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

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. 1.

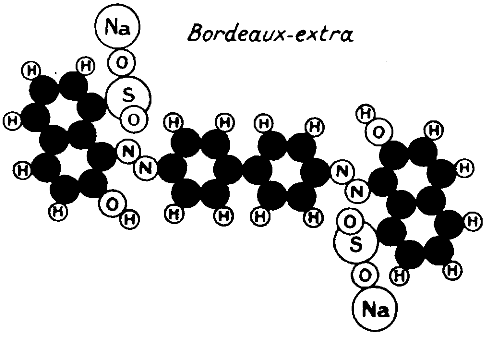


FIG. 2.

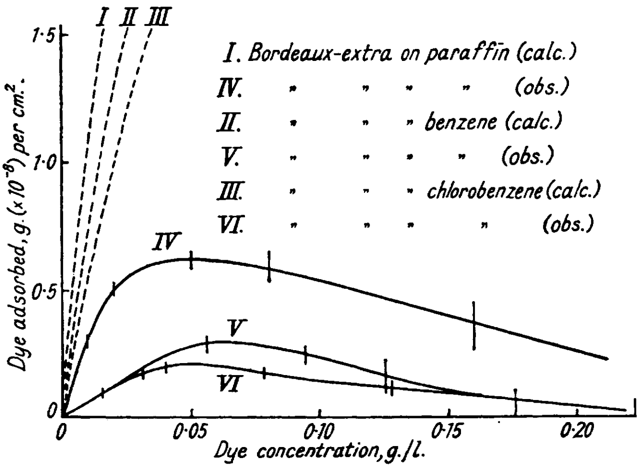


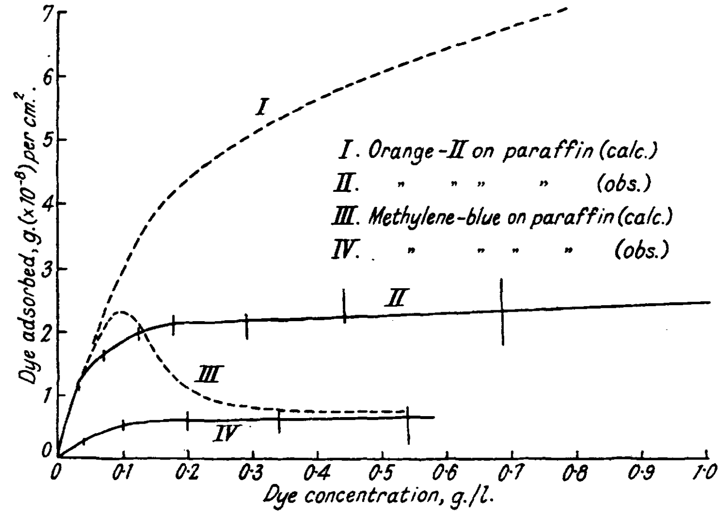
TABLE I.

