

sates) at different gelatin concentrations, over a wide range of hydrogenion adjustments. Except at very high and very low (> 2 and < 11) values of P_H , the rigidity does not vary very rapidly, the maximum being at P_H 7 to P_H 9.

2. Amounts of aluminum equivalent to 0.01 to 0.1% of aluminum trioxide based on dry gelatin, produced considerable changes in the rigidity— P_H curve, and markedly increased the rigidity.

3. These results are discussed in connection with the theory of gelatin viscosity and elasticity.

4. A misleading statement on Poisson's ratio (for gelatin jellies) in a previous paper and in the literature of the subject is corrected.

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ADSORPTION BY ACTIVATED SUGAR CHARCOAL. I¹

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The greater part of the vast amount of work that has been done in connection with the study of the mechanics of adsorption of substances from solution by charcoal has been done with animal or blood charcoal. In view of the fact that the highly complex blood charcoal and the almost equally complex, but less active, wood or vegetable charcoal are not readily purified, it is not surprising that the results obtained with them have varied greatly in the hands of different investigators.

The recent development of methods for the activation of charcoal^{2,3,4} for the adsorption of gases suggested to us the possibility of preparing from sugar an active charcoal which would be free from the objectionable features of animal charcoal, such as high ash, high nitrogen content, and the necessity of treatment with reagents for its purification, and using this charcoal in a study of the nature of adsorption of electrolytes from solution.

Preparation of Activated Sugar Charcoal

Ten-pound lots of cane sugar were repeatedly recrystallized from conductivity water in order to free the sugar, as far as possible, from inorganic matter, such as calcium, etc. After recrystallization the sugar was carbonized and activated by the following method.

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² Lamb, Wilson and Chaney, *J. Ind. Eng. Chem.*, **11**, 420 (1919).

³ Sheldon, *Phys. Rev.*, **16**, 165 (1920).

⁴ Winter and Baker, *J. Chem. Soc.*, **117**, 319 (1920).

The sugar was charred in a large platinum dish and ignited at a low red heat to drive off the greater part of the volatile matter. This charcoal was then reduced to granules about the size of a kernel of wheat and heated at a temperature of about 1000° . Under proper conditions a marked increase in activity was obtained. The heating was carried out in 18 mm. silica tubes 30 cm. long, closed at one end. An asbestos box was made to fit over the top of a large Meker burner. Holes were provided in the sides of the box to carry the silica tubes in a nearly horizontal position while a small hole in the top of the box permitted the escape of the burner gases. When the silica tubes were half filled with the charcoal and the filled parts of the tubes heated for a period of 24 to 48 hours, or longer, it was found that the layer of charcoal nearest the open end of the tubes had changed its appearance from a bright, gray black to a dull, dead black and was capable of decolorizing considerable amounts of methylene blue solution. The charcoal farther back in the tubes had not changed appreciably in appearance or activity. It was thought from this that a certain amount of oxygen from the air might be necessary for the activation of the charcoal. As a further test a tube was heated to the highest temperature obtainable with this apparatus, the unsealed end closed with a stopper, and the heating continued in this manner for 48 hours. The activity of the charcoal remained practically unchanged.

After the charcoal was for 24 hours in the silica tubes it was transferred to silica crucibles with tightly fitting covers. When the crucibles and covers were not close fitting, too much air entered during the heating and the charcoal was entirely burned up during the 24 hours. When they fitted too closely, the charcoal was not activated. Finally, we were able to provide conditions such that satisfactory charcoal was fairly easily produced. A crucible, filled with the charcoal and heated for several days over a protected Meker burner, yielded from $\frac{1}{2}$ to $\frac{2}{3}$ the crucible volume of active material. Heating for longer periods gave a more active material but was accompanied by a correspondingly larger consumption of charcoal.

The charcoal so obtained had a soft, velvety-black appearance. When finely ground in an agate mortar and suspended in conductivity water it did not produce in the reaction of the water any change detectable by the sensitive indicators of the Clark and Lubs selection prepared for hydrogen-ion determinations. It was, of course, free from chlorides, and a Kjeldahl determination indicated the absence of combined nitrogen. Ash determinations made on a sample before activation showed 0.0002 g. in 3.0486 g. of charcoal; after activation 2.7686 g. gave 0.0003 g. of ash.

Work of Other Investigators

Many attempts have been made to answer the question as to whether or not adsorption by charcoal results in decomposition of an electrolyte so that either an acid or a base is set free in solution.

