

curve of silver perchlorate in benzene, leading to a nearly perpendicular section such as occurs where a binary system forms two liquid phases. In the curve for silver perchlorate and aniline (Fig. 2) no corresponding rise is found, and no corresponding binodal curve appears in the ternary system.

Summary

1. The system consisting of silver perchlorate and aniline has been studied from the eutectic at -6.6° to temperatures slightly higher than 70° , at which extensive decomposition occurs. Four new compounds have been described, namely, $\text{AgClO}_4 \cdot 6\text{C}_6\text{H}_5\text{NH}_2$, $\text{AgClO}_4 \cdot 3\text{C}_6\text{H}_5\text{NH}_2$, $\text{AgClO}_4 \cdot 2\text{C}_6\text{H}_5\text{NH}_2$ and $\text{AgClO}_4 \cdot \text{C}_6\text{H}_5\text{NH}_2$. Of these only the first is stable in contact with the solution at ordinary temperatures, and has been shown to have a congruent melting-point at 60.52° and a transition point at 48.3° . The other three compounds have been isolated from the ternary system, but not wholly pure. The transition point of $\text{AgClO}_4 \cdot 3\text{C}_6\text{H}_5\text{NH}_2$ is 66.6° ; the temperatures for the last two compounds were not obtainable.

2. The system consisting of water and aniline has been studied and the results of previous workers amplified.

3. The ternary system consisting of silver perchlorate, water and aniline has its eutectic at -58.8° , and in a rise of temperature to 66.6° nine invariant equilibria were realized and studied with 28 monovariant equilibria originating from them.

4. Isothermal diagrams have been drawn to represent schematically the equilibria existing in the above-mentioned temperature range.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MICHIGAN AGRICULTURAL COLLEGE EXPERIMENT STATION, No. 29]

ADSORPTION BY ACTIVATED SUGAR CHARCOAL. I. PROOF OF HYDROLYTIC ADSORPTION^{1,2}

BY ELROY J. MILLER

RECEIVED JANUARY 17, 1924

It has been the object of many investigations to determine whether hydrolysis of electrolytes is increased during adsorption from solution by charcoal. It is unnecessary to review in detail the many discrepancies and contradictory results and conclusions existing in the literature on this subject. It is sufficient to state that recent general conclusions arrived at are (1) hydrolysis of electrolytes is not increased during adsorption and (2) when a solution is more acid or more alkaline after ad-

¹ Published by permission of the Director of the Michigan Agricultural College Experiment Station.

² Presented at the Milwaukee meeting of the American Chemical Society, September, 1923.

sorption the effect is due to displacement of adsorbed impurities from the adsorbent.^{3,4}

In two recent papers⁵ the writer in collaboration with Dr. F. E. Bartell reported results of a study of adsorption of electrolytes from solution by pure, activated, ash-free, sugar charcoal. These results were free from the irregular and discordant findings of previous investigators. They indicated clearly that hydrolysis is increased during adsorption.

In the present paper are presented data that furnish the final link in the chain of evidence which proves that hydrolytic or decomposition adsorption does take place.

Preparation of Charcoal

The charcoal used in this investigation was prepared by two methods. In the first method cane sugar, after repeated crystallization from conductivity water, was charred at a low temperature. The char was then heated in the absence of air for 24 hours at a temperature of 1200°. Activation was accomplished by continuing the heating for 24 to 48 hours at the same temperature in the presence of a limited supply of air.

In the second method the recrystallized sugar was charred by treatment with hot, concd. sulfuric acid. After the char was washed to remove part of the sulfuric acid it was heated and activated by the procedure outlined above. It was expected that carbon prepared by this method might be very active since it is produced in an extremely finely divided form and should be relatively, if not entirely, free from hydrocarbons. This expectation was not realized, however, and it was necessary to activate the char. Heating and activation were carried out in platinum and silica ware in an electric furnace.

The charcoals so prepared equalled, or surpassed, in adsorptive power the best blood charcoal found on the market. They contained 0.01% or less of ash, were nitrogen-free and were neutral in reaction when suspended in water and organic solvents. The charcoals yielded identical results and exhibited the same behavior when used in the adsorption experiments. They were ground in an agate mortar to pass through a 300-mesh sieve.

