[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF MICHIGAN AND THE MICHIGAN AGRICULTURAL COLLEGE EXPERIMENT STATION]

ADSORPTION BY ACTIVATED SUGAR CHARCOAL. II[1,2]

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The results of a study of adsorption of methylene blue by charcoal were presented in a previous paper.[3] In that paper it was shown that charcoal has the power of hydrolytically adsorbing methylene blue and crystal violet, two basic dyes of the electrolyte type. These results with basic dyes led to conclusions which are the exact opposite of those recently presented by Michaelis and Rona[4] who, after an investigation of the adsorption of a number of acid and basic dyes of the electrolyte type by blood charcoal, came to the conclusion that these dyes are not hydrolytically adsorbed by charcoal.

In the present paper are presented the results obtained when work similar to that of Michaelis and Rona with blood charcoal and acid dyes was carried out under the same conditions employed by them, but with an activated sugar charcoal; there are also given the results which have so far been obtained with acids, bases and salts in a study of the nature of adsorption from solution by activated ash-free sugar charcoal.

The charcoal used in this investigation was prepared as described in the previous paper.

Adsorption of Acid Dyes by Activated Sugar Charcoal

The acid dyes used were sodium and ammonium picrates and the sodium and ammonium salts of eosin. The sodium and ammonium eosins were used in solutions 0.0025 *M* and the picrates in solutions 0.005 *M*, to correspond with those used by Michaelis and Rona.

Preliminary tests with sodium eosin solution and activated sugar charcoal indicated that the adsorption was accompanied by considerable hydrolysis.

These results were obtained under conditions which precluded the origin of the free base from being any other than the sodium in the sodium eosin. The source of the free base remaining in solution after decoloration could not have been the charcoal for it carried only a few hundredths of a per cent. of ash, was nitrogen-free and, moreover, was sufficiently active so that it was necessary to use only 0.25 g. or less to secure satisfactory results.

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[1] Presented at the Pittsburgh meeting of the American Chemical Society, September, 1922.

[2] Published as Journal Article No. 27 from the Chemical Laboratory of the Michigan Agricultural College Experiment Station. Published by permission of the Director of the Experiment Station.

[3] Bartell and Miller, THIS JOURNAL, **44**, 1866 (1922).

[4] Michaelis and Rona, *Biochem. Z.*, **97**, 57 (1919).

It is apparent that it was the conditions under which Michaelis and Rona worked that prevented them from attributing, with certainty, the alkalinity of their decolorized solutions to decomposition of the adsorbed acid dye. Their charcoal contained 7–8% of ash and gave a water extract, the Sörensen value of which was P_H 8.0. The Sörensen value of their potassium eosin solution was P_H 7.11 and of the filtrate after adsorption 8.59, and they were justified, therefore, in concluding that the alkalinity was due to the impurities in the charcoal.

Hydrolytic Adsorption of Acid Dyes

With the information derived from these preliminary experiments at hand, it was deemed desirable to study more closely the adsorption of acid dyes by activated ash-free sugar charcoal, in order to see how this type of adsorption compared with that of the basic dyes, methylene blue and crystal violet. Accordingly, samples of charcoal of 0.25 g. each were placed in 100cc. Erlenmeyer flasks and the stated amounts of the dye solutions added. The flasks were evacuated with a good water pump to remove as much as possible of the adsorbed air from the charcoal, vigorously

Table I

Hydrolytic Adsorption of Acid Dyes

Amount and conc. of each addition	Cc. of 0.02 N alkali set free with each successive addition of solution					
Cc.	1st	2nd	3rd	4th	5th	6th
		0.005 M sodium picrate				
5	0.95	0.75	0.45	0.25	0.05	0.05
5	1.00	.75	.40	.25	.07	.05
15	2.00	.65	.20	.05	..	..
20	2.15	.60	.10	.05	..	..
25	2.10	.50	.10	.05	..	..
25	2.30	.55	.10	.05	..	..
50	2.55	.35	.10	.05	..	..
50	2.60	.30	.05	..	..	..
		0.005 M ammonium picrate				
5	0.80	0.70	0.40	0.20	0.05	0.05
5	1.10	.80	.60	.20	.10	.05
25	2.10	.35	.10	.00	.05	..
25	2.45	.40	.10	.05	..	..
50	2.50	.35	..	..	..	..
50	2.75	.35	0.05	..	..	..
		0.0025 M sodium eosin				
10	0.75	0.35	0.30	0.20	..	..
25	1.10	.35	.40	.20	..	..
50	1.25	.20	.10	.05	..	..
		0.0025 M ammonium eosin				
10	0.70	0.35	0.20	0.15	..	..
25	1.50	.40	.30	.15	..	..
50	1.75	.30	.20	.05	..	..

