviation from ideal behaviour is not immediately apparent from these curves, the results obtained with these two dyes are also shown as graphs of FA plotted against F, (Figure 14). These curves are of forms similar to the PV-P curves for gases deviating somewhat from Boyle's Law, and represent the behaviour of "gaseous" layers. At low surface pressures, the product FA is approximately constant, and the deviations with increasing pressure are of the form shown by gases.

2) Methylene Blue and Orange II on the benzene interface present a rather different case. For small values of F, (Figures 11 and 14) the curves indicate that the layers have a gaseous nature, but on increasing the value of F, A becomes constant, and remains so up to the highest values of F investigated. This is shown in Figure 11 by a straight line parallel to the F axis, and more clearly in Figure 14, curves 5 and 6, as a straight line relation between FA and A. This suggests a transition, with increasing surface pressure, from a gaseous to a condensed adsorbed film. In other words, the adsorption increases with concentration until a point is reached such that the interface is completely covered by a layer of closely packed molecules. Under these conditions, the only effect of any increase of surface pressure will be to compress the actual molecules. Such a change in area, brought about by the

FIG. 11.

F-A RELATION FOR ORANGE II AND METHYLENE BLUE.

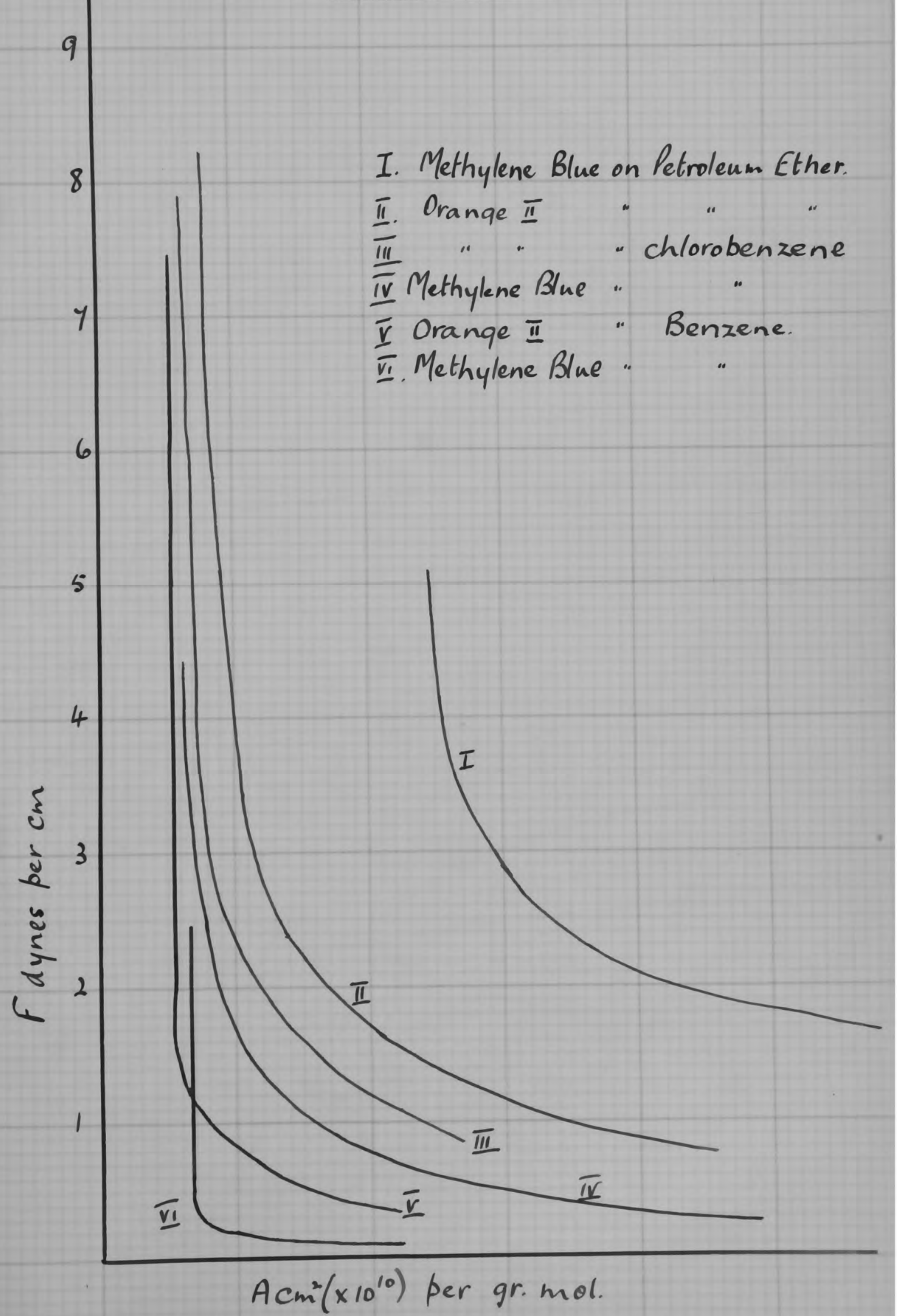


FIG. 12.

F-A RELATION FOR METHYL ORANGE AND CONGO RED.

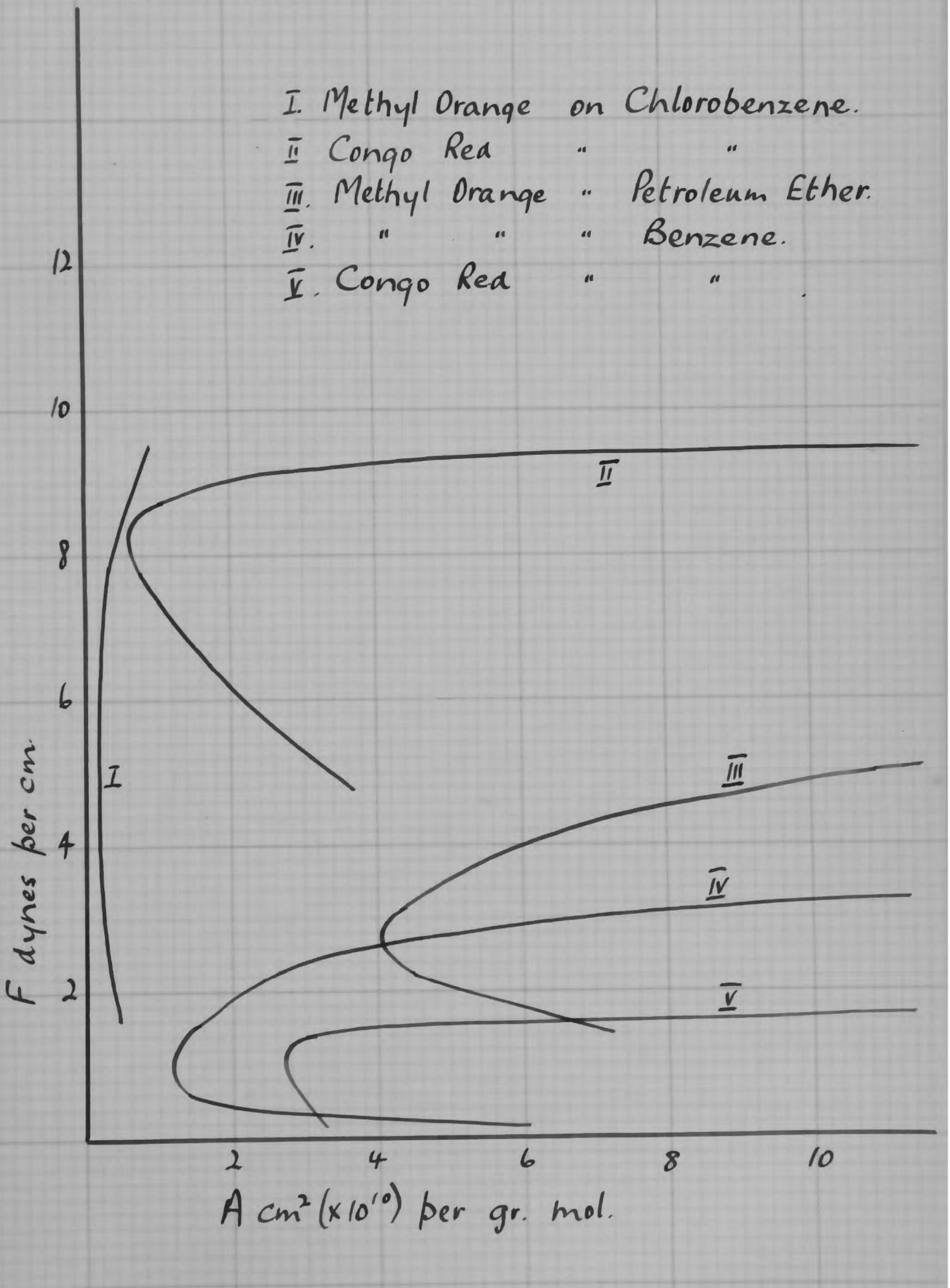


FIG. 13.

F-A RELATION FOR BORDEAUX EXTRA AND CONGO RED.

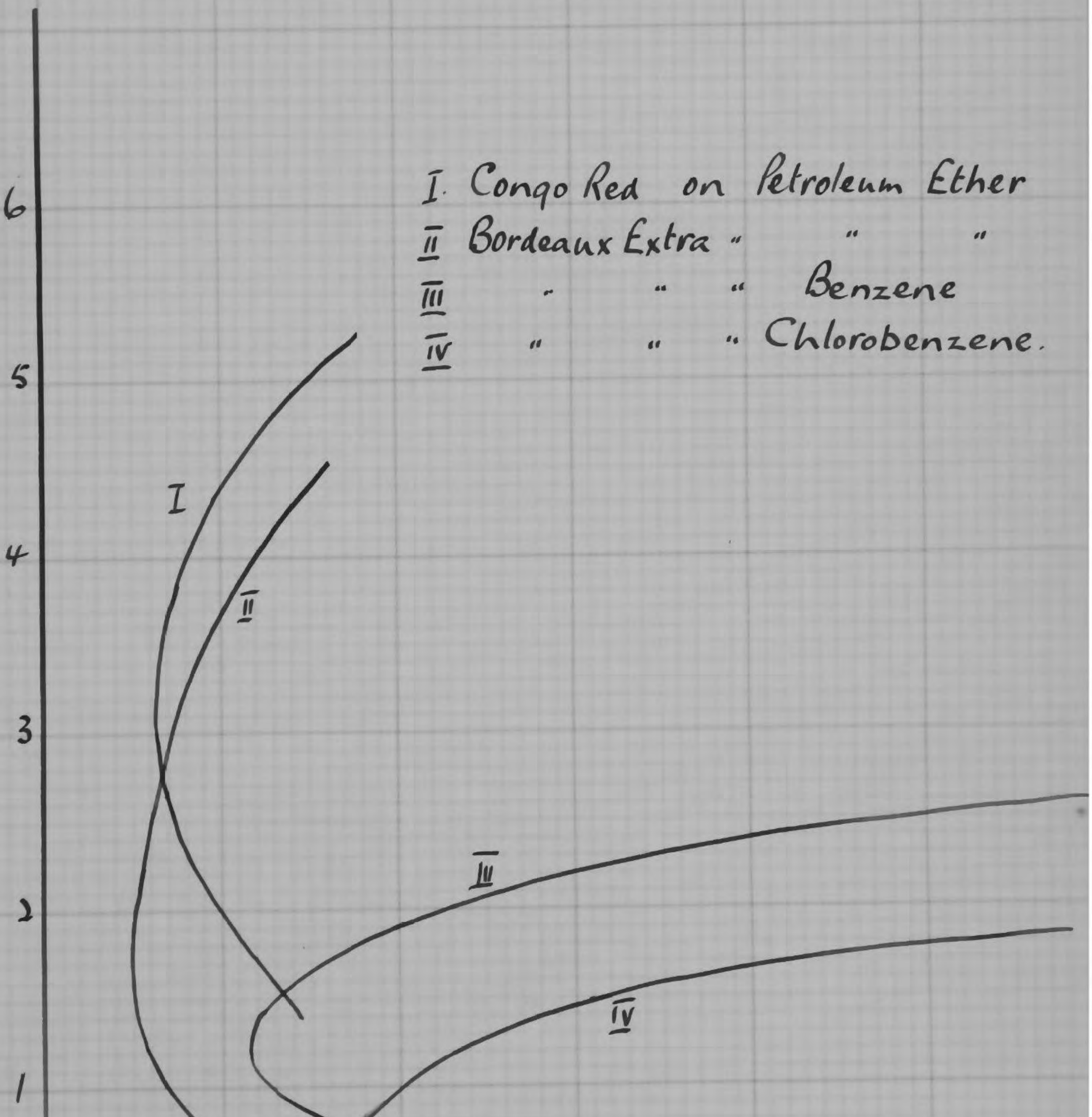
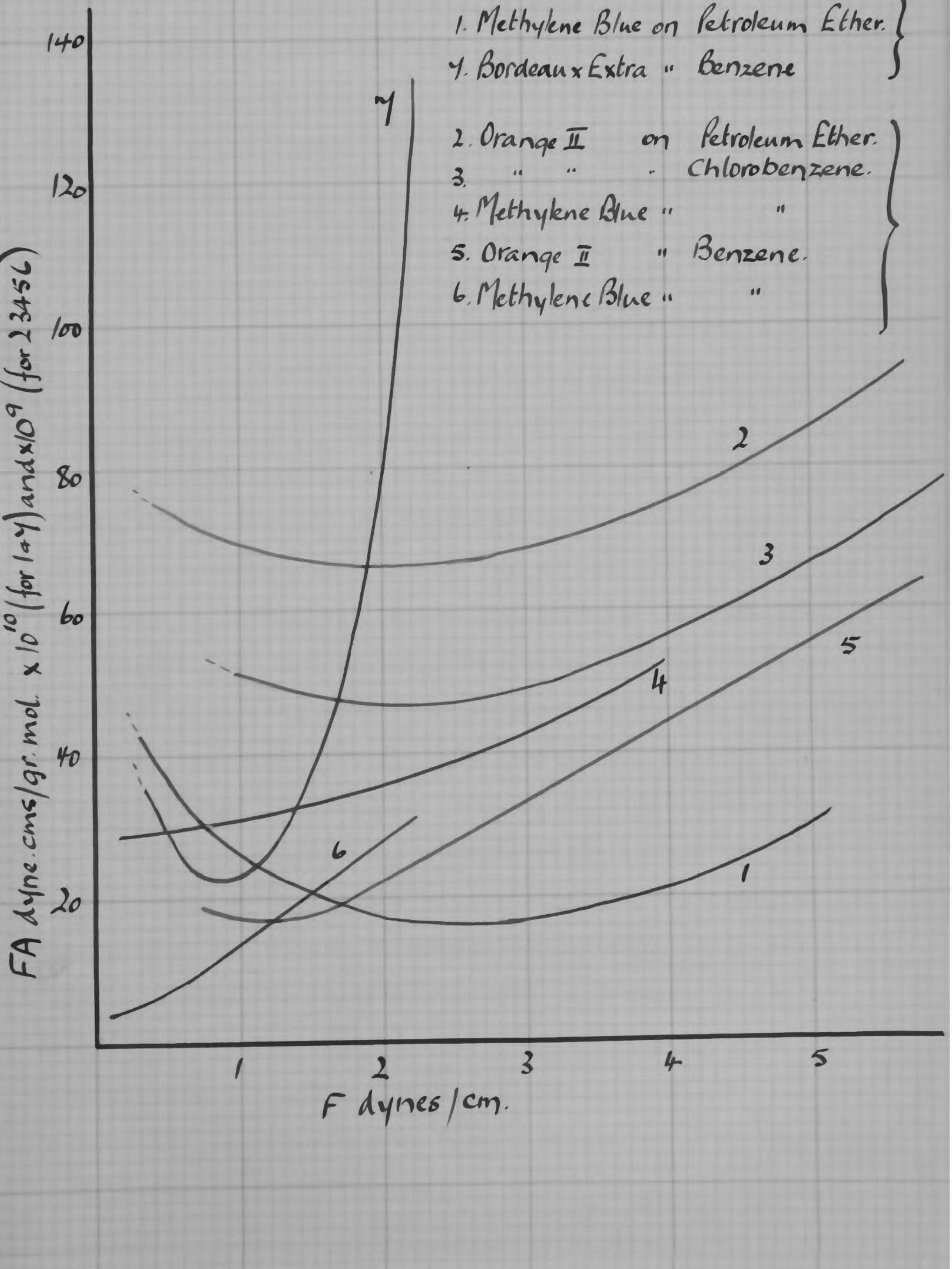


FIG. 14.