Change in Appearance of Charcoals on Activation

Certain changes in appearance of the charcoals upon activation were observed. Both charcoals after being heated in the absence of air had a bright gray, coke-like appearance. They were hard and devoid of any decolorizing or adsorbing power. After activation they had a soft, velvety black appearance.

This change in appearance is, in all probability, due to oxidation of part of the carbon with the formation of minute pits and pores. These minute pits and pores impart to the surface of the charcoal the black appearance by virtue of their power to trap or absorb incident light. This is strikingly similar to the phenomenon displayed by a bundle of steel needles which, when viewed from the point end, appears black, due to

³ Odén and Andersson, *J. Phys. Chem.*, **25**, 311 (1921).

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

⁵ Bartell and Miller, (a) *THIS JOURNAL*, **44**, 1866 (1922); (b) **45**, 1106 (1923).

the absorption of the incident light.⁶ Bancroft⁷ ascribes the black appearance of pulverulent silver to the same cause and Pease⁸ attributes a change in appearance of metallic copper to the same phenomenon.

Additional evidence that this pitting causes the change in appearance of the charcoal is found in the fact that a large granule of the activated charcoal which has the black surface shows, when broken, the original bright appearance at the surface of the fracture.

Proof of Hydrolytic or Decomposition Adsorption

As stated in the previous papers, when an acid dye and certain salts are adsorbed by these charcoals, alkali is set free. If, as some investigators maintain, this base set free and remaining in solution after adsorption of a salt were simply displaced impurities or retained base from the charcoal, the charcoal should be neutral. On the other hand, if the base set free is a result of hydrolysis, there should be on the charcoal, after adsorption, an amount of acid equivalent to the base remaining in solution. That the latter is the case has been completely demonstrated with a number of representative salts such as sodium benzoate, potassium oxalate, sodium chloride, potassium nitrate, etc.

Method of Procedure

In the light of a previous investigation^{5b} sodium benzoate was chosen as the salt most likely to yield the desired results. It was there shown that the strong inorganic bases are not adsorbed by pure activated sugar charcoal. It was also shown that benzoic acid is more readily adsorbed than any of the other acids. Under these conditions a salt of a strong base and benzoic acid should be most readily decomposed during adsorption. This premise proved to be correct and was demonstrated as follows. Sodium benzoate solutions were treated with the charcoal and the amounts of sodium hydroxide set free determined. The charcoal was then extracted with suitable organic solvents and benzoic acid was found in the extracts. The amounts of benzoic acid in the extracts were equivalent to the sodium hydroxide set free in the sodium benzoate solutions.

The method of recovering the adsorbed benzoic acid from the charcoal depends upon the well-known principle that a given solute is not adsorbed to the same extent from different solvents and that, in general, adsorption is less from organic solvents than from aqueous solutions. This is especially true of benzoic acid.

An attempt was made to use alcohol for the extraction of the benzoic acid but this was found to be unsatisfactory because too many extractions

⁶ Wood, "Physical Optics," The Macmillan Co., 1911, p. 449.

⁷ Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., 1921, p. 199.

⁸ Pease, *THIS JOURNAL*, 45, 2304 (1923).

were required and the alcohol interfered with the indicator in the titration of the acid. The ease with which benzoic acid volatilizes prevented the evaporation of the solvent without loss of acid.

The same objections applied to the use of acetone as a solvent.

Benzene proved to be more satisfactory. By repeated extraction it was found possible to remove all the acid from the charcoal. The acid in the combined extracts could be determined by shaking out with water and titrating with standard alkali, using phenol red as indicator. An indicator of the type of methyl red cannot be used, since it is completely removed from the water phase by the benzene.

While satisfactory results could be obtained by this method of extraction, the following simpler and preferable procedure was evolved. The charcoal, carrying the adsorbed benzoic acid, is washed into a glass-stoppered Erlenmeyer flask, benzene added, and the mixture is shaken to remove the charcoal from the water phase. The indicator is added and goes to the water phase. The acid is then titrated with standard alkali, the flask stoppered and shaken thoroughly and considerable time allowed to elapse between the later additions. The last portions of benzoic acid are removed somewhat slowly and it is preferable to add an excess of standard alkali and, after shaking the mixture at intervals for some time, to titrate back with standard acid.

