STUDIES ON ACTIVE CARBON

Part V. Adsorption of Methylene Blue by Activated Charcoal: Examination of the Theory of Hydrolytic Adsorption

By M. V. C. Sastri

It has been established that the adsorption of methylene blue by active charcoal is accompanied by a change in the pH of the solution. While Bartell and Miller (*J. Amer. Chem. Soc.,* 1922, 44, 1866) observed the liberation only of acid in the process, Chambers and King (*J. Chem. Soc.*, 1938, 688) found that either acid or base may be liberated depending on the conditions of activation. Activation with air at temperatures below 500° C. gave carbons which formed free acid during the adsorption of methylene blue. On the other hand, those produced at higher temperatures gave rise to free base in the solution.

In the earlier experiments (Part IV of this series) on the adsorption of methylene blue by commercial specimens of decolorising charcoal, a substantial lowering of pH was noticed when blood charcoal, Carboraffin and Darco were added to methylene blue in alkaline, neutral and moderately acid solutions. With solutions which were strongly acid at the outset, the same carbons produced a small but definite increase in the pH-value. This is clearly seen from the data given in Table I below. The behaviour of Norit was, however,

TABLE I

Specimen	Initial pH	Equilibrium pH
Blood charcoal ..	2·46 2·60 2·83	2·56 2·68 2·93
Carboraffin ..	2·46 2·54 2·60 2·83	2·60 2·77 2·72 2·94
Darco ..	2·60 2·83	2·69 2·98

slightly different in that it produced an increase in the pH at all but high initial pH-values of the solution.

In the present paper, investigations on the adsorption of methylene blue on charcoal have been carried further with special reference to the effect of carbon on the pH of the solution. In order to eliminate the effect of soluble impurities, the specimens of charcoal (blood charcoal, Carboraffin, Norit and Darco) were each washed with 40 litres of specially distilled water per gram of carbon. The procedure adopted for washing the specimens was the same as described in Part III of this series (page 122). It should be mentioned here that in the case of Carboraffin only the coarse portion was taken for the present experiments as the fine portion was found to be unsuitable for the experimental technique employed. The adsorption experiments were carried out with pure methylene blue in aqueous solution without the addition of any electrolyte.

Bartell and Miller (*loc. cit.*) and Chambers and King (*loc. cit.*) estimated the amount of acid formed during the adsorption of methylene blue by titrating the solution with standard alkali after filtering off the carbon. This method cannot, however, be regarded as acurate, as the pH of the solution changes on filtration. In the present experiments the amount of acid formed in the solution is deduced from the observed pH by reference to the curve (Fig. 2*a*) in which the pH-values of the solutions containing known amounts of either hydrochloric acid or sodium hydroxide have been plotted. Readings of the pH of the suspension and colorimetric estimations of the dye in the solution were made at regular intervals of time, so that the progress of the adsorption and the liberation of acid could be observed at various stages simultaneously. In order to ascertain if the pH of the solution was affected by the dilution that took place during adsorption, the pH-values of 0·075-0·150 per cent. solutions of methylene blue were determined, and the effect of adding hydrochloric acid or caustic soda to these solutions were studied separately. The methylene blue chloride employed in this work was of the purest variety and was prepared by repeated re-crystallisation from alcohol.

Experimental

Measurements of the rate of adsorption of methylene blue and the rate of fall of pH.—The arrangement shown in Fig. 1 enables the measurement of the pH of the solution as well as the withdrawal of half-c.c. aliquots at various intervals for colorimetric estimation of methylene blue.

