2. The dielectric constants of six binary mixtures at 25° have been determined at various concentrations. The systems studied are benzene-*p*-xylene, benzene-*o*-xylene, benzene-ethyl ether, benzene-chloroform, benzene-chlorobenzene and benzene-phenol.

3. The systems have been grouped for discussion according to whether or not the molar polarization of the solute in solution changes with concentration.

4. The electric moments of each of the solute molecules in benzene solution have been calculated. These results have been critically discussed.

NOTE—Since this paper was written there has appeared an article by Smyth and Morgan [THIS JOURNAL, 49, 1030 (1927)] in which the electric moments of certain substituted benzene molecules were calculated from dielectric-constant and density data. Smyth and Morgan have apparently obtained dielectric-constant and density data for but one system reported in this paper, namely, benzene-chlorobenzene. The data used for the calculations for the moment of phenol were taken from a paper by Philip and Haynes [*J. Chem. Soc.*, 87, 998 (1905)]. Since Smyth and Morgan have withheld their dielectric-constant data for a future publication, and since all the dielectric-constant data used by these authors were obtained using bridge methods rather than one of the newer and more accurate electrical resonance methods, the authors of the present paper have decided to submit their paper in its original form.

MADISON, WISCONSIN

ADSORPTION FROM SOLUTION BY ASH-FREE ADSORBENT CHARCOAL. IV. THE NON-INVERSION OF SUCROSE BY ADSORBED ACIDS AND ITS SIGNIFICANCE FOR THEORIES OF ADSORPTION AND CATALYSIS[1]

BY ELROY J. MILLER AND SELMA L. BANDEMER

Information that will throw light on the properties and behavior of substances in the adsorbed state is much needed for a better understanding of the nature of adsorption, catalysis, and reactions at interfaces. In the present paper are presented the results of a study of the properties of acids when adsorbed on pure ash-free adsorbent charcoals.

In a previous paper[2] methods were described whereby adsorbed acids can be removed from pure ash-free charcoal and quantitatively estimated. By means of these methods it was demonstrated[3] with hydrochloric acid and pure charcoal that a certain amount of adsorbed acid is held so firmly

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[1] Published by permission of the Director of the Experiment Station as Journal Article No. 41.

[2] Miller, THIS JOURNAL, 46, 1150 (1924).

[3] Miller, *ibid.*, 47, 1270 (1925).

that it cannot be removed by washing with water alone, either at room temperature or at boiling temperature. Evidence of the tenacity with which adsorbed acids are held by charcoal is also furnished by the fact that acid is hydrolytically adsorbed from a neutral salt, such as potassium chloride, even in the presence of 0.01 N potassium hydroxide and that in order to remove the acid quantitatively it is necessary to extract the charcoal several times by boiling with an amount of alkali somewhat in excess of that equivalent to the acid on the charcoal.

These facts seemed to indicate that the adsorption forces were sufficiently strong to affect profoundly the properties of the acid. They also suggest that the adsorption is not simply a concentration of the acid in the water side of the charcoal-water interface. Further evidence on the properties of adsorbed acids was sought by attempting to determine whether or not adsorbed acids are capable of inverting sucrose and, if so, whether the action is catalyzed by the increased concentration of acid and sugar through adsorption. The ash-free adsorbent charcoals prepared as previously described,[4] because of their purity and high adsorption capacity, are ideal substances for use in such a study. The amounts of adsorbed acid can be controlled accurately and there can be no doubt that the acids are truly adsorbed and not combined with impurities. The fact that known amounts of acids can be added and quantitatively removed and estimated gives further assurance that the conditions are under strict control.

Materials and Methods Used

The charcoals used in this investigation were from three sources: activated sugar charcoal, Norite and blood charcoal. The method of preparation of the sugar charcoal was essentially the same as that previously described.[4a] The Norite and blood charcoal were purified by the method described in a previous publication.[4b] All three charcoals were practically ash-free, containing at the most only a few hundredths of a per cent. of ash. They were all ground to pass through a 300-mesh sieve. The usual tests[5] for the presence of adsorbed acids and alkaline impurities were applied to each lot of charcoal before use, in order to insure the absence of these substances. The sugar used was recrystallized cane sugar practically free from invert sugar. One g. contained less than a milligram of invert sugar and this was corrected for in blank determinations. The sugar solutions were analyzed for total sugar and invert sugar before and after treatment with the charcoal. Two methods were used: the Shaffer-Hartmann[6] modification of the Benedict method for the determination of the invert sugar, and Willaman and Davison's[7] modification of the picric acid method for the determination of both total sugars (sucrose, glucose and fructose) and invert sugar remaining in solution after adsorption.