shaken for half an hour, and then allowed to stand for approximately 15 hours with occasional shaking. The charcoal was then filtered off with suction through a small disc of ash-free filter paper in a 25cc. Gooch crucible and the alkali in the filtrate determined by titration with 0.02 *N* hydrochloric acid, using phenol red as indicator. The charcoal was returned to the flask and the next addition of solution made. This procedure was repeated until the solutions were no longer sufficiently decolorized to permit accurate titrations to be made. The results are summarized in Table I.

A glance at Table I reveals the striking fact that in the adsorption of acid dyes the greater amounts of alkali are set free when the first additions of the solutions are decolorized, the amount set free diminishing rapidly with successive additions of solution and with decrease in adsorption.

This is just the reverse of the order in which acid is set free during the adsorption of the basic dyes, methylene blue and crystal violet. With successive additions of 16 cc. of 0.0025 *M* methylene blue solution to 0.25 g. of charcoal, the first 2 or 3 additions were completely decolorized, leaving the solutions neutral, while each subsequent addition was decolorized to a less degree and the resulting solution contained increasingly greater amounts of hydrochloric acid. It was also found that from a mixture of small amounts of the methylene blue solution and hydrochloric acid charcoal adsorbed both the solutes and left the solution neutral. Parallel experiments with acid dyes and sodium hydroxide were carried out by decolorizing the dye solutions alone and in the presence of known amounts of sodium hydroxide and determining the amount of sodium hydroxide remaining in solution after complete removal of the color.

It was found that the presence of a small amount of added alkali had no appreciable effect on the amount of base set free during adsorption from the solution of acid dye. These results also offer further evidence that, whereas activated ash-free sugar charcoal will decolorize certain amounts of the basic dyes, methylene blue and crystal violet, leaving the solutions neutral and still have the power to take up certain amounts of acids, it decolorizes solutions of the acid dyes, *but in this case leaves the resulting solutions alkaline and does not have the power of taking up the base set free by hydrolysis of the acid dye in solution.*

At first thought these results may seem somewhat surprising. Reasoning from the behavior of basic dyes, which in small amounts were completely adsorbed, it might have been expected that the adsorption of small amounts of acid dyes would likewise result in a neutral solution and that the adsorption of larger amounts would leave the solution alkaline. A consideration of the theory of hydrolytic adsorption of dyes, and of the fact that in general charcoal adsorbs either organic or inorganic acids far more readily than inorganic bases, gives us at once a simple and satisfactory explanation for the preceding results; and it will be seen that the foregoing data, obtained in the study of adsorption of acid and basic dyes by activated ash-free sugar charcoal, are convincing evidence in support of this hydrolytic adsorption theory.

Relative Adsorption of Acids and Bases

Before taking up in detail a discussion of the data and theory it is necessary to consider the relative adsorption of acids and bases by activated sugar charcoal. The adsorption of a number of the more common organic and inorganic acids and inorganic bases by activated ash-free sugar charcoal was determined. In Table II is summarized the amount of acid or base adsorbed by 0.25 g. of the charcoal from 100 cc. of 0.01 *N* solution.