The mechanism of this procedure and the principles involved are as follows. The charcoal carrying the adsorbed benzoic acid is wetted or adsorbed more readily by the benzene than by water and consequently is removed from the water phase. When the charcoal is wetted by the benzene the adsorbed benzoic acid, because it is adsorbed less from benzene than from water, dissolves in the benzene until the adsorption equilibrium for benzoic acid and charcoal in benzene is reached.

Benzoic acid in benzene, in contact with water, is distributed between the two liquids according to its partition coefficient. Neutralization of the acid in the water phase destroys these equilibria, and more and more acid leaves the charcoal until all has passed into the benzene and thence to the water.⁹

Control experiments were performed using charcoal alone and also charcoal carrying known amounts of adsorbed benzoic acid.

The results indicated clearly (1) that the charcoal is free from adsorbed acid, (2) that adsorbed benzoic acid can be quantitatively recovered from the charcoal by this method, (3) that adsorption of sodium benzoate from solution is accompanied by hydrolysis with subsequent adsorption of

⁹ Because of the numerous principles involved this procedure makes an interesting and instructive experiment for the student in the colloid laboratory, since it illustrates (1) hydrolytic adsorption, (2) adsorption of a solid by a liquid, (3) variation of adsorption of a given solute from different solvents by the same adsorbent, and (4) the distribution of a solute between two immiscible liquids.

benzoic acid and liberation of sodium hydroxide, and (4) that the benzoic acid on the charcoal is exactly equivalent in amount to the sodium hydroxide appearing in solution.

Chloroform and carbon tetrachloride also wet the charcoal more readily than does water and extract the benzoic acid, but they introduce an error, since they decompose and liberate hydrochloric acid which neutralizes the standard alkali.

Results with Various Types of Acids

With proof of the hydrolytic decomposition of sodium benzoate at hand it was, of course, expected that similar results would be obtained with salts of other acids. Experiments were first carried out to see whether acids other than benzoic when adsorbed could be quantitatively recovered from the charcoal. It was found that they could be recovered but that in some cases it was necessary to continue the extraction for a longer period. In some cases three or more days were required. Salicylic acid, like benzoic, was readily recovered. Succinic, oxalic and sulfuric acids, on the other hand, required a longer period due, probably, to their relative insolubility in benzene.

The results obtained with the various types of acids are given in Table I. In control experiments using the same quantities of charcoal, benzene, water and indicator (Phenol Red) 0.10 cc. of 0.01 *N* sodium hydroxide was required to change the color of the indicator.

TABLE I
RECOVERY OF ADSORBED ACIDS FROM CHARCOAL

Acid	Amount of acid adsorbed Equivalent to cc. of 0.01 <i>N</i>	Amount of acid recovered Equivalent to cc. of 0.01 <i>N</i>
GROUP 1. AROMATIC ACIDS		
Benzoic	50:30	50.24
	50.30	50.12
Salicylic	50.30	50.18
	50.30	50.30
GROUP 2. DICARBOXYLIC ACIDS		
Succinic	52.10	52.02
	50.00	49.80
Oxalic	48.10	48.00
	48.10	48.00
GROUP 3. ALIPHATIC ACIDS		
Acetic	50.30	49.54
	50.30	50.14
GROUP 4. INORGANIC ACIDS		
Sulfuric	51.18	50.36
	51.18	51.16
Hydrochloric	50.60	50.26
	20.06	20.02

Hydrolytic Adsorption of Salts of Organic Acids

The data in Table I indicated that the various acids could be quantitatively recovered from the adsorbent. The next step was to determine whether sufficient hydrolysis took place when solutions of salts of acids of the various types were treated with charcoal. It was found that results of sufficient magnitude could readily be obtained with salts of organic acids by simply suspending the charcoal (0.25–1.5 g.) in the salt solution (50–500 cc. 0.02 *N*). The amount of decomposition varied as would be expected, the salts of the strongly adsorbed acids yielding higher values than the salts of the less strongly adsorbed ones.

It is necessary at this point to describe in detail the method of procedure and certain precautions that must be observed in carrying it out. The charcoal is suspended in the salt solution and after a few minutes filtered off with the aid of suction on a disk of hardened ash-free filter paper in a Gooch crucible and washed several times with conductivity water. The charcoal is again suspended in a fresh portion of salt solution, filtered and washed as before. The amount of alkali in the combined filtrates and washings is determined by titration with standard acid using Phenol Red (phenol sulfonephthalein) as indicator.