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[4] (a) Bartell and Miller, THIS JOURNAL, **44**, 1866 (1922). (b) Miller, *J. Phys. Chem.*, **30**, 1031 (1926).

[5] Ref. 4 b, p. 1162.

[6] Shaffer and Hartmann, *J. Biol. Chem.*, **45**, 375 (1920–1921).

[7] Willaman and Davison, *J. Agr. Research*, **28**, 479 (1924).

Outline of Procedure

The charcoal (2 g.) was suspended in conductivity water in an Erlenmeyer flask and the system evacuated to remove air and insure thorough wetting. The acid was then added and the suspension allowed to stand with occasional shaking for approximately 16 hours. After this period the charcoal was filtered off with the aid of suction in a Gooch crucible, the filtrate tested for acid, and the charcoal transferred to an Erlenmeyer flask containing 100 cc. of a 5% sugar solution. This suspension was digested with frequent shaking for one and a half hours in a water-bath at 80°. Near the end of the digestion period the charcoal was allowed to settle to the bottom of the flask so that the supernatant solution could be decanted while the temperature was still at 80°. (Since the charcoal suspensions in many cases filtered rather slowly, decantation was necessary in order to keep the suspension from cooling, with the consequent greater adsorption of the solutes at lower temperatures, as would have occurred had the suspension been filtered. Also, by decanting the solution it could be quickly cooled and the inverting action of the acid stopped. While, theoretically, the inversion would go on to some extent in the cold, in practice this action was of negligible magnitude because of the small quantities of acid in the solutions.) The decanted solution was cooled as quickly as possible in running water and then filtered through a disk of filter paper in a Gooch crucible in order to remove the small amount of charcoal that had not settled out. The acid in the filtrate was determined on an aliquot. Since the quantity of acid in the filtrate was usually small, a 50cc. portion was used for titration with 0.02 N sodium hydroxide solution. Phenol red was used as indicator. Aliquots of suitable size were taken for use in the methods mentioned above for the determination of total sugar and for invert sugar.

Experimental Part

After a number of preliminary experiments it seemed certain that the only inversion which took place was with the acid and sucrose remaining in solution in equilibrium with adsorbed acids and sugars, for not the slightest trace of invert sugar was ever detected when the charcoal was free from adsorbed acid or when the amount of adsorbed acid was sufficiently small to be adsorbed irreversibly at 80° and was not displaced by the adsorption of sugar at that temperature. It was decided, therefore, to test this point further, using the charcoals with hydrochloric and benzoic acids as representatives, respectively, of groups of acids of low and of high adsorbability. The amount of adsorbed acid held irreversibly adsorbed at 80° depended upon the activity of the charcoal and the adsorbability of the acid. For example, 2 g. of blood charcoal adsorbed irreversibly nearly 10 cc. of 0.02 N hydrochloric acid and nearly 50 cc. of the highly adsorbed benzoic acid. When larger quantities of acid were added to the charcoals some acid appeared in solution at 80° in the presence of sugar. In these instances inversion of sugar, of course, always took place. Since relatively large amounts of sugar were also adsorbed, the amount of total sugar (sucrose+invert sugar) remaining in solution at 80° was determined as stated above. The amount of total sugar adsorbed varied with the amount of adsorbed acid on the charcoal. The presence of a large amount of adsorbed acid cut down appreciably the adsorption of the sugar.

