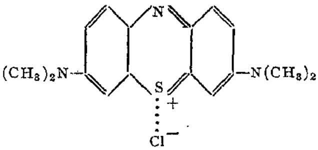
STUDIES ON ACTIVE CARBON

Part IV. Adsorption of Methylene Blue by Activated Charcoal: Effect of Anions and Cations

By M. V. C. Sastri

Measurement of the adsorption of methylene blue chloride from aqueous solution has often been considered to yield quantitative data for the surface and the activity of adsorbent carbon (Paneth and Radu, *Ber.*, 1924, 57, 1221; Berl and Herbert, *Z. angew. Chem.*, 1930, **43**, 904; Rideal and Wright, *J. Chem. Soc.*, 1925, **127**, 1347). In Part I of this series, a convenient method has been described in detail for the measurement of the adsorption of methylene blue by carbon and the relation between this quantity and the heat of wetting with benzene has also been discussed.

Methylene blue is a basic dye. Although, strictly speaking, it is a colloid, it dissociates in aqueous solution like an electrolyte into the methylene blue cation and the chloride ion thus:



The coloured cation is adsorbed by several adsorbents preferentially to a very great extent. Methylene blue has therefore been found to be very suitable for the study of non-equivalent adsorption by adsorbents such as, kaolin and fullers-earth. Its adsorption on charcoal has also been widely investigated from this standpoint.

It has been known for a long time that if activated charcoal were placed in a solution of a neutral electrolyte the reaction of the solution changes, apparently due to the liberation of acid or base. The origin of these acids and bases in the solution has been the subject of much controversy, and many attempts have been made to answer the question whether or not the adsorption of an electrolyte by charcoal results in hydrolytic decomposition. Much of the earlier work on the subject was carried out with impure specimens and the results were inconclusive and contradictory (Michaelis and Rona, *Biochem. Z.,* 1919, **97**, 57; *ibid.,* 1920, **103**, 19; Oden and Andersson, *J. Phys. Chem.,* 1921, **25**, 311). Bartell and Miller (*J. Amer. Chem. Soc.,* 1922, **44**, 1866; 1923, **45**, 1106; 1924, **46**, 1150) were the first to employ purified sugar-charcoal for the study of the adsorption of electrolytes. They established by direct titration that acid was liberated during the adsorption of basic dyes and alkali during the adsorption of acid dyes. Their investigations extended also to neutral salts such as potassium chloride. They explained the phenomenon on the basis of the *hydrolytic adsorption theory.* For example, to account for the liberation of free acid, presumably hydrochloric acid, when methylene blue was adsorbed by charcoal they suggested that there existed in the solution the following hydrolytic equilibrium:

$$MCl + H_2O \rightleftharpoons MOH + HCl$$

where 'M' denotes the methylene blue radical. The products of hydrolysis were considered to be adsorbed unequally by carbon, MOH being taken up more than HCl, thereby causing further hydrolysis with liberation of free acid. In accordance with their theory, Bartell and Miller (1923) found that the same charcoal that gave rise to an excess of acid in the adsorption of a basic dye gave an alkaline solution when an acid dye (*e.g.,* eosin) was adsorbed. It is significant that this theory of hydrolytic adsorption excluded the possibility of the adsorption of the individual ions. Further, the same explanation based on hydrolysis was advanced also in the case of neutral salts, *e.g.,* potassium chloride.

Chambers and King (*J. Chem. Soc.,* **1938**, 488) investigated the adsorption of methylene blue, potassium chloride and sodium benzoate by pure sugar-charcoal, which had been activated at temperatures varying from 300° to 1000° C. They also determined the amount of acid or base liberated by titration. They observed, in the first place, that the adsorption of an electrolyte was partly molecular and partly hydrolytic, the relative amounts sorbed hydrolytically and molecularly depending upon the conditions of activation.

Secondly, they found that while acid was liberated during the adsorption of methylene blue and potassium chloride by carbons activated at temperatures below 500° C., free *base* was liberated when the same electrolytes were adsorbed by specimens prepared at higher temperatures. With these two electrolytes they observed that the maximum acid-liberation was obtained with carbons prepared at 350° to 400° and the maximum base-liberation with those activated at 700° to 750°. Carbons activated at an intermediate temperature of 500° did not produce any appreciable change in the reaction of the solution.