In this connection the work of Freundlich⁵ and of Michaelis⁶ and their co-workers has been referred to more frequently than that of any others in recent years. Their earlier researches were put forth to substantiate the theory that the ions of an electrolyte are not adsorbed in equivalent amounts with the result that the solution was left either acid or alkaline in reaction. Recently Michaelis and Rona^{6,7} have repeated some of their earlier work on adsorption and have come to the opposite conclusion, namely, that the ions of an electrolyte are adsorbed in equivalent quantities and that the hydrolytic adsorption of one or the other ion does not take place. Odén and Andersson⁸ also have recently presented data to show that adsorption is equivalent and they maintain that a so-called "decomposition" adsorption is only apparent.

It is worth while at this point to note that all these investigators used the same kind of adsorbent, namely, Merck's blood charcoal. In some cases the preparation was used without any attempt at purification; in others, attempts were made to remove the acid-soluble material.

Freundlich and Losev repeatedly boiled the charcoal with conc. hydrochloric acid. By this process the ash content was reduced from 8% before treatment to 5-7% after treatment.

Odén and Andersson used the same method of extraction but dried their preparation at 125°.

Michaelis and Rona used blood charcoal without any attempt at purification. They were aware that their material was far from ideal for the purpose but stated that a sample of cane sugar charcoal prepared by them could not be reduced finely enough, mechanically, to give sufficient adsorption.

When the process of carbonization of animal matter is studied and the possibility of mechanical occlusion considered, it is not difficult to understand why it is impossible to effect any considerable degree of purification of such charcoal by subsequent treatment with acid. The following experiment illustrates this point rather convincingly and also shows what may be expected from commercial charcoal. A sample of sugar charcoal purchased on the open market gave an acid extract upon treatment with water. Burning off the carbon left a brown ash which was almost completely soluble in hydrochloric acid and which was to all appearances largely iron. A portion of this charcoal was repeatedly boiled with conc. hydrochloric acid until no more iron could be detected in the filtrate. It was then thoroughly washed and an ash determination again made. This ash was almost completely soluble in hydrochloric acid and carried a large amount of iron. Determination of ash in 4.7846 g. of the charcoal before extraction gave 0.0288 g. or 0.57%; and after extraction the same weight of charcoal gave 0.0263 g. of ash or 0.55%. This experiment shows clearly the difficulty of purifying commercial sugar charcoal by acid treatment.

Adsorption of Dyes

Organic acid and basic dyes of the electrolyte type, because of their

⁵ Freundlich and Losev, *Z. physik. Chem.*, **59**, 284 (1907).

⁶ Michaelis and Rona, *Biochem. Z.*, **97**, 57 (1919).

⁷ Rona and Michaelis, *ibid.*, **103**, 19 (1920).

⁸ Odén and Andersson, *J. Phys. Chem.*, **25**, 311 (1921).

high adsorbability, have proved to be nearly ideal substances for use in a study of adsorption of electrolytes by charcoal. They have the disadvantage that they are with difficulty produced in a state of high purity.

In beginning the study of the nature of adsorption by activated sugar charcoal we deemed it advisable to see how this product compared in its behavior toward dyes with the animal charcoal used by Michaelis and Rona. Its action toward methylene blue, a basic dye of the electrolyte type whose cation is an organic radical and whose anion is chlorine, was first investigated. The purity of the methylene blue preparation was found to be approximately the same as that used by them. A 0.0025 *M* solution gave a Sørensen value of P_H 4.02, whereas their 0.002 *M* solution gave P_H 4.26. A sample of 1.0005 g. was charred and ignited with conc. sulfuric acid. A residue of 0.0022 g. of ash, or 0.22%, compared favorably with their 0.17% ash. The solution of the ash and the dye solution both gave a strong flame test for sodium. The preparation evidently contained as an impurity a small amount of sodium chloride and was in this respect also very similar to theirs.

Since the state of combination of the chlorine after adsorption determines whether or not the adsorption of methylene blue is equivalent or hydrolytic in its nature, a solution of methylene blue, 0.0025 *M* with respect to its chlorine content was prepared. The chlorine was determined by dissolving the methylene blue in conc. sulfuric acid and collecting the evolved hydrogen chloride in standard silver nitrate solution. This displacement was accomplished by aeration with an ammonia and carbon dioxide-free stream of air, using a somewhat modified form of apparatus described by Weiser and Sherrick.⁹ It was found that 0.3197 g. of methylene blue required 4.98 cc. of 0.02 *N* silver nitrate solution (average of 4 samples), whereas the calculated amount was 5.00 cc.