Table II

Adsorption of Acids and Bases by Charcoal

Acid or base	Amount of acid or base adsorbed by 0.25 g. of charcoal expressed in cc. of 0.01 *N* solution	Acid or base	Amount of acid or base adsorbed by 0.25 g. of charcoal expressed in cc. of 0.01 *N* solution
Group 1. Aromatic acids		Group 4. Inorganic acids	
Benzoic	75.80	Hydrochloric	11.22
Hydroxybenzoic (salicylic)	73.76	Perchloric	10.86
o-Aminobenzoic (anthranilic)	67.00	Nitric	10.08
Group 2. Dicarboxylic acids		Sulfuric	9.66
Succinic	48.00	Hydrobromic	8.54
Hydroxysuccinic (malic)	35.88	Group 5. Inorganic hydroxides	
Dihydroxy-succinic (tartaric)	31.76	Sodium	0.10[a]
Aminosuccinic (aspartic)	8.78	Potassium	0.00
Group 3. Aliphatic acids		Calcium	0.00
Formic	15.70	Barium	0.40[b]
Acetic	16.44	Ammonium	0.00
Propionic	24.36	Magnesium	0.00
Butyric	35.52		
Hydroxypropionic (lactic)	17.86		
Amino-acetic (glycocoll)	0.0		

[a] Nearly saturated solution.

[b] These small values are probably due to carbon dioxide.

The data in this table indicate the marked selective adsorption by activated, ash-free sugar charcoal for the various groups of acids and bases. It is significant that the organic acids are as a rule adsorbed to a greater extent than inorganic acids. The most striking fact, however, is that the strong inorganic bases are not adsorbed at all. In this connection it may be well to point out that, if precautions are not taken to exclude carbon dioxide, results may be obtained which would indicate the adsorption of considerable amounts of these bases. Failure to take this precaution, together with the presence in many charcoals of undetected adsorbed acids, is undoubtedly responsible for the positive values usually assigned to the adsorption of inorganic bases by charcoal. When this property of the charcoal is considered, the results obtained during adsorption of the acid and basic dyes can be easily and satisfactorily explained by accepting the theory of preferential adsorption of either or both the acid and base set free by hydrolysis of the salts in solution.

In the case of methylene blue and crystal violet it was shown that certain amounts were completely adsorbed leaving the solutions neutral, although during the course of adsorption the solutions contained relatively great amounts of acid. The adsorption of still greater amounts of dye left the solutions increasingly acid. In this case both products of hydrolysis, the dye base and hydrochloric acid, were adsorbed although at different rates and to different degrees, the methylene blue hydroxide being taken up more readily than the hydrochloric acid. When small amounts of these dyes are adsorbed the charcoal is still able to take up the hydrochloric acid, but as it reaches its limit of adsorptive capacity more and more of the acid remains in solution.

With the acid dyes the conditions are quite different. The products of hydrolysis are organic acids and sodium or ammonium hydroxide. The organic acids are strongly adsorbed while the sodium and ammonium hydroxides are not adsorbed at all. The reason is evident, therefore, why in Table I the larger amounts of alkali appear during the first additions of the acid dye solutions. The base is not adsorbed by the charcoal and remains in solution. It is also evident that the adsorption of acid dyes is not entirely hydrolytic, since only part of the base remains in solution after complete adsorption of the acid. It is probable that a part of the dye is removed as undissociated molecules of the salt.

From the study of the adsorption of basic and acid dyes of the electrolyte type, where in one case the dye is a product of a strongly adsorbed base and a feebly adsorbed acid, and in the other a product of a strongly adsorbed acid and a feebly adsorbed base, and also from a knowledge of the relative adsorbability of the more common acids and bases, it should be possible to predict in a general way what the relative acidic or basic reaction of almost any salt solution would be after treatment with activated ash-free charcoal.

In order to try this out experimentally a number of solutions of various salts were prepared and the reaction before and after treatment with charcoal roughly estimated by means of the indicators of the Clark and Lubs series for hydrogen-ion determinations. The concentration of the solutions was 0.02 N except in those cases where the salt was not sufficiently soluble. Fifteen cc. (approximately) was shaken with 0.2–0.3 g. of charcoal and the mixture allowed to stand for about $^1/_2$ hour, filtered and the reaction of the filtrate determined. The Sörensen values of the solutions before and after treatment are recorded in the following table.