Whatever may be the mechanism of the formation of acid or base during the adsorption of electrolytes by carbon, this behaviour is characteristic of polar adsorbents, such as kaolin and fullers-earth, which upon adsorption of electrolytes liberate by exchange fresh ions into the solution. A further analogy between carbon and typical polar adsorbents is that the adsorption of electrolytes by active carbon is influenced generally by the presence of other ions in the system. Siegrist (*"Contribution a' l'etude des phenomenes d' adsorption"*, *Diss.*, Lausanne, 1910) has made the interesting observation that charcoal treated with acids takes up crystal ponceau, an acidic dye, more strongly and methylene blue, a basic dye, more weakly, than untreated charcoal. Hauge and Willaman (*Ind. Eng. Chem.*, 1927, **19**, 943) carried out a detailed investigation of the effect of pH on the adsorption of acidic, basic, amphoteric and neutral substances. They found that while increasing acidity of the solution favoured the adsorption of negatively charged colloids like benzo-azurin and caramel, alkalinity enhanced the adsorption of electropositive substances, such as methylene blue. In these cases, it was further observed that the amount adsorbed changed more or less abruptly at a particular pH-value, which was characteristic for each specimen of charcoal. The adsorption of amphoteric substances, such as proteins, was maximum in the general region of the iso-electric pH of the protein, and was minimum at the extremes of acidity and alkalinity. The adsorption of non-electrolytes, *e.g.*, dextrose, was unaffected by variations in the pH of the solution. The explanation offered by Hauge and Willaman was based primarily on the electrical theory of adsorption, which interprets the process in terms of electrical attraction between oppositely charged particles. The charge carried by the carbon-particle was attributed to the adsorption by $H^{\cdot}$ and OH'-ions on its surface and the magnitude and sign of the charge, and hence the adsorption of electropolar substances, varied with the activities of the $H^{\cdot}$ and OH'-ions in the solution.

Apart from $H^{\cdot}$ and OH'-ions, other anions and cations must naturally influence the adsorption of electrolytes by carbon. The phenomenon has obviously an important bearing on hydrolytic adsorption. In the present paper the influence of $H^{\cdot}$, OH', Cl', SO_4 and Na-ions has been investigated.

Experimental

Methylene blue chloride employed in this work was of very high purity. The specimen supplied by Kahlbaum was purified by repeated recrystallisation from alcohol. Several stock solutions, containing 0·15 per cent. of methylene blue and different amounts of hydrochloric acid, or sulphuric acid, or caustic soda or sodium chloride were prepared so as to obtain solutions with different activities of $H^{\cdot}$, OH', Cl', SO_4'' and $Na^{\cdot}$ ions. The amount of methylene blue adsorbed by charcoal from each of these solutions was determined as described in Part I of this series. Suitable amounts of the well-dried carbon were shaken up with methylene blue solution for two hours. The amounts of carbon were so adjusted as to leave an end-concentration of 0·1 per cent. of methylene blue in the solution. The solution, after adsorption, was centrifuged and two c.c. of the supernatant clear solution were pipetted out for colorimetric estimation. The amount of dye adsorbed was determined by comparison with the original solution. The pH-values of the same solutions before and after adsorption, in the latter case without filtering off the carbon, were determined with a glass-electrode assembly as described earlier in Part III (p. 124) of this series.

The pH of a 0·15 per cent. solution of methylene blue in pure water was found to be between 6·20 and 6·50. It was also found that the colour of the solution was unaffected when the pH of the solution was changed between the values, 2 and 9.

