

109. Adsorption at the Interface between Two Fluids. Part III. The Adsorption of Five Dyes at a Mercury-Water Interface.

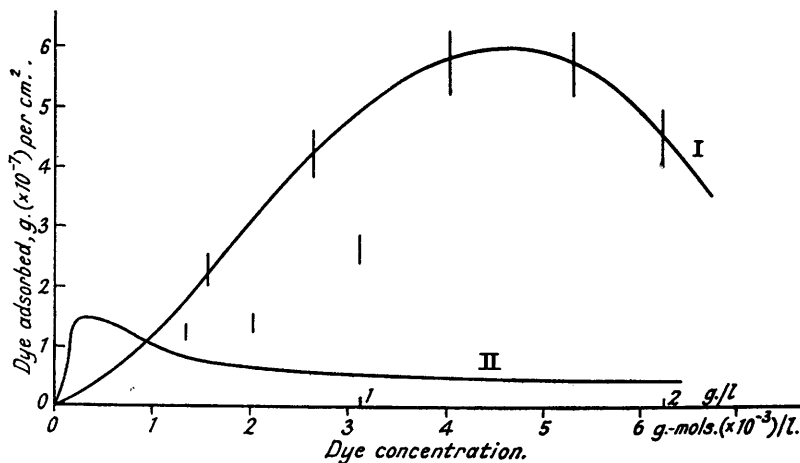
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The adsorptions of methylene-blue, Congo-red, Bordeaux extra, indigo-carmin X, and Solway ultra-blue B at mercury-aqueous solution interfaces have been measured. In each case the adsorption passes through a maximum as the concentration increases, and is always positive. Interfacial-tension measurements have also been made, and values of the adsorption calculated from them by means of Gibbs's equation. These are not in agreement with the measured values, and are in some cases negative.

IN Parts I and II (J., 1936, 119, 1306) the adsorptions of certain dyes at water-organic liquid interfaces were measured, and compared with those calculated by means of Gibbs's equation, $\Gamma = -c(d\sigma/dc)/RT$, from measured values of interfacial tensions.

The present report deals with the adsorptions, at the mercury-water interface, of three of these same dyes, Congo-red, Bordeaux extra, and methylene-blue, and also of two

FIG. 1.



I. Methylene-blue (measured).
II. Methylene-blue (theoretical).

others, indigo-carmin X (the potassium salt of indigotin-5 : 5'-disulphonic acid) and Solway ultra-blue B (the sodium salt of 1-amino-4-anilinoanthraquinone-2-sulphonic acid). The last two were chosen to include two types of structure, indigoid and anthraquinonoid, not previously studied. Attempts to carry out measurements of this type for the mercury-water interface seem to be limited to those of Patrick (*Z. physikal. Chem.*, 1914, **86**, 545), whose determinations are only comparative.

With all five dyes the measured adsorption passes through a maximum with increasing concentration (Figs. 1, 2, 3; Table I). A similar phenomenon was observed in many of the cases previously studied (*loc. cit.*), though both the adsorbing liquid and the experimental method were entirely different.

The areas of interface per molecule adsorbed at the concentration of maximum adsorption are shown in Table II, together with the approximate areas of the molecules, found by drawing projections of their outlines to scale on a plane, as in Parts I and II. It has been assumed that the molecule of Solway ultra-blue B is coplanar, hence the area estimated in this case is a maximum value. The ratios of the two sets of values suggest considerable orientation of the molecules at the interfaces. The difference between the ratios for Congo-red and Bordeaux extra is striking, as the structures of these two dyes are closely related.