FA - F RELATION FOR METHYLENE BLUE, ORANGE II AND BORDEAUX EXTRA.



comparatively small surface pressures set up in these experiments, will be negligible.

3) The curves obtained with those dyes whose adsorption curves go through a maximum, i.e. Congo Red, Methyl Orange and Bordeaux Extra, are of a still different type. (See Figures 12 and 13; one FA-F curve for Bordeaux Extra is also included in Figure 14 for comparison.) For very small values of F, the curves may possibly be of the gaseous type, but as soon as F reaches an appreciable value, the curves reverse direction. They thereby infer an impossible set of conditions, in that as A increases, F increases. That is , as the number of dye molecules which are present to exert surface pressure decreases, the surface pressure actually exerted becomes greater.

It is very probable that in these cases, adsorption takes place throughout a surface layer more than one molecule thick, under which circumstances the above two-dimensional treatment is not applicable.

The only other apparent conclusion to be drawm from these curves is that the dyestuff actually adsorbed on to the interface is not the only factor influencing surface tension. As adsorption is decreasing with concentration, some other factor with the property of lowering tension must be increasing with concentration. When the adsorption becomes zero, this factor becomes responsible for the total lowering of tension.

It is suggested here that lowering of interfacial tension is not due entirely to adsorbed material. Even if adsorption influences be completely absent, it is to be expected that the interfacial tension between (say) benzene and water will be appreciably different from that between benzene and a strong dye solution, since in such a case the distribution of dye molecules on the interface must necessarily be the same as that throughout the bulk of the dye solution. This effect is held to constitute the factor referred to above.

In a private communication regarding the theoretical interpretation of the tension and adsorption curves obtained in this work, Dr.N.K.Adam (U.C.L.) pointed out an apparent anomaly, in that for dyes which showed points of maximum adsorption, experiments indicated zero adsorption at concentrations where the interfacial tension curves were still falling. If lowering of tension is assumed to be due entirely to adsorption, the results are not immediately explicable.

Dr. Adam suggested the presence of some capillary active impurity replacing the dye on the interface, thus causing an undue fall in the adsorption of the dyestuff. Such an impurity could scarcely be inorganic, since most inorganic compounds raise surface tension, and so would not be attracted to the interface. Extensive purification of the Methyl Orange has verified that no colourless organic impurities which could behave as capillary active impurities are present. (see chapter 6)

It is contended, therefore, that interfacial tensions of strong solutions of those dyes showing a maximum in their adsorption curves, are less than those in dilute solutions because the percentage of dye molecules at the interface in concentrated solutions, even when no adsorption takes place, is greater than that percentage in dilute solutions, when adsorbed dye is present.

In contradiction to this theory, however, it was feared that if the dye adsorbed did actually raise the concentration from its value at the point of maximum adsorption to that value where zero adsorption was found, it would do so through more than just a surface layer, since the solutions employed are so dilute. The thickness of this layer will obviously be small if a concentration much higher than that where adsorption first becomes zero is considered, and it is in considering this latter value that a limiting value is reached. The thickness of the layers formed by the adsorbed dye in raising the concentration to this limiting value have been calculated, and therefore maximum figures are given.

Two points on the tension curves are taken; one at a concentration giving maximum dye adsorption, and the other at a concentration where zero adsorption is first reached. For the purposes of this approximate calculation, the lowering produced by the stronger solution will be taken as being at least as great as that for the weaker solution, and the comparatively small difference between the two actual values will be neglected. Also, the difference in dye concentration at the interface which this difference in tension implies can be neglected here. Actually, since the drop in tension at the lower concentration is less than that at the higher, the surface concentration of dye will be less, and the layer will be slightly thicker than subsequent figures indicate. However, from the shapes of the interfacial tension curves, it follows that when large concentrations are being considered, these influences will make no important difference to the calculated figures; they only become appreciable in the limiting cases.

The two points are therefore considered as having about the same dye concentration at the surface as in the bulk solution, and the difference in bulk concentration is made up by the adsorbed dye. It follows that since this amount is a fixed quantity, then the greater concentration of dye to be reached, the less the volume, and therefore the thinner will be the layer formed.

Congo Red on benzene is taken as an example :-

The concentration of dye molecules at the interface in a strong solution, 0.8 gr/litre, where no adsorption is found, should cause the lowering in tension to be at least as great as that for the weaker solution at the point of maximum adsorption, i.e. 0.04 gr/litre.

Therefore :-

Concentration for zero adsorption = 0.8 gr/l = 0.00114 N
" " maxm. " = 0.04 " = 0.00006 N
Increase due to adsorption = 0.00108 N
Thickness of layer = 0.4 molecules (by expt.)
Area of molecule = 200 Å (from figure of molecule)

From which data,

Number of gr.molecules on 100 cm^2 of surface

$$= \frac{100 \times 10^{16}}{200 \times 2.5 \times 6 \times 10^{23}}$$

$$= 0.33 \times 10^{-8}$$

Hence 0.33×10^{-8} gr.mols. are equivalent to a 0.00108 N solution, whose volume must be $\frac{0.33 \times 10^{-8}}{0.00108}$ litres.

Therefore thickness over area of 100 cm^2 $= \frac{0.33 \times 10^{-8} \times 10^{3} \times 10^{8}}{1.08 \times 10^{-3} \times 100}$

$$= \underline{3000\ \text{Å}}$$

Maximum values for the thickness which will be reached when minimum concentration values consistent with zero adsorption are taken, have been similarly worked out for the following three cases :-

Dye	Concn for max.adsn. gr./l	Concn for zero adsn gr/l	Ratio	Layer Thickness	
				Å	Mols.
M.Orange -benzene	0.1	0.6	0.16	5500	275
C.Red - benzene	0.04	0.4	0.13	6500	217
C.Red on chloro-benzene.	0.7	1.8	0.4	8500	283

These results are not unreasonably inconsistent with the requirements of Gibbs's Equation. The previous reasoning can, therefore, provide a partial explanation of the apparent paradox.

It can be seen from the Congo Red figures, that as the ratio $\frac{\text{Concn for max. adsn.}}{\text{" \quad " zero adsn.}}$ increases, i.e. as the concentration representing zero adsorption approaches a minimum value, the thickness of the layer also increases, since the fixed quantity of dye adsorbed naturally fills a greater volume at a smaller concentration.

The two sets of curves can, then, be correlated by assuming that lowering of tension is not due solely to adsorbed material. A solute is adsorbed because its movement to the interface reduces the tension, and thus the potential energy, of the system. Hence the fact that dye is sometimes adsorbed shows that the replacement of water molecules by dye molecules on the surface is a movement towards equilibrium. In dilute solutions, the excess of benzene-dye attraction over benzene-water attraction results in adsorption. $\frac{d\sigma}{dc}$ is large in dilute solutions, and therefore the driving force is large. In sufficiently concentrated solutions, $\frac{d\sigma}{dc}$ is zero. This means that adsorption from the bulk of the solution produces no lowering in interfacial tension, and so it does not take place.

In all the cases investigated, the value of $\frac{d\sigma}{dc}$ is diminishing as concentration increases. Methylene Blue and Orange II show long, flat maxima in their adsorption curves, and in both these cases, $\frac{d\sigma}{dc}$ is still large up to fairly large concentrations. The adsorption should ultimately return to zero.

Again, adsorption is influenced by electrical and other effects at the interface. It cannot, therefore, be argued that the adsorption must come to zero exactly when $\frac{d\sigma}{dc}$ is zero, but only that two such variables do come to zero at some, but not necessarily the same, concentration.

Another mechanism whereby the interfacial tension of a solution may be lowered in the absence of any actual Gibbs adsorption has been put forward by J.W.McBain (48). He suggests that immediately a new surface is created, the "tension is lowered, not merely by the orientation of dissolved molecules which chance to be exposed on the surface, but also that there is an interchange of positions between molecules of solute and solvent within a few molecular diameters of the surface".

By this means, "a solution might almost immediately be covered by a layer of solute exposing only hydrocarbon groups, and overlying another layer that would be mainly water".

Whereas Gibbs adsorption takes an appreciable time, such a pre-Gibbs equilibrium could be attained in a negligible time. The tension could be considerably reduced, and yet the average composition of the surface sandwich layers would still be that of the bulk solution.

Chapter 6.

EXPERIMENTAL.

1. Interfacial Tension Measurements.

Theoretical Considerations.

Interfacial tensions of dye solutions against benzene, chlorobenzene, and petroleum ether have been measured by the drop weight method. This consists essentially in allowing the liquid under test to rise or fall from a jet of known size, through any required medium. The drop is held by surface tension forces, and therefore the greater the tension, the greater will be the weight of the drop. This drop weight therefore affords a measure of surface or interfacial tension; the method is applicable to both.

In these experiments, the number of drops from a fixed volume of organic liquid were counted as they left a jet immersed in an aqueous solution of the dyes under test, and which pointed up or down according to density. The drop size is deriveable from the drop number so obtained.

The method was chosen because of its accuracy and reproducibility. It has been found possible to reproduce the results to one drop in several hundreds, thereby reducing the experimental error to a fraction of a percent.

Though this method is extensively used, the theory connecting drop weight with interfacial tension is by no means clear, and the correst result is even now only obtained by a series of standardisations with known values. This is due to the dynamic complexity of the drop release. Guye and Perrot's photographs of a falling drop, (49) illustrate that only part of the bulk of the liquid outside the jet is released as a drop. Part is retained, and part follows as a minute drop in the wake of the larger one. It is not surprising, therefore, that no simple formula exists.

In these experiments with organic liquids, a similar phenomenon has been noticed.

Tate (50) suggested that

$$W = 2\pi r\sigma$$

where W = drop weight, and r = jet radius.

This simple relation between W and σ was rapidly disproved.

Another static formula has been employed by Lewis (10), viz.

$$2\pi a\sigma - \frac{2\pi a^2\sigma}{r} = \frac{4\pi r^3}{3}(d_{H_2O} - d_{liq})$$

This formula, again, is scarcely applicable to a dynamic phenomenon.

The dynamic conception of a falling drop, which must take into account the size of the drop at the point where it breaks away, and the fraction of the bulk which falls, is more nearly portrayed in the interpretation put on the drop weight by Lohnstein. The Lohnstein-Kohlrauch formula (51) states that :-

$$g = r\sigma\Phi$$

where g = drop weight, and r = radius of drop.

Φ is a function of $\frac{r}{a}$, where $a^2 = \frac{2\sigma}{\delta\rho}$ (ρ = density)

A value for σ is assumed, and $\frac{r}{a}$ is calculated. A linear relation given by Kohlrauch yields Φ directly. The value of g calculated from $r\sigma\Phi$ is compared with the value actually obtained by experiment, and therefore may by trial be given the value such as to make the calculated and observed values of g identical.

Lewis (loc.cit.) preferred this method, and used it for the calculation of the theoretical adsorption coefficients by employing Gibbs's Equation.

In the experiments here recorded, however, the values of $\frac{r}{a}$ obtained called for an extrapolation of Lohnstein's $\frac{r}{a} - \Phi$ relation to such an extent as to be unjustified. The more comprehensive figures of Harkins and Brown (52) were therefore used.

Like Lohnstein, they found that :-

$$\text{Weight of drop} = W = \text{function of } \frac{r}{a}$$

$$= 2\pi r\sigma f\left(\frac{r}{a}\right)$$

They point out that $f\left(\frac{r}{a}\right)$ is also a function of $\frac{r}{V^{1/3}}$

where V = volume of one drop.

Therefore, $W = 2\pi r\sigma\psi\left(\frac{r}{V^{1/3}}\right)$

If F is a function of $\frac{V}{r^3}$, such that $F = \dfrac{1}{2\pi\psi\left(\frac{r}{V^{1/3}}\right)}$

Then $\sigma = \frac{mg}{r} \times F$ where m = mass of drop.

The following table is an extract, over the relevant range, from the tables connecting $\frac{V}{r^3}$ and F given by Harkins and Brown, obtained by standardisations against liquids of known properties. Hence σ may be evaluated.

$\frac{V}{r^3}$	F
5000	0.172
250	0.198
58.1	0.215
24.6	0.2256
17.7	0.2305

Example of calculation.

The interfacial tension of benzene against pure water will be worked out as example. The necessary densities etc. are taken from the International Critical Tables.

Radius of jet = r = 0.082 cms

Volume of pipette = 29.328 ccs.

Drop number = 228

$$\left.\begin{aligned} d^{17^\circ C}_{H_2O} &= 0.9986 \\ d^{17^\circ C}_{C_6H_6} &= 0.8835 \end{aligned}\right\} \quad d_{H_2O} - d_{C_6H_6} = 0.1151$$

Therefore, $\frac{V}{r^3} = \frac{29.328}{228 \times (0.082)^3} = 233.9$

From tables, $F = 0.200$

Hence, $\sigma = \frac{mg}{r} \times F = \frac{29.328 \times 0.1151 \times 0.200}{228 \times 0.082} = 35.4$ dynes/cm.

The interfacial tensions for the three liquids against pure water are here compared with the values given by I.C.Tables (vol.4, 436).

Liquid	Temp.	Observed value d./cm	I.C.T. value d./cm
Benzene	17°C	35.4	35.2 (at 17°C)
Chlorobenzene	17°C	37.41	37.41(at 20°C)
Petroleum Ether	17°C	51.35	c.f.Hexane 51.1 Octane 50.8

For the present purpose, these results compare quite satisfactorily.

The values of the benzene-water interfacial tension as calculated by the various methods, using the same experimental data, are quoted for comparison.

(a) From Harkins and Brown's figures = 35.4 dynes/cm

(b) " Lohnstein's " = 36.43 "

(c) " Static Formula = 39.15 "

It is obvious that the static formula completely fails to record the phenomenon.

Experimental Procedure.

A pipette was constructed of the form shown in Text Figure 15. The pipette was filled by suction, and the liquid allowed to emerge in drops from a jet which was immersed below the surface of the aqueous dye solution. The number of drops issuing while the level in the pipette fell from a mark K to a calibration mark L, was noted. The volume contained by the pipette between the two calibration marks was measured by weighing the water content. During experiments with chlorobenzene, the tip was turned downwards.

This tip was made by drawing out a piece of glass tubing to a circular aperture, and the radius was measured on a travelling microscope. Decrease in the interfacial tension results in a decrease in the drop size, and therefore a corresponding increase in the drop number. For measurements on chlorobenzene, it was found necessary to grind the tip to a knife edge. This was done by filling the tube with Wood's Metal, grinding with carborundum powders of increasing degrees of fineness, and then immersing the whole in hot water. The tip was finally cleaned with concentrated nitric acid. Benzene and petroleum ether showed less tendency to cover the surface of the glass, and therefore the edge of the aperture was not necessarily made sharp. The drop sizes were independent of the lip width of the aperture.

Pipette dimensions.

1) Pipette used for chlorobenzene and all five dyes.

Radius of jet = 0.092 cm.
Volume of pipette = 29.328 ccs.
Drop number against water = 188

2)Pipette used for benzene and all dyes save Bordeaux Extra.

Radius of jet = 0.082 cms.
Volume of pipette = 29.328 ccs.
Drop number against water = 228

3) Pipette used for a) petroleum ether and five dyes
b) benzene and Bordeaux Extra

Radius of jet = 0.1435 cms.
Volume of pipette = 28.595 ccs.
Drop number petroleum ether-water = 228
Density of petroleum ether(80°-100°) = 0.716
Drop number benzene-water = 136

This pipette gives 35.38 dynes/cm as the benzene-water interfacial tension. This agrees almost exactly with the value obtained with the other pipette.