The proper amount of methylene blue was then used in making up the 0.0025 *M* solution. The chlorine in an aliquot of this solution was determined in the same way. Twenty-five cc. of this 0.0025 *M* methylene blue solution required 3.16 cc. of 0.02 *N* silver nitrate solution, whereas the calculated amount was 3.13 cc.

The decolorizing action of a number of charcoals using this methylene blue solution was then studied. Particular attention was given to the reaction of the decolorized solution after adsorption.

Results with Animal Charcoal

Two samples of animal charcoal obtained from different sources were used. The general results obtained with them were similar, as is shown below.

Acidity of Water Extract of Animal Charcoal No. 1.—Samples of charcoal of 2 g. each were suspended in 50 cc. of water and allowed to

⁹ Weiser and Sherrick, *J. Phys. Chem.*, **23**, 205 (1919).

stand for 3 hours with frequent shaking. They were then filtered, and washed, and the amount of acid set free determined by titration with 0.02 *N* sodium hydroxide solution, using methyl red as indicator. The amount of acid set free both with and without methylene blue is indicated below.

TABLE I
ACIDITY OF SOLUTION AFTER ADSORPTION WITH CHARCOAL 1
Amount of charcoal: 2 g.

Water used Cc.	0.0025 <i>M</i> methylene blue added Cc.	0.02 <i>N</i> acid set free Cc.
50	..	0.15
50	..	0.15
..	16	0.75
..	16	0.80

The larger amount of acid is set free when methylene blue is present.

Acidity of Water Extract from Animal Charcoal No. 2.—Experiments similar to those with Charcoal 1 were carried out.

TABLE II
ACIDITY OF SOLUTION AFTER ADSORPTION WITH CHARCOAL 2
Amount of charcoal: 0.5 g.

Expt.	Water used Cc.	0.0025 <i>M</i> methylene blue added Cc.	0.02 <i>N</i> NaOH added Cc.	0.02 <i>N</i> acid set free Cc.
1	50	0.15
2	..	50	..	3.75
3	..	25	..	1.65
4	..	50	..	3.60
5	..	50	3.60	1.70

From Tables I and II it is noted that the adsorption of methylene blue by acid animal charcoals results in setting free considerable amounts of acid. Also, even though enough alkali was added before adsorption to this solution to neutralize the acid set free by these amounts of charcoal and methylene blue, it did not prevent setting free a considerable amount of acid. This is shown in Expts. 4 and 5. Qualitative tests for chlorides were made on the solutions after decolorization of methylene blue and in all cases it was found that fairly large amounts were present.

The commercial sugar charcoal which we have previously described in connection with the extraction with hydrochloric acid, before activation, gave an acid water extract and was entirely devoid of any decolorizing

Commercial sugar charcoal G.	Treatment	0.02 <i>N</i> HCl required Cc.
1.0	Boiled with water and filtered	2.00
0.5	+50 cc. cold water and filtered	2.00
0.5	+16 cc. 0.0025 <i>M</i> methylene blue	0.20
0.5	+16 cc. 0.0025 <i>M</i> methylene blue	0.30

power for the methylene blue solution. After activation its water extract was strongly alkaline. The activated material gave the preceding results.

Samples of activated coconut charcoal and activated sugar charcoal prepared from beet sugar which had not been recrystallized also gave aqueous extracts that were strongly alkaline. When methylene blue solutions were decolorized by these charcoals the resultant solutions were alkaline but less so than the aqueous extract of the same amount of charcoal.

Adsorption with Ash-Free Carbon

The decolorizing action of the ash-free, activated sugar charcoal on methylene blue solution was studied under the same conditions as those chosen by Michaelis and Rona in their work with animal charcoal. They found that when methylene blue solutions were completely decolorized by animal charcoal the resulting solution was neutral or faintly alkaline and from 5.5 to 35% of the chlorine of the methylene blue remained in solution as neutral chlorides. They concluded from this and from similar data obtained with other basic and acid dyes that adsorption is equivalent and that in no case was there any indication of hydrolytic adsorption with the resultant setting free of acid or alkali. The appearance of calcium and other chlorides in solution was easily accounted for by the presence of these bases as impurities in their charcoal.

Provided ash-free, activated sugar charcoal were to behave in a similar manner it should be found that there is only equivalent adsorption of methylene blue. The filtrate after decolorization should be neutral and there should be no chlorides in solution. In our work these expectations were only partially fulfilled. The filtrates were found to be absolutely neutral. It was somewhat surprising, however, to find a small amount of chloride in these neutral filtrates. The method of preparation of the charcoal precluded the possibility of any contamination by neutral chlorides and the only source of the neutral chlorides remaining was the methylene blue. As stated before, the methylene blue contained sodium chloride as an impurity. Further evidence indicating this as the source of the neutral chloride will appear later.