It was deemed desirable to determine whether the amount of invert sugar found in the solution after digestion was the same as would be produced by the action of the unadsorbed acid on the unadsorbed sucrose
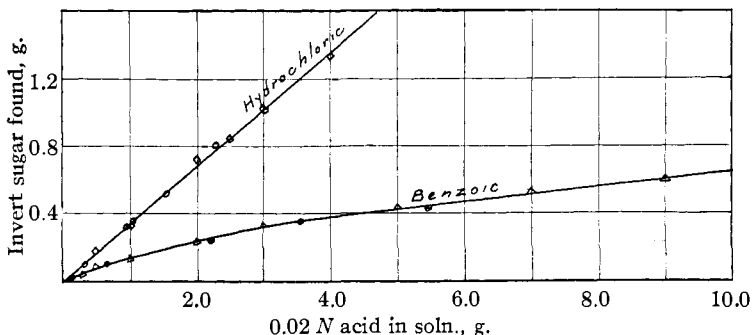
Fig. 1.—Data for blood charcoal. O, Hydrochloric acid and invert sugar in solution after digestion with charcoal; □, invert sugar with hydrochloric acid and 3.92% sucrose; ●, benzoic acid and invert sugar in solution after digestion with charcoal; △, invert sugar with benzoic acid and 4.35% sucrose.

found in the solution at 80°.   If this were found to be the case it would be additional evidence that adsorbed acids are incapable of inverting sucrose.   Since it would involve an unnecessarily large amount of work

Fig. 2.—Data for Norite. O, Hydrochloric acid and invert sugar in solution after digestion with charcoal; □, invert sugar with hydrochloric acid and 4.40% sucrose; ●, benzoic acid and invert sugar in solution after digestion with charcoal; △, invert sugar with benzoic acid and 4.64% sucrose.

to determine the amount of inversion by the various amounts of sugar and acid found in solution at 80° and since considerable error might be

introduced in titrating a small quantity of acid (0.1–1.0 cc., 0.02 N), a slightly different procedure was followed. The average of the amounts of unadsorbed sucrose found in solution in the experiments with varying amounts of a given acid was calculated. The amount of inversion produced at 80° by given amounts of the acid in question on this amount and concentration of sugar was determined, and from these data a curve was constructed from which could be read the amount of invert sugar that would be produced by the action of any quantity of acid within the range of that found in the solutions in contact with the charcoal in the experiments.

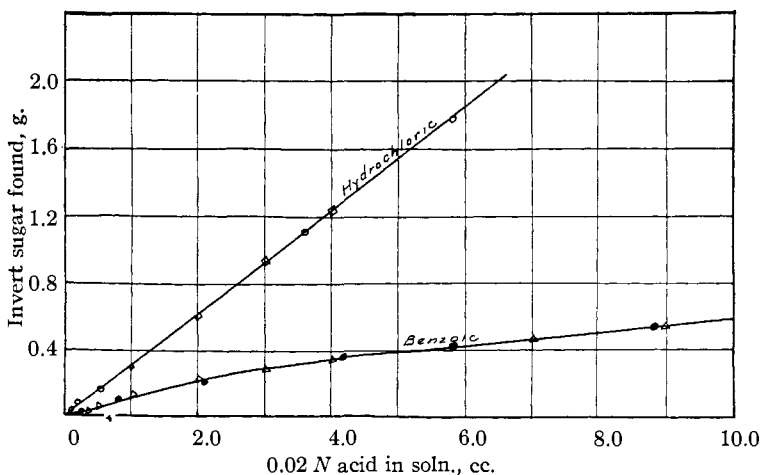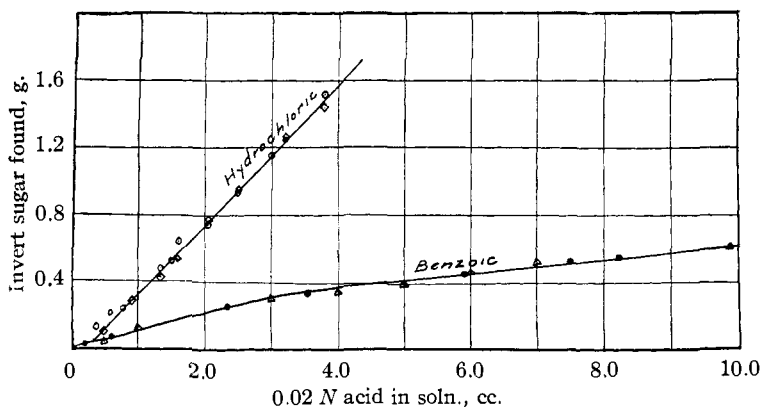Fig. 3.—Data for activated sugar charcoal. ○, Hydrochloric acid and invert sugar in solution after digestion with charcoal; □, invert sugar with hydrochloric acid and 4.60% sucrose; ●, benzoic acid and invert sugar in solution after digestion with charcoal; △, invert sugar with benzoic acid and 4.70% sucrose.