Rate of flow.

The rate of flow was controlled by a fine air leak, made by drawing out to a long tail a piece of finely bored capillary tube. The required drop rate was obtained by breaking off the tail to a suitable length. The pipette bulb was blown as broad as possible to minimise alteration in drop rate due to changes in head of pressure.

In his original experiments, Tate (loc.cit.) quoted 40 seconds for each drop release as the minimum time for reproducible results. Other investigators,e.g. Lewis (loc.cit.) and Lord Rayleigh (53) have found this unnecessary, and Lewis suggests 12 to 15 seconds per drop as a necessary minimum time. In this investigation, it has been found that results reproducible to one drop could be obtained if the drops were each given a minimum time of 12 seconds to form. Any increase of this rate up to 20, 30, etc. seconds per drop made no difference to the drop number ; the results were not reliable if much less than 12 seconds were allowed for each drop.

Temperature Control.

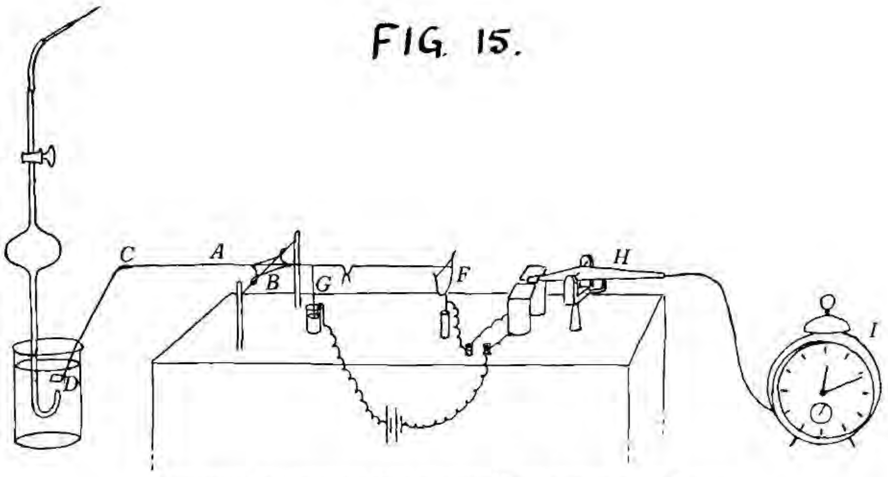
All drop numbers were taken at 17 ± 0.5°C. If the room temperature was outside this range, the solutions under test were first raised or lowered to 17°C, and placed in a Dewar vessel, in which the experiments were then carried out. Measurements showed a maximum variation of 0.5°C during the period of one experiment, of average duration about one hour.

The I.C.Tables (vol.4,437) state that the temperature coefficient of interfacial tension of benzene against pure water is constant, and has a value of 0.058dynes per cm. per degree. It follows that a temperature fluctuation of 0.5°C would produce a negligible change in the tension. No corresponding results can be found for chlorobenzene or petroleum ether. However, Harkins and Cheng (54) quote values of temperature coefficients for a range of liquids, and in each case the coefficient is small. The coefficients for hexane and octane are respectively 0.3 and 0.2. The petroleum ether used in these experiments will almost certainly have a similar value. It has been assumed, then, that for these two liquids also, any influences due to temperature fluctuations will be negligible.

Automatic Device.

Since the number of drops to be counted was of the order of several hundreds, and the rate of flow small, the mechanical device here described was constructed.

FIG. 15.



Automatic device for recording drop numbers

Donnan and Barker (17) refer to the counting of drops of liquid falling through air by allowing them to strike a vane which actuated a morse inker. The motive power of drops of benzene rising through water is, of course, much less. This apparatus possesses a further advantage, in that without its help it would be almost impossible to count bubbles of organic liquid passing through deeply coloured solutions. The device was particularly useful in measurements on Methylene Blue and Bordeaux Extra, whose solutions are so intensely coloured that even a strong light can only penetrate thin layers of solution of extremely small concentration.

A beam A, made of aluminium wire, is suspended at B by means of a cotton thread round which it is looped. At C it is fastened by shellac to a thin glass rod less than one mm. diameter, to which is sealed a piece of microscope cover glass D. Drops of benzene or petroleum ether rising from the pipette strike the underside of the inclined vane D, and deflect the beam, (previously balanced by means of a rider), causing the platinum wire fastened to its other extremity to make contact with a transverse platimum wire held in an adjustable stirrup F. One permanent electrical connection is made by a platinum wire G, dipping into mercury. The closing of the circuit operates the relay arm H, which terminates in a stiff wire passing through a small hole in the escapement lever of the clock I. The balance wheel of the clock was removed, and the seconds dial replaced by one so divided that the seconds hand reads directly in bubbles, and the minute hand in hundreds of bubbles. It is essential that C should be thin, or readjustment of the height of F is necessary, on account of the increasing upthrust of the accumulating organic liquid.

The same apparatus was used for chlorobenzene, except that the beam A was so balanced that the platinum wire was under the wire held in F. The heavier drops of chlorobenzene falling on top of the vane D thus cause contact by deflecting the beam in the opposite direction.

The interfacial tensions between the three organic liquids and aqueous solutions of the dyes, over a sufficient range of concentration, have been measured, and the adsorptions calculated. The results are shown as Tables in Appendix 4, and as tension-concentration curves in Figures 7,8, and 9.

Calculation of theoretical adsorption values.

The theoretical adsorption coefficients according to Gibbs's Equation were calculated as follows :-

The values of $\frac{d\sigma}{dc}$ were read off directly from the σ - c curves, by laying a fine wire on the curve at a series of points. These slopes were graphed against concentration, and a smooth curve drawn through the points. The values of $\frac{d\sigma}{dc}$ required for substitution in Gibbs's Equation were read off directly from this curve.

An attempt was made to obtain values of $\frac{d\sigma}{dc}$ by integrating equations fitted to the curves. Schofield and Rideal (31) state that the equation

$$\sigma_{H_2O} - \sigma_{solution} = \alpha + \beta \log_{10} C$$

applies to acetic acid solutions in not too dilute solution. This equation was found to apply exactly to the σ - c curves for these dyes, but only at concentrations above about 0.3 gr/litre. Since in several cases the adsorption curves obtained by experiment lie completely below a concentration value of 0.3 gr/litre, this method was abandoned.

Since some of these dyes exist in micellular form in solution, the exact value to be assigned to the molecular weight in Gibbs's Equation is therefore uncertain. Since, however, no method of determining how the degree of aggregation varies with the concentration is at hand, the molecular weight used throughout has been that of the simple molecule.

Example.

$$\Gamma = - \frac{c}{RT} \cdot \frac{d\sigma}{dc}$$

Considering the tension curve for Orange II against chlorobenzene,

$$c = 0.14 \text{ gr/litre} - 0.00014 \text{ gr/cc.}$$

$$R = \frac{2 \times 4.2 \times 10^{7}}{\text{molec.wt.}} \text{ ergs, for one gram of solute.}$$

$$T = \text{Absolute temperature} = 290^{\circ} \text{A.}$$

From curve, $\frac{d\sigma}{dc} = - 1.8 \frac{\text{dynes per cm.}}{\text{grams per cc.}} \times 10^{4}$

Substituting these values,

$$\Gamma = \frac{0.00014 \times 350 \times 1.8 \times 10^{4}}{2 \times 4.2 \times 10^{7} \times 290} = 3.66 \times 10^{-8} \text{ gr./cm}^{2}.$$

Several other methods for interfacial tension were tried, e.g. Bartell's U-tube method. Their unsuitability lay in their inability to differentiate with sufficient accuracy between solutions of only slightly different interfacial tension.

2. Surface Tension Measurements.

The surface tensions of the dye solutions were measured by the capillary rise method, using a falling meniscus. A uniform capillary tube was obtained, and was cleaned frequently with an alcohol-nitric acid mixture. The heights of surface and meniscus were measured on a travelling microscope.

The following table gives the results obtained, which were all perfectly reproducible.

Dye	Concn. grs./l	Capillary Rise, mms.	Surface Tension dynes/cm.
Pure water	-	50.4	74.0
Bordeaux Extra.	0.1900 0.0950	50.2 50.3	73.7 73.85
Orange II	1.8420 0.9210	49.8 50.0	73.11 73.41
Methyl Orange.	1.4710	50.0	73.41
Congo Red	1.0000	50.2	73.7
Methylene Blue	0.5840	49.9	73.26

In no case, therefore, is any lowering of tension observed of sufficient magnitude ~~observed~~ to give a curve. The maximum lowering is less than one dyne, although the dye solutions are in many cases much stronger than those used hitherto.

3. Adsorption Measurements.

The moving bubble method was used for all experimental determinations of adsorption. This method has several advantages over the emulsion method for investigating adsorption at liquid-liquid interfaces, particularly in that it allows of an exact evaluation of the surface area exposed.

The apparatus here described is a modified and developed form of the original type of apparatus used by Lewis (loc.cit.)

a) Adsorption at the benzene-water interface.

FIG. 16.

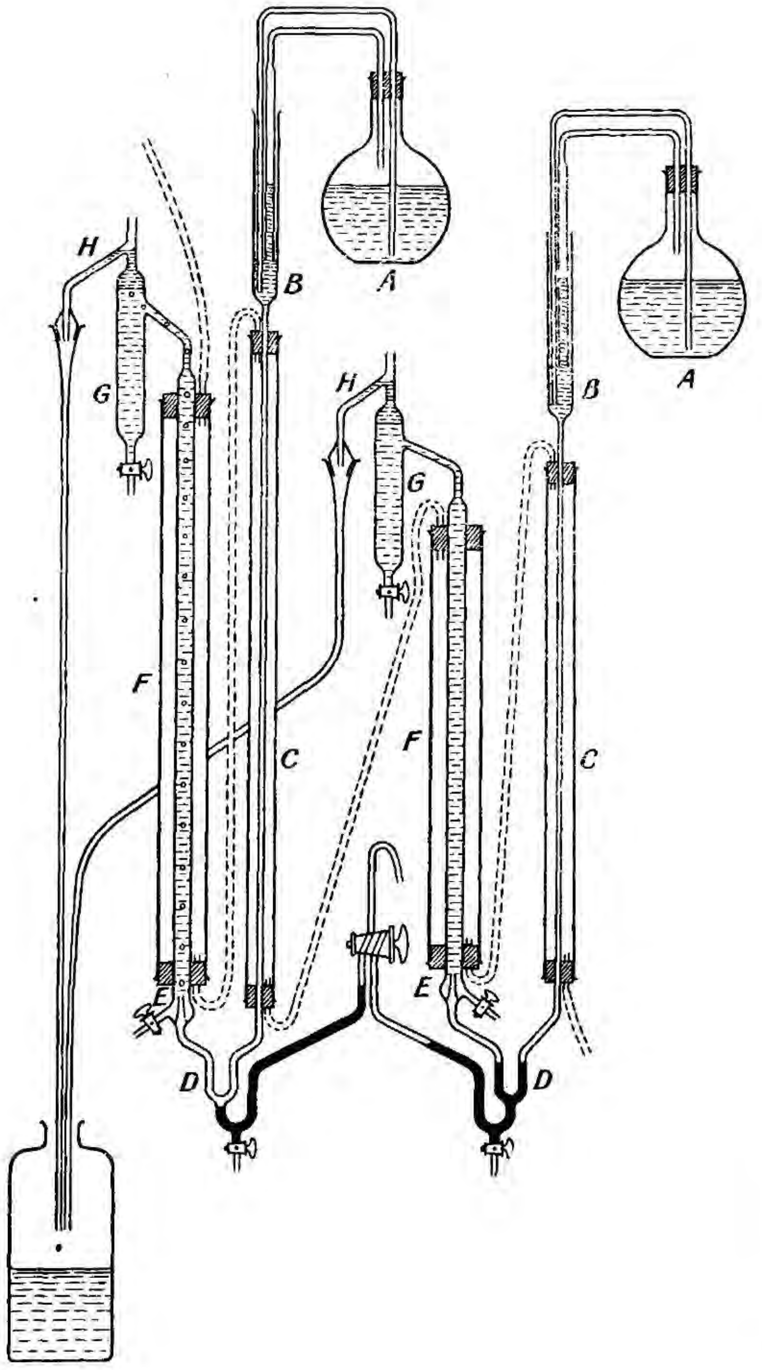
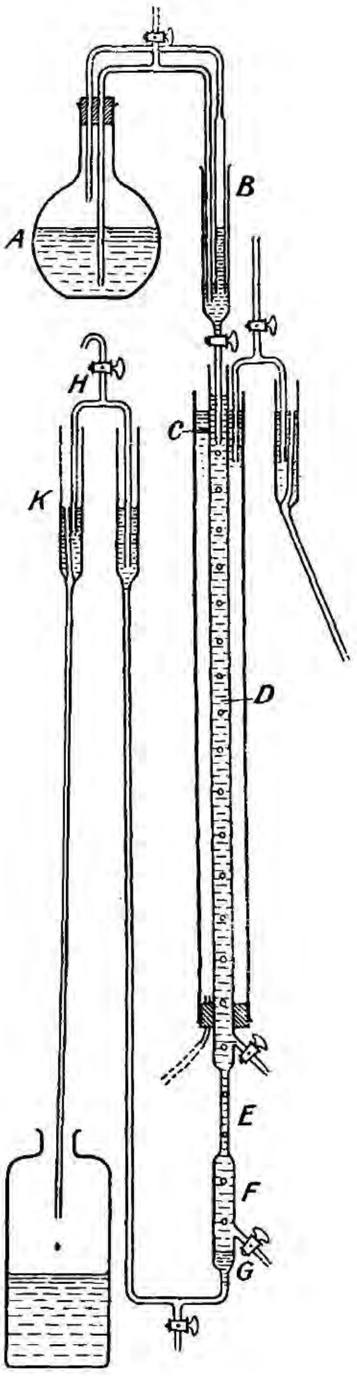


FIG. 17.



Benzene, stored in a reservoir A, (Text Figure 16) flowed through a constant pressure head B, down a long tube C, and past a mercury trap D. This was connected to a water pump, and the two-way tap made it possible, by filling or emptying the trap with mercury, to control at will the flow of benzene in either column. A glass tap was undesirable, as the dissolved rubber grease would have fouled the benzene, and locked the tap. The benzene issued through a jet E, and rose by gravity in drops through the dye solution in the column F. This column was surrounded by a water jacket, through which water at any desired temperature could be circulated. The drops passed out through an inclined tube at the top of F, which was only slightly larger than the drops themselves, and into a reservoir G. There they coalesced with a layer of benzene, which overflowed through a side tube H, and was collected. The adsorbed layer of dye was shed in G, and experiments showed, (see below), that no appreciable back diffusion into F took place during the period of one experiment. The apparatus was of glass throughout. The quantities and dimensions used will be evidenced by the following approximations :-

The average duration of an experiment was about 20 hours, during which time 3 to 5 litres of benzene passed through the apparatus in drops of volume about 0.1 cc, and issuing at a frequency of about 60 drops per minute. The apparatus was so standardised that a run could be commenced during an afternoon, allowed to run overnight, and the solutions withdrawn the following morning. The area of interface exposed during one experiment was of the order of 3.5 square metres. The rate of flow was determined by weighing the benzene overflowing in a measured time, and was maintained substantially steady by the constant pressure head. The number of drops passing in a measured time was counted at frequent intervals. By fixing the pressure head, it was found possible to keep the fluctuations in rate to within ± 1 drop per minute, although the apparatus was so arranged that this could be varied at will. In order to prove that the surface was saturated, the apparatus was constructed in duplicate, with columns of different heights, having jets of diameters 0.58 and 1.26mms.

b) Adsorption at the Petroleum ether-water Interface.

The apparatus used in this case was identical in form with that used for benzene. The height of the constant pressure head was increased because of the smaller density of the petroleum ether. The jet diameters were 0.5 and 0.85 mms.

c) Adsorption at the Chlorobenzene-water Interface.