Results

Table I gives the amounts of methylene blue adsorbed from solutions of varying pH-values prepared by the addition of decinormal hydrochloric or sulphuric acid or caustic soda. The variation

TABLE I

Adsorption of Methylene Blue by Activated Charcoal

Specimen	(*a*) In presence of HCl			(*b*) In presence of H_2SO_4			(*c*) In presence of NaOH		
	Intl. pH	Eqbm. pH	Adsn. mg./g.	Intl. pH	Eqbm. pH	Adsn. mg /g.	Intl. pH	Eqbm. pH	Adsn. mg./g.
Blood charcoal	2·46	2·56	601	2·60	2·68	627	7·55	3·82	610
	3·40	2·79	602	2·83	2·93	619	8·59	3·96	680
	6·04	3·12	594	3·04	2 99	620	8·64	4·79	710
	6·09	3·27	586	3·14	3·02	594	8·72	5·65	712
	6·16	3·36	579	3·59	3·22	547	9·29	6·47	730
	6·72	3·71	584	3·95	3·60	560	9·40	7·04	788
Carboraffin	2·46	2·60	362	2·60	2·72	375	6·96	3·96	366
	2·54	2·77	362	2·83	2·94	362	7·50	4·00	371
	2·95	2·98	347	3·04	3·04	363	8·59	4·57	396
	3·13	3·06	350	3·14	3·04	359	8·72	5·07	439
	3·23	3·16	329	3·59	3·21	334	8·95	6·10	482
	3·31	3·21	316	3·95	3·35	328	9·24	6·85	505
	6·04	3·45	335	..	..	..	9·30	6·96	514
	6·58	3·47	345	..	..	..	..	..	..
Norit	2·92	4·99	164	2·60	2·86	175	6·96	7·50	187
	3·13	6·70	159	2·83	4·47	175	7·50	7·80	190
	3·23	6·99	158	3·04	6·55	173	8·59	7·93	192
	3·45	7·12	155	3·14	6·77	170	8·72	8·13	196
	3·68	7·38	157	3·59	7·11	166	9·24	8·65	205
	6·04	7·40	167	3·95	7·39	164	..	..	..
	6·58	7·43	180	..	..	..	..	..	..
Darco	2·92	2·90	96	2·60	2·69	109	7·50	4·77	112
	3·13	3·10	98	2·83	2·98	107	8·59	6·12	122
	3·31	3·39	95	3·04	3·07	108	8·72	6·65	136
	6·09	3·72	96	3·14	3·12	110	9·24	7·77	146
	6·58	3·95	110	3·59	3·39	106	9·59	8·06	155
	..	..	..	3·95	3·65	103	..	..	..
Philburgin	2·26	2·36	33	..	..	..	7·28	7·04	46
	2·94	3·05	34	..	..	..	8·66	7·38	49
	6·15	4·53	33	..	..	..	9·41	8·45	67
	6·23	6·92	47	..	..	..	..	..	..
Animal charcoal	2·26	2·29	13	..	..	..	..	..	..
	2·94	3·41	29	..	..	..	..	..	..
	6·15	5·63	34	..	..	..	..	..	..
	6·23	6·97	38	..	..	..	..	..	..

of methylene blue-adsorption with the equilibrium-pH is also shown by the curves in Fig. 1. The amounts of methylene blue adsorbed

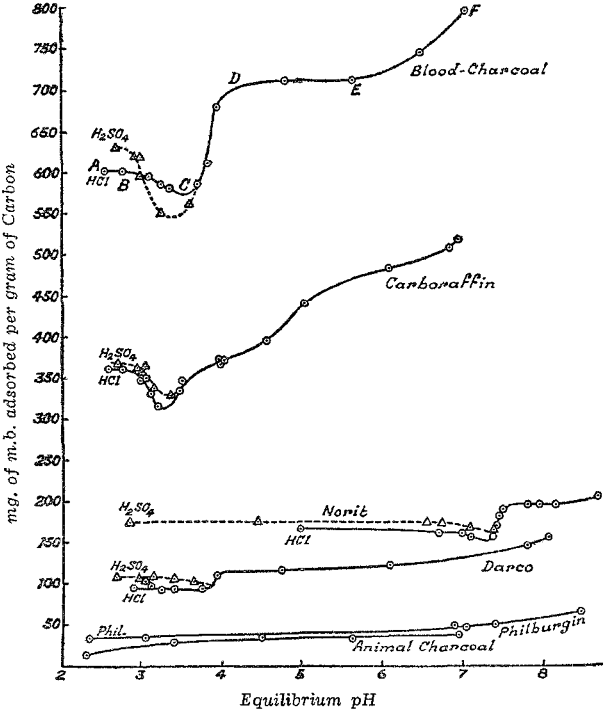


FIG. 1

from solutions containing sodium chloride are given in Table II, in which the figures shown in parenthesis represent the amounts of methylene blue adsorbed in the presence of hydrochloric acid instead of sodium chloride.