The data for the three charcoals with hydrochloric and benzoic acids and for these acids with the sugar solutions of given concentrations are

TABLE I

DATA FOR PURIFIED BLOOD CHARCOAL AND HYDROCHLORIC ACID

0.02 N acid added to 2 g. of charcoal, cc.	0.02 N acid in soln. at room temp., cc.	0.02 N acid in soln. at 80°, cc.	0.02 N acid on the charcoal at 80°, cc.	Total sugar left in solution at 80°, g.	Invert sugar found after digestion, g.	Invert sugar calcd., g.
0.00	0.00	0.00	0.00	....	0.00	0.00
2.00	.00	.00	2.00	3.88	.00	.00
5.00	.00	.00	5.00	3.94	.00	.00
7.00	.00	.00	7.00	3.92	.00	.00
10.00	.00	.05	9.95	3.88	.01	.02
12.00	.00	.10	11.90	3.89	.04	.04
14.00	.00	.20	13.80	3.87	.08	.08
16.00	.00	.55	15.45	3.91	.16	.16
25.00	.95	3.60	20.45	4.00	1.10	1.14
30.00	2.00	5.80	22.20	3.99	1.78	1.78

presented in Tables I to XII and in the curves in Figs. 1, 2 and 3.   The values are the averages of the results with two or more samples of charcoal.

TABLE II

INVERT SUGAR FORMED IN 100 CC. OF SOLUTION CONTAINING 3.92 G. OF SUCROSE AND VARYING QUANTITIES OF HYDROCHLORIC ACID

0.02 N acid in soln., cc.	1.00	2.00	3.00	4.00
Invert sugar in soln. after digestion, g.	0.31	0.61	0.94	1.24

TABLE III

DATA FOR PURIFIED BLOOD CHARCOAL AND BENZOIC ACID

0.02 N acid added to 2 g. of charcoal, cc.	0.02 N acid in solution at room temp., cc.	0.02 N acid in solution at 80°, cc.	0.02 N acid on the charcoal at 80°, cc.	Total sugar left in soln. at 80°, g.	Invert sugar found after digestion, g.	Invert sugar calcd., g.
0.00	0.00	0.00	0.00	....	0.00	0.00
10.00	.00	.00	10.00	4.28	.00	.00
49.90	.00	.25	49.65	4.22	.04	.04
74.85	.00	.80	74.05	4.31	.12	.11
99.81	.00	4.15	120.31	4.43	.37	.36
149.72	.45	5.81	143.46	4.34	.43	.43
174.67	.95	8.82	164.90	4.36	.55	.54
199.63	2.00	11.78	185.85	4.36	.65	....

TABLE IV

INVERT SUGAR FORMED IN 100 CC. OF SOLUTION CONTAINING 4.33 G. OF SUCROSE AND VARYING QUANTITIES OF BENZOIC ACID

0.02 N acid in soln., cc.	0.30	0.50	1.00	2.00	3.00	4.00	7.00	9.00
Invert sugar in soln. after digestion, g.	.04	.08	0.14	0.23	0.29	0.35	0.47	0.55

TABLE V

DATA FOR PURIFIED NORITE AND HYDROCHLORIC ACID

0.02 N acid added to 2 g. of charcoal, cc.	0.02 N acid in soln. at room temp., cc.	0.02 N acid in soln. at 80°, cc.	0.02 N acid on the charcoal at 80°, cc.	Total sugar left in soln. at 80°, g.	Invert sugar found after digestion, g.	Invert sugar calcd., g.
0.00	0.00	0.00	0.00	....	0.00	0.00
6.00	.00	.40	5.60	4.38	.12	.06
8.00	.00	.80	7.20	4.39	.22	.22
10.00	.00	1.35	8.65	4.52	.47	.46
12.00	.05	1.60	10.35	4.45	.63	.57
14.00	.20	2.05	11.75	4.42	.75	.76
16.00	.72	2.50	12.78	4.33	.92	.94
18.00	1.35	3.20	13.45	4.42	1.25	1.24
20.00	2.10	3.80	14.10	4.33	1.51	1.48