TABLE III

CHANGE IN HYDROGEN-ION CONCENTRATION DUE TO ADSORPTION

Solution	P_H before adsorption	P_H after adsorption	Solution	P_H before adsorption	P_H after adsorption
Sodium chloride	7.0	9.0	Barium acetate	7.2	8.+
Sodium potassium tartrate	7.2	8.6	Calcium acetate	7.4	8.4
Sodium citrate	7.8	8.8	Magnesium chloride	6.8	8.0
Sodium salicylate	7.0	9.4	Magnesium nitrate	6.8	8.0
Sodium acetate	7.2	8.2	Lead nitrate	5.0	6.2
Sodium phosphate (Na_3PO_4)	8.2	8.2	Cadmium chloride	6.7	7.4
Potassium nitrate	6.8	9.4	Manganese sulfate	4.4	7.4
Potassium chlorate	7.0	8.8	Copper acetate	4.8	4.8
Potassium bromide	7.0	8.6	Zinc sulfate	6.8	7.0
Potassium iodide	7.0	8.8	Zinc lactate	7.0	7.0
Potassium ferrocyanide	7.0	7.8	Aluminum sulfate	<4.4	<4.4
Potassium phosphate (KH_2PO_4)	4.4	6.6	Ferric chloride	<4.4	<4.4
Ammonium bromide	5.6	8.4	Mercuric chloride	4.4	3.8
Ammonium chloride	5.6	8.4	Silver nitrate	6.8	4.4
Ammonium sulfate	6.8	8.4	Silver sulfate	6.8	4.4
Ammonium thiocyanate	5.5	7.8	Silver acetate	7.+	5.0
Ammonium picrate	4.4	8.6	Platinic chloride	<4.4	<4.4
Barium chloride	6.8	8.0	Auric chloride	<4.4	<4.4
Barium benzoate	7.0	9.0			

The results in this table agree well with those that would be expected from an *a priori* consideration of the conditions obtaining in each instance. As would be anticipated, solutions of the salts of sodium, potassium, ammonium, barium, calcium and magnesium, after treatment with charcoal were distinctly alkaline. The total amount of alkali found in the solutions after adsorption varied from a few hundredths of a cc. of 0.02 *N* solution in the case of solutions such as sodium chloride to 2 cc. or more of solutions of barium benzoate and sodium salicylate. This, too, is in accord with what would be expected, since sodium chloride is derived from a feebly adsorbed acid and a non-adsorbed base and is hydrolyzed only to a very slight extent, while sodium salicylate, derived from a non-adsorbed base and a very strongly adsorbed acid, is hydrolyzed to a greater extent and consequently should offer ideal conditions for considerable hydrolytic adsorption.

The salts of metals such as lead, cadmium, copper, manganese, iron, aluminum, etc., could not be expected to yield strongly alkaline solutions because they are precipitated by a low concentration of hydroxyl ions. Their solutions would not change greatly in their reactions during adsorption.

Solutions of iron and of the noble metals undergo reduction as well as adsorption. Silver, gold and platinum are apparently quantitatively reduced to the metallic form, while ferric chloride is reduced to ferrous chloride, along with the adsorption of considerable amounts of the iron. When relatively small amounts of solutions of iron, silver, gold and platinum salts are decomposed, both the metal and the acid are completely adsorbed leaving the solution neutral. With larger amounts of the solutions more acid remains in solution, the amount depending upon the salt in question. Thus, under certain conditions, with an excess of the approximately neutral solutions of silver nitrate, silver sulfate, and silver acetate, the solution after adsorption is left acid and contains the equivalent of about 1 cc. of 0.02 N acid. Under similar conditions solutions of auric and platinic chlorides contain the equivalent of about 16 cc. of 0.02 N acid.