Initial concn., g./l.	Time of flow, mins.	Surface area, cm.^{2}.	Adsorption coefficient, g./cm.^{2} × 10^8.	Initial concn., g./l.	Time of flow, mins.	Surface area, cm.^{2}.	Adsorption coefficient, g./cm.^{2} × 10^8.
(A) *Methylene-blue on paraffin.*				(B) *Orange-II on paraffin.*			
0·0210	1420	59,330	0·10 ± 0·01	0·0302	1185	40,520	1·09 ± 0·03
0·0421	1420	46,850	0·28 ± 0·03	0·0678	1260	33,890	1·58 ± 0·06
0·1012	1103	47,570	0·60 ± 0·06	0·1180	1054	39,950	1·9 ± 0·1
0·2023	1187	41,780	0·60 ± 0·15	0·1715 *	1136	29,100	2·1 ± 0·2
0·3380	1200	60,710	0·6 ± 0·2	0·2826	1395	45,600	2·0 ± 0·2
0·5400	1200	57,280	0·6 ± 0·3	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.*				(D) *Congo-red on paraffin.*			
0·0166	1176	35,530	0·14 ± 0·01	0·00738	1370	69,720	0·14 ± 0·004
0·0554	930	31,210	0·55 ± 0·05	0·0203	1080	42,420	0·46 ± 0·02
0·1108	1275	43,580	0·81 ± 0·08	0·0304	1260	44,860	0·47 ± 0·02
0·1754	1200	36,560	0·6 ± 0·15	0·0407	1080	39,200	0·45 ± 0·03
0·2338	900	34,100	0·4 ± 0·2	0·0738	1330	58,660	0·23 ± 0·04
0·4962	1155	44,420	0·00 ± 0·35	0·1215	1215	46,310	0·00 ± 0·08
(E) *Bordeaux-extra on paraffin.*				(F) *Bordeaux-extra on benzene.*			
0·0100	1580	61,120	0·300 ± 0·003	0·0310	1357	51,710	0·17 ± 0·02
0·0200	1400	44,330	0·5 ± 0·15	0·0558	1310	57,350	0·29 ± 0·03
0·0500	1200	43,050	0·62 ± 0·03	0·0939	936	46,190	0·25 ± 0·06
0·0800	1515	37,450	0·60 ± 0·06	0·1261	1260	44,020	0·16 ± 0·08
0·1605	1200	49,230	0·36 ± 0·09	0·1765	1440	47,610	0·00 ± 0·1
(G) *Bordeaux-extra on chlorobenzene.*							
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.		
Concn., g./l.	Drop no.	σ, dynes/cm.	Concn., g./l.	$d\sigma$/* dc.	Adsorption, g./cm.^{2} × 10^8.
(A) *Methylene-blue on paraffin.*					
0·0000	228	51·35	0·05	24·0	1·58
0·1038	243	48·36	0·10	18·0	2·36
0·2000	248	47·43	0·15	8·9	1·75
0·3460	250	47·07	0·20	3·8	1·00
0·7200	252	46·72	0·25	2·8	0·92
1·0380	255	46·21	0·30	2·4	0·95
			0·40	1·8	0·95
			0·50	1·15	0·76
			0·60	0·8	0·63
(C) *Methyl-orange on paraffin.*					
0·0000	228	51·35	0·05	22·0	1·47
0·1272	243	48·29	0·10	19·0	2·55
0·2544	252	46·73	0·15	13·0	2·61
0·4070	260	45·42	0·20	11·4	3·06
0·6784	270	43·78	0·25	10·5	3·52
1·0176	279	42·46	0·30	9·2	3·70
			0·40	7·4	3·97
			0·50	6·5	4·36
			0·60	5·5	4·42
(E) *Bordeaux-extra on paraffin.*					
0·0000	228	51·35	0·04	26·0	2·9
0·1000	241	48·67	0·06	24·0	4·1
0·2000	248	47·38	0·10	16·8	4·8
0·3650	256	45·94	0·20	10·2	5·8
0·5520	264	44·63	0·30	8·0	6·9
0·7360	268	44·03	0·40	6·6	7·6
0·9210	272	43·46	0·50	5·2	7·4
(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

			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.
(B) *Orange-II on paraffin.*					
0·0000	228	51·35	0·05	29·0	2·08
0·1460	253	46·55	0·10	21·0	3·02
0·2910	266	44·39	0·15	19·0	4·09
0·5820	284	41·71	0·20	16·0	4·60
1·0200	305	38·96	0·25	13·0	4·67
			0·40	9·6	5·52
			0·60	7·0	6·03
			0·80	6·3	7·24
			1·00	5·95	8·55
(D) *Congo-red on paraffin.*					
0·0000	228	51·35	0·02	76·0	4·34
0·0357	245	47·98	0·05	45·0	6·43
0·0520	249	47·25	0·08	25·0	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	3·70
			0·30	4·5	3·80
(F) *Bordeaux-extra on 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	0·10	11·9	3·41
0·3600	152	31·82	0·20	8·1	4·64
0·5000	157	30·81	0·30	6·6	5·67
0·6305	161	30·00	0·40	5·9	6·76
			0·50	5·5	7·88