TABLE II

Adsorption of Methylene Blue of Activated Charcoal in presence of NaCl

c. c. of $\frac{N}{10}$ NaCl added per L. of m.b. soln.	Intl. pH	Blood charcoal		Carboraffin		Norit		Darco	
		Eqbm. pH	Adsn. mg./g	Eqbm. pH	Adsn. mg./g.	Eqbm. pH	Adsn. mg./g.	Eqbm. pH	Adsn mg./.g.
5	6·20	3·23	578 (588)	3·41	352 (330)	7·76	159 (190)	3·59	93 (95)
10	6·34	3·19	582 (592)	3·46	359 (337)	7·77	166 (190)	3·53	110 (95)
15	6·32	3·18	591 (592)	3·52	360 (345)	7·76	171 (190)	3·56	111 (95)
20	6·30	3·20	601 (590)	3·54	360 (347)	7·75	171 (190)	3·54	111 (95)
25	6·30	3·20	610 (590)	3·53	362 (346)	7·75	173 (190)	3·52	112 (95)
30	6·29	3·19	610 (592)	3·54	362 (347)	7·75	175 (190)	3·54	114 (95)

The figures given in parenthesis represent the amount of adsorption at corresponding equilibrium pH-values when HCl was present instead of NaCl.

Discussion

It will be noted from the figures given in Tables I and II that the addition of charcoal to a solution of methylene blue produces a marked change in the pH-value of the solution. It was also observed in the course of these experiments that the equilibrium-pH was practically unaffected by changes in the concentration of adsorbent employed.

From the curves in Fig. 1, the following features of the effect of pH on the adsorption of methylene blue by the more active specimens, *viz.*, Blood charcoal, Carboraffin, Norit and Darco, can be noted:

(1) The adsorption changes abruptly in a narrow range of pH, which is characteristic for each specimen (*e.g.*, CD in Fig. 1). These critical pH-regions are given in Table III.

TABLE III

Specimen	pH-region of maximal change in adsorption
Blood charcoal ..	3·75 to 3·95
Carboraffin ..	3·35 to 3·50 and 3·90 to 4·80
Norit ..	7·37 to 7·50
Darco ..	3·80 to 3·90

(2) At pH-values higher than the critical range the adsorption tends to reach a steady value (DE, Fig. 1), but at still higher pH-values, *i.e.,* in the extreme alkaline region, the adsorption again increases (EF, Fig. 1).

(3) The amount adsorbed by any carbon is at a minimum at about the lower limit of the critical range of pH. As the pH is reduced still further the adsorption increases again (CB, Fig. 1).

(4) In the region of very low pH-values, *i.e.*, in highly acid solutions, the amounts adsorbed by any carbon are nearly the same (AB, Fig. 1).

In the case of Carboraffin, the increase of adsorption with pH is gradual over a wide pH-range. On closer examination of the curve for Carboraffin in Fig. 1, it is seen that there are actually two pH-regions in which the adsorption rises rather steeply. These are 3·35 to 3·50 and 3·90 to 4·80.

Animal charcoal and Philburgin have very low adsorptive power and do not exhibit the features enumerated above.

The general trend of the curves in Fig. 1 do not conform simply with the statement of Hauge and Willaman that the adsorption of methylene blue increases with the pH of the solution. It can be seen from these curves that at low pH-values the adsorption actually increases as the pH is reduced.