B is a micro-burette with a fixed mark near the top and a delivering capacity of 0·5 c.c. To the inlet tube *A*, which is bent into S-shape as shown, is joined a small fritted-glass filter *F* (Jena G. 3). The filter *F*, the glass-quinhydrone electrode *G*, the

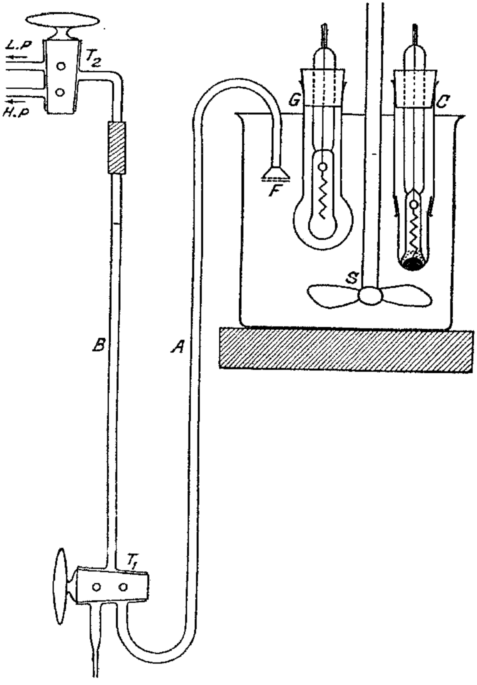


FIG. 1

calomel electrode *C* and the stirrer *S* were supported in a 250 c.c. beaker. The top-end of the burette is connected through a three-way stop-cock T_2 to compressed air and suction lines. To draw the solution into the burette *B*, the tap T_1 is connected to the tube *A* and gentle suction applied to *B*, by turning T_2 to the low-pressure line. To force the solution out of the burette, T_2 was turned to the compressed-air line; the solution could be returned to the beaker or delivered into a receptacle by manipulating the tap T_1.

200 c.c. of 0·15% aqueous methylene blue solution were placed in the 250 c.c. Pyrex beaker and the pH of the solution was determined with a Leeds and Northrup Valve Potentiometer. The solution was then drawn into the burette, which was previously empty to the delivery tip, and the level of the solution carefully adjusted to the fixed mark. The solution was then run out completely into a glass-stoppered vessel of resistance-glass and diluted with 25 c.c. of water. The solution thus prepared served as the standard for colorimetric comparison with subsequent aliquot portions of the solution. The solution remaining in *A* was then forced back into the beaker.

A weighed sample of the charcoal-specimen (washed with 40 litres of water per gram of carbon) was tipped into the methylene blue solution and the stop-watch timed. The pH readings were taken at one-minute intervals for the first ten minutes, when the pH fell rapidly, and subsequently at 15-minute intervals, when the pH hardly changed. It was not convenient to draw aliquot samples of the solution at one-minute intervals for colorimetric comparison. The first sample during adsorption was taken between three and five minutes after addition of the adsorbent, and subsequent portions were drawn at 15-minute intervals. Care was taken to rinse the filter *F* with the solution about fifteen seconds before drawing an aliquot sample, by turning in the high- and low-pressure lines alternately. The aliquots drawn at various intervals during adsorption were each diluted with 25 c.c. of water and compared by means of a Kober colorimeter with the original solution, similarly prepared at the beginning of the experiment. The amounts of methylene blue adsorbed at different times were then calculated. In almost all cases the adsorption equilibrium was reached in about an hour.

Effect of adding standard sodium hydroxide and hydrochloric acid solutions on the pH of methylene blue solutions of concentrations varying between 0·075% *and* 0·150%.—Stock solutions containing 0·075, 0·100, 0·125, 0·150% of pure methylene blue chloride in water were prepared. 200 c.c. (*i.e.*, the same volume as in the previous experiment) of any of these solutions were placed in a Pyrex beaker in which a glass-quinhydrone electrode, a calomel electrode and a stirrer were supported as described already. After reading the pH-value of the original solution, quantities of 0·1 N hydrochloric acid up to 3 c.c. were added, in portions of 0·1 c.c. from a burette, graduated in 0·01 c.c., and the pH measured after each addition. The pH-values of the solutions when 0·1 N sodium hydroxide was added were determined in a similar manner.

