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.

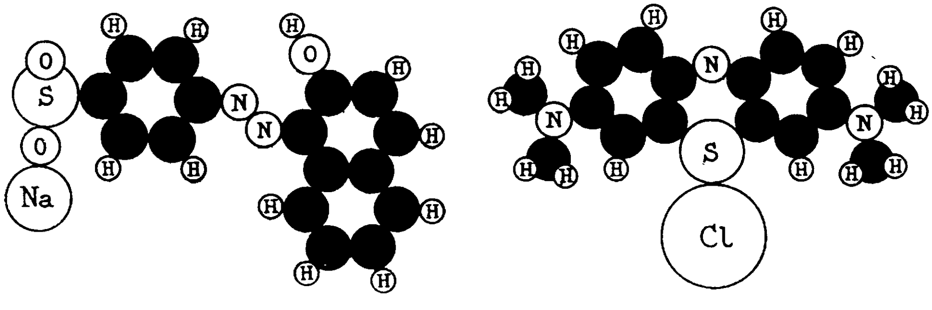
We have measured (i) the adsorptions of four dyes from various concentrations of each in water, at water–benzene and water–chlorobenzene interfaces, near 17°; (ii) the interfacial tensions of the systems. The four dyes mentioned in the title were specially purified. Benzene and chlorobenzene were chosen 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.

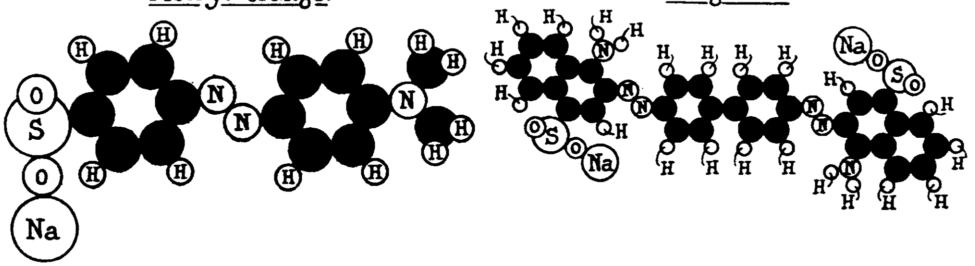
It is particularly to be observed that Gibbs's equation in this form is intended to apply only to the adsorption of a single component from a solution in which its behaviour is ideal with reference to concentration, and that in this, or in its original form, it applies only to interfaces unaffected by 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.

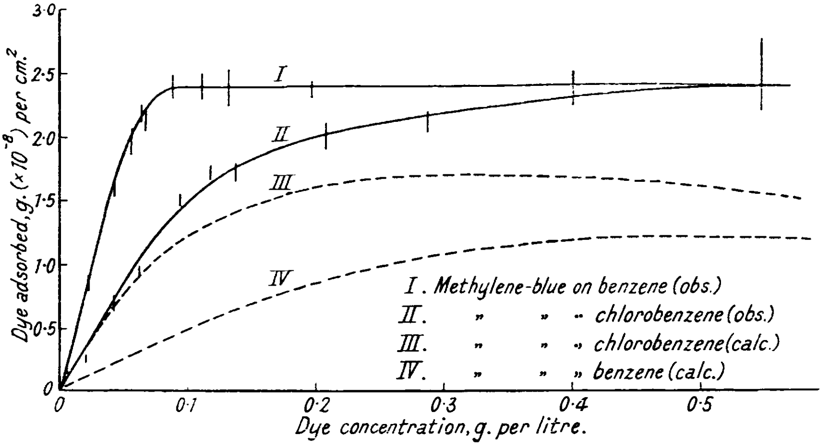
Congo-red.

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.