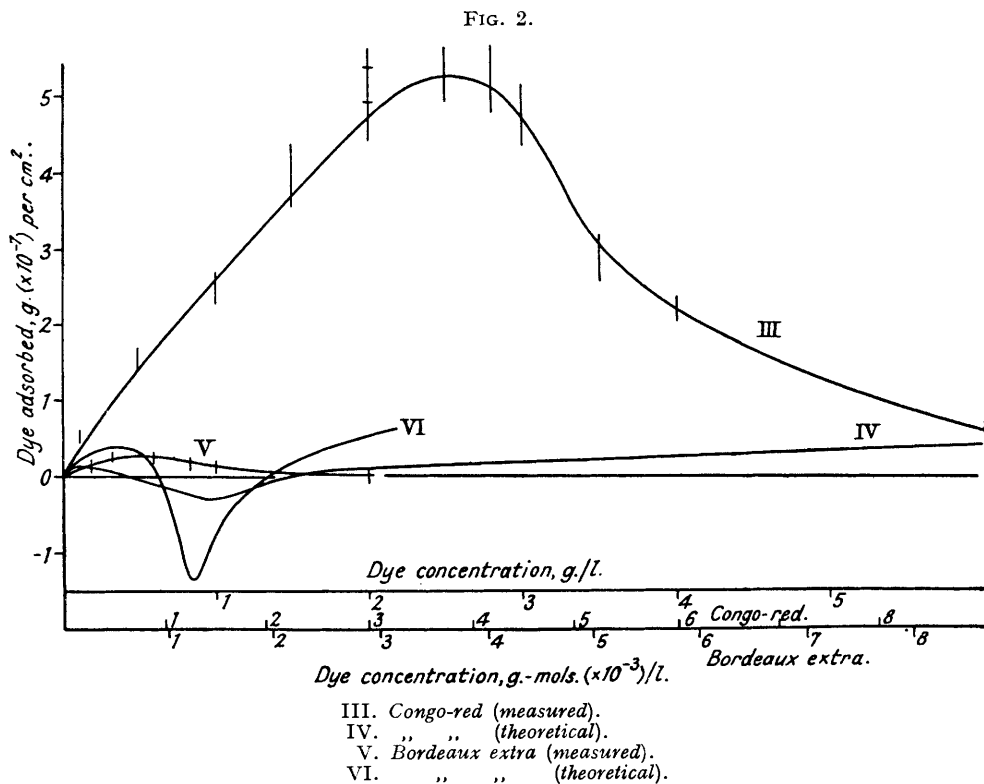


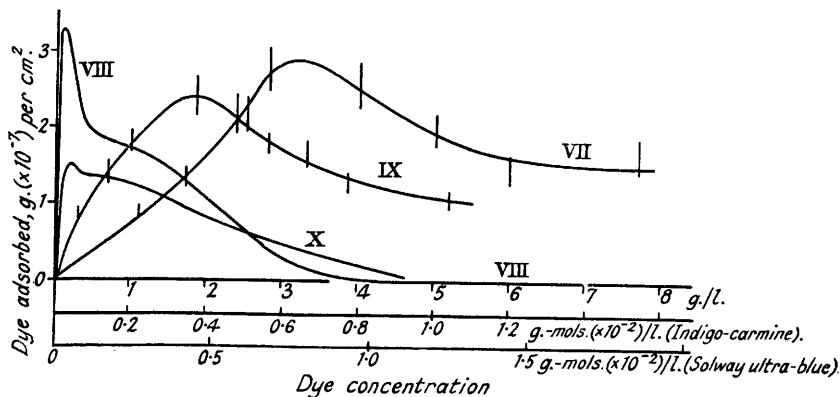
TABLE I.