The most significant feature of these observations is the sharp alteration in the extent of adsorption of methylene blue within a narrow range of pH-values and that this feature is characteristic for each carbon. That this effect is due entirely to the nature of the adsorbent and not to any effect on the dye follows from the fact that this critical range of pH-values varies widely from carbon to carbon. A reference to the investigations of Hauge and Willaman (*loc. cit.*) shows that for each carbon there is a characteristic region of pH in which maximum variations of adsorption are noticeable, irrespective of the nature of dye employed, *viz.*, whether it is acidic or basic. These authors referred to this region of pH as the "*iso-electric zone*" of the carbon, and they suggested that the change in adsorption in this region was due to a sharp variation in the sign and magnitude of the charge carried by the adsorbent. This view was fully supported by the later work of Olin, Lykins and Munro (*Ind. Eng. Chem.*, 1935, 27, 690) on the cataphoretic velocities of carbon-particles suspended in media whose pH-values were varied between the extremes of acidity and alkalinity. They observed that the speed and direction of the migration of the carbon-particles changed in a marked manner with the pH of the media. The curves in Fig. 2 give the results obtained by them with two typical carbons: one, a highly active cocoanut charcoal, and the other, a specimen of peat charcoal activated at 650° C. In these curves the relative magnitude and sign of the charge on the carbon-particle are plotted against the pH of the suspension. It is at once noticed that the carbon-particles retain their negative charge even in acid solution. When the solution is made increasingly acidic, there is at first a gradual decrease in the negative charge on the carbon. Then, within a characteristic range of pH-values (1·7–3·0 for cocoanut charcoal and 3·0–6 0 for peat charcoal) the negative charge decreases abruptly and the charge on the carbon becomes positive. At the pH-values, 2·4 for cocoanut charcoal and 4·2 for peat charcoal, the carbon-particles assume a "null-charge" and therefore remain stationary in the cataphoretic cell; these pH-values are the iso-electric pH-values of the respective carbons. The positive charge on the carbon-particle reaches its maximum at the lower limits of the pH-ranges mentioned above, *viz.*, at the pH-values 1·7 and 2·9 for cocoanut charcoal and peat-charcoal respectively. Below these pH-values, the position is again reversed, the positive charge on the carbons decreasing rapidly with further fall of pH. In the case of peat charcoal, there is also a deflexion in the curve at a pH of 2·4, and the positive charge tends to attain a steady value.

The striking similarity between these curves in Fig. 2 and those

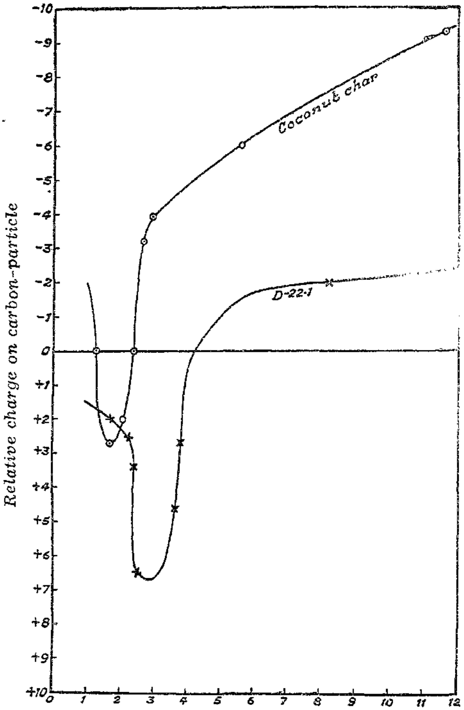


FIG. 2

in Fig. 1, giving the variation of methylene blue-adsorption with pH, offers conclusive proof that in the latter case also the effect observed was due to a fundamental property of the adsorbent. The charge on the carbon is generally ascribed to the presence of ions adsorbed, or chemisorbed, on it. Consequently, a variation in this ionic superstructure on the adsorbent produces a corresponding difference in the electro-kinetic charge and also in the adsorption of electrolytes such as methylene blue. The relative proportions of the various anions and cations present on the surface of the carbon and, therefore, the charge, which is the algebraic sum of the individual charges of the adsorbed ions, will naturally depend on the activities of the various ions in solution. Any explanation which accounts for the observed variation of the charge on the carbon-particles with the pH of the solution will also serve to explain the variation of the adsorption of methylene blue from solutions containing various amounts of acid or alkali.