A number of samples of the ash-free, activated charcoal were tested as follows.

The charcoal, finely ground in an agate mortar, was placed in small Erlenmeyer flasks, the methylene blue solution added, and the flasks evacuated for a few minutes with a good water pump to remove as much of the occluded air as possible in order to allow better contact with the methylene blue solution. The suspension was allowed to stand, with occasional shaking, for a length of time sufficient for complete decolorization. The charcoal was then filtered off through a small disc of ash-free filter paper in a 30cc. Gooch crucible and repeatedly washed. The reaction of the filtrate was tested and the amount of chloride present determined by concentrating the filtrate and washings to a volume of approximately 10 cc. and titrating with 0.02 *N* silver nitrate solution, using potassium chromate as indicator.

TABLE III
 ADSORPTION OF METHYLENE BLUE BY CHARCOAL
 Using a small amount of methylene blue

Charcoal G.	0.0025 <i>M</i> methylene blue	0.02 <i>N</i> AgNO ₃ required
	Cc.	Cc.
0.25	16	0.24
1.00	50	0.60
1.00	50	0.56
0.25	56	0.47
0.25	16	0.10
0.25	16	0.24

In every instance the filtrate was colorless, neutral, and contained a small amount of neutral chloride. These data seemed to confirm the results obtained by Michaelis and Rona and seemed to substantiate their statement that hydrochloric acid is not set free under these conditions.

Since the methylene blue in solution is hydrolyzed to a certain extent, there are present in addition to the methylene blue molecules and the ions resulting from its dissociation, also methylene blue hydroxide and hydrochloric acid. The above data give no clue to the manner in which all these are removed from solution. The methylene blue molecules alone might be adsorbed, thus causing the eventual complete association of the ions and the reaction of the hydrolytic products. The hydrolytic products might be adsorbed with the result that all of the methylene blue would be hydrolyzed. Another possibility is that the methylene blue molecules, the methylene blue hydroxide molecules, and the hydrochloric acid molecules might all be adsorbed. This would result in complete adsorption of all solutes present.

It was found that the charcoal, after adsorption of methylene blue under the above conditions, was still able to take up a considerable quantity of hydrochloric acid. This was shown by the following two experiments.

1. Two g. of charcoal, after completely decolorizing 80 cc. of 0.0025 *M* methylene blue solution, took up 12.11 cc. of 0.02 *N* hydrochloric acid. 2. To a mixture of 58 cc. of 0.0025 *M* methylene blue solution and 2.00 cc. of 0.02 *N* hydrochloric acid sufficient charcoal was added to decolorize the solution completely. The charcoal was filtered off and washed. In the filtrate was found 0.20 cc. of 0.02 *N* hydrochloric acid.

These results immediately suggested the possibility that, if the charcoal were more nearly saturated with methylene blue, there might be set free either acid or base. This, proved to be the case as shown by the data following in Table IV.

To a given weight of charcoal was added sufficient methylene blue solution so that at the end of a day or two there still remained in solution a small amount of color equivalent to about 0.05 cc. of 0.0025 *M* methylene blue. The charcoal was then filtered off in the usual way and the acid and chloride content of the filtrate determined.

TABLE IV
ADSORPTION OF METHYLENE BLUE BY CHARCOAL

Using a large amount of methylene blue

Charcoal taken G.	0.0025 M methylene blue added Cc.	0.02 N NaOH	0.02 N AgNO ₃
		required to neutralize filtrate Cc.	required by filtrate Cc.
0.30	160	3.32	5.38
0.25	100	3.72	4.50
0.25	100	3.22	3.73

Here, indeed, was evidence of a hydrolytic adsorption. It appeared probable that the methylene blue hydroxide was adsorbed to a greater extent than the hydrochloric acid. In order to study this action more closely, the following experiment was performed.

0.25 G. samples of charcoals of different degrees of activity were treated with successive portions of 16 cc. of 0.0025 M methylene blue solution. The charcoal was filtered off and washed after each addition of methylene blue and the amount of acid and chlorine in the filtrate determined. *This procedure was repeated until the charcoal no longer decolorized the solution sufficiently for the determinations to be made on the filtrate.* In the case of Charcoal 3 the second addition was 64 instead of 16 cc. of 0.0025 M methylene blue. Charcoal 5, before the addition of the first 16 cc. of methylene blue solution, had been treated with hydrochloric acid by suspending it for 24 hours in 10.17 cc. of 0.02 N hydrochloric acid. It was then centrifuged and 5.0 cc. pipetted off, titrated with 0.02 N sodium hydroxide solution (3.02 cc. required), and the chloride determined by titration with 0.02 N silver nitrate solution (3.03 cc.). The charcoal was filtered from the remainder of the solution, the filtrate and washings were also titrated with 0.02 N sodium hydroxide solution (2.97 cc.), and chloride determination made (3.10 cc. of silver nitrate solution required.) The charcoal, therefore, carried 4.18 cc. of 0.02 N hydrochloric acid before it was used to adsorb the methylene blue.