Initial concn., g./l.	Surface area $\times 10^{-4}$, cm. ² .	Adsorption coeff. $\times 10^7$, g./cm. ² .	Initial concn., g./l.	Surface area $\times 10^{-4}$, cm. ² .	Adsorption coeff. $\times 10^7$, g./cm. ² .	Initial concn., g./l.	Surface area $\times 10^{-4}$, cm. ² .	Adsorption coeff. $\times 10^7$, g./cm. ² .
Methylene-blue.								
0.425	2.15	1.4 \pm 0.1	0.850	1.55	4.1 \pm 0.4	1.710	1.40	5.8 \pm 0.6
0.500	1.61	2.1 \pm 0.2	1.000	2.11	2.6 \pm 0.3	2.000	1.16	4.6 \pm 0.5
0.650	1.74	1.6 \pm 0.2	1.300	1.33	5.7 \pm 0.6			
Congo-red.								
0.125	1.61	2.5 \pm 0.3	2.000	1.87	53.5 \pm 5.4	3.000	1.57	47.8 \pm 4.8
0.250	2.06	5.7 \pm 0.6	2.000	2.34	49.0 \pm 5.0	3.500	1.41	29.1 \pm 2.9
0.500	1.61	15.2 \pm 1.5	2.500	1.40	54.0 \pm 5.4	4.000	1.96	22.2 \pm 2.2
1.000	1.32	24.5 \pm 2.5	2.800	1.74	53.0 \pm 5.3	6.000	1.18	5.7 \pm 0.6
1.500	1.36	39.3 \pm 4.0						
Bordeaux extra.								
0.100	3.05	0.9 \pm 0.1	0.500	1.54	3.7 \pm 0.4	1.000	1.56	1.1 \pm 0.1
0.200	3.80	1.4 \pm 0.1	0.600	1.70	2.3 \pm 0.2	2.000	1.45	0.8 \pm 0.1
0.330	1.91	2.4 \pm 0.2	0.730	1.77	1.6 \pm 0.2			
Indigo-carmine.								
1.110	1.50	0.9 \pm 0.1	2.810	1.30	2.8 \pm 0.3	6.000	1.33	1.5 \pm 0.2
1.730	1.46	1.4 \pm 0.1	4.000	1.56	2.5 \pm 0.3	7.700	0.84	1.7 \pm 0.2
2.500	1.42	2.2 \pm 0.2	5.000	1.48	2.0 \pm 0.2			
Solway ultra-blue.								
0.300	2.08	0.8 \pm 0.1	1.850	1.96	2.4 \pm 0.2	3.300	1.61	1.7 \pm 0.2
0.700	2.84	1.4 \pm 0.1	2.400	1.43	2.2 \pm 0.2	3.860	1.85	1.3 \pm 0.1
1.000	1.29	1.8 \pm 0.2	2.800	1.27	1.8 \pm 0.2	5.000	1.56	1.1 \pm 0.1

TABLE II.

	Actual area, \AA^2 .	Area of interface per molecule at maximum adsorption, \AA^2 .
Methylene-blue	140	53
Congo-red	192	2
Bordeaux extra	153	33
Indigo-carminc	168	27
Solway ultra-blue	176	28

FIG. 3.



VII. Indigo-carminc (measured).
 VIII. " " (theoretical).
 IX. Solway ultra-blue (measured).
 X. " " (theoretical).

Interfacial tensions between mercury and aqueous solutions of the dyes have been determined by a drop-number method, and are shown in Fig. 4 and Table III. Exact agreement between measured adsorption and that calculated from the form of Gibbs's equation quoted above is not to be expected, on account of the latitude in evaluating $d\sigma/dc$, the use of concentrations instead of activities, and of factors such as the influence of electrical double layers, of which Gibbs's equation takes no account. The values of the interfacial tensions and of the adsorption coefficients calculated from them are nevertheless

FIG. 4.