Results

The variation of the pH-value when either 0·1 N HCl or 0·1 N NaOH is gradually added to methylene blue solutions of 0·075 to 0·150% strengths is expressed by the data in Table II. It is to be remembered that these figures are valid for 200 c.c. of the solution, *i.e.*, the same volume as that involved in the adsorption experiments. On plotting the pH against c.c. of acid or alkali added to 200 c.c. of 0·15% solution the familiar "titration curve" shown in Fig. 2(*a*) is obtained. From this curve one can deduce the pH-shift produced when a known amount of acid or alkali is added, and conversely, the amount of acid or alkali required for a given variation of pH.

Table III gives the simultaneous values of pH and adsorption at various intervals of time when a given weight of charcoal is added to 200 c.c. of 0·15% methylene blue solution. The rates of adsorption by the different specimens of charcoal are shown by the firm lines in Fig. 2(*b*). With the aid of the "titration-curve" in Fig. 2(*a*), the pH readings in Table II are converted into c.c. of 0·1 N acid liberated. Assuming that each molecule of hydrochloric acid set free corresponds to the hydrolytic adsorption of one molecule of methylene blue $C_{16}H_{18}N_3SCl$ of molecular weight = 319·5, the amounts of methylene blue thus adsorbed at various intervals of

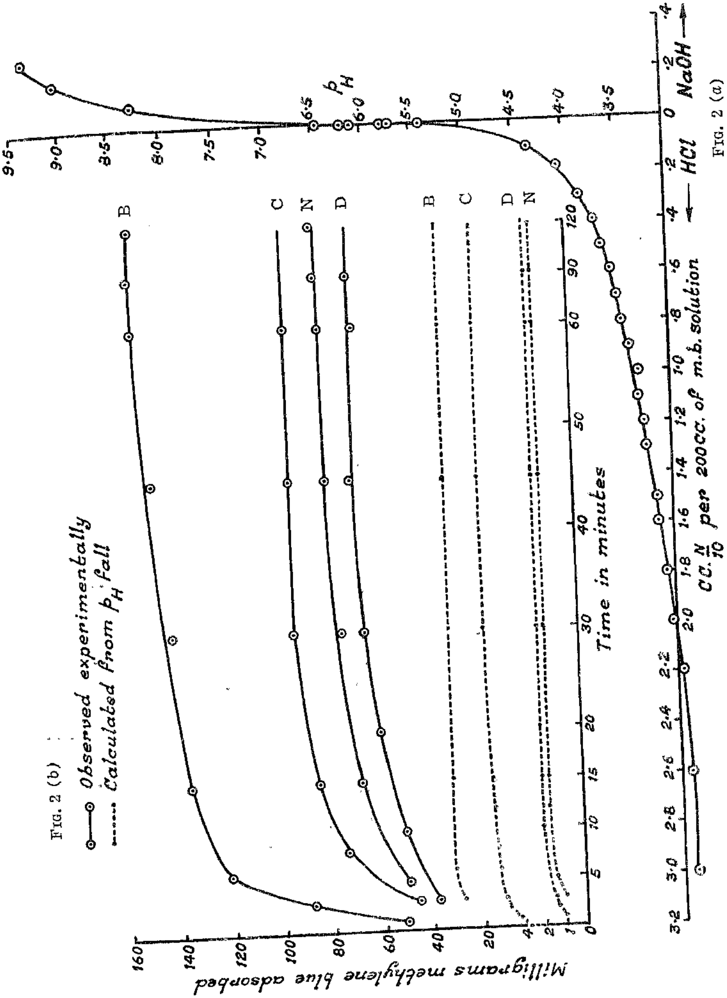

pH
9·5
9·0
8·5
8·0
7·5
7·0
6·5
6·0
5·5
5·0
4·5
4·0
3·5
·4
·2
0
·2
·4
·6
·8
1·0
1·2
1·4
1·6
1·8
2·0
2·2
2·4
2·6
2·8
3·0
3·2
← HCl
NaOH →
cc. N/10 per 200cc. of m.b. solution
Observed experimentally
Calculated from pH fall
B
C
N
D
B
C
D
N
Time in minutes
0
1
2
4
5
10
15
20
30
40
50
60
90
120
Milligrams methylene blue adsorbed
0
20
40
60
80
100
120
140
160

Fig. 2 (a)

Fig. 2 (b)

time can be calculated. The calculated rates of hydrolytic adsorption are shown by the dotted lines in Fig. 2(*b*).