In the case of chlorobenzene, similar sets of apparatus were used, (Text Figure 17), but because the density of chlorobenzene is greater than that of water, (1.1062 at 17°C), the essential features of the apparatus are reversed. To prove saturation of the drops, the apparatus was constructed in duplicate, and the two columns used concurrently. The liquid, stored in A and maintained at a constant pressure head in B, fell in drops from jets C,of diameters 0.4 and 0.32 mms., dipping into dye solution in the jacketed column D. They passed through a constriction E, about 10 cms. long, and just large enough to accomodate the bubbles and so prevent back diffusion, and coalesced with the chlorobenzene surface G at the bottom of the reservoir F, in which the adsorbed dyestuff collected. The chlorobenzene passed through only one tap, in the constant pressure head. This was lubricated only once with a small quantity of rubber grease. The chlorobenzene overflowed through a syphon H, and by adjusting the moveable syphon limb K, the level of the interface G could be kept constant. In filling, the chlorobenzene was first added down H until the surface was at G, as shown. The chlorobenzene and dye solution were then added down the respective limbs at such a rate as to keep the interface stationary.

Cleaning of Apparatus.

Benzene and Petroleum ether showed less tendency to cover a glass surface than did chlorobenzene. Therefore in the two former cases, little trouble was experienced from bubbles attaching themselves to the glass and blocking the tubes. An occasional flush with acetone was found to be adequate to remove organic impurities from the glass surface. In the chlorobenzene apparatus, however, the bubbles readily blocked the restriction tube E unless the latter was scrupulously clean. Therefore before each experiment, the apparatus was rinsed with "Analar" acetone, and dried. After every two or three experiments, the restriction was "bubble" cleaned with concentrated nitric acid and ethyl alcohol. In certain attempts to adsorb inorganic salts on chlorobenzene, a large interfacial area was obtained by forcing a shower of very small droplets from the jet by means of a large head of pressure. These experiments could not be completed unless the apparatus was "bubble" cleaned between each experiment.

Tintometric Estimation of Adsorbed Dyestuff.

At the termination of each experiment, the reservoir solutions were run out and weighed. In the benzene and petroleum ether apparatus, the solution from G could be run out directly. In the chlorobenzene apparatus, the column solution and the chlorobenzene were each run out, the latter through the tap below G, at such a relative rate as to keep the interface G in position. The reservoir solution was then withdrawn, and its concentration compared with that of a sample of the original solution, in a Dubosq Tintometer.

The latter was equipped with two cups of fixed heights which contained the dye solution, and two glass plungers of variable heights. By fixing the plunger, the height of the column of original dye solution was taken for all readings as 30mms. The height of the column of reservoir dye solution was altered by the moveable plunger, until the two tints matched in the divided eyepiece, when the height of the column could be read off from a circular scale, reading in tenths of a millimeter. The concentrations were assumed to be inversely proportional to the column heights.

Beer's Law, which states that the value of the absorption (or extinction) coefficient is proportional to the concentration of the absorbing material, and that no actual colour change takes place with change in concentration, was assumed to hold throughout. A match in the tintometer was always possible; this would not have been the case if Beer's Law had not applied.

To obtain reproducible results, it was found necessary to carry out all comparisons out of doors, away from large objects affecting the illumination, and whenever possible in direct, bright sunlight.

Comparison of concentrated solutions was difficult and less accurate than that of dilute solutions, and so the solutions were diluted whenever necessary to a suitable depth of colour.

Evaluation of Experimental Error.

It was found possible to reproduce the scale readings to ± 0.05 mms. The experimental errors quoted in the tables, and shown in the graphs, are calculated on this basis. The percentage error on the adsorption coefficient was obtained in the following manner :-

Depth of original solution = 30 mms.

Concn. " " = c

Depth of reservoir " = x

Therefore, concn. of reservoir $= \frac{30}{x} \times c$

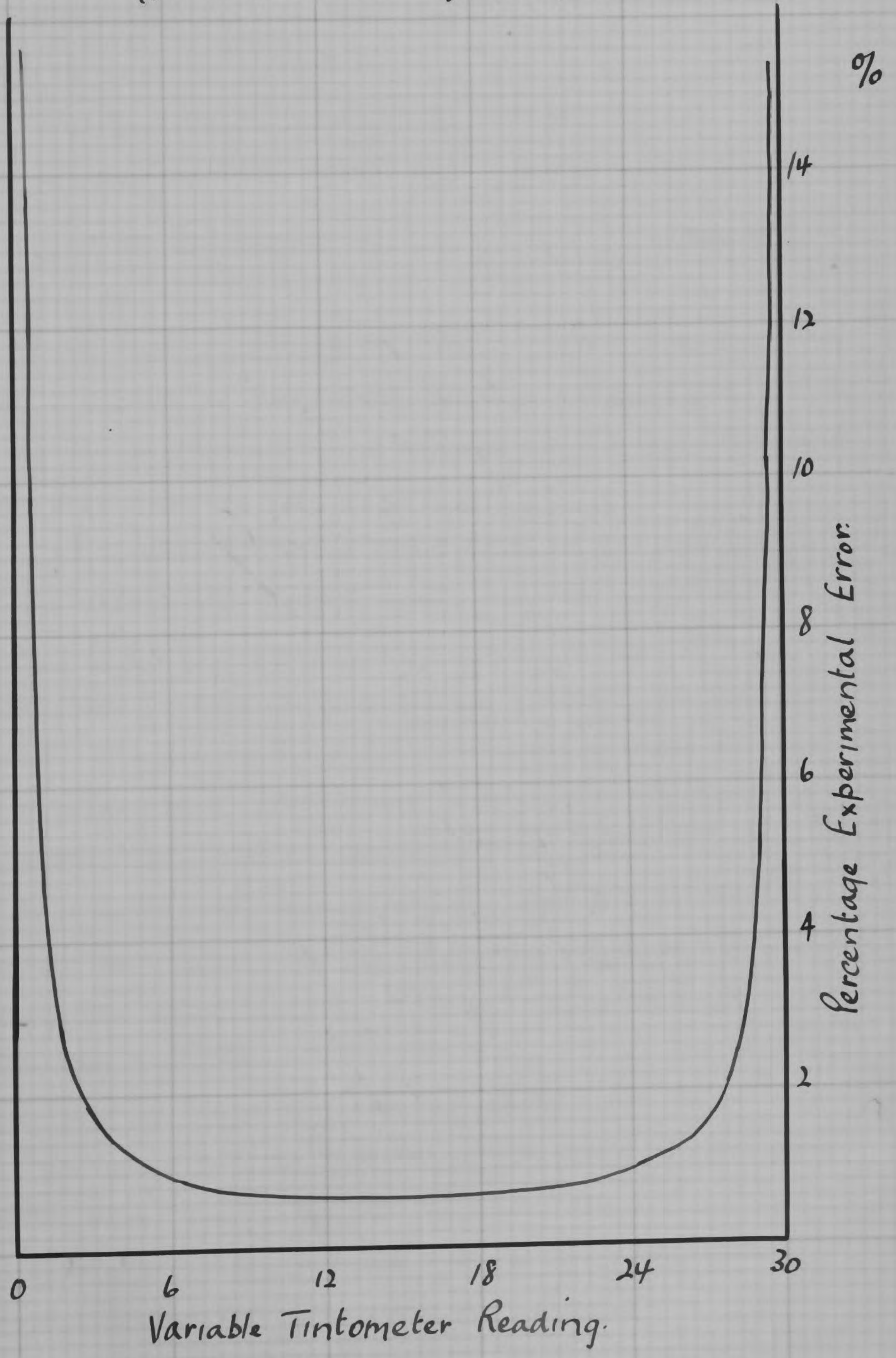
Concn, increase due to adsorption $= \left(\frac{30}{x} - 1\right) c$

Now, adsorption coefficient $= \frac{\text{Increase}}{\text{surface area}}$

FIG. 18.

EXPERIMENTAL ERROR IN ADSORPTION COEFFICIENT.

(for a fixed setting of 30.)



i.e. Adsorption Coefficient $= \dfrac{\left(\dfrac{30}{x} - 1\right) c}{\text{surface area}}$

Its limiting values are therefore proportional to:-

$$\left(\frac{30}{x \pm 0.05} - 1\right)$$

Hence, maximum % error $= \pm \dfrac{\left(\dfrac{30}{x} - \dfrac{30}{x + 0.05}\right)}{\left(\dfrac{30}{x} - 1\right)} \times 100$

Taking an actual reading,

Height of reservoir solution = 27 mms.

Then, $\left(\dfrac{30}{27} - 1\right) = 0.1111$ and $\left(\dfrac{30}{27.05} - 1\right) = 0.10906$

Therefore, % experimental error $= \dfrac{0.00204}{0.1111} \times 100 = 1.84\ \%$

These values were graphed against the tintometer scale readings, so that the percentage error on the adsorption coefficient could be read off directly from the tintometer reading. (Figure 18)

It is obvious that as the heights of the two liquid columns become more nearly equal, then the experimental error, which is inversely proportional to the difference in heights, becomes greater. Even a constant quantity of adsorbed dye alters the relative concentrations, and thus the relative heights, less and less as the concentration increases. Therefore an upper limit is set to the range of concentration which can be used, when the difference between the heights, and therefore the relative difference between the concentrations, is of the same order as the experimental error.

Evaluation of Interfacial Surface Area.

The drops were assumed to be spherical, and to be of uniform size. The latter they must be, since the drop rate and flow rate remain constant. Successive drops kept a constant distance from one another along the tube, and travelled at a rate of about 6 cms. per second. Stokes' Law implies that any irregularity in size would be evidenced by different rates of fall.

The surface area was calculated from the total number of drops and the total mass of liquid passing.

Example.

An adsorption coefficient for Methyl Orange on chlorobenzene will be calculated :-

Concentration of Methyl Orange = 0.1308 grs/litre

Weight of reservoir solution = 76.1 grams

Period of experiment = 1260 minutes

Bubble Rate = 92 bubbles per minute

Flow Rate = 151.7 grs. in 63 minutes

Volume of one drop $= \frac{4\pi r^3}{3} = \frac{151.7}{63\times 92\times 1.1062}$ ccs.

(Density of chlorobenzene at 17°C is 1.1062)

Surface area of one drop $= 4\pi r^2 = \left(\frac{151.7\times 3}{63\times 92\times 1.1062\times 4\pi}\right)^{2/3} 4\pi$

Therefore total area $= 4\pi r^2 \times 92\times 1260$

$= \underline{46{,}220\ \text{cm}^2}$.

Tintometer Readings :-	Original solution		Reservoir soln.
	20		32.3
	50		52.5
Therefore column heights =	30	and	20.2

Reservoir concentration $= \frac{30}{20.2}\times 0.1308 = 0.1928$ grs/litre

Increase in concn. $= 0.1928 - 0.1308 = 0.0620$ grs/litre

Weight of dyestuff adsorbed $= 0.0620\times\frac{76.1}{1000}$ grams,

Hence adsorption coefficient $= \frac{0.0620\times 76.1}{1000\times 46{,}220}$

$= 10.21\times 10^{-8}$ grams/cm^2.

From the graph, experimental error on a tintometer reading of 20.2 is 0.75 % of the adsorption coefficient

$= 0.077\times 10^{-8}$ grs./cm^2.

Therefore,

Adsorption Coefficient $= 10.2 \pm 0.1\times 10^{-8}$ grams/cm^2.

Test for Diffusion.

a) Benzene and petroleum ether apparatus.

In order to test the possibility of back diffusion of solute from the reservoir in which the adsorbed dye collected, the latter was filled with a 0.088 N sodium chloride solution, and the saturation columns with pure water. The salt solution lost only 3.5 % in concentration in 20 hours, and this value was unaltered even if benzene bubbles were passing up. The greatest concentration difference of dye set up in any experiment was 0.000014 gram. mols. per litre, from which back diffusion would be negligible.

b) Chlorobenzene apparatus.

Because of the actual structure of the apparatus, the amount of back diffusion from the reservoir in the case of chlorobenzene will be much less than that for benzene. Since the downward diffusion of strong solution in the benzene apparatus was only 3.5%, then the upward diffusion here must be negligible.

Proof of saturation of surface.

With all dyes, two adsorption columns of different heights were used :-

Apparatus.	Tower Heights.
Benzene	88 and 125 cms
Chlorobenzene	100 and 145 cms
Pet. Ether	110 and 150 cms.

The results obtained with the two columns were found to coincide within the limits of experimental error. For each dye, approximately equal numbers of points on the adsorption curves were obtained from each column. The volume of solution in the saturating columns was at least eight times that of the reservoir; the adsorption therefore took place from a solution of virtually constant concentration.

During experiments with chlorobenzene, it was observed that adsorption was not complete from a column 50 cms. long. This suggests that adsorption on the drops is not absolutely spontaneous, but that the interface must be exposed to the dye solution for more than a definite minimum time. The drops took about 10 seconds to travel this column.

Temperature Control.

Throughout the duration of these experiments, the room temperature remained at 17 ± 1.5°C. The apparatus was lagged with water jackets to minimise small fluctuations in temperature. Experiments with the chlorobenzene apparatus were also carried out at 22°C, by pumping water at this temperature from a thermostat through the water jackets by means of a Suddo water circulator. The flow of water was increased to such a rate as to keep the towers and the thermostat at the same temperature. The results agree, within the usual experimental error, with those for the same concentrations at 17°C.

Dye	Concentration grams/litre	Temp.	Adsn. Coeff. $gr.\times 10^{-8}/cm^2$
Methylene	0.1177	22°C	1.73 ± 0.05
Blue	0.1177	17°C	1.71 ± 0.05
Orange II	0.1995	22°C	2.7 ± 0.1
	0.1995	17°C	2.7 ± 0.1
Congo Red	0.1981	22°C	3.7 ± 0.1
	0.1981	17°C	3.7 ± 0.1
Methyl	0.8155	22°C	7.8 ± 0.3
Orange	0.5826	22°C	9.8 ± 0.2

The two points for Methyl Orange were both taken at 22°C, and fell on the curve obtained at 17°C.

----

d) Adsorption on the Air-water Interface.

The apparatus constructed for these experiments is shown in Figure 19.