TABLE VI

INVERT SUGAR FORMED IN 100 CC. OF SOLUTION CONTAINING 4.40 G. OF SUCROSE AND VARYING QUANTITIES OF HYDROCHLORIC ACID

0.02 N acid in soln., cc.	0.50	0.90	1.35	1.50	1.60	2.05	2.50	3.20	3.80
Invert sugar in soln. after digestion, g.	.10	.28	0.46	0.52	0.53	0.76	0.94	1.26	1.44

TABLE VII
DATA FOR PURIFIED NORITE AND BENZOIC ACID

0.02 N acid added to 2 g. of charcoal, cc.	0.02 N acid in soln. at room temp., cc.	0.02 N acid in soln. at 80°, cc.	0.02 N acid on the charcoal at 80°, cc.	Total sugar left in soln. at 80°. g.	Invert sugar found after digestion. g.	Invert sugar calcd., g.
0.00	0.00	0.00	0.00	....	0.00	0.00
50.00	.00	.20	49.80	4.59	.03	.01
74.06	.00	.60	73.46	4.64	.07	.06
100.00	.10	1.98	97.92	4.63	.23	.24
108.63	.60	2.36	105.67	4.60	.27	.26
123.44	.30	3.55	119.59	4.66	.35	.36
133.30	.95	5.90	126.45	4.62	.46	.46
143.17	1.80	7.50	133.82	4.68	.53	.52
148.13	1.85	8.22	138.06	4.68	.55	.55

TABLE VIII
INVERT SUGAR FORMED IN 100 CC. OF SOLUTION CONTAINING 4.64 G. OF SUCROSE AND VARYING QUANTITIES OF BENZOIC ACID

0.02 N acid in soln., cc.	1.00	2.00	3.00	4.00	5.00	6.00	7.00	9.88
Invert sugar in soln. after digestion, g.	0.13	0.23	0.31	0.35	0.40	0.46	0.50	0.61

TABLE IX
DATA FOR PURIFIED SUGAR CHARCOAL AND HYDROCHLORIC ACID

0.02 N acid added to 2 g. of charcoal, cc.	0.02 N acid in soln. at room temp., cc.	0.02 N acid in soln. at 80°, cc.	0.02 N acid on the charcoal at 80°. cc.	Total sugar left in soln. at 80°. g.	Invert sugar found after digestion, g.	Invert sugar calcd., g.
0.00	0.00	0.00	0.00	....	0.00	00.0
5.00	.00	.35	4.65	4.57	.10	.10
8.00	.00	.93	7.07	4.56	.32	.32
10.00	.10	1.04	8.86	4.62	.36	.36
12.00	.30	1.56	10.14	4.57	.52	.52
14.00	.88	2.28	10.84	4.64	.81	.76
16.00	1.45	3.01	11.54	4.59	1.02	1.01

TABLE X
INVERT SUGAR FORMED IN 100 CC. OF SOLUTION CONTAINING 4.60 G. OF SUCROSE AND VARYING QUANTITIES OF HYDROCHLORIC ACID

0.02 N acid in soln., cc.	0.50	1.00	2.00	2.50	3.00	4.00
Invert sugar in soln. after digestion, g.	.18	0.33	0.72	0.84	1.03	1.34

TABLE XI
DATA FOR PURIFIED SUGAR CHARCOAL AND BENZOIC ACID

0.02 N acid added to 2 g. of charcoal, cc.	0.02 N acid in soln. at room temp., cc.	0.02 N acid in soln. at 80°, cc.	0.02 N acid on the charcoal at 80°. cc.	Total sugar left in soln. at 80°, g.	Invert sugar found after digestion, g.	Invert sugar calcd., g.
0.00	0.00	0.00	0.00	....	0.00	0.00
25.00	.00	.10	24.90	4.70	.01	.01
50.00	.00	.63	49.37	4.68	.10	.09
75.00	.15	2.20	72.65	4.72	.24	.25
85.00	.25	3.56	81.19	4.71	.36	.36
100.00	.40	5.44	94.20	4.67	.43	.44
125.00	1.90	10.89	112.21	4.73	.66	....