Starting with carbon suspended in pure water, we can follow the nature of the adsorbed ionic layer when increasing amounts of hydrochloric acid or sodium hydroxide are added to the suspension. When sodium hydroxide is introduced into the medium, the activities of both the $Na^{\cdot}$ and OH'-ions are increased. Since the adsorption of Na-ions is negligible when compared with that of OH'-ions the negative charge on the carbon particles increases progressively with the pH of the suspension. On the other hand, when hydrochloric acid is added the activities of $H^{\cdot}$ and Cl'-ions are increased. Both these ions are adsorbed by charcoal, but the $H^{\cdot}$ ions are by far the more strongly adsorbed. Therefore, for the initial amounts of acid added, the carbon becomes increasingly positive, due to the preferential adsorption of $H^{\cdot}$-ions. Meanwhile, the activity of the Cl'-ions left behind in solution increases steadily. At a critical concentration of the acid in solution, the Cl'-ion activity becomes so much in excess of the $H^{\cdot}$-ion activity that the Cl'-ions are taken up as much as the $H^{\cdot}$-ions. At this point the positive charge on the carbon particles reaches a maximum value. With further addition of acid, Cl'-ions are adsorbed more than $H^{\cdot}$-ions and the positive charge diminishes accordingly. Finally, when a state of saturation is reached on the surface, no further adsorption of ions takes place, and the charge remains unaffected by increase of acid-strength.

The electrical charge on the carbon depends, naturally, on the balance between the various ions adsorbed. If the anions predominate on the surface, the carbon assumes a negative charge. On the other hand, if the cations predominate, the charge is positive. Between the two extremes there is a balanced state when the anions and cations are present in equivalent proportions and the carbon manifests a "null-charge". This happens at the "iso-electric point" at which the carbon manifests no tendency to migrate in a cataphoretic cell.

It is noteworthy that the variation of electrical charge with pH is greatest in the narrow range of pH-values immediately above and below the iso-electric point. From the remarkable parallelism between electrical charge and adsorption, it may be concluded that the maximum variation of adsorption also occurs at the iso-electric point. The system is more or less "buffered" at the iso-electric point and the result is that any fresh addition of acid or alkali produces a comparatively slight alteration in the pH of the solution in equilibrium with the carbon, although it effects a considerable change in the charge on the adsorbent.

The "buffer" action of activated carbons has already been referred to in Part III of this series (page 157). It was observed there that each specimen of carbon maintained its own characteristic pH in aqueous suspension and that variations of the initial pH of the water and of the concentration of the carbon had little influence on this value. It is to be expected, however, that this value will be affected, though only slightly, by the presence of electrolytes in the solution. From the data given in Table I, it will be noticed that the equilibrium pH-values of each carbon lie within a narrow region around the iso-electric point even when the initial pH-values of the solution are varied over a wide range. This is clearly shown by the curves in Fig. 3, where the equilibrium pH-values are plotted against the corresponding initial pH-values. It is seen that for each carbon there is a certain characteristic pH which remains constant over a wide range of initial pH-values. In the case of Carboraffin, there are two such values. The characteristic equilibrium pH-values for the four specimens of activated charcoal are given in Table IV.

It is seen that the figures in Table IV can be compared with those in Table III, which gives the pH-range in which the maximum change in adsorption takes place. In other words, the maximum variation in the extent of electrolyte-adsorption occurs in the region of the characteristic equilibrium-pH.

It is possible that on the addition of acid or alkali to a suspension of adsorbent charcoal at the iso-electric point, the $H^{\cdot}$ or the OH'-ions just introduced are immediately taken up by the adsorbent so that a

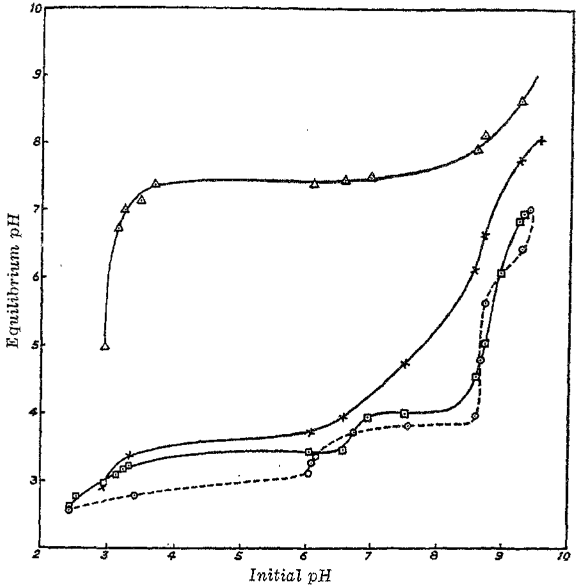


Fig. 3

Table IV

Specimen	Characteristic equilibrium pH
Blood charcoal ..	3·8
Carboraffin ..	3·5 and 4·0
Norit ..	7·5
Darco ..	3·6 (*ca*)