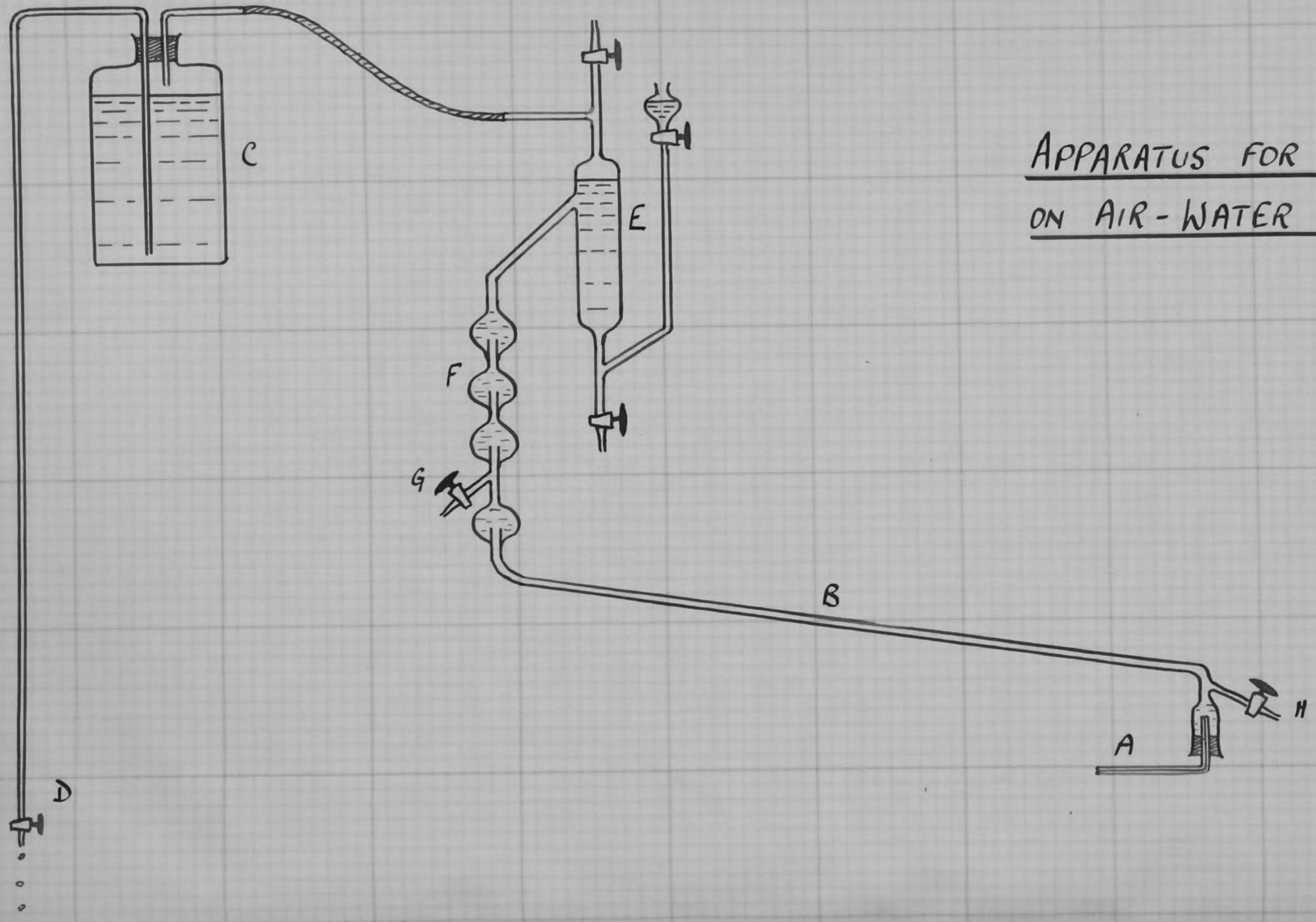
Air was drawn into the apparatus by means of the vacuum created when water from a tank C, connected to the apparatus, was run out through the tap D. Small bubbles, of approximate diameter 1.5 mm., were thereby drawn in through the thermometer tubing A, and passed along the slightly inclined tube B, of relatively large diameter, and about 80 cms. long. Besause of their small diameter, the bubbles were not obviously distorted. The bubbles took about 25 seconds to travel this tube, during which time it was assumed that any forces causing adsorption would have reached equilibrium. The bubbles then passed up a series of baffle chambers F, of the form found to be most effective in preventing back diffusion, and into a reservoir E, where they collapsed on reaching the surface.

The rate of bubbling could be readily controlled by regulating the flow of water from D. Bubble rates of the order of 150 per minute were used, at which rate the bubbles were about 1 cm. apart in the adsorption tube. The volume of air passing was that of the water flowing from C, plus a slight adjustment for the difference in pressure between A and E. Thus the surface area exposed could be directly evaluated.

Air bubbles travel much faster through a liquid than do bubbles of (say) benzene, and therefore set up a much stronger tendency for back diffusion to take place from E. Blank experiments showed that the three top baffle chambers were sufficient to prevent diffusion of dye from E into the fourth and lowest bulb. In attempts to detect adsorption, the solution from the tube B was compared tintometrically with the original. Any diffusion into B will take place from this lower bulb. Therefore on completion of an experiment, the solution from the top three bulbs was run

FIG. 19.

APPARATUS FOR ADSORPTION ON AIR-WATER INTERFACE.



out through the tap G, and by withdrawing the remaining solution through the tap H, the liquid in the lower bulb was included in the solution drawn from B. By so including the solution from which any diffusion would take place, diffusion influences are eliminated.

The tendency for the bubbles to coalesce in B presented an interesting case. When the apparatus was filled with pure water or very dilute dye solutions, the bubbles readily coalesced. When stronger dye solutions were used, this tendency was not apparent; the bubbles passed along B in a perfectly regular manner, as though the separation was being caused by a similar electrical charge on each bubble. Such a charge might be due to orientated polar dye molecules, on the surface of the bubbles, but it need not necessarily follow that this concentration of dye molecules on the interface is any greater than that in the bulk of the solution.

In attempts to measure the adsorption at this air-water interface, the method of McBain and Davies (18), in which the bulk solution drains away from the bubbles as they pass over an inverted U tube, was tried with apparatus of various dimensions, but was found to be impracticable. Since the surface tension of the dye solutions is almost the same as that of water, the bubbles collapsed before passing over the tube. It was verified that the apparatus constructed was suitable for the adsorption of substances which lowered the tension sufficiently to allow the formation of stable bubbles, since very attractive qualitative experiments were carried out with solutions of saponine and soap.

Three experiments, at various concentrations, were carried out with each dye. In no case could any adsorption be detected by the tintometric means employed.

The concentrations used, and areas of interface exposed, are given in the following table. (over)

Dye	Concentration grs/l	Surface Area cm^2.	Adsorption Coefficient
Orange II	0.0431	35,000	zero
	0.2150	53,000	"
	0.6530	71,000	"
Methylene Blue	0.0108	70,000	"
	0.0861	"	"
	0.2582	"	"
Bordeaux Extra	0.0190	70,000	"
	0.0950	90,000	"
	0.1900	70,000	"
Methyl Orange	0.1052	70,000	"
	0.2105	70,000	"
	0.4210	90,000	"
Congo Red	0.0526	70,000	"
	0.1051	"	"
	0.2102	"	"

Purity of substances used.

This section will be treated under the following headings :-

1. Organic Fluids.
2. Dyestuffs.
3. Water.
4. Special purification of Methyl Orange.

1. Organic Fluids.

a) Benzene.

The benzene used throughout was Messrs. Burgoyne and Burbridges' Ltd. A.R.Benzene, but the results were not affected by the substitution of benzene supplied as "Extra Pure". The following experiment was carried out with this benzene :-

Dye :- Methylene Blue

Concentration:- 0.1310 grs/l

Adsorption Coefficient:- 2.4 ± 0.14 $grs/cm^2 \times 10^{-8}$.

This point was found to lie on the curve obtained with the A.R.Benzene.

b) Chlorobenzene.

The chlorobenzene used throughout was Messrs. B.D.H. "Purified".

c) Petroleum Ether.

Ordinary petroleum ether, boiling point range 80°-100° C, was used in these experiments. A sample was distilled:-

The distillation range was 83° - 97° C. No distillate came over outside this range. Further,

74 % distilled between 83° and 90° C,
26 % " " 90° and 97° C.

The density of the ether used was 0.716 gr/cc (by density bottle).

The percentage of aromatic hydrocarbons in the sample was determined as follows:-

A sample was completely purified from aromatic hydrocarbons by shaking with concentrated sulphuric acid. An emulsion of equal quantities of this pure ether and aniline was heated, and the temperature at which the mixture cleared was noted. This was repeated with the ordinary ether. The percentage of aromatic hydrocarbons in the latter sample is given directly by the difference in degrees centigrade between the two cloud temperatures.

	Cloud Point.
Pure ether - aniline	58° C.
Ordinary ether - aniline	55° C.

Therefore the ordinary petroleum ether has 3 % of aromatic hydrocarbons.

The results were unaffected by the substitution of Messrs. B.D.H. "Analar" product, guaranteed to contain not more than 0.5 % of aromatics. The following experiments were carried out with this adsorbent and Orange II.

Concentration. grs/l	Adsorption Coefficient $gr \times 10^{-8}/cm^2$
0.1715	2.4 ± 0.3
0.4340	2.4 ± 0.3

These points fall on the curve obtained with the ordinary sample of ether.

2. Dyestuffs.

The dyes were purified until a drop number of benzene against a particular concentration of the dye was not altered by further purification.

a) Orange II.

The sample used was a student's preparation. It was recrystallised from water three times, after which a solution of concentration 0.3510 gr/l gave a drop number of 291, which lies on the curve obtained before purification. Further purification was therefore unnecessary.

Since insufficient of this stock was at hand, more dye was synthesised by diazotising p-aminobenzenesulphonic acid, and coupling the product with b-naphthol. This yield was purified in the same manner.

To prove the identity of the two dyes, a chlorobenzene drop number was taken against a solution of this dye. The drop number was 240 at concentration 0.5423 gr/l. This point falls on the chlorobenzene curve given by the dye taken from stock, and the two samples must therefore be identical.

b) Methyl Orange.

The sample used was taken from laboratory stock, and was recrystallised from water five times. Several drop numbers taken with this dye fell on the curve obtained with the dye before purification.

c) Congo Red.

The dye (laboratory commercial stock) was treated ina hot Soxhlet apparatus with absolute alcohol for a period of two days to remove any organic impurity of simpler constitution which might be soluble in the alcohol. The dye itself is only very slightly soluble. On applying the chromyl chloride test, the dye was found to contain traces of chloride. It was therefore treated in the manner advised by C.Robinson and H.A.T.Mills (55), by salting out with 40 % sodium acetate. This was repeated three times, after which no trace of chloride could be found. The acetate was removed by boiling with absolute alcohol, and the filtrate well washed with absolute alcohol. This was repeated four times, when no trace of acetate could be detected by the cacodyl test. Drop numbers were taken on this pure solution.

Drop Number.	Concentration. gr/l
271	0.4610
276	0.6305

These points coincide with those obtained beforepurification.

An adsorption experiment was also carried out with this pure dye :-

At concentration 0.0423 gr/l, adsorption coefficient is found to be $2.6 \pm 0.05 \times 10^{-8}$ gr/cm^2. This point also falls, within the usual experimental error, on the curve obtained before purification of the dye.

Congo Red solutions, even when made from the purified dye, faded on standing for several days, but not to any appreciable extent during the period of one experiment. All Congo Red solutions were therefore made up specially for each experiment.

d) <u>Methylene Blue</u>.

The sample used was taken from laboratory stock. The most probable impurities are sodium and zinc chlorides, by which the commercial product is salted out. No residue on ignition proved the absence of all possible inorganic impurities except zinc salts, which can volatilise. A solution of the dye was decolourised by reducing to the leuco compound with sodium hydrosulphite. This solution on treatment with ammonium sulphide gave only sulphur. The dye was therefore assumed to be pure.

e) <u>Bordeaux Extra</u>.

A sample of this compound was kindly prepared and given for this work by Messrs. I.C.I. Ltd., Blackley.

When this sample was used in experiments with benzene, a total loss of dye throughout the whole apparatus was noticed. The reservoir solution was stronger than the column, denoting some adsorption, but since the dye is insoluble in benzene, it must have disappeared from solution into an unpleasant scum which formed at the interface. The same result was obtained with chlorobenzene. The dye was therefore purified by the method used for Congo Red ; it was salted out four times with sodium acetate from redistilled water. It was extracted with boiling absolute alcohol four times, and then treated with the same agent in a hot Soxhlet apparatus for several hours. No acetate could be detected by the cacodyl test, and no acetate crystals were apparent under the microscope.

Experiments with this purified dye gave an interface free from scum, and it was therefore possible to investigate its adsorption.

Bordeaux Extra is a very intense dye in solution, being almost comparable in this respect with Methylene Blue.

3. Purity of Water.

The water used in making up the dye solutions throughout was laboratory distilled water, which is contained in a metal tank. A private communication, (C.Robinson) intimated that the presence of a minute trace of copper altered the conductivity of the water solutions by its effect on the degree of aggregation of the dyestuffs. Since this effect may also influence surface phenomena, some specially pure water was made by redistilling the laboratory distilled water, and collecting in a silica vessel. This water was tested for metal impurities, and its purity compared with that of the ordinary distilled water.

a) Laboratory distilled water.

Copper was tested for with sodium diethyldithiocarbamate, according to Messrs. B.D.H. instructions. A standard copper solution of one part in a million was compared in a tintometer with the test solution. The tank solution was found to contain one part of copper in 7 million.

<u>Tin.</u> was tested for with a-dinitrodiphenylaminesulphoxide, when no trace of tin was found.

<u>Lead</u> was absent; the darkening in colour of the water with hydrogen sulphide was due to the copper present.

<u>Ammonia</u> was found with Nessler's solution to be present as a very slight trace. The darkening did not appear immediately.

b) <u>Redistilled water</u>.

This water was found to contain no trace of metals, and only the slightest trace of ammonia. Its specific conductivity was tested with a "Megger" earth tester, and found to be approximately 8×10^{-6} mhos. It cannot therefore have sufficient of any impurity to influence the adsorption.

An experiment was carried out with the ordinary Methyl Orange and this pure water.

At concentration 0.8570 gr/l, Adsorption Coefficient was found to be $7.1 \pm 0.2 \times 10^{-8}$ gr/cm^2.

This point falls, within experimental error, on the curve given with the ordinary distilled water, and the small trace of copper cannot therefore have influenced the results.

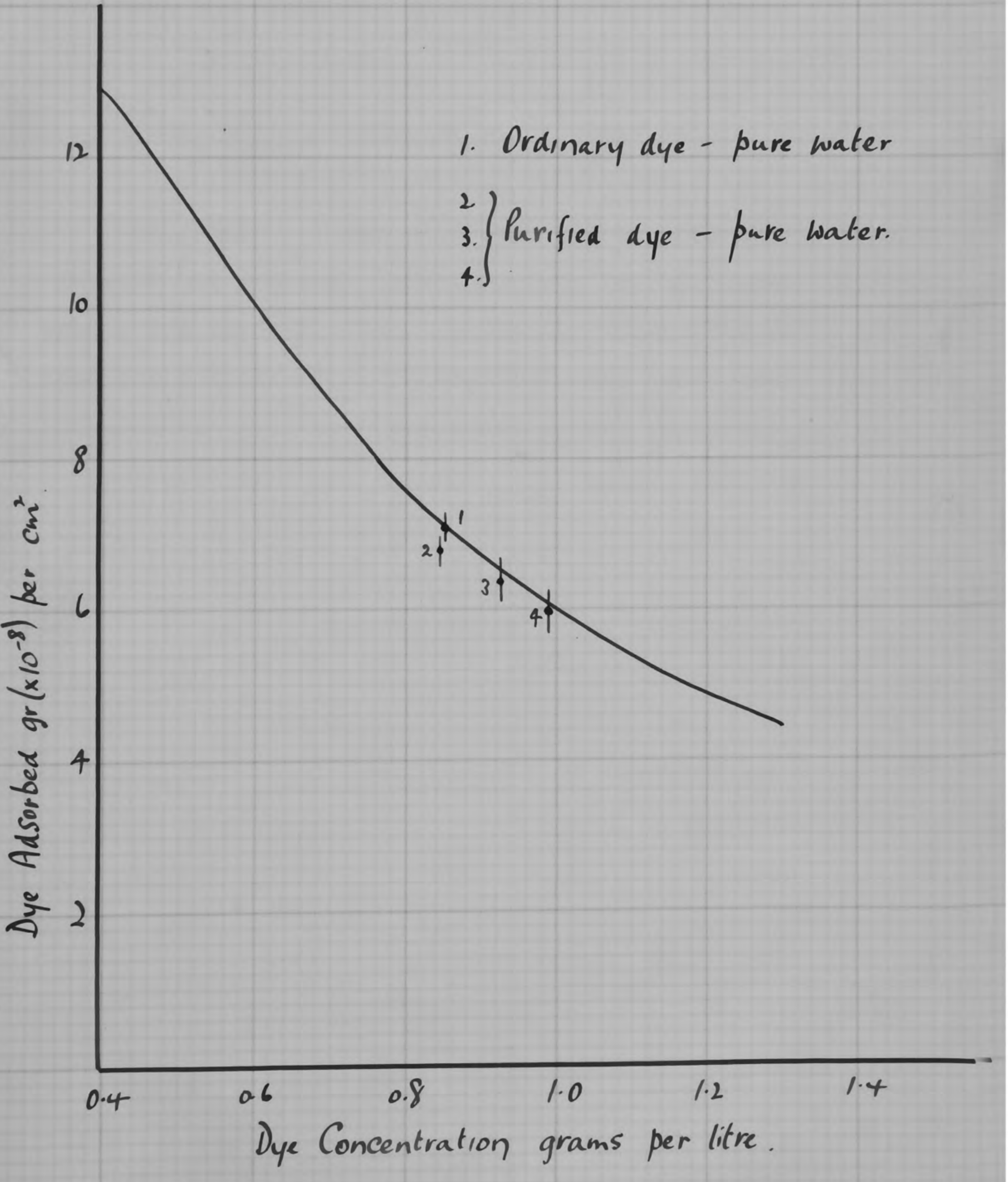
4. <u>Special purification of Methyl Orange</u>.