The data for the 5 charcoals are given in Table V.

TABLE V
HYDROLYTIC ADSORPTION OF METHYLENE BLUE

Successive additions of 16 cc. of methylene blue and amounts of reagents required in titrations

Char. coal	0.02 N solution	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th
1	NaOH, cc.	0.00	0.00	0.00	0.20	0.30	0.40	0.45
	AgNO ₃ , cc.	0.19	0.19	0.32	0.53	0.71	0.69	0.91
2	NaOH, cc.	0.00	0.00	0.00	0.30	0.30	0.40	0.45	0.45	0.50	0.55
	AgNO ₃ , cc.	0.23	0.35	0.18	0.54	0.66	0.62	0.72	0.76	0.95	0.90
3	NaOH, cc.	0.00	2nd Addition			0.70	0.45	0.55
	AgNO ₃ , cc.	0.19	64 cc. of 0.0025 M			1.64	0.91	0.86
4	NaOH, cc.	0.00	0.05	0.20	0.75	0.45	0.65
	AgNO ₃ , cc.	0.24	0.34	0.54	0.87	0.91	1.10
5	NaOH, cc.	1.11	1.15	1.02	1.07
	AgNO ₃ , cc.	1.41	1.43	1.31	1.44

It is clearly shown by the data in this table that (1) up to a certain amount, the adsorption of methylene blue or its hydrolytic products is

complete or equivalent, but beyond that amount free hydrochloric acid remains in solution; (2) when the charcoal is first treated with hydrochloric acid and then washed until no more acid is removed, it is still capable of decolorizing methylene blue solution (four 16cc. additions were made) but hydrochloric acid remains in the solution; (3) the small but definite amount of neutral chloride (0.2–0.3 cc. of 0.02 *N* per 16 cc. of 0.0025 *M* methylene blue) remaining after adsorption comes, as previously stated, from the sodium chloride in the methylene blue.

Further evidence that the sodium chloride remains in solution under these conditions is shown by the data obtained in the following experiments.

To a solution containing 16 cc. of 0.0025 *M* methylene blue and 1.02 cc. of 0.02 *N* sodium chloride solution was added 0.25 g. of the charcoal. After the solution had been completely decolorized the charcoal was filtered off and washed. The filtrate was neutral and required 1.21 cc. of 0.02 *N* silver nitrate solution. Thus it is seen that all of the 1.02 cc. of added chloride, together with 0.19 cc. in addition, which must have come from the methylene blue solution, remained in solution after the adsorption of the methylene blue. The same charcoal was again suspended in 16 cc. of 0.0025 *M* methylene blue solution, but this time without the addition of any sodium chloride. After complete decolorization the filtrate was found to be neutral and contained 0.20 cc. of 0.02 neutral chloride solution.

Neutralization of Sodium Hydroxide by Adsorbed Methylene Blue

When activated, ash-free sugar charcoal that has adsorbed a known amount of methylene blue is suspended in sodium hydroxide solution, the sodium hydroxide is neutralized and there appears in solution an amount of sodium chloride equivalent to the chloride originally held by the charcoal. No trace of color, however, is imparted to the solution by this treatment. At room temperature it requires a considerable length of time with shaking, or a number of extractions with 0.02 *N* sodium hydroxide solution, to remove all the chloride from the charcoal. Boiling for a few minutes

TABLE VI
NEUTRALIZATION OF SODIUM HYDROXIDE BY ADSORBED METHYLENE BLUE

Expt.	Char- coal G.	Extractions with NaOH	Period of contact of NaOH with adsorbent	0.02 <i>N</i> NaOH used in each extraction Cc.	0.02 <i>N</i> chlor- ide originally adsorbed on the charcoal Cc.	0.02 <i>N</i> chloride removed by the extractions Cc.
1 ^a	1.0	3	10 days	10	5.69	5.55
2 ^a	1.0	2	9 days	10	8.13	6.33
3 ^a	0.25	1	3 hrs.	5.04	1.90	1.39
4 ^b	0.25	1	10 min.	14.10	10.46	11.07
5 ^b	0.25	1	10 min.	20.14	14.09	14.45
6 ^b	0.30	1	10 min.	20.14	14.62	15.01
7 ^a	0.25	2	1 day	5.04	1.76	1.72

^a Room temperature.