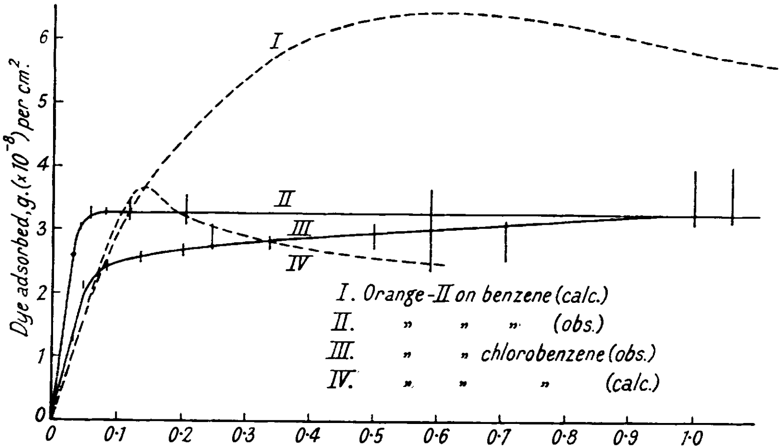
Two distinct types of concentration–adsorption curve are found here. The type differs according to the absorbate, but is independent of whether the interface is water–benzene or water–chlorobenzene.

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.

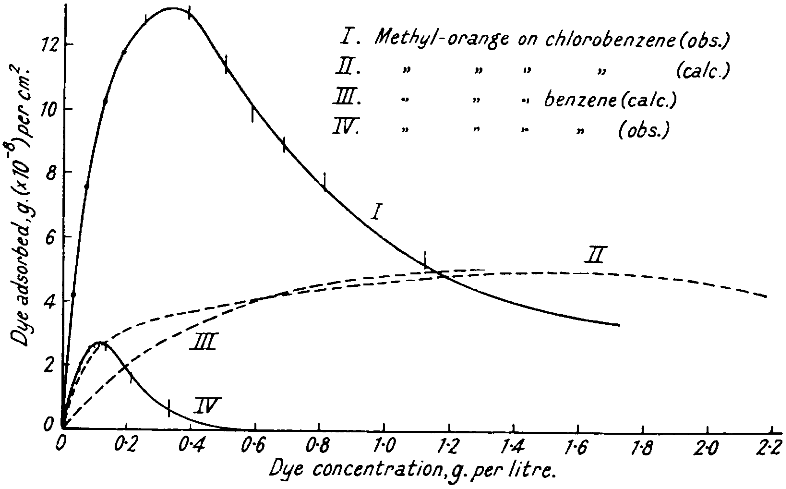
FIG. 3.



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.

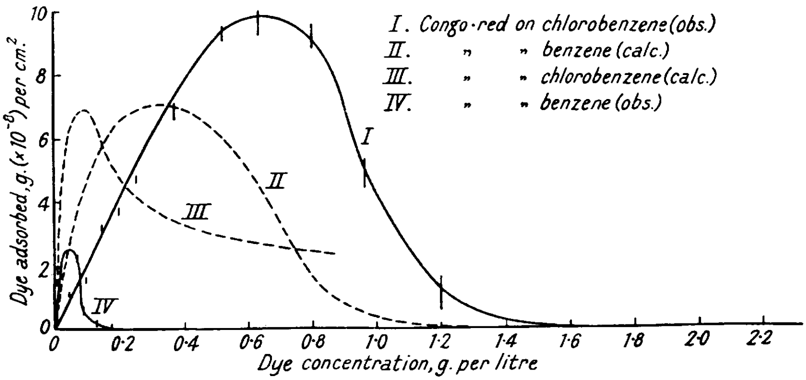
The shapes of the experimental curves for Congo-red and methyl-orange, although similar to those required by Gibbs's equation, could equally well be accounted for qualitatively on the assumption that only single molecules are adsorbed. Two opposing factors are then operating simultaneously : on the low-concentration 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.