The suggestion by Dr.N.K.Adam (see previous theory), that some capillary active impurity may be replacing the dye on the interface in the cases where the interfacial adsorption falls from its maximum value, was tested in the following manner :-

Methyl Orange was chosen as a suitable substance for careful purification. It was treated in a Soxhlet apparatus for several hours with pure chloroform; the extract was

FIG. 20.

EXPERIMENTAL POINTS WITH SPECIALLY PURIFIED METHYL ORANGE.



green in thin layers, and red in thick. The dye was then treated similarly with petroleum ether, when nothing seemed to dissolve. This treatment should remove any simple components of the dye which may have remained from the synthesis, and inorganic impurities have already been removed. The Methyl Orange was then recrystallised four times from the specially purified water already described, when it was assumed to be as pure as was possible. Adsorption experiments on chlorobenzene were then carried out with this pure dye dissolved in the redistilled water.

Concentration. gr/l	Adsorption Coefficient. $gr. \times 10^{-8}/cm^2$.
0.8568	6.8 ± 0.2
0.9951	6.0 ± 0.37
0.9280	6.4 ± 0.3

The removal of any capillary active impurity would result in an increase in adsorption. In Figure 20, these points are shown plotted against the chlorobenzene adsorption curve already obtained, and signify that the results have not been influenced by any capillary active impurity.

Appendix 1.

Other adsorbents used.

a) Mercury.

An apparatus was constructed of a similar type to that used for chlorobenzene. The use of single drops of mercury was not practicable, since only a small surface area could be exposed. The mercury was therefore forced out of the jet in a fine spray, by means of a large head of pressure. The particle size was obtained by direct measurement, and also by Stokes' Law.

Picric acid was used as adsorbate, and the mercury was carefully purified. Even then, conductivity measurements showed a total loss of picric acid throughout the whole apparatus, probably due to reaction with the mercury.

As other work was on hand at the moment, this particular investigation was postponed. No particular difficulties were encountered, and further work should yield interesting results.

b) Nitrobenzene.

Nitrobenzene was considered as an adsorbent because of its strongly polar nature. All the dyes except Methyl Orange were, however, soluble in nitrobenzene. Further, the brown colour of the nitrobenzene was found to be due to an oxidation product which could not be permanently removed. The nitrobenzene imparted this colour to solutions in contact with it, and was therefore an unsuitable adsorbent for these experiments.

Appendix 2.

Other adsorbates used.

a) Attempts to repeat Lewis's experiments with sodium glycocholate were abandoned, because no pure sample could be obtained. Its solution became turbid on standing, and settled out during the course of an experiment.

b) Inorganic Salts.

Attempts were made to adsorb a range of inorganic salts at the benzene and chlorobenzene interfaces. The surface area exposed was increased by forcing the organic liquid through the jet as a fine spray, but in no case could any adsorption be detected.

The salts used were :-

Sodium and potassium chlorides,
" " " carbonates,
Silver and aluminium nitrates,
Zinc sulphate.

The reservoir and original solutions were compared by titration, conductivity and density measurements. These methods, however, are not capable of detecting a small enough difference in concentration, and interferometer measurements will probably be required before work on these inorganic salts can be continued.

Appendix 3 (a)

Details of adsorption experiments on

Benzene.

Methylene Blue.

(on Benzene)

Initial Concn gr/1	Time of Flow(mins)	Flow Rate gr/min.	Bubble Rate (per min)	Reservoir Weight(grs)	Tintometer Reading.	Surface Area(cm^2)	Adsorption Coefficient (gr×10^{-8}/cm^2)
0.00436	1164	2.024	26	230.43	29.3	29,100	0.103 ± 0.007
0.0218	1035	2.109	34	230.18	28.9	29,070	0.85 ± 0.03
0.0436	900	3.130	44	231.23	28.1	41,800	1.60 ± 0.06
0.0550	1463	1.827	23	252.58	28.7	32,790	1.92 ± 0.07
0.0621	1862	2.193	26	251.78	28.0	50,240	2.18 ± 0.05
0.0653	810	2.428	34	235.13	28.9	27,580	2.11 ± 0.10
0.0872	1348	1.864	27	231.10	28.6	32,300	2.40 ± 0.10
0.1100	1250	2.820	30	253.28	29.0	40,880	2.41 ± 0.12
0.1310	818	3.000	45	221.88	29.1	37,920	2.40 ± 0.14
0.1960	1190	3.050	46	236.33	29.5	59,540	2.38 ± 0.06
0.4598	1292	2.143	24	235.60	29.8	32,680	2.6 ± 0.6
0.5475	1327	3.440	88	229.08	29.6	68,570	2.5 ± 0.3

Congo Red. (on Benzene)

Initial Concn gr/1	Time of Flow(mins)	Flow Rate gr/min.	Bubble Rate (per min)	Reservoir Weight(grs)	Tintometer Reading.	Surface Area(cm^2.)	Adsorption Coefficient ($gr \times 10^{-8}/cm^2$.)
0.01196	1498	1.211	21	229.58	26.3	24,770	1.56 ± 0.02
0.0239	1141	2.916	47	228.45	22.5	44,320	2.58 ± 0.02
0.0283	836	3.378	34	254.40	27.2	32,150	2.29 ± 0.05
0.0329	1013	2.530	35	235.28	27.2	32,460	2.45 ± 0.05
0.0423	1156	1.780	36	229.10	27.9	29,560	2.46 ± 0.05
0.0425	520	4.021	42	249.40	28.5	24,470	2.28 ± 0.08
0.0486	837	3.074	32	254.00	28.3	30,040	2.50 ± 0.07
0.0624	1446	1.820	28	232.20	28.5	34,620	2.21 ± 0.08
0.0729	953	2.970	30	250.80	29.1	32,270	1.75 ± 0.1
0.0851	882	3.083	40	233.33	29.7	33,680	0.57 ± 0.09
0.1276	1180	2.768	42	232.78	29.9	42,310	0.20 ± 0.1
0.1822	1181	2.108	34	218.10	30.0	33,170	-
0.1881	1164	2.090	32	232.70	30.0	31,850	-
0.3300	1556	2.181	38	231.50	30.0	46,390	-

Orange II.

(on Benzene)

Initial Concn gr/1	Time of Flow(mins)	Flow Rate gr/min.	Bubble Rate (per min)	Reservoir Weight(grs)	Tintometer Reading.	Surface Area(cm^2)	Adsorption Coefficient (gr×10^{-8}/cm^2.)
0.0191	1099	1.744	22	233.93	27.9	23,550	1.75 ± 0.03
0.0296	1506	1.498	24	229.33	26.9	30,020	2.61 ± 0.05
0.0411	1170	2.884	46	225.78	26.2	44,800	3.02 ± 0.04
0.0592	1405	1.620	30	229.43	27.8	33,160	3.25 ± 0.08
0.0823	1085	2.971	27	250.18	28.4	35,500	3.27 ± 0.04
0.0883	1383	1.898	41	233.00	28.2	38,560	3.38 ± 0.11
0.1183	975	2.085	31	231.53	29.1	26,370	3.25 ± 0.18
0.2006	847	2.577	42	234.90	29.3	29,200	3.37 ± 0.24
0.2057	3423	1.287	21	230.48	29.0	54,370	3.09 ± 0.11
0.3445	599	2.227	41	230.00	29.7	18,620	4.20 ± 0.67
0.4433	1394	1.985	24	244.00	29.7	33,500	3.21 ± 0.51
0.5890	1119	2.330	46	240.78	29.7	37,150	2.98 ± 0.74

Bordeaux Extra.

(on Benzene)

Initial Concn gr/1	Time of Flow(mins)	Flow Rate gr/min.	Bubble Rate (per min.)	Reservoir Weight(grs)	Tintometer Reading.	Surface Area(cm^2)	Adsorption Coefficient $(gr \times 10^{-9}/cm^2)$
0.0310	1357	2.063	86	168.15	29.5	51,710	1.7 ± 0.2
0.0558	1310	2.367	102	176.6	29.5	57,350	2.9 ± 0.3
0.0939	936	2.683	114	169.8	29.8	46,190	2.5 ± 0.6
0.1261	1260	1.930	78	178.0	29.9	44,020	1.6 ± 0.8
0.1765	1440	1.904	68	177.25	30.0	47,610	0.0 ± 1.0

Methyl Orange.

(on benzene

Initial Concn gr/1	Time of Flow(mins)	Flow Rate gr/min.	Bubble Rate (per min)	Reservoir Weight(grs)	Tintometer Reading.	Surface Area(cm^2)	Adsorption Coefficient ($gr \times 10^{-8}/cm^2$)
0.01332	1120	1.172	28	229.50	29.0	19,940	0.5 ± 0.03
0.0305	830	2.858	84	231.50	28.7	38,610	0.96 ± 0.04
0.0333	1163	2.673	30	250.20	28.9	28,150	1.12 ± 0.05
0.0500	591	2.554	30	258.10	29.2	18,100	1.90 ± 0.10
0.0800	1135	1.445	30	237.30	29.1	23,770	2.47 ± 0.10
0.0828	1263	2.451	68	220.18	28.3	49,430	2.21 ± 0.06
0.1093	851	2.591	32	260.50	29.3	26,750	2.50 ± 0.20
0.1332	1240	3.020	88	229.20	28.7	60,780	2.50 ± 0.10
0.2120	1448	2.492	30	253.00	29.6	43,610	1.63 ± 0.20
0.3278	1368	2.479	31	257.80	29.9	41,530	0.68 ± 0.34
0.5337	1364	2.485	31	255.90	30.0	41,470	-
1.0673	973	1.836	50	232.80	30.0	28,340	-

Appendix 3 (b)

Details of adsorption measurements on Chlorobenzene.

Methylene Blue.

(on Chlorobenzene)

Initial Concn gr/1	Time of Flow(mins)	Flow Rate gr/min.	Bubble Rate per min.	Reservoir Weight(grs)	Tintometer Reading.	Surface Area(cm^2)	Adsorption Coefficient ($gr \times 10^{-8}/cm^2$)
0.0210	1052	2.327	66	90.9	28.8	33,700	0.24 ± 0.01
0.0420	932	1.888	42	76.4	28.7	22,380	0.65 ± 0.03
0.0627	905	2.043	47	77.0	28.7	23,790	0.92 ± 0.04
0.0941	982	2.997	61	89.3	28.5	32,660	1.50 ± 0.05
0.1383	1148	1.981	44	74.1	28.6	28,910	1.74 ± 0.07
0.2074	893	2.787	66	89.1	29.0	32,320	2.0 ± 0.1
0.2879	1295	3.076	63	88.2	28.8	49,290	2.1 ± 0.1
0.4030	1292	2.144	44	74.8	29.2	34,290	2.4 ± 0.15

Methyl Orange.

(on Chlorobenzene)

Initial Concn gr/1	Time of Flow(mins)	Flow Rate gr/min.	Bubble Rate per min.	Reservoir Weight(grs)	Tintometer Reading.	Surgace Area(cm.^{2})	Adsorption Coefficient (gr $\times 10^{-8}$/cm.^{2})
0.0343	1243	2.429	93	76.00	17.3	46,020	4.16 ± 0.03
0.1308	1260	2.408	92	76.10	20.2	46,220	10.2 ± 0.1
0 0.2501	955	2.458	95	89.60	24.9	35,880	12.8 ± 0.1
0.3852	1073	2.289	102	80.60	25.7	39,900	13.0 ± 0.2
0.5022	930	1.755	56	89.50	28.3	23,410	11.5 ± 0.4
0.6816	1050	2.364	108	77.70	28.1	40,130	8.9 ± 0.2
1.1224	1300	2.986	83	84.00	29.1	54,500	5.3 ± 0.3

Bordeaux Extra.

(on Chlorobenzene)

Initial Concn gr/1	Time of Flow(mins)	Flow Rate gr/min.	Bubble Rate per min.	Reservoir Weight(grs)	Tintometer Reading.	Surface Area.(cm^2)	Adsorption Coefficient. (gr×10^{-9}/cm^2)
0.0162	1353	2.147	78	77.65	29.0	43,480	1.0 ± 0.05
o.0408	1257	2.082	72	78.55	29.3	38,560	2.0 ± 0.15
0.0783	1327	2.371	86	77.75	29.6	47,080	1.8 ± 0.2
0.1280	1292	2.503	94	78.60	29.8	48,980	1.3 ± 0.3
0.2227	1325	2.352	92	78.35	30.0	47,820	0 ± 0.07

Congo Red.

(on Chlorobenzene)

Initial Concn gr/1	Time of Flow(mins)	Flow Rate gr/min.	Bubble Rate (per min)	Reservoir Weight(grs)	Tintometer Reading.	Surface Area(cm^2)	Adsorption Coefficient ($gr \times 10^{-8}/cm^2$.)
0.0205	1130	2.766	54	87.1	24.1	38,540	1.13 ± 0.01
0.0409	1130	2.000	40	77.3	26.7	36,140	1.08 ± 0.02
0.0629	1410	2.132	47	75.3	27.2	39,220	1.24 ± 0.03
0.0943	1230	2.887	56	91.5	27.8	42,640	1.59 ± 0.04
0.1425	912	2.149	46	77.5	28.0	24,610	3.18 ± 0.08
0.2503	1525	1.939	31	76.0	27.7	33,670	4.7 ± 0.1
0.3755	1380	2.855	47	89.4	28.8	38,880	6.8 ± 0.2
0.5247	1145	2.958	62	89.8	27.7	42,230	9.3 ± 0.2
0.6305	1047	1.941	35	75.3	28.6	24,110	9.6 ± 0.4
0.8000	965	2.111	43	75.7	28.9	25,150	9.2 ± 0.4
0.9608	876	2.866	54	89.8	29.5	30,210	4.9 ± 0.5
1.2000	913	2.908	54	90.2	29.9	31,800	1.1 ± 0.6

Orange II.

/on Chlorobenzene

Initial Concn gr/1	Time of Flow(mins)	Flow Rate gr/min.	Bubble Rate (per min)	Reservoir Weight(grs)	Tintometer Reading.	Surface Area(cm^2)	Adsorption Coefficient (gr$\times10^{-8}$/cm^2)
0.0298	1086	2.233	35	80.2	26.1	27,450	1.30 ± 0.02
0.0447	990	2.809	43	89.4	26.5	31,250	2.13 ± 0.03
0.0814	895	2.200	34	77.6	27.6	22,180	2.47 ± 0.06
0.1378	1077	2.083	35	77.5	28.2	26,800	2.55 ± 0.07
0.2444	861	2.184	34	91.3	29.2	21,230	2.90 ± 0.02
0.3353	1273	2.744	49	90.0	28.9	41,290	2.80 ± 0.10
0.5029	1142	2.241	70	77.1	29.2	36,440	2.9 ± 0.2
0.7071	1227	2.345	42	77.9	29.5	33,520	2.8 ± 0.3
1.0606	1098	2.773	53	89.4	29.6	35,490	3.6 ± 0.5

Appendix 3 (c).

Details of adsorption measurements on

Petroleum Ether.

Methylene Blue.

(on Pet. Ether.)