marked difference in the distribution of ions on the surface, and hence in the charge on the carbon-particles, is produced without appreciable change in the pH of the solution. Since the buffer-effect of the carbon depends almost entirely on its selective adsorptive power for various ions, it follows that the buffered pH-range will be fundamentally characteristic of the specimen and will therefore depend on the conditions of preparation of the specimen.

Having explained the salient features of the variation of the electrical charge on carbons with the pH of the medium, we can proceed to account for the influence of pH on the adsorption of electrolytes by carbon using the following postulates due to Chaney, Ray and St. John (*Ind. Eng. Chem.*, 1923, 15, 1244) to express the relation between electrical charge and adsorption:

1. A given carbon will be most effective as an adsorbent if it carries an electrical charge opposite to that carried by the particle to be adsorbed.
2. Active carbon may be neutral or may readily become positively or negatively charged by the adsorption of H˙ or OH′-ions from solution.
3. The carbon may be caused to assume the desired charge by the adsorption of H˙ or OH′-ions from solution.
4. The fact that a carbon is electrically charged does not influence its adsorptive capacity when it happens to react towards neutral particles.
5. The differences in adsorptive power caused merely by differences in electrical charges on the carbon are not fundamental in estimating the intrinsic character of the carbon.

The tendency of the adsorption of methylene blue to reach a state of saturation (DE, Fig. 1) as the equilibrium pH of the solution rises just above the iso-electric point is probably due to steric limitations on the surface of the adsorbent. The increase in adsorption beyond the region of saturation (EF, Fig. 1) may be due to the fact that in these cases the solution was initially highly alkaline and under such conditions methylene blue tends to coagulate.

In the case of Carboraffin two iso-electric points have been observed (Figs. 1 and 3) in the course of the present investigation. The first is at 3·4–3·5 and the second at 4·0–4·5. In both these regions the adsorption of methylene blue manifests accelerated variation with pH and the system simulates a buffer. This could only be due to the co-existence of two different carbons. In this connection it may be recalled that in the paper on the pH of carbon-suspensions

(Part III) reference was made to a fine and a coarse portion of Carboraffin having the characteristic pH-values of 3·05 and 5·13 respectively in water.

The iso-electric pH-value represents a very important characteristic of decolorising carbons, especially when the substance sought to be removed is of the nature of an electrolyte. At this point there is produced a sharp change in the decolorising properties of the carbon. Also, it can be said to be the characteristic equilibrium-pH of the carbon in a given solution. At this point the equilibrium-pH remains constant for a comparatively large variation of the initial pH of the solution. This is in accordance with the definition given by Kroetz (*Biochem. Z.*, 1924, **153**, 173) that the iso-electric point is the pH of the buffer which is not changed in reaction by the addition of the charcoal. Since the effect of the carbon on the pH of a solution is due to the selective adsorption of ions from the solution, the characteristic equilibrium-pH will depend upon the electrolytes present in the solution. The iso-electric point of a given specimen of charcoal will, therefore, vary in different electrolyte-solutions, though these variations may be slight.

The effect of the Cl-ion.—The effect of the Cl-ion on the adsorption of methylene blue is clearly shown by the figures in Table II. As increasing amounts of sodium chloride are added the amount of methylene blue adsorbed increases progressively. The amounts adsorbed at corresponding pH-values in presence of hydrochloric acid instead of sodium chloride, as shown by the figures in parenthesis, are distinctly lower than those obtained with sodium chloride. This is due to the fact that the adsorption of the $Na^{\cdot}$ ion is practically negligible when compared with that of the $H^{\cdot}$ ion with the result that in the presence of NaCl the carbon takes a greater negative charge and adsorbs more methylene blue than when HCl is present in the solution.