In carrying out these operations the alkaline solutions and conductivity water take up carbon dioxide from the air. This carbon dioxide must be eliminated by boiling the solutions after the later additions of the standard acid until the red color of the indicator is permanently discharged.

The charcoal is next washed into a 300cc. glass-stoppered Erlenmeyer flask, benzene added and the mixture is shaken until the charcoal is entirely removed from the water layer. The indicator and an amount of standard alkali slightly in excess of that set free from the salt solution are then added. The flask is vigorously shaken at intervals during the time necessary for the complete extraction of the acid as indicated by con-

TABLE II
HYDROLYTIC ADSORPTION OF SALTS OF ORGANIC ACIDS

Salt	Alkali set free during adsorption from aqueous solution Equivalent to cc. of 0.01 <i>N</i>	Acid extracted from charcoal after adsorption Equivalent to cc. of 0.01 <i>N</i>
Sodium benzoate	9.40	9.50
	29.00	28.16
Barium benzoate	9.30	9.30
	3.50	3.50
Sodium salicylate	7.84	7.90
	13.50	13.54
Sodium succinate	6.00	6.12
	2.30	2.20
Potassium oxalate	3.90	3.76
	25.36	25.02
Sodium acetate	7.06	6.90
	3.20	2.80

trols. When this time has elapsed the excess of alkali is titrated with standard acid.

The results obtained by this method with salts of various types of organic acids are illustrated by the data in Table II. They show conclusively that hydrolysis is involved and that the charcoal after adsorption carries an amount of adsorbed acid exactly equivalent to the alkali set free.

Hydrolytic Adsorption of Salts of Inorganic Acids

Demonstration of decomposition of the common stable salts of inorganic acids such as sodium chloride, potassium sulfate, potassium nitrate, etc., was accomplished by a slight modification of the foregoing procedure. As would be expected, from an *a priori* consideration of the fact that the strong inorganic acids are least adsorbed by pure charcoal, the amount of alkali set free and remaining in solution after adsorption of these salts is comparatively small. Equilibrium between the adsorbed acid and the free alkali in solution is reached when the concentration of the latter is extremely low. When, however, advantage is taken of this fact and the equilibrium destroyed by removal of the alkali as fast as it is set free, ample decomposition can be obtained so that accurate quantitative determinations may be made. This can be accomplished by percolating the salt solutions through the charcoal. The solutions are added in small quantities with an occasional washing with conductivity water between additions. Under these conditions the concentration of the alkali is kept low and the amount of acid on the charcoal increases. In these experiments 300–500 cc. of 0.02 *N* salt solutions were percolated through the charcoal in a Gooch crucible of approximately 30cc. capacity. The alkali in the filtrate was determined, as before, by titration with 0.02 *N* acid using Phenol Red as indicator and boiling to remove carbon dioxide.

Recovery of the adsorbed acids could be accomplished by the usual extraction with benzene. Since the inorganic acids are very slowly removed from the charcoal by benzene it was found more expedient to extract the charcoal a number of times by boiling it with an excess of 0.02 *N* sodium hydroxide solution. The amount of acid extracted was determined again by titrating the excess of the standard alkali, taking the usual precautions to expel carbon dioxide.

As an additional check on the results in the case of chlorides and sulfates the amount of chloride or sulfate in the extract was quantitatively determined. The values obtained correspond closely with the amount of alkali neutralized by the adsorbed acid on the charcoal. These values are given in Col. 3 of Table III.

Data obtained with a number of the simple, stable salts appear in Table III. The data indicate clearly that when a solution of sodium chloride is treated with the charcoal, sodium hydroxide appears in solution and

an equivalent amount of hydrochloric acid is adsorbed on the charcoal. Likewise from a solution of potassium sulfate the charcoal adsorbs sulfuric acid and sets free potassium hydroxide, and similarly for other salts.