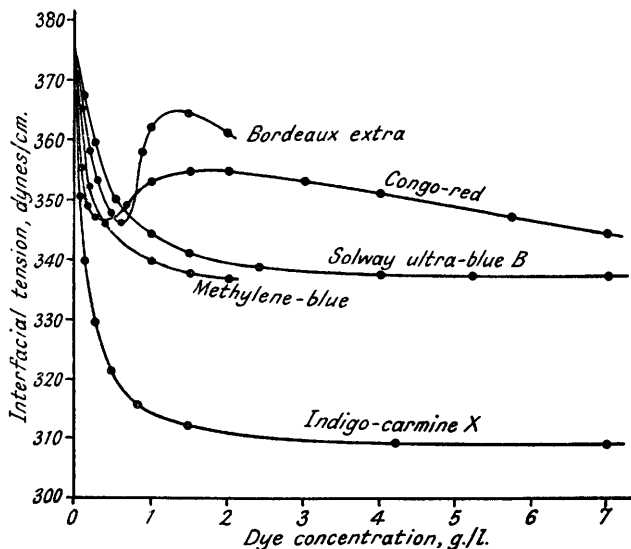


TABLE III.

Concn., g./l.	Drop no.	σ , dynes/cm.	Concn., g./l.	Drop no.	σ , dynes/cm.	Concn., g./l.	Drop no.	σ , dynes/cm.
Methylene-blue.								
0.000	208	374	0.200	222	352	1.000	230	340
0.100	215	363	0.400	226	346	2.000	232	337
Congo-red.								
0.000	208	374	0.250	225	347	2.000	220	354
0.022	213	366	0.500	225	347	3.000	221	353
0.044	216	361	0.750	224	348	4.000	222	351
0.063	220	354	1.000	221	352	5.700	225	347
0.125	224	348	1.500	220	354	7.000	227	344
Bordeaux extra.								
0.000	208	374	0.400	223	350	1.000	216	361
0.050	212	368	0.500	225	347	1.500	214	364
0.100	214	365	0.600	226	346	2.000	216	361
0.200	218	358	0.750	225	347			
0.300	221	353	0.910	218	358			
Indigo-carmine.								
0.000	208	374	0.500	244	322	2.800	254	310
0.063	223	350	1.000	249	316	4.200	254	310
0.125	230	340	1.500	251	313	7.000	254	310
0.250	238	329	2.000	253	311			
Solway ultra-blue.								
0.000	208	374	0.500	223	359	4.000	232	337
0.050	210	371	1.000	227	344	5.000	232	337
0.100	212	368	1.500	229	341	7.000	232	337
0.200	217	360	2.400	231	339			

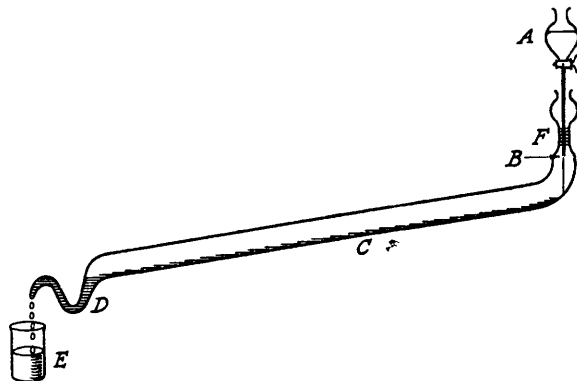
recorded (Table III, Fig. 4; Figs. 1, 2, 3) because of the great discrepancies between the latter and the measured values. With methylene-blue, Solway ultra-blue B, and indigo-carmine X the interfacial tension falls with increasing concentration to a practically constant value, leading to a "theoretical" adsorption curve of the same form as that found by measurement, though of different dimensions. In this they resemble the behaviour of methyl-orange, Congo-red, and Bordeaux extra when adsorbed on benzene, chlorobenzene, and light petroleum. For the last two dyes the interfacial tension-concentration curves show two inflexions, similar to those found for the surface tension of laurylsulphonic acid and quoted by McBain and Mills ("Report on Progress of Physics," 1938, 5, 30, where references are given to other tension curves which reach or pass through a minimum). These lead to "theoretical" values for the adsorption which change from positive to negative and again from negative to positive with increasing concentration. This change of sign is independent of the use of concentrations instead of activities in Gibbs's equation, and of errors in assessing the numerical magnitude of $d\sigma/dc$. In none of the cases investigated do the curves representing the "theoretical" and measured adsorptions coincide at small concentrations, as would be the case if the only cause of the discrepancy were the omission of activity coefficients. No evaluation of possible activity coefficients could be carried out, therefore, as was done for methylene-blue (on chlorobenzene), Congo-red (on benzene), and Orange-II (on light petroleum) in Part II.