^b Boiling temperature.

seems to remove it completely. An exhaustive investigation of the conditions for the removal of the adsorbed chloride such as the amount of shaking, period of contact, and temperature was not made and the preceding data are presented merely to indicate the general trend of the action.

In connection with this table it is noteworthy that Expts. 4 and 5 were performed using Charcoals 1 and 2, respectively, of Table V. After adsorption of methylene blue with the results given in Table V these charcoals were suspended in water and the stated amounts of 0.02 *N* sodium hydroxide solution added, after which the solutions were boiled for about 10 minutes. They were then filtered and the chloride in the filtrate determined. With this information at hand all the chlorine originally contained in the methylene blue solutions used in these two cases is accounted for.

Summed up in terms of 0.02 *N* solutions it is as follows.

	Charcoal	
	4	5
	Cc.	Cc.
HCl set free during adsorption.....	1.35	2.95
Neutral chloride in solution after adsorption.....	2.39	2.96
NaCl formed by boiling with 0.02 <i>N</i> NaOH.....	11.07	14.45
Chloride accounted for.....	14.61	20.36
Chloride in the methylene blue (calc.) decolorized.....	14.00	20.00

If, to a methylene blue solution an amount of sodium hydroxide equivalent to, or slightly in excess of, that necessary to combine with the chlorine of the methylene blue (assuming it is set free as hydrochloric acid during adsorption) be added and the solution decolorized with the activated charcoal, it is found that the chlorine of the methylene blue remains quantitatively in solution as sodium chloride and that the sodium hydroxide has been neutralized. The data in the following table show clearly that this is what happens.

TABLE VII
SELECTIVE ADSORPTION OF METHYLENE BLUE HYDROXIDE
0.25 g. of charcoal used

0.02 <i>N</i> NaOH added	0.0025 <i>M</i> methylene blue decolorized	0.02 <i>N</i> NaCl possible	0.02 <i>N</i> NaCl found
Cc.	Cc.	Cc.	Cc.
16.17	128.00	16.00	15.53
7.05	50.00	6.25	5.95
7.05	50.00	6.25	5.90
7.05	50.00	6.25	6.00

From the above data it would be anticipated that if a methylene blue solution were decolorized by a blood charcoal that gives an alkaline extract with water, there would, after adsorption, be more or less neutral

chloride remaining in solution, the amount depending of course upon the amount of base available in the charcoal. Under these conditions it would be impossible to detect any hydrolytic adsorption with the corresponding liberation of hydrochloric acid, because the free acid would be immediately neutralized. This clearly accounts for the fact that Michaelis and Rona⁶ did not detect any free hydrochloric acid in those cases in which their charcoal was not used in excess and their solutions were not completely decolorized. This also explains why they found as high as 35% of the chlorine of methylene blue remaining in solution as neutral chloride.

Still another point which is opposed to the theory that hydrolytic adsorption does not exist is the fact that even during the process of adsorption of small amounts of methylene blue there actually exists in solution much free hydrochloric acid. Evidently the methylene blue hydroxide is taken up more rapidly than the hydrochloric acid, although at the end of the adsorption it is found that both have been completely removed from solution. Experiments were carried out using 0.25 g. samples of activated charcoal such as easily decolorized 48 cc. of 0.0025 *M* methylene blue solution and left the solution neutral. When the charcoal was filtered off quickly with suction while the solution was still deeply colored it was found that there was in the filtrate as much as 0.6 cc. of 0.02 *N* hydrochloric acid. When the charcoal was again suspended in this same filtrate and the decolorization allowed to go on to completion after which the charcoal was again filtered off, the filtrate was found to be neutral. There may be several explanations for this action but the simplest, and perhaps the most logical one is that the charcoal adsorbs, at different rates, the methylene blue hydroxide and hydrochloric acid molecules resulting from the hydrolysis of methylene blue. The adsorption of the hydrolytic products that are already present in solution before the charcoal is added would result in the hydrolysis of additional methylene blue molecules. If the rate of adsorption of the methylene blue hydroxide were greater than that of the hydrochloric acid, there would be an excess of hydrochloric acid present. The facts seem to substantiate this view.