TABLE III
HYDROLYTIC ADSORPTION OF SALTS OF INORGANIC ACIDS

Salt	Alkali set free during adsorption. Equivalent to cc. of 0.01 N	Acid extracted from charcoal after adsorption. Equivalent to cc. of 0.01 N	Amount of chloride or sulfate found in extract. Equivalent to cc. of 0.01 N HCl or H ₂ SO ₄
Sodium chloride	11.36	11.33	11.13
	27.42	27.03	27.23
Potassium chloride	13.10	12.90	13.22
	25.86	25.26	25.94
Potassium nitrate	40.54	40.22	...
	25.18	24.67	...
Potassium sulfate	30.58	30.76	30.99
	24.06	23.99	24.37

The salts listed in Tables II and III were selected merely as representative of the various types. Similar results have been obtained with many other salts of sodium, potassium, ammonium, barium, calcium, magnesium, etc., with a wide variety of acids.

Discussion of Results

The data presented in the preceding tables prove conclusively that adsorption of salts from aqueous solutions by pure activated sugar charcoal is accompanied by hydrolysis or decomposition and that the acid arising from the hydrolysis is adsorbed by the charcoal while the base is set free and remains in solution. The proof is based on the following facts. (1) The method of preparation of the charcoal precludes the possibility of ascribing the effects to impurities in the adsorbent. (2) The base set free in the aqueous solution is exactly equivalent to the acid recovered from the charcoal after adsorption. (3) The acid recovered from the charcoal is identical with the one from which the original salt is derived.

It was observed in the course of this investigation that a given sample of charcoal may be used over and over again in the experiments by simply washing with water and heating after the adsorbed acid has been removed from the charcoal. The adsorptive power of the charcoal remains practically unchanged. This, obviously, would not be the case if the effects were due to adsorbed impurities on the charcoal.

It was also observed that under the same conditions of experiment the amount of decomposition of the alkali salts of the different acids varies in the same order as the adsorbability of the acids themselves. For example, there were set free, from solutions of sodium benzoate, potassium oxalate and sodium chloride, the equivalent of 74.80, 25.36 and 11.36 cc. of 0.01 N alkali, respectively. These figures parallel very

closely the relative adsorption of benzoic, oxalic and hydrochloric acids by this charcoal.

The question arose whether the charcoal adsorbs from solution only the acid resulting from hydrolysis of the salt or whether part of the salt is adsorbed as such. To obtain some evidence on this question the behavior of a number of potassium salts was studied. Determination of the potassium in solution before and after adsorption indicated that from the potassium chloride solution absolutely no potassium is removed and the adsorption, therefore, is entirely hydrolytic, only hydrochloric acid being adsorbed. With potassium benzoate, however, it was found that a considerable amount of the salt as such is adsorbed in addition to the benzoic acid resulting from hydrolysis. Further evidence is being procured on this point.

Summary

1. Methods for the quantitative recovery of adsorbed acids from charcoal are described.

2. By means of these methods it has been demonstrated that when alkali is set free in salt solutions during adsorption by pure activated sugar charcoal there exists on the charcoal after adsorption an equivalent amount of adsorbed acid.

3. Data are given for the hydrolytic adsorption of a number of salts of representative organic and inorganic acids.

4. The results obtained in this investigation make untenable the present widely accepted view that hydrolytic or decomposition adsorption does not take place.

EAST LANSING, MICHIGAN

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE HEAT OF WETTING OF LEAD SULFATE¹

W. A. KOEHLER AND J. H. MATHEWS

RECEIVED FEBRUARY 13, 1924

It has been known for the past hundred years that when some finely divided powders, or porous materials, are wetted with a liquid in which they are not soluble, the wetting is accompanied by a thermal change.²

¹ This paper constitutes a portion of a thesis presented by W. A. Koehler to the Graduate School of the University of Wisconsin, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in January, 1924.

² Pouillet, *Ann. chim. phys.*, **20**, 141 (1822). Junck, *Pogg. Ann.*, **125**, 292 (1865). Chappuis, *Wied. Ann.*, **19**, 21 (1883). Meissner, *ibid.*, **29**, 114 (1886). Fitzgerald, *Nature*, **49**, 293, 316 (1894). Gore, *Phil. Mag.*, **37**, 306 (1894). Lagergren, *Kgl. Vetenskaps Akad.*, **24B**, adf. ii (1898). Ercolini, *Nuovo cimento*, [4] **9**, 110 (1899). Linebarger, *Phys. Rev.*, **13**, 48 (1901). Parks, *Phil. Mag.*, [6] **4**, 240 (1902). Schwalbe,