Table IV shows the constancy of the equilibrium pH-value obtained when different amounts of carbon are added to 50 c.c. of methylene blue solution.

TABLE II

c.c. 0·1 N HCl per 200 c.c. of m. b. solution	pH of solution			
	Concentration of methylene blue in solution			
	0·150%	0·130%	0·110%	0·075%
0·00	6·06	6·20	6·30	6·45
0·06	5·40	5·73	5·78	5·81
0·10	4·30	4·34	..	..
0·20	4·02	4·04	4·04	4·05
0·30	3·83	3·83	..	..
0·40	3·71	3·71	3·70	3·72
0·50	3·63	..	..	..
0·60	3·53	3·53	3·52	3·53
0·70	3·50	3·50	3·50	3·50
0·80	3·43	3·43	3·44	3·43
0·90	3·38	2·38	..	3·38
1·00	3·31	3·31	..	3·32
1·10	3·28	..	..	..
1·20	3·25	..	..	3·25
1·30	3·23	..	..	3·23
1·50	3·16	3·16	3·16	3·15
1·60	3·13	..	..	3·14
1·80	3·06	..	3·06	..
2·00	3·02	3·01	3·02	3·02
2·20	2·96	..	..	2·96
2·60	2·92	2·92	..	2·92
3·00	2·89	2·88	2·89	2·89
c.c. 0·1 N NaOH				
0·00	6·06	6·20	6·30	6·45
0·09	8·24	..	8·24	..
0·19	9·04	9·04	..	9·05
0·28	9·35	9·35	9·35	9·35

TABLE III

Specimen	Time Mins.	pH	c.c. 0·1N HCl liberated from start = 10^4 x no. of mols of methylene blue adsorbed hydrolytically	mg. of methylene blue adsorbed hydrolytically (calculated)	total mg. of methylene blue adsorbed by actual wt. of charcoal (experimental)
Blood charcoal 0·2680 g.	Start	6·04	..	..	..
	1	3·71	0·40	12·8	51
	3	3·40	0·84	26·8	88
	6	3·36	0·93	29·7	121
	15	3·36	0·93	29·7	136
	30	3·36	0·93	29·7	141
	45	3·36	0·93	29·7	148
	60	3·36	0·93	29·7	154
	90	3·36	0·93	29·7	153
	120	3·36	0·93	29·7	154
Carboraffin (coarse) 0·3049 g.	Start	6·20	..	..	..
	1	4·00	0·21	6·4	..
	2	3·83	0·30	9·6	..
	3	3·78	0·34	10·9	45
	6	3·72	0·40	12·8	..
	8	3·68	0·43	13·7	74
	12	3·66	0·46	14·7	..
	15	3·63	0·48	15·3	85
	20	3·58	0·54	17·3	..
	30	3·56	0·55	17·6	93
	45	3·56	0·55	17·6	94
	60	3·56	0·55	17·6	94
Norit 0·5140 g.	Start	5·47	..	..	..
	3	4·75	0·03	0·96	49
	5	4·69	0·04	1·28	..
	12	4·64	0·05	1·60	..
	15	4·64	0·05	1·60	68
	30	4·64	0·05	1·60	74
	45	4·63	0·05	1·60	80
	60	4·63	0·05	1·60	80
	90	4·63	0·05	1·60	81
	120	4·62	0·05	1·60	82
Darco 0·6550 g.	Start	6·18	..	..	..
	1	4·79	0·03	0·96	..
	2	4·70	0·04	1·28	..
	3	4·67	0·04	1·28	38
	7	4·60	0·05	1·60	..
	10	4·58	0·06	1·82	51
	15	4·58	0·06	1·82	..
	20	4·58	0·06	1·82	60
	30	4·58	0·06	1·82	65
	45	4·59	0·06	1·82	69
	60	4·58	0·06	1·82	67
	90	4·57	0·06	1·82	68