Results with Acid Treated Charcoals

The widely differing and apparently erratic results obtained in the adsorption of basic dyes by treated charcoals becomes somewhat clearer after a study of adsorption of such dyes by acid treated, ash-free sugar charcoal. When ash-free, activated charcoal is suspended in an excess of 0.02 *N* hydrochloric acid considerable amounts of the acid are adsorbed and cannot be washed out with cold water. By the use of sufficient charcoal an acid solution is so completely freed from acid that not a trace, detectable by sensitive indicators, remains. If this charcoal, carrying adsorbed acid, is used to decolorize methylene blue solution, hydrochloric

acid is immediately set free and is not subsequently removed from solution. The following experiment will illustrate this point. A number of samples of ash-free charcoals were suspended in known amounts of 0.02 *N* hydrochloric acid for varying periods of time; all were then washed until no more acid could be detected in the filtrate and washings and each sample was treated with 0.0025 *M* methylene blue solution. The amounts of charcoal used, adsorbed acid, methylene blue solution used, and acid remaining in solution after decolorization are given in the following table.

TABLE VIII
ADSORPTION OF METHYLENE BLUE BY ACID TREATED CHARCOAL

Charcoal G.	0.02 <i>N</i> HCl adsorbed Cc.	0.0025 <i>M</i> methylene blue solution decolorized Cc.	0.02 <i>N</i> HCl left in solution Cc.
1.00	9.73	50.00	2.80
1.00	9.58	50.00	3.00
0.25	4.17	64.00	4.35
0.25	2.72	24.00	1.25

It is thus seen that the results of adsorption of methylene blue by acid-treated, ash-free sugar charcoals are, in some respects, the exact opposite of those obtained with the untreated material. In all cases in the above table the same weight of untreated charcoal, that is, charcoal free from adsorbed acids, would have decolorized the solutions, leaving them strictly neutral. The conclusion drawn from results obtained from the adsorption of basic dyes by acid-extracted charcoals, supposedly washed free from acid, would naturally be that the adsorption is entirely hydrolytic since, as shown in the case of Charcoal 5 of Table V, the adsorption of even small amounts of methylene blue results in an acid solution instead of a neutral one. This is exactly the conclusion that Freundlich and Losev⁵ held after using the acid treated charcoals prepared as described earlier in this paper. Using blood charcoal and sugar charcoal, washed until the filtrates were free from acid and chlorides, they studied the adsorption of crystal violet, a basic dye of the same type as methylene blue. They found that the adsorption of this dye resulted in the setting free of hydrochloric acid and came to the conclusion that the adsorption of basic dyes by charcoal is accompanied by the setting free of hydrochloric acid which "remains quantitatively in solution as such." This conclusion was hardly justified in view of the fact that they tested the reaction of the decolorized solution with litmus paper and then determined the chloride content quantitatively and assumed that it was all present in the form of hydrochloric acid.

In order to confirm our own views further, a 0.0025 *M* solution of crystal violet was prepared and small amounts were decolorized with un-

treated ash-free, activated sugar charcoal. The resulting solution was found, as expected, to be strictly neutral. With larger amounts of the crystal violet some hydrochloric acid remained in solution.

At this point it may be well to include results of one experiment in which an activated, ash-free sugar charcoal apparently gave a hydrolytic adsorption with small amounts of methylene blue. A sample of ignited, ash-free charcoal was heated in a shallow, uncovered platinum dish in an attempt to activate it at a low temperature. The charcoal was repeatedly heated to incipient redness over a free flame from a Meker burner and, as it cooled, was stirred to bring it in contact with air. This process produced an active, ash-free charcoal that decolorized methylene blue solutions readily but always with the liberation of hydrochloric acid. Another sample was activated in a silica dish in the same manner and acted in the same way. This was opposed to all the results so far obtained. Upon investigation it was found that the water suspension of this charcoal was acid. The charcoal had evidently adsorbed acid gases from the burner, for when this acid charcoal was removed and heated to a high temperature in silica tubes, excluding the possibility of such contamination, the adsorbed acid gases were driven off and the charcoal was again neutral in water, and no longer left acid in solutions when small amounts of methylene blue solutions were completely decolorized.

Discussion

Nearly all of our present theories relating to the adsorption of electrolytes from solution by charcoal are based upon results of researches which have been carried out with animal or blood charcoal as adsorbents. Although it has been recognized that these are of complex composition and that no two samples from different sources may be identical either in composition or behavior, the results obtained by their use have been employed in making generalizations and formulations in which the assumption was tacitly made that no complicating factors were in operation.