In this connection it is interesting to note that when the charcoal is added to the solutions of the noble metals without certain precautions an evolution of gas results which seems to be in no manner connected with the decomposition of the solute except that it is a displacement of adsorbed or dissolved gas by the substances adsorbed. When a water suspension of the charcoal and the solution of the salt are first boiled to remove the adsorbed and dissolved gases and then mixed, there is no evidence of any evolution of gas even when the containing vessel is evacuated to a point at which the liquid boils. This evidence is contrary to the theory that carbon dioxide is evolved in the decomposition of these salts.[5]

Adsorption of Substituted Organic Acids

A study of the adsorption of the organic acids listed in Table II reveals the effect on the adsorption produced, by the introduction of hydroxyl and amino groups into benzoic, succinic, acetic and propionic acids. The introduction of these groups, in general, decreases the adsorption of the acid to a more or less marked degree, the amount of the decrease depending upon the nature of the group and the acid in which it is substituted. The introduction of the hydroxyl group produces a smaller effect than the introduction of the amino group (which is far more basic) both in the case of aliphatic and aromatic acids. The effect of each group is much more pronounced when substituted in the aliphatic than in the aromatic acids.

From Table II it is seen that *o*-hydroxybenzoic (salicylic) acid is adsorbed to a slightly less extent than benzoic acid. Hydroxysuccinic (malic) and dihydroxy-succinic (tartaric) acids are adsorbed to a much less extent than succinic acid. Hydroxypropionic (lactic) acid is adsorbed much less than propionic acid.

The effect of the amino group is even more striking. Thus *o*-aminobenzoic (anthranilic) acid is slightly less adsorbed than either benzoic or salicylic acid. Aminosuccinic (aspartic) acid is very much less adsorbed than succinic, malic or tartaric acids. Amino-acetic acid (glycocoll) is not adsorbed at all.

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[5] For a discussion of this theory see Bancroft, *J. Phys. Chem.*, **24,** 361 (1920).

In Group 3 of Table II it is also evident that beginning with formic acid and extending through the fourth member of the homologous series of aliphatic acids there is a marked increase in adsorption of aliphatic acids with increase in molecular weight. In the case of the series succinic, malic, and tartaric acids, where an increase in molecular weight is due to the introduction of hydroxyl groups, adsorption decreases with increase in molecular weight.

Results Obtained by Other Investigators

With the data obtained in the investigation of the nature of adsorption of electrolytes from solution by activated ash-free sugar charcoal at hand, it becomes of interest to compare them with those obtained by various investigators with animal and vegetable charcoals.

The results obtained by the use of activated ash-free sugar charcoal in the adsorption of acid and basic dyes of the electrolyte type have led us to conclusions just the reverse of those of Michaelis and Rona[4] who believe that adsorption is not accompanied by hydrolysis. They maintain that there is but one form of adsorption of organic acid and basic dye salts from pure water by pure charcoal, that in all cases the anion and cation are removed in equivalent amounts, and that a measurable hydrolytic splitting never results from adsorption. The results with neutral, activated, ash-free sugar charcoal described in this paper seem to indicate that the alkaline impurities in their blood charcoal prevented them from attributing with certainty the presence of alkali in their decolorized acid dye solutions to hydrolytic adsorption of the substance in solution. In their work with blood charcoal and basic dyes two factors prevented them from detecting acid set free. The first was the fact that their charcoal carried alkaline impurities and gave an alkaline water extract. The second was that in some instances they used such large quantities of charcoal that any acid that might have been set free would also have been adsorbed.

Bancroft,[6] in a discussion of selective adsorption of salts by charcoal, cites the results obtained by Liebermann with bone black and a number of salt solutions. Liebermann found that from solutions of barium formate, sodium acetate, ammonium oxalate and sodium potassium tartrate the basic constituents were removed by bone black to a greater extent than the acid ones, thus leaving the solutions acid.

When 0.02 *N* solutions of these salts were prepared and treated with neutral, activated, ash-free sugar charcoal it was found, as would be anticipated from the theory and data presented in this paper, that the solutions left were not acid but, on the contrary, strongly alkaline.

Liebermann reported also that calcium and barium benzoates, sodium

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[6] Bancroft, *J. Phys. Chem.*, **24,** 360 (1920). The original appeared in *Sitzungsber. Akad. Wiss. Wien,* **75,** II, 331 (1878) and has not been accessible to the writers.

chloride, sodium nitrate and sodium sulfate were adsorbed without change in reaction of the solutions. Here again it was found by us that the activated ash-free sugar charcoal adsorbed the acid constituents of the solutes to a greater extent than the basic ones and left the solutions distinctly alkaline in the case of the sodium salts and very strongly alkaline in the case of the barium and calcium benzoates.