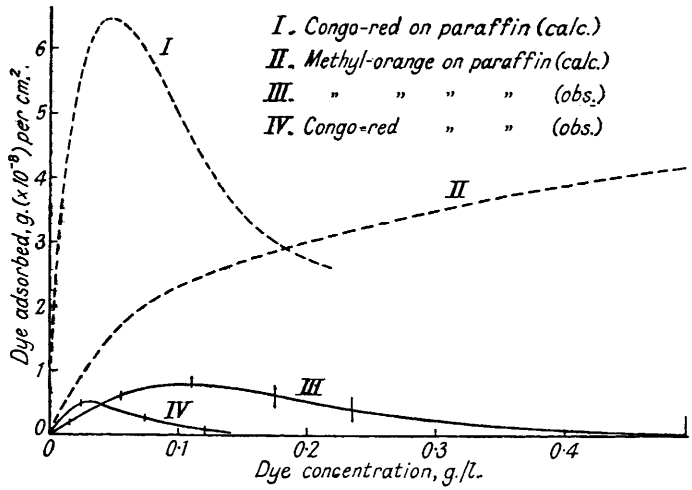
* Smoothed.

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.

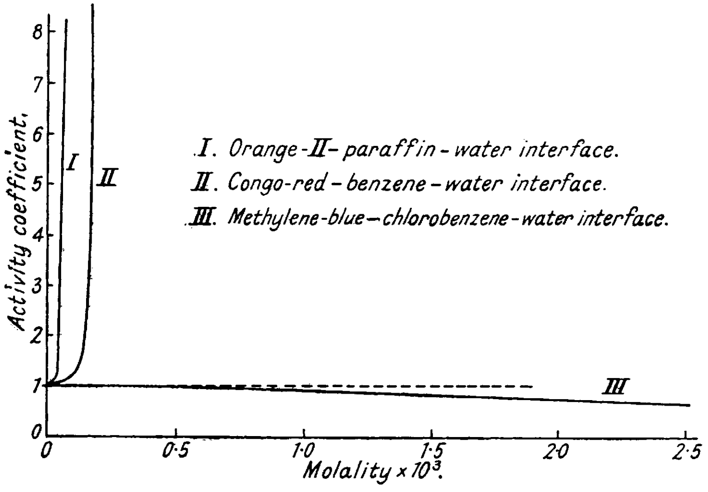
Calculation of Activity Coefficients.—Much emphasis is often, and rightly, laid upon the approximate nature of the equation $\Gamma = -c(d\sigma/dc)/RT$, and the desirability of replacing concentrations (c) by activities (a) as in the exact equation $\Gamma = -a(d\sigma/da)/RT$. Since, however, activity 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.

(A) *Congo-red on benzene.*

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.
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		

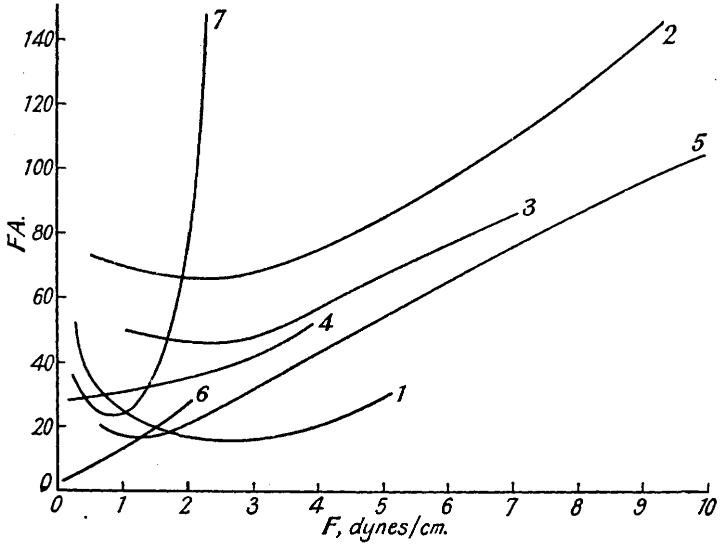
c_1 = (A) 0·01; (B) 0·08; (C) 0·03.

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.*
5. *Orange-II on benzene.*

(2.–5.) A = *cm.*^{2} *per g.-mol.* × 10^9.

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 $\varkappa = 8 \times 10^{-6}$ 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./cm^2. × 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," $d_{4°}^{17°}$ 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.

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THE DURHAM COLLEGES IN THE UNIVERSITY OF DURHAM. [*Received, July 6th*, 1936.]