The effect of the SO_4'' *ion.*—The results in Table I and the dotted lines in Fig. 1, show that the amount of methylene blue adsorbed in the presence of sulphuric acid is generally higher than that adsorbed in the presence of hydrochloric acid at the same pH. In the case of blood charcoal, however, the adsorption from solutions acidulated with sulphuric acid is initially lower than from those containing hydrochloric acid, but at higher concentrations of the acid sulphuric acid enables greater sorption of the dye. This may be due to two reasons: firstly, the SO_4''-ion may be more strongly adsorbed by the carbon than the Cl'-ion thereby giving the carbon a greater negative charge. However, Rona and Michaelis (*Biochem. Z.*, 1919, **94**, 240) have found that blood charcoal adsorbs Cl'-ions more than SO_4''-ions. In the case of Merck's purified blood charcoal employed in the present investigation also, the indications are that the SO_4''-ions are less strongly adsorbed than the Cl'-ions. Otherwise, the decolorisation of the solution should have been greater at all concentrations of sulphuric acid and the observed superiority of the Cl'-ion over the SO_4''-ion in this respect at lower concentrations would not have been possible.

A more satisfactory explanation is found in the bivalency of the SO_4''-ion. Each SO_4''-ion adsorbed contributes two negative charges to the carbon as compared with a single negative charge of the Cl'-ion. As 1, 2, 3, 4, ... etc. SO_4''-ions are adsorbed the negative charges on the carbon increase in the order 2, 4, 6, 8, ... etc. In other words the adsorption of the SO_4''-ions will produce a more rapid rise in the negative charge on carbon than the adsorption of the Cl'-ion so that, eventually, the SO_4''-ion gives rise to a greater negative charge than the Cl'-ion. The greater the negative charge, the greater is the adsorption of methylene blue.

The data presented in this paper show clearly the effect of various anions and cations on the adsorption of methylene blue by active carbon. The impressive correlation between the adsorption of this basic dye and the electrical charge on the adsorbent suggests that the same factors that influence the electrical charge affect likewise the adsorption of methylene blue. The relation between the electrical charge of carbon and the adsorption of methylene blue can be summarised by the simple rule, the more negative the carbon the greater is the amount of basic dye adsorbed. The electrical charge on carbon is attributed to the unequal adsorption of anions and cations. The variation of electrical charge in solutions of varying pH-values have been fully explained in this paper on the basis of changes in the adsorption of $H^{\cdot}$, OH' and Cl'-ions on carbon. Thus, the curves obtained by Olin, etc. (*loc. cit.*), give a useful indication of the relative adsorptive affinities of various ions at different concentrations of acid and alkali in the solution. The relation between the pH of the solution and the amount of methylene blue adsorbed show how such changes in the relative sorptive affinities of the various ions affect the adsorption of methylene blue. Briefly, it is found that the conditions that favour the adsorption of anions, like OH′, Cl′ and SO_4'', enhance the adsorption of methylene blue. On the other hand, under conditions that favour the adsorption of cations, like $H^{\cdot}$, the amount of methylene blue taken up is decreased.

Summary

1. The adsorption of methylene blue from acidic and alkaline solutions has been studied.

2. The variation of the adsorption of methylene blue with the equilibrium-pH of the solution has been noted. The general trend of these results has been correlated with the variation of electrical charge on carbon-particles, suspended in media of varying pH-values.

3. The equilibrium pH-value has been found to remain constant over a wide range of initial pH-values and to be characteristic of the specimen.

4. The adsorption of the dye has been found to change markedly in the region of the characteristic equilibrium pH-values of the respective specimens. It is suggested that this effect is due to the buffer-action of activated carbon.

5. The buffer-action of active carbon and the variation in extent of adsorption, produced by various anions and cations, have been explained on the basis of the selective adsorption of ions on the surface.

6. In conclusion, it is observed that conditions that favour the adsorption of anions enhance the adsorption of methylene blue.

The author's thanks are due to Dr. K. R. Krishnaswami, D.SC., F.I.C., for his kind advice and encouragement, and to the Indian Institute of Science, Bangalore, for the award of a Research Scholarship.

General Chemistry Section,
Indian Institute of Science,
Bangalore (India).

[Received, 15-8-1942.]