Initial Concn gr/1	Time of Flow(mins)	Flow Rate gr/min.	Bubble Rate per min.	Reservoir Weight(grs)	Tintometer Reading.	Surface Area(cm^2)	Adsorption Coefficient ($gr \times 10^{-8}/cm^2$)
0.0210	1420	1.64	62	176.0	29.5	59,330	0.1 ± 0.01
0.1012	1103	1.695	128	167.2	29.5	47,570	0.6 ± 0.06
0.2023	1187	1.767	64	180.0	29.8	41,780	0.6 ± 0.15
0.3380	1200	1.93	160	170.9	29.8	60,710	0.62±0.2
0.0421 ~~0.4210~~	1420	1.54	60	180.0	29.~~8~~5	46,850	0.28±0.03
0.5400	1200	2.35	90	183.9	29.9	57,280	0.55±0.3

Initial Concn gr/1	Time of Flow(mins)	Flow Rate gr/min.	Bubble Rate per min.	Reservoir Weight(grs)	Tintometer Reading.	Surface Area(cm^2)	Adsorption Coefficient ($gr \times 10^{-8}/cm^2$)
			Orange II. (on Pet. Ether)				
0.0302	1185	1.719	62	185.0	27.8	40,520	1.09 ± 0.03
0.0678	1260	1.080	84	174.7	28.7	33,890	1.58 ± 0.06
0.1180	1054	1.916	68	184.9	29.0	39,950	1.9 ± 0.1
0.2826	1395	1.662	58	187.3	29.5	45,600	2.0 ± 0.2
0.6775	1100	1.636	66	186.3	29.8	37,150	2.3 ± 0.6
0.9801	3504	1.380	56	186.3	29.6	100,000	2.4 ± 0.3
			Methyl Orange. (on Pet. Ether)				
o.0166	1176	1.185	90	170.9	29.5	35,530	0.14 ± 0.01
0.0554	930	1.36	100	174.8	29.5	31,210	0.55 ± 0.05
0.1108	1275	1.692	60	185.7	29.5	43,580	0.81 ± 0.08
0.1754	1200	1.181	92	173.6	29.6	36,560	0.6 ± 0.15
0.2338	900	3.44	36	182.5	29.9	34,100	0.4 ± 0.2
0.4962	1155	1.91	72	182.0	30.0	44,420	0.0 ± 0.3

Initial Concn gr/1	Time of Flow(mins)	Flow Rate gr/min.	Bubble Rate per min.	Reservoir Weight(grs)	Tintometer Reading.	Surface Area(cm^2)	Adsorption Coefficient (gr$\times10^{-8}$/cm^2.)
Bordeaux Extra. (on Pet. Ether)							
0.0100	1580	1.975	68	184.6	27.3	61,120	0.3 ± 0.003
0.0200	1400	1.610	56	179.8	28.2	44,330	0.5 ± 0.15
0.0500	1200	1.330	120	172.9	29.1	43,050	0.62±0.03
0.0800	1515	0.887	88	162.1	29.5	37,450	0.6 ± 0.06
0.1605	1200	2.000	80	178.4	29.8	49,230	0.36±0.09
Congo Red. (on Pet. Ether)							
0.00738	1370	2.07	140	147.5	27.9	69,720	0.14 ± 0.004
0.0203	1080	1.785	122	183.6	28.5	42,420	0.46 ± 0.02
0.0304	1260	1.335	116	181.3	28.9	44,860	0.47 ± 0.02
0.0407	1080	1.85	68	180.0	29.3	39,200	0.45 ± 0.03
0.0738	1330	2.37	70	181.1	29.7	58,660	0.23 ± 0.04
0.1215	1215	1.70	60	181.6	29.5- 30.0	46,310	0.0 ± 0.08

Appendix 4 (a)

Drop Numbers, Interfacial Tensions, and Calculated Adsorption Values for

Benzene.

			Reading	from	σ-c curve.
Concn gr/l	Drop Number	σ dynes /cm.	Concn gr/l	$\frac{d\sigma}{dc}$	Adsorption ($gr \times 10^{-8}/cm^2$.)
Methylene Blue - Benzene.					
0.0000	228	35.4	0.1	3.875	0.519
0.1340	232.5	34.7	0.2	3.19	0.837
0.2681	236	34.4	0.3	2.65	1.056
0.5475	241	33.7	0.4	2.2	1.156
0.8580	244	33.4	0.5	1.81	1.190
1.0725	246	33.2	0.6	1.5	1.182
			0.7	1.25	1.149
			0.8	1.025	1.077
			0.9	0.875	1.034
			1.0	0.75	0.985
Orange II - Benzene.					
0.0000	228	35.4	0.1	21.0	3.02
0.1003	254	32.1	0.2	15.5	4.46
0.2006	271	30.3	0.3	12.5	5.39
0.3396	290	28.4	0.4	10.5	6.04
0.5230	311	26.6	0.5	9.0	6.47
0.6970	329	25.3	0.6	7.5	6.47
1.0460	354	23.6	0.7	6.25	6.29
			0.8	5.25	6.04
			0.9	4.5	5.88
			1.0	4.0	5.75
Methyl Orange - Benzene.					
0.0000	228	35.4	0.1	8.8	1.184
0.1334	237.5	34.01	0.2	7.5	2.013
0.2669	245	33.13	0.3	6.63	2.67
0.5337	259	31.5	0.4	6.0	3.22
0.8518	273	30.0	0.5	5.4	3.64
1.0673	281	29.2	0.6	4.95	3.99
			0.7	4.55	4.25
			0.8	4.15	4.48
			0.9	3.90	4.71
			1.0	3.75	4.97
Congo Red - Benzene.					
0.0000	228	35.4	0.1	15.5	4.43
0.0911	241	33.5	0.2	11.0	6.49
0.1254	243	33.4	0.3	8.25	6.86
0.1881	252	32.2	0.4	6.0	6.86
0.2370	257	31.7	0.5	4.5	6.07
0.3696	266	30.7	0.6	3.0	5.14
0.4435	271	30.3	0.7	1.75	3.50
0.6650	278	29.5	0.8	0.75	1.71
0.8308	280	29.4	0.9	0.25	0.64
1.0730	281	29.3	1.0	0.00	-

			Reading from σ-c curve.		
Concn gr/1	Drop Number	σ dynes /cm.	Concn gr/1	$\frac{d\sigma}{dc}$	Adsorption $(gr \times 10^{-8}/cm^2.)$
		Bordeaux Extra - Benzene.			
0.0000	136	35.38	0.02	19.1	1.09
0.1200	144	33.44	0.06	14.6	2.51
0.2400	149	32.31	0.1	11.9	3.41
0.3600	152	31.82	0.2	8.1	4.64
0.5000	157	30.81	0.3	6.6	5.67
0.6305	161	30.00	0.4	5.9	6.76
			0.5	5.5	7.88

Appendix 4 (b)

Drop Numbers, Interfacial Tensions, and Calculated Adsorption Values for

Chlorobenzene.

			Reading from σ-c curve.		
Concn gr/l	Drop Number	σ dynes /cm.	Concn gr/l	$\frac{d\sigma}{dc}$	Adsorption $(gr \times 10^{-8}/cm^2)$
		Methylene Blue - Chlorobenzene.			
0.0000	188	37.41	0.1	10.1	1.34
0.0867	196	36.00	0.2	6.0	1.59
0.2167	202	34.95	0.3	4.2	1.67
0.4334	208	34.09	0.4	3.2	1.70
0.5778	210	33.72	0.6	1.85	1.47
1.0219	214	33.20	0.8	1.3	1.38
2.0438	219	32.50	1.0	1.0	1.33
			1.2	0.9	1.43
			1.4	0.75	1.39
			1.6	0.6	1.27
			1.8	0.5	1.19
			2.0	0.42	1.11
		Orange II - Chlorobenzene.			
0.0000	188	37.41	0.08	21.8	2.53
0.0532	205	36.00	0.1	21.5	3.12
0.1064	213	33.35	0.12	20	3.48
0.2128	225	31.70	0.14	18	3.66
0.5319	240	29.86	0.16	14	3.48
1.0638	255	28.21	0.18	12.5	3.3
2.1275	283	25.58	0.2	11.1	3.22
			0.3	6.8	3.96
			0.4	4.7	2.73
			0.5	3.94	2.86
		Methyl Orange - Chlorobenzene.			
0.0000	188	37.41	0.1	18.2	2.47
0.1244	207	34.24	0.2	11.6	3.15
0.3111	222	32.08	0.3	8.7	3.54
0.6222	237	30.20	0.4	6.7	3.63
0.9334	248	29.00	0.6	4.85	3.95
1.2445	258	27.88	0.8	4.0	4.34
1.8667	273	26.47	1.0	3.4	4.61
			1.2	3.0	4.88
			1.4	2.6	4.94
			1.6	2.3	4.99
			1.8	2.0	4.88
			2.0	1.7	4.61
		Congo Red - Chlorobenzene.			
0.0000	188	37.41	0.02	43	2.49
0.0495	210	33.79	0.04	43	5.02
0.1503	228	31.32	0.06	37	6.34
0.1981	232	30.82	0.08	29	6.62
0.3962	241	29.73	0.10	23.5	6.71
0.6604	246	29.17	0.15	13.6	5.83
1.3208	256	28.10	0.20	8.1	4.63
1.9812	263	27.38	0.3	4.45	3.81
			0.4	3.17	3.62
			0.5	2.30	3.29

			Reading from σ-c curve.		
Concn gr/l	Drop Number	σ dynes /cm.	Concn gr/l	$\frac{d\sigma}{dc}$	Adsorption $(gr \times 10^{-8}/cm^2)$
Bordeaux Extra - Chlorobenzene.					
0.0000	188	37.41	0.02	16.2	0.93
0.0820	194	36.33	0.06	12.0	2.06
0.1640	198	35.60	0.10	9.3	2.66
0.2907	202	35.08	0.20	6.1	3.50
0.4100	206	34.48	0.30	4.8	4.13
0.5200	208	34.07	0.4	3.8	4.35
0.5726	209	33.90	0.5	3.1	4.44
			0.6	2.5	4.29

Appendix 4 (c)

Drop Numbers, Interfacial Tensions, and Calculated Adsorption Values for

Petroleum Ether.

			Reading from σ-c curve.		
Concn gr/l	Drop Number	σ dynes /cm.	Concn gr/l	$\frac{d\sigma}{dc}$	Adsorption ($gr\times10^{-8}/cm^2$)
		Methylene Blue - Petroleum Ether.			
0.0000	228	51.35	0.05	24.0	1.58
0.1038	243	48.36	0.1	18.0	2.36
0.2000	248	47.43	0.15	8.9	1.75
0.3460	250	47.07	0.2	3.8	0.998
0.7200	252	46.72	0.25	2.8	0.92
1.0380	255	46.21	0.3	2.4	0.946
			0.4	1.8	0.946
			0.5	1.15	0.755
			0.6	0.8	0.631
		Orange II - Petroleum Ether.			
0.0000	228	51.35	0.05	29	2.08
0.1460	253	46.55	0.1	21	3.02
0.2910	266	44.39	0.15	19	4.09
0.5820	284	41.71	0.2	16	4.60
1.0700	305	38.96	0.25	13	4.67
			0.3	10.6	4.57
			0.4	9.6	5.52
			0.5	8.2	5.89
			0.6	7.0	6.03
			0.7	6.5	6.54
			0.8	6.3	7.24
			0.9	6.15	7.95
			1.0	5.95	8.55
		Methyl Orange - Petroleum Ether.			
0.0000	228	51.35	0.05	22	1.47
0.1272	243	48.29	0.1	19	2.55
0.2544	252	46.73	0.15	13	2.61
0.4070	260	45.42	0.2	11.4	3.06
0.6784	270	43.78	0.25	10.5	3.52
1.0176	279	42.46	0.3	9.2	3.70
			0.4	7.4	3.97
			0.5	6.5	4.36
			0.6	5.5	4.42
		Congo Red - Petroleum Ether.			
0.0000	228	51.35	0.02	76	4.34
0.0357	245	47.98	0.05	45	6.43
0.0520	249	47.25	0.08	25	5.71
0.1070	258	45.69	0.10	18.5	5.29
0.4000	269	43.92	0.15	8.3	3.56
0.8000	273	43.32	0.20	6.3	3.60
1.2094	280	42.29	0.25	5.3	3.79
			0.30	4.5	3.86

			Reading	from σ-c	curve.
Concn gr/l	Drop Number	dynes /cm.	Concn gr/l	$\frac{d\sigma}{dc}$	Adsorption ($gr\times10^{-8}/cm^2$)
Bordeaux Extra - Petroleum Ether.					
0.0000	228	51.35	0.04	26	2.9
0.1000	241	48.67	0.08	21	4.8
0.2000	248	47.38	0.1	16.8	4.8
0.3650	256	45.94	0.2	10.2	5.8
0.5520	264	44.63	0.3	8.0	6.9
0.7360	268	44.03	0.4	6.6	7.6
0.9210	272	43.46	0.5	5.2	7.4

Appendix 5.

Surface Pressures (F) and Areas (A)
of
Adsorbed Molecules.

Methylene Blue.

Concn. gr/1	Adsorption Coefficient gr/cm^2.	Area A cm^2/gr.mol	Pressure F dynes/cm.
a) On Petroleum Ether.			
0.01	0.06 $\times 10^{-8}$	5.30 $\times 10^{11}$	0.6
0.02	0.13	2.44	1.0
0.04	0.26	1.22	1.6
0.06	0.39	0.80	2.1
0.08	0.48	0.66	2.6
0.10	0.55	0.59	3.0
0.20	0.64	0.50	3.95
0.30	0.63	0.50	4.25
0.40	0.62	0.53	4.45
0.50	0.60	0.53	4.6
b) On Benzene.			
0.02	0.85 $\times 10^{-8}$	3.80 $\times 10^{10}$	0.1
0.04	1.6	2.00	0.2
0.06	2.1	1.52	0.3
0.08	2.35	1.34	0.4
0.10	2.4	1.34	0.48
0.2	2.4	1.34	0.82
0.3	2.4	1.34	1.12
0.4	2.4	1.34	1.37
0.5	2.4	1.34	1.58
0.6	2.4	1.34	1.78
0.7	2.4	1.34	1.9
c) On Chlorobenzene.			
0.02	0.35 $\times 10^{-8}$	9.10 $\times 10^{10}$	0.3
0.04	0.70	4.60	0.7
0.06	1.0	3.23	1.00
0.08	1.25	2.57	1.25
0.10	1.5	2.13	1.40
0.15	1.8	1.78	1.95
0.2	2.0	1.60	2.35
0.3	2.2	1.45	2.95
0.4	2.35	1.37	3.2
0.5	2.4	1.33	3.5
0.6	2.4	1.33	3.68

Orange II.

Concn. gr/l	Adsorption Coefficient gr/cm^2.	Area A cm^2/gr.mol	Pressure F dynes/cm.
a) On Petroleum Ether.			
0.01	0.5×10^{-8}	7.0×10^{10}	1.0
0.02	0.8	4.4	1.6
0.04	1.3	2.7	2.45
0.06	1.55	2.28	3.0
0.10	1.8	1.96	3.95
0.15	2.0	1.75	4.95
0.2	2.1	1.67	5.85
0.3	2.13	1.64	7.1
0.4	2.19	1.58	8.15
0.5	2.20	1.57	9.0
0.6	2.25	1.56	9.75
0.7	2.32	1.52	10.45
b) On Benzene.			
0.01	1.0×10^{-8}	3.5×10^{10}	0.45
0.02	1.8	1.95	0.9
0.03	2.6	1.35	1.3
0.04	3.0	1.17	1.65
0.05	3.15	1.11	1.95
0.06	3.2	1.09	2.2
0.1	3.25	1.08	3.2
0.3	3.25	1.08	6.45
0.4	3.26	1.07	7.6
0.6	3.27	1.07	9.4
0.7	3.28	1.07	10.05
c) On Chlorobenzene.			
0.02	1.0×10^{-8}	3.45×10^{10}	1.4
0.04	1.8	1.96	2.4
0.06	2.2	1.59	3.0
0.08	2.4	1.45	3.6
0.10	2.5	1.41	3.9
0.2	2.7	1.30	5.6
0.3	2.8	1.25	6.4
0.4	2.87	1.22	7.0
0.5	2.92	1.20	7.4
0.6	3.0	1.16	7.8
0.7	3.1	1.12	8.1

Congo Red.