In all probability Liebermann's results were due to other constituents than the carbon of the bone black, for we have found that an activated, ash-free sugar charcoal carrying a small amount of adsorbed acid leaves these solutions neutral, the alkali set free by hydrolysis being neutralized by the adsorbed acids already on the charcoal. This also was the result obtained by us when acid dyes were adsorbed by a charcoal carrying small amounts of adsorbed acids. The solutions were left neutral.

From the data presented in this and in the previous paper the conclusion is drawn that hydrolysis accompanies and is a considerable factor in the adsorption of electrolytes, especially the acid and basic dyes, by activated, ash-free sugar charcoal. The contention that this phenomenon is due to impurities in the charcoal does not hold in the case of activated, ash-free sugar charcoal. The method of preparation precludes the possibility of ascribing the effects to impurities such as alkaline inorganic matter, combined nitrogen, and adsorbed hydrogen and hydroxyl ions in the charcoal.

We ascribe many of the contradictory effects described by previous investigators to alkaline impurities or to retained acid or base used in attempts to purify complex animal or vegetable charcoals. This view is made more probable by the fact that these effects can be reproduced by treatment of neutral, ash-free sugar charcoal before use, with acids or bases and then washing until the reagents have apparently all been removed.

If the acidity or alkalinity of the solutions after adsorption by ash-free sugar charcoal were due to the displacement or setting free of acid or base previously adsorbed by the charcoal it would be difficult to explain the fact that the same charcoal sets acid free when treated with basic dyes and sets alkali free when treated with acid dyes. Under these conditions it would be necessary to assume that this charcoal carries simultaneously both adsorbed acid and adsorbed base.

On the basis of our experimental results the most logical explanation for the hydrolytic adsorption of electrolytes by charcoal (which adsorption may constitute but a small part of the whole adsorption) seems to be that the charcoal selectively adsorbs the acid or base set free by hydrolysis of the electrolyte in aqueous solution, thus disturbing the equilibrium and causing further hydrolysis of the dissolved substance.

Summary

1. Data have been presented in support of a theory of hydrolytic adsorption of electrolytes from solution by activated, ash-free sugar charcoal.

2. It has been demonstrated that the adsorption of acid dyes is accompanied by considerable hydrolysis and liberation of alkali which remains in solution.

3. The adsorption by this charcoal of a number of acids, bases and salts has been investigated. It has been found that pure charcoal does not adsorb the strong inorganic bases. The adsorption of a salt of a strong base and a readily adsorbed acid results in the liberation of free base.

4. The effect, on adsorption, of the substitution of hydroxyl and amino groups in organic acids has been noted. The introduction of the hydroxyl group decreases the adsorption of the acid to a more or less marked extent, depending upon the nature of the acid into which it is introduced. The introduction of the amino group decreases the adsorption of the acid, the extent also depending upon the nature of the acid into which it is introduced. The effect of the amino group is considerably greater than that of the hydroxyl group.

5. A number of the conflicting results of other investigators have been reproduced by means of neutral, activated, ash-free charcoal and an explanation of their causes have been offered.

6. In an early paper a theory for hydrolytic adsorption will be presented in which it will be shown that we must consider that molecules become oriented at the interface as a result of adsorption.

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THE USE OF BROMATE IN VOLUMETRIC ANALYSIS. I. THE STABILITY OF BROMIC ACID IN BOILING SOLUTIONS

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The use of bromic acid in volumetric analysis was first suggested by Kratschmer.[1] The sodium salt was prepared and shown to be stable when dried at 180°. The oxidation of potassium iodide to iodine in dil. hydrochloric, nitric, sulfuric and phosphoric acid solutions was shown to be quantitative. Feit and Kubierschky[2] used 0.1 *N* solutions of potassium bromate acidified slightly with sulfuric acid, and stated that under ordinary conditions of storage such solutions were stable during quite long periods of time. They suggested the use of this reagent in the oxidation

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[1] Kratschmer, *Z. anal. Chem.*, **24**, 546 (1885).

[2] Feit and Kubierschky, *Chem.-Ztg.*, **15**, 351 (1891).