In the present investigation we wished to obtain a pure type of amorphous carbon, one with a minimum of ash and nitrogen, and one which would lend itself readily to activation. The difficulty of removing the last traces of hydrogen and oxygen from charcoal has been reviewed by Bancroft¹⁰ and it is unnecessary to repeat it here.

It seems probable that activation effected by prolonged heating at a temperature somewhat above 1000° would result in either oxidation or vaporization of practically all the hydrogen or hydrocarbons present.

If the activated charcoal be permitted to cool down without the complete exclusion of air, there will result some oxidation, also some subsequent adsorption of carbon dioxide together with oxygen and nitrogen. It

¹⁰ Bancroft, *J. Phys. Chem.*, **24**, 127 (1920).

seems very improbable, however, that these were factors of any appreciable importance in connection with the results obtained in this investigation. Care was taken to allow the charcoal to come to room temperature before fully exposing to the air, thereby preventing much oxidation and the adsorption of large amounts of carbon dioxide. As previously mentioned, when the charcoal was suspended in water in a flask and the flask evacuated, a small amount of gas could be withdrawn from the charcoal. A test showed no carbon dioxide; furthermore, removal of the gas from the carbon made no observable difference in the results.

In the light of the data presented in this paper, it seems extremely probable that the statement made by Odén and Andersson⁸ that "the so-called decomposition by adsorption is only apparent, the cause being adsorbed impurities (H or OH ions) which are partially thrown out by the adsorbed solution," does not hold true in the case of adsorption by pure activated, ash-free sugar charcoal. It does, however, hold true in those cases in which the charcoal is first "purified" by treatment with acids or bases and it is, as stated by them, "a striking fact with regard to these researches that those adsorbents which are said to adsorb the base and set the acid free are derived from acid solutions or have been treated with acids, whereas the adsorbents which appear to adsorb the acid and set the base free are prepared from alkaline solutions.

"This can hardly be due to chance only, but depends, on the contrary, on the circumstance that the disintegrated constituent which is said to be set free, is in reality retained as traces of acid or base, not washed out, and not detected until thrown out by the addition of neutral salt solution."

To these considerations may be added the effect of impurities in the adsorbent such as ash contained in animal charcoal. This ash cannot all be removed from the charcoal by extraction with acids and the adsorbed acids in turn cannot be readily removed by washing with water. Re-igniting the charcoal removes the acid but leaves the charcoal alkaline in reaction as in the beginning.

If there can be any doubt remaining that there is hydrolysis or decomposition when activated sugar charcoal adsorbs basic dyes, this doubt must become even more remote when facts mentioned below are considered. It will be shown in another paper that this same charcoal that sets free acid from basic dyes, adsorbs acid dyes with the liberation of free base. Were we to consider the theory that adsorbed hydrogen or hydroxyl ions cause the decomposition to be only apparent it is difficult to see what the origin of this acid and of this base would be in the case of activated, ash-free sugar charcoal, inasmuch as neither carbon dioxide nor ammonia was detected in the adsorption experiments and combined nitrogen was proved to be absent by the Kjeldahl determination. In view of the magnitude of the decomposition of the adsorbed substances and the method of

preparation of the charcoal, it seems that we have precluded the possibility of the cause being adsorbed acids and bases.

It seems logical to assume, therefore, that decomposition or hydrolysis of methylene blue results when a water solution of it is treated with activated, ash-free charcoal and that the products of hydrolysis, namely, methylene blue hydroxide and hydrochloric acid are, up to a certain point, both adsorbed, although at different rates. Beyond this point methylene blue hydroxide is adsorbed to a greater extent than hydrochloric acid and some hydrochloric acid remains in solution.

This process of preferential adsorption may be regarded as a general phenomenon, differing only in degree for different systems.

Summary

1. Adsorption of methylene blue, a basic dye of the electrolyte type, by activated, ash-free sugar charcoal has been studied.
2. Evidence has been presented to show that this adsorption is partially, if not entirely, hydrolytic in nature.
3. It has been demonstrated that activated, ash-free sugar charcoal will completely adsorb a certain maximum amount of methylene blue from solution and still leave the solution neutral. During this process of adsorption there is set free a considerable amount of hydrochloric acid which is readily and completely adsorbed. Adsorption of amounts of methylene blue greater than the above mentioned maximum results in the setting free of hydrochloric acid which is not subsequently removed from solution.
4. The contradictory results obtained by previous investigators who have used blood charcoal as adsorbent have been reproduced with pure sugar charcoal and an explanation of these results given.

Further investigation is being made along the above lines. Results, covering the action of activated, ash-free sugar charcoal on acid dyes, acids, bases, salts, etc., have been obtained and will shortly be submitted for publication.

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