TABLE IV

Equilibrium pH of charcoals in methylene blue solutions

(c.c. of methylene blue solution = 50)

Blood charcoal		Carboraffin (coarse)		Norit		Darco	
Wt. in g.	Eqbm. pH	Wt. in g.	Eqbm. pH	Wt. in g.	Eqbm. pH	Wt. in g.	Eqbm. pH
0·1020	3·37	0·0960	3·56	0·1468	4·62	0·2340	4·56
0·1550	3·37	0·1450	3·57	0·1694	4·62	0·3010	4·56
0·1700	3·36	0·1860	3·57	0·1980	4·63	0·3460	4·57
0·2030	3·37	0·2100	3·56	0·2160	4·62	0·3826	4·57
0·2345	3·36	0·2490	3·56	0·2890	4·62	0·5264	4·57
0·2680	3·36	0·2820	3·56	0·4220	4·62	0·6550	4·56
0·2770	3·36	0·3049	3·56	0·5140	4·63	0·7126	4·57

Discussion

It is clear from the results presented in this Part that adsorption of methylene blue is always accompanied bv a fall in pH. Since these results were obtained with specimens which have been freed from soluble impurities, the pH-effects observed in the present series of experiments can be regarded as definite evidence of polar adsorption by active carbon.

To explain the reported liberation of acid during the adsorption of methylene blue by carbon, Bartell and Miller (*loc. cit.*) suggest that methylene blue chloride is hydrolysed in solution into its free base and hydrochloric acid and that by selective adsorption of the undissociated base, free acid accumulates in the solution.

The figures given in Table II reveal that the pH-value of the methylene blue solution is practically unchanged when it is diluted from a concentration of 0·15 per cent. to half this value. The pH-value obtained from a dilute solution of the dye in specially distilled water lies between 6·2 and 6·5. The low value of pH = 4 obtained by Bartell and Miller (*loc. cit.*) may be due to impurities present in the samples of methylene blue employed by them. The present results, obtained with pure samples, show that there is very little hydrolysis of the dye in aqueous solution.

A comparison of the experimental values of methylene blue adsorbed with the values calculated from the pH-variations (Table III and Fig. *2b*) will show that the acid liberated corresponds to a small part of the total adsorption. Bartell and Miller assumed, however, that a quantitative relationship exists between the adsorption of methylene blue and the concurrent hydrolysis so that each molecule of acid liberated corresponds to a molecule of methylene blue-base adsorbed.

The slight discrepancy between the amount of dye adsorbed and the acid liberated in the process was attributed by Bartell and Miller to the adsorption of part of the acid by charcoal, as free acid was noticeable in the solution only in the later stages of adsorption. In the present experiments, however, it is found that the equilibrium pH-value is attained in about ten minutes, whereas it takes nearly two hours to obtain a maximum value for the adsorption (Fig. *2b.*). It would appear, therefore, that any hydrolysis of methylene blue should be induced by the carbon and should necessarily be completed almost instantaneously and independently of the adsorption. This conclusion does not agree with the theory of hydrolytic adsorption according to which adsorption and hydrolysis take place concomitantly.

The data given in Table IV show that the equilibrium pH-value is unaffected by changes in the concentration of the charcoal present. In a previous part of this series (*This volume,* p. 157) it was noticed that the equilibrium pH was constant over a wide range of initial pH-values. It is clear, therefore, that the equilibrium pH is truly characteristic of the adsorbent. If, on the other hand, the pH-change produced on addition of carbon to a solution of methylene blue were due to acid formed by hydrolytic adsorption then the acidity of the solution would depend upon the amount of methylene blue adsorbed. The pH-value of the solution would in that case vary with the concentration of charcoal as well as with the initial pH of the solution.

Lastly, the observed increase in pH (base-liberation) when specimens of active carbon are added to highly acid solutions of methylene blue (Table I), and the observation of Chambers and King (*loc. cit.*) that free base is formed with high temperature-carbons, conflict with the theory of hydrolytic adsorption according to which acid-liberation should be expected under all circumstances when methylene blue is hydrolytically adsorbed by active charcoal.