EXPERIMENTAL.

Adsorption Measurements.—Mercury stored in a reservoir *A* (Fig. 5) fell in a very rapid stream of small drops through a fine jet *B*, dipping below the dye solution contained in the inclined tube *C*. The drops moved slowly down to the syphon *D*, through which they passed as a sludge, aided if necessary by gentle stirring with a glass rod, and fell into a beaker *E*. The stability of the drops was such that in all the recorded experiments, except some of those with the most dilute solutions, very little coalescence could be detected in the syphon *D*. In some cases, particularly with Bordeaux extra, the drops remained stable for as long as two months, and coalescence of the mercury could be brought about only by centrifuging at high speed. In the cases of greatest stability the mixture of mercury and solution was uniformly semi-solid,

and only after centrifuging could a distinct layer of solution be seen on top of the mercury. The volume of the mercury used was measured directly, centrifuging being carried out first if necessary. The volume of the solution carried through with the mercury was that added from a burette to keep a constant level in the graduated neck *F*. The difference in concentration between the original solution and that in *E* was measured in a tintometer. It was found necessary to centrifuge the solution again before comparison, to remove a large number of extremely minute drops of mercury, probably secondary drops formed at the jet, which otherwise produced a spurious deepening of the tint. The size of the mercury drops was found by catching a number of them on a lightly greased glass plate held under the surface of a solution a short distance below the jet. The diameters were then measured on the calibrated eyepiece scale of a microscope. A large majority of the drops were of uniform diameter within 2%, and very little variation was caused by changes in the concentrations of the solutions, the drops not being formed under quasi-equilibrium conditions, as was the case in the measurement of interfacial tensions. The values so obtained, of the order of 0.02 cm., were confirmed by measurements on drops caught on greased plates as they emerged from the syphon *D*, and on others which had been flowing for some time down a gentle slope. Different times of contact between the mercury and the solution were ensured by using alternately two adsorption tubes of different lengths, 45 and 60 cm., and by varying the angle of slope. In the majority of the experiments recorded the time of contact was 1.5–2 mins. The drop sizes were varied by using different

FIG. 5.



jets. As variation in these factors produced no corresponding variation in the results, it was concluded that the interfaces were saturated. All measurements were carried out at approximately 17°.

Interfacial Tensions.—The drop pipette used for the determination of drop numbers against the dye solutions was made from fine-gauge capillary tubing, blown out into a bulb of 1.206 c.c. capacity, measured between two constrictions formed above and below it. The lower constriction was of such a size that about 10 mins. were required to fill the bulb with mercury from below by evacuating from above with a pump. The average radius, measured along several diameters with a travelling microscope, was 0.0400 ± 0.0002 cm. The falling drops were counted automatically, as in previous work, and an average of several successive readings with each solution was taken when exact agreement to 1 drop was not obtained. The values of σ and $d\sigma/dc$ were calculated (as in Parts I and II) from smoothed curves of drop number plotted against concentration. No difference in drop number for a single solution was found by altering the time of formation of the drops from 4 to 20 secs. The time of formation used was 12–15 secs.

Materials.—The mercury was purified at frequent intervals by the method of Russell and Evans (J., 1925, 127, 2221). The methylene-blue, Congo-red, and Bordeaux extra were from the samples used in Parts I and II. The indigo-carmin and Solway ultra-blue had been purified by Messrs. Imperial Chemical Industries, Ltd. (to whose Research Department of the Dyestuffs Group we are indebted for the gift of these and other dyes) and were not further treated. All solutions were made in distilled water.