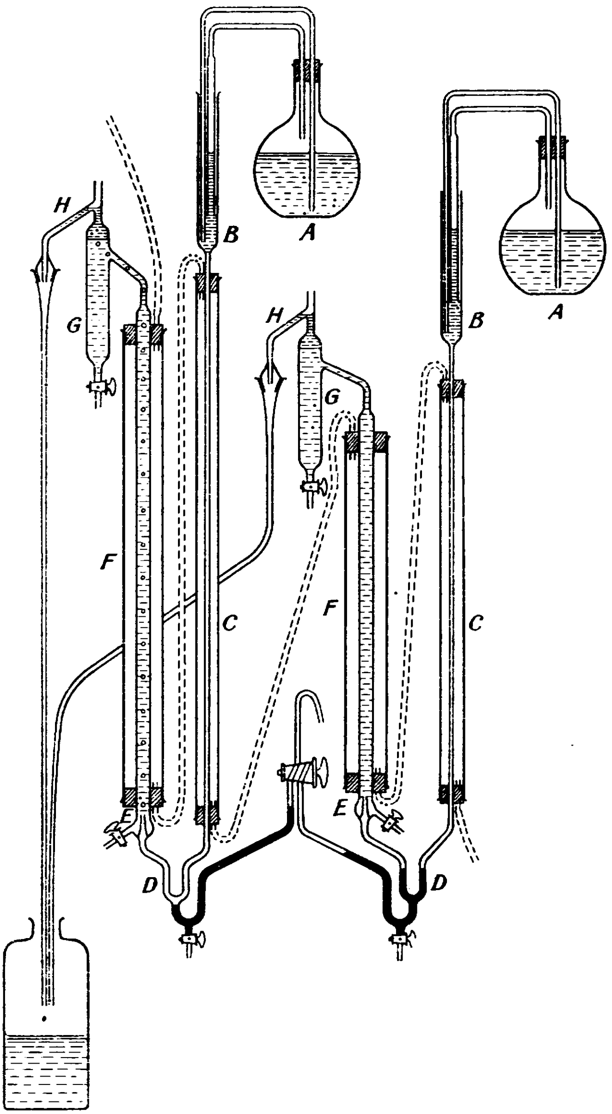
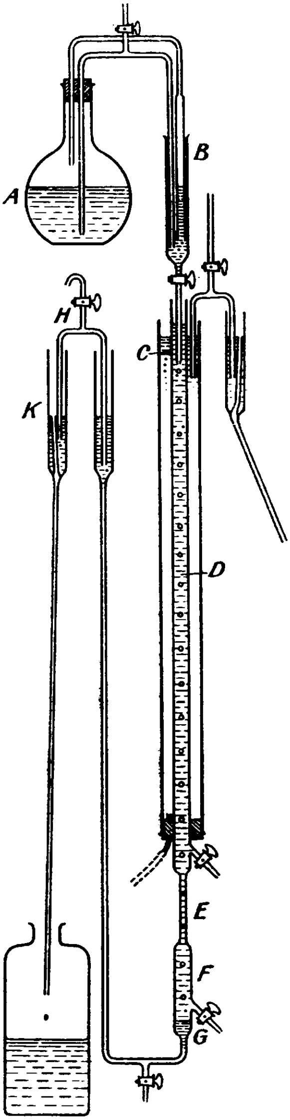


FIG. 7.



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 0·088N-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} × 10^8.
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} × 10^8.
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.

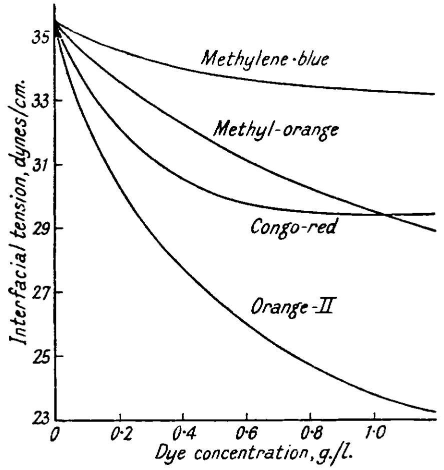
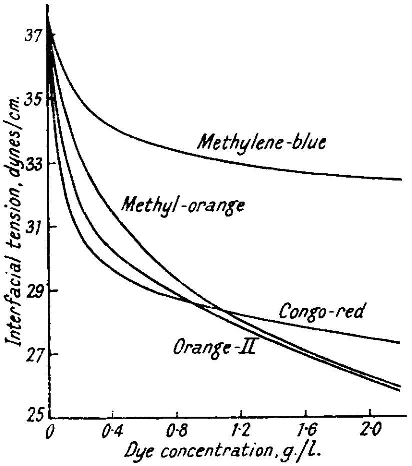


FIG. 9.



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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