It is seen from the foregoing that the results of this work cannot be fully explained by the theory of hydrolytic adsorption, except, perhaps, with the aid of *ad hoc* assumptions.

In developing their theory of hydrolytic adsorption, Bartell and Miller have assumed that the surface of pure carbon does not contain any ions and that the excess of hydrogen-ions is liberated during the adsorption of methylene blue with hydrolysis. Subsequent work (referred to in Part II) has shown that when active carbon is placed in aqueous media it adsorbs anions and cations non-equivalently. The existence of ionic layers on the surface of carbon is now widely accepted. It should therefore be expected that by "ion-exchange adsorption" some ions can be transferred from the surface to the solution, a possibility which was not mentioned by Bartell and Miller.

When active carbon is suspended in pure water it takes up hydrogen and hydroxyl ions in non-equivalent proportions with consequent change in the pH-value. Most carbons (except those prepared at high temperature) adsorb OH'-ions preferentially with the result that the pH of water is lowered by the addition of these carbons. This aspect of the non-equivalent adsorption of $H^{\cdot}$ and OH'-ions has been discussed more fully in Part III of this series. The pH-change that is observed when active charcoal is added to a solution of methylene blue may be treated as the effect of methylene blue on the pH-effect of the carbon in pure water.

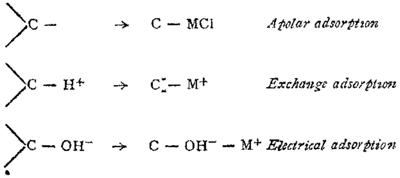
If methylene blue is added in sufficient concentration to an aqueous suspension of active carbon, most of the dye will be taken up equivalently (*i.e.*, as undissociated molecules, or as the *gegenions* $M^{\cdot}Cl'$). This is apolar adsorption and does not cause any change in the pH of the suspension. A small proportion is, however, adsorbed non-equivalently, with resultant change in the pH. In the latter case, the methylene blue cation may be preferentially adsorbed by the carbon by two mechanisms: (1) the positively charged ion may be attached to the OH'-ions present on the surface in accordance with the principles of electrical adsorption set forth by Chaney, Ray and St. John (*This volume,* p. 158); (2) the methylene blue ion can also replace by exchange a H·-ion from the surface. The exchange adsorption between the hydrogen and the methylene blue ions produces an increase in the H·-ion activity in the suspension. This explains the observation that the equilibrium pH of a specimen of active carbon in methylene blue solution is always lower than the pH-value of the same specimen in water (Table V).

TABLE V

Specimen	Equilibrium pH in water	Equilibrium pH in methylene blue
Blood charcoal	3·4	3·3
Carboraffin (Coarse)	5·1	3·6
Norit	6·3	4·6
Darco	6·0	4·6

Since the adsorbent is in a state of equilibrium with the H·, OH′, Cl′ and methylene blue ions, which are themselves in equilibrium with one another, the activities of the various ions in solution are maintained at stable equilibrium values, which depend almost wholly on their relative affinities for the adsorbent. This explains why the equilibrium pH-value of a specimen is almost unaffected by variations in the concentration of the carbon and of the initial pH of the solution.

Combining the apolar and the two polar mechanisms for the adsorption of methylene blue by activated charcoal, the changes in the ionic-layer on carbon, produced by the addition of methylene blue to an aqueous suspension of the adsorbent, can be pictured as shown below:



In water. *In methylene blue.*

The ions on the surface of the adsorbent are sensitive to changes in the activities of various ions in the solution. Thus, the addition of acid to the solution of $H^{\cdot}$-ions will lead to an increase in the adsorption of $H^{\cdot}$-ions and, consequently, the replacement of $H^{\cdot}$-ions by methylene blue cations is decreased. Hence the observation that the adsorption of methylene blue decreases with increasing $H^{\cdot}$-ion activity. If, on the other hand, adsorbable anions, such as OH' and Cl'-ions, are added, more anionic groups will be formed on the surface leading to an increase in the "electrical" adsorption of methylene blue.