Concn. gr/l	Adsorption Coefficient gr/cm^2.	Area A cm^2/gr.mol	Pressure F dynes/cm.
a) On Petroleum Ether.			
0.01	0.25 × 10^{-8}	2.78 × 10^{11}	1.4
0.02	0.43	1.61	2.4
0.03	0.49	1.42	3.2
0.04	0.46	1.5	3.7
0.05	0.40	1.75	4.1
0.06	0.31	2.04	4.5
0.08	0.21	3.3	5.1
0.10	0.12	5.9	5.54
0.12	0.05	14	5.86
0.14	0.01	72	6.04
b) On Benzene.			
0.02	2.0 × 10^{-8}	3.0 10^{10}	0.5
0.04	2.5	2.78	1.0
0.06	2.3	3.03	1.3
0.08	0.9	7.7	1.6
0.10	0.4	17.8	2.0
0.12	0.25	27.8	2.3
0.14	0.17	41.6	2.55
0.16	0.05	139.0	2.8
c) On Chlorobenzene.			
0.1	2.1 × 10^{-8}	3.3 × 10^{10}	5.0
0.2	4.1	1.69	6.6
0.3	6.0	1.16	7.2
0.5	9.0	0.77	7.9
0.6	9.7	0.72	8.1
0.7	9.6	0.72	8.3
0.8	8.6	0.83	8.5
1.0	4.1	1.69	8.9
1.1	2.2	3.12	9.1
1.2	1.1	6.25	9.3
1.3	0.4	16.5	9.5

Methyl Orange.

Concn. gr/l	Adsorption Coefficient gr/cm^2.	Area A cm^2/gr.mol	Pressure F dynes/cm.
a) On Petroleum Ether.			
0.05	0.53 × 10^{-8}	6.2 × 10^{10}	1.6
0.10	0.80	4.15	2.6
0.15	0.70	4.76	3.4
0.20	0.50	6.7	4.1
0.25	0.35	9.0	4.6
0.30	0.22	14.3	5.15
0.35	0.13	25.0	5.5
0.40	0.08	41.5	5.9
0.45	0.05	67.0	6.25
0.50	0.03	110	6.6
b) On Benzene.			
0.01	0.5 × 10^{-8}	6.2 × 10^{10}	0.12
0.02	0.75	4.35	0.2
0.06	2.20	1.49	0.6
0.10	2.55	1.28	0.95
0.2	1.70	1.93	1.8
0.3	0.83	4.0	2.5
0.4	0.30	11.9	3.15
0.5	0.05	66.8	3.7
c) On Chlorobenzene.			
0.1	9.1 × 10^{-8}	0.36 × 10^{10}	2.4
0.2	12.0	0.27	4.1
0.3	13.1	0.25	5.17
0.4	12.8	0.256	5.9
0.5	11.4	0.286	6.5
0.6	9.9	0.333	7.0
0.7	8.8	0.37	7.5
0.8	7.8	0.416	7.95
0.9	6.4	0.50	8.35
1.0	6.0	0.555	8.7

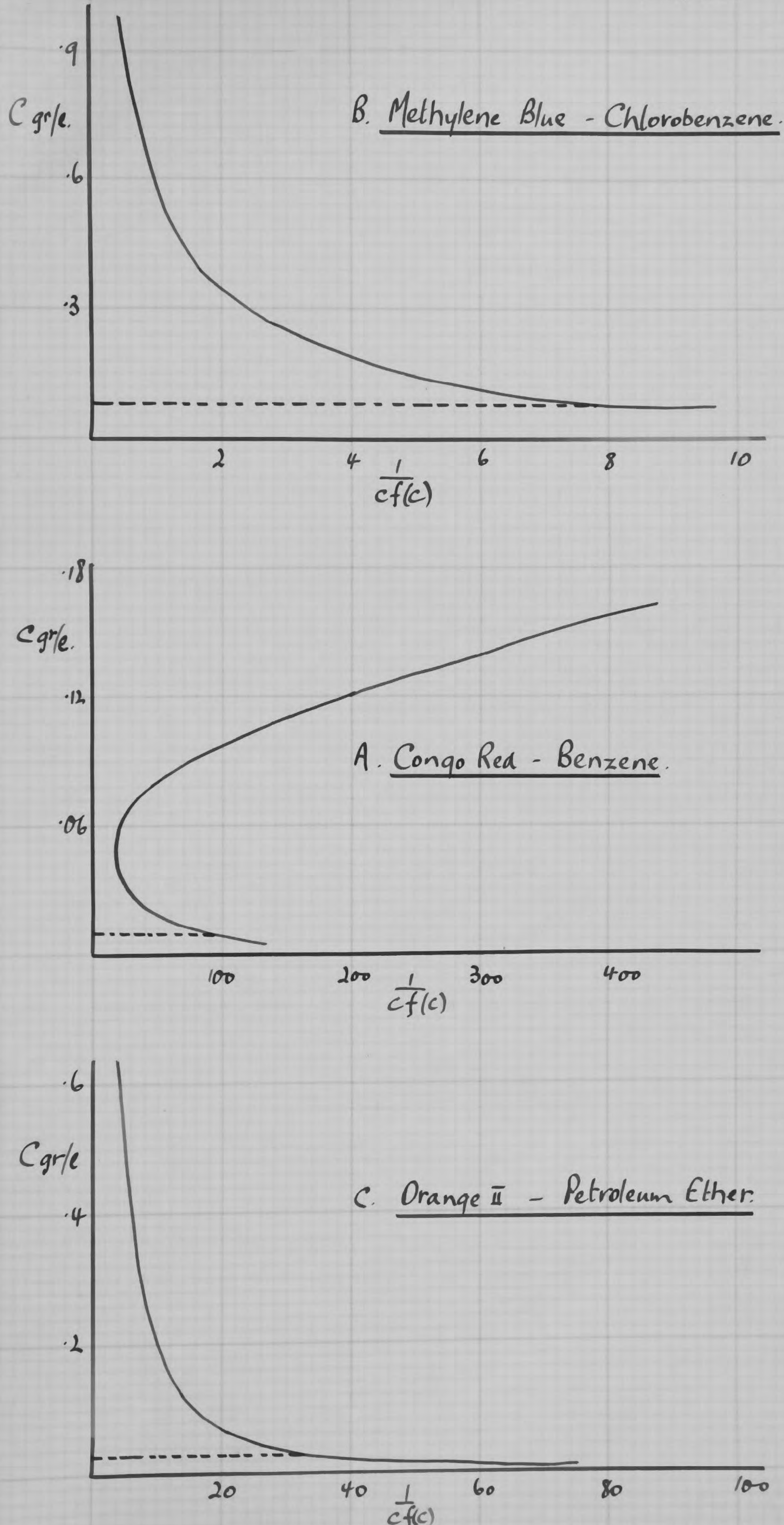
Bordeaux Extra.

Concn. gr/l	Adsorption Coefficient gr/cm .	Area A cm /gr.mol	Pressure F dynes/cm.
a) On Petroleum Ether.			
0.02	0.50 × 10^{-8}	1.39 × 10^{11}	1.0
0.04	0.62	1.11	1.65
0.06	0.60	1.20	2.1
0.08	0.57	1.22	2.4
0.10	0.53	1.33	2.8
0.15	0.40	1.75	3.5
0.20	0.26	2.70	4.1
b) On Benzene.			
0.01	0.06 × 10^{-8}	1.163×10^{12}	0.3
0.02	0.125	0.556	0.5
0.04	0.24	0.291	0.85
0.06	0.3	0.233	1.15
0.08	0.28	0.25	1.4
0.10	0.235	0.30	1.7
0.15	0.11	0.633	2.25
0.20	0.04	1.75	2.7
c) On Chlorobenzene.			
0.01	0.06 ×10^{-8}	1.163×10^{12}	0.15
0.02	0.125	0.556	0.3
0.04	0.20	0.35	0.5
0.06	0.20	0.35	0.75
0.08	0.175	0.40	1.0
0.10	0.15	0.465	1.2
0.15	0.09	0.77	1.6
0.20	0.04	1.75	2.0

Appendix 6.

Graphs and Tables employed in Activity Calculations.

FIG. 21.



B. Methylene Blue - Chlorobenzene.

A. Congo Red - Benzene.

C. Orange II - Petroleum Ether.

Concn. gr/1	$\Gamma_c \times 10^8$	$\Gamma_0 \times 10^8$	$f(c) = \frac{a}{c}\cdot\frac{dc}{da}$	$\int_{c=c_1^*}^{c=c} \frac{dc}{cf(c)}$	$2.303 \log_{10} a$	a	Activity Coefficient.
a) Congo Red on Benzene.							
0.01	1.0	1.0	1.0	0.00	-4.606	0.01	1.0
0.06	3.3	2.3	0.69	1.88	-2.72	0.068	1.3
0.08	4.0	1.0	0.25	2.50	-2.10	0.12	1.5
0.10	4.6	0.3	0.065	4.02	-0.58	0.56	5.6
0.12	5.1	0.2	0.391	7.22	+2.62	13.8	115
0.14	5.6	0.12	0.021	12.42	+7.82	251	1793
0.16	6.0	0.1	0.016	19.62	+15.00	2.8×10^6	1.75×10^7
b) Methylene Blue on Chlorobenzene.							
0.08	1.15	1.15	1.0	0.00	-2.47	0.08	1.0
0.1	1.20	1.50	1.25	0.17	-2.30	0.10	1.0
0.2	1.60	1.95	1.22	0.82	-1.65	0.19	0.95
0.3	1.70	2.20	1.30	1.14	-1.33	0.26	0.87
0.4	1.67	2.57	1.42	1.35	-1.12	0.33	0.83
0.5	1.60	2.4	1.50	1.50	-0.97	0.38~~0.43~~	0.76
0.6	1.50	2.4	1.60	1.61	-0.86	0.43	0.72
0.7	1.44	2.4	1.67	1.71	-0.76	0.47	0.67
0.8	1.38	2.4	1.74	1.79	-0.68	0.51	0.64
c) Orange II on Petroleum Ether.							
0.03	1.1	1.1	1.0	0.00	-3.51	0.03	1.0
0.06	2.0	1.55	0.775	8.1	+4.59	100	↓
0.08	2.5	1.70	0.68	12.1	+8.59	5370	∞
0.1	3.0	1.80	0.60	15.5	+12.03	16,600	
0.2	4.3	2.10	0.49	28.8	+25.33	↓	
0.3	5.0	2.13	0.426	38.0	+34.53	∞	
0.4	5.6	2.18	0.39	45.2	+41.73		
0.5	6.0	2.20	0.367	51.0	+47.53		

* Note.

Values of c_1 are
(A) 0.01
(b) 0.08
(c) 0.03

Bibliography.

(1) Langmuir, Chem.Met.Eng. 15,468,1916.
(2) " J.A.C.S. 39,1848,1917.
(3) Harkins, Davies, and Clark, J.A.C.S. 39,541,1917.
(4) E.L.Griffin, " 45,1648,1923.
(5) Van der Meulen and Riemann, " 46,876,1924.
(6) " " , " 47,2507,1925.
(7) W.D.Harkins and N.Beeman, " 51,1674,1929.
(8) E.K.Fischer and Harkins, J.Phys.Chem. 86,1932.
(9) W.C.McLewis, Phil.Mag. 15,499,1908.
(10) " " " 17,466,1909.
(11) Patrick, Zeit.Phys.Chem. 86,545,1914.
(12)Nonaka, J.Chem.Soc.Ind.Japan, 31,297,1928.
(13) " " " , 32,115,1929.
(14) Seymour, Tartar, and Wright, J.Phys.Chem. 38,839,1934.
(15) Zawidski, Zeit.Phys.Chem. 35,77,1900.
(16) Milner, Phil.Mag. 13,96,1907.
(17) Donnan and Barker, Proc.Roy.Soc.A, 85,557,1911.
(18) J.W.McBain and G.P.Davies, J.A.C.S. 49,2230,1927.
(19) " " R.Dubois, " 51,3534,1929.
(20) M.E.Laing, J.W.McBain and E.W.Harrison,
Coll.Symp.Monograph, 6,63,1928.
(21) Harkins and Gans, " " " , 5,40,1927.
(22) " " " , " " " , 6,36,1928.
(23) J.W.McBain and C.W.Humphreys, J.Phys.Chem. 36,300,1932.
(24) " " R.C.Swain,Proc.Roy.Soc.a,154,1936.
(25) " " D.A.Wilson, J.A.C.S. 58,379,1936.
(26) " " T.F.Ford, " 58,378,1936.
(27) W.D. and C.E.Barrett, Coll.Symp.Monograph,6,73,1928.
(28) Kolthoff and Rosenbaum, J.A.C.S. 2664,1933.
(29) Paneth, Radioactive Indicators, p.72.
(30) N.Ando, J.Chem.Soc. Japan,A, 697,1935.
(31) Schofield and Rideal, Proc.Roy.Soc.A,109,1925.
(32) " " " , " ,110,1926.
(33) " " " , Phil.Mag. 13,806,1932.
(34) Wynne-Jones, " " 12,907,1931.
(35) R.Dubrisay, Compt.Rend. 182,1217,1926.
(36) Harkins and Wampler, J.A.C.S. 53,850,1931.
(37) Butler and Wightmah, J.C.S. 2089,1932.
(38) J.L.Shereshefski, J.Phys.Chem. 36,1271,1932.
(39) J.W.Belton, Trans.Farad.Soc. 31,1642,1935.
(40) " , " " " , 31,1413,1935.
(41) " , " " " , 31,1648,1935.
(42) Sidgwick and Bowen, Annual Reports, 28,402,1931.
(43) Valko, Farad.Soc.Discn.Colloidal Electrolytes,230,1935.
(44) Robinson, ibid.p.245.
(45) Quesnel, ibid.p.259.
(46) Alty, Proc.Roy.Soc.A, 106,315,1924.
(47) Lewis, Zeit.Phys.Chem. 73,143,1910.
(48) J.W.McBain, Nature, 659,137,1936.
(49) Guye and Perrot, Arch.Sci.Phys.Nat.Geneva,15,178,1903.
(50) Tate, Phil.Mag. 27,176,1864.
(51) Lohnstein, Ann.der Physik,1906. 20,798,237,606.
21,1030.22,191.
(52) Harkins and Brown, J.A.C.S. 499,1909.
(53) Rayleigh, Phil.Mag. 48,321,1899.
(54) Harkins and Cheng, J.A.C.S. 43,35,1921.
(55) Robinson and Mills, Proc.Roy.Soc.A,131,576 & 596,1931.

SUMMARY.

The adsorption of Methylene Blue, Orange II, Methyl Orange, Congo Red and Bordeaux Extra, from various concentrations of each, has been measured at the benzene-water, chlorobenzene-water, petroleum ether-water and air-water interfaces at 17°C, by the moving bubble method. The adsorbed material was determined colorimetrically. Interfacial tensions of the same systems were measured by the drop weight method, and surface tensions by capillary rise.

Considerable deviations from the consequences of Gibbs's Adsorption Equation have been found. They can be ascribed to the action of factors not considered by him, but not to that of any one factor. Activities of dye solutions have been calculated.

Two types of concentration-adsorption curve have been found, differing according to the adsorbate, but independent of the interface. The adsorption of Methylene Blue and Orange II rises to a maximum and remains there up to the highest concentrations used. That of Congo Red, Bordeaux Extra and Methyl Orange passes through a maximum, and returns to or towards zero at higher concentrations. The numerical value of the adsorption reached in the two former cases is the same whether benzene or chlorobenzene is used; for Congo Red or Methyl Orange the influence of polar strength of the adsorbent is outstanding. Bordeaux Extra shows anomalous behaviour, and adsorption on petroleum ether is small throughout. In no case was adsorption observed on the air-water interface, and lowering of surface tension was only slight.

Methylene Blue and Orange II on benzene and chlorobenzene interfaces form approximately monomolecular layers, which

show transition, with increasing concentration, from a gaseous to a condensed nature. The adsorption curves for the other three dyes, although similar to those required by Gibbs's Equation, could also be accounted for qualitatively by assuming selective adsorption of single molecules. Methyl Orange and Congo Red, at maximum adsorption, form sparse monomolecular layers on benzene, but on chlorobenzene their layers are approximately two molecules thick.

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