In a strongly acidic medium the large excess of $H^{\cdot}$-ions will not only reduce the dissociation of the $H^{\cdot}$-ion from the surface but will also draw some of the firmly held OH'-ions into the solution. This will lead to an increase in pH, as observed in the present work.

Carbon activated at high temperature manifests a preferential affinity for $H^{\cdot}$-ions, and when it is suspended in water it produces an alkaline reaction. This accounts in part for the observation of Chambers and King that *base* is liberated when such a carbon is employed to decolorise methylene blue. As opposed to the case of low temperature-carbons, the $H^{\cdot}$-ions on the surface of a high temperature-carbon are very firmly fixed and are consequently difficult to replace by exchange with other cations. On the other hand, the hydroxyl ions are more labile on high temperature-carbons and can therefore be exchanged with other anions. For instance, in solutions of methylene blue the OH'-ions may be partly replaced by Cl'-ions with consequent liberation of OH'-ions in the solution.

This difference between the two types of carbon, while affecting polar adsorption by the ion-exchange mechanism, will not interfere with the electrical adsorption of the methylene blue ion on anionic centres on the carbon-surface. For either type of carbon, the general rule holds that the adsorption of methylene blue will be enhanced by conditions favouring the adsorption of anions.

Chambers and King (*loc. cit.*) studied the adsorption of methylene blue, sodium benzoate and potassium chloride by ash-free sugar-charcoal activated at different temperatures. They found that either acid or base was liberated depending on the specimen employed. Since it was established that the temperature of activation governed the composition and constitution of the oxide complexes found on the surface of carbon, they concluded that hydrolytic adsorption was due to the presence of these surface-oxides. This was also shown clearly by Burstein and Frumkin (*Z. physikal Chem*,. 1929, **141**, 219) who found that when a sample of activated charcoal was outgassed thoroughly at 1000° C. and then placed in a salt-solution in vacuum, no sign of hydrolysis was noticed; but on admitting air or oxygen into the solution hydrolytic adsorption took place. The surface-oxides therefore act as centres of polar adsorption. As the oxide-layer on carbon constitutes only about half per cent. of its total adsorptive surface (Rideal and Wright, *J. Chem. Soc.,* 1925, **27**, 1347), the magnitude of the polar adsorption would be very small, and by far the greater part of an electrolyte would be taken up without the liberation of acid or base. This view emerges from the present observations and is in agreement with those of Chambers and King.

Summary

1. Only specimens which had been thoroughly washed with water were employed in this investigation.

2. The amounts of methylene blue adsorbed by the specimens from a pure aqueous solution at various stages have been determined. Simultaneously, the pH-values of the solution at various stages of the adsorption-process have also been noted.

3. The pH-value of a solution of methylene blue is found to be practically unaffected by dilution from 0·150 per cent. to 0·075 per cent.

4. The pH-values of methylene blue solutions containing various amounts of either acid or alkali have been determined. From these values, a curve has been drawn connecting the pH of the solution with the amount of acid or alkali present in the solution. This curve is valid for methylene blue concentrations varying from 0·075 to 0·150 per cent.

5. From the above data, the amounts of acid liberated at various stages of the adsorption-process have been calculated from the pH-variations during adsorption. The amounts of methylene blue adsorbed with hydrolytic effect were thus derived.

6. The experimental results presented here cannot be explained satisfactorily by the theory of hydrolytic adsorption.

7. Ion-exchange mechanism has been proposed to account for the pH-change observed during the adsorption of methylene blue by activated charcoal. This mechanism is valid for all cases of electrolyte-adsorption by active carbon.

In conclusion, the author records his thanks to Dr. K. R. Krishnaswami, D.SC., F.I.C., for his kind advice and encouragement. The author is also grateful to the Indian Institute of Science, Bangalore, for the award of a Research Scholarship.

General Chemistry Section,
Indian Institute of Science,
Bangalore.

15*th August* 1942.

1180-42 Printed at The Bangalore Press, Bangalore City, by G. Srinivasa Rao, Superintendent