TABLE XII

INVERT SUGAR FORMED IN 100 CC. OF SOLUTION CONTAINING 4.70 G. OF SUCROSE AND VARYING QUANTITIES OF BENZOIC ACID

0.02 N acid in soln., cc.	0.30	0.50	1.00	2.00	3.00	5.00	7.00	9.00
Invert sugar in soln. after digestion, g.	.04	.07	0.10	0.24	0.33	0.44	0.54	0.61

The data show conclusively the following facts. (1) Pure charcoal free from adsorbed acids does not invert sucrose. (2) When the acid is irreversibly adsorbed there is no inversion of sucrose at 80°, even though as much as 1 g. of sucrose was adsorbed by 2 g. of charcoal carrying varying quantities of acids. This would seem to imply a very high concentration of sucrose on the carbon. (3) When sufficient amounts of acid were added to the charcoal so that at 80° there was reversible adsorption and displacement of some of the acid by the sugar, there was always inversion. The amount of sugar inverted under these conditions was the same as that inverted by an amount of acid and sugar equivalent to the unadsorbed acid and sugar under the same conditions but in the absence of charcoal. It is certain that the only inversion is that produced by the acid not adsorbed. (4) Large amounts of adsorbed acid and adsorbed sucrose can be held by the charcoal without producing any inversion at 80°.

Results with Acids of Various Types

In order to determine whether the non-inversion of sucrose by adsorbed acid is a general phenomenon, the behavior of a number of acids of various types was investigated. The procedure was practically the same as above. To 2 g. of blood charcoal was added (1) a quantity of acid sufficiently small so that it was completely and irreversibly adsorbed at 80° in the presence of sugar and (2) a quantity of acid large enough so that at 80° in the presence of sugar some acid appeared in solution. The data appear in Table XIII. The results show conclusively that inorganic, aliphatic,

TABLE XIII

RESULTS WITH ACIDS OF VARIOUS TYPES

0.02 N acid added to 2 g. of blood charcoal, cc.	0.02 N acid in soln. at 80°, cc.	Invert sugar found, g.	0.02 N acid added to 2 g. of blood charcoal, cc.	0.02 N acid in soln. at 80°, cc.	Invert sugar found, g.
5.00 hydrochloric	0.00	0.000	10.00 malic	0.00	0.000
5.00 sulfuric	.00	.000	10.00 tartaric	.00	.000
5.00 nitric	.00	.000	10.00 oxalic	.00	.000
10.00 acetic	.00	.000	39.00 anthranilic	.25	.04
10.00 stearic	.00	.000	40.00 salicylic	.60	.21
10.00 benzoic	.00	.000	20.00 succinic	1.42	.08
10.00 salicylic	.00	.000	20.00 malic	1.62	.17
10.00 anthranilic	.00	.000	20.00 tartaric	1.32	.18
10.00 succinic	.00	.000			

dicarboxylic and aromatic acids, when adsorbed, are incapable of inverting sugar and that inversion takes place only when the adsorbed acids have been displaced from the charcoal.

Results with Salt Solutions and Acid-Salt Mixtures

The data thus far presented show definitely that whatever the mechanism of the adsorption and whatever the condition of the adsorbed acids and sugar on the charcoal, there is no inversion of the sugar by the acid. It has been shown in previous papers[2,8] that pure ash-free charcoal adsorbs acid hydrolytically from solutions of neutral salts and sets free an equivalent amount of alkali which remains in solution. There is, at the same time, adsorption of some of the solvent, for in the case of the inorganic salts such as potassium chloride, sulfate and nitrate the solution remaining after adsorption is more concentrated with respect to the positive ion than before.[3] The inversion or non-inversion of sucrose by the charcoal in salt solutions should yield information regarding the state of the adsorbed acid and adsorbed water. Provided sugar were inverted it would indicate that the acid is free in solution. Non-inversion would show that either or both the acid and sugar and possibly the water, too, are bound in such a manner that they no longer have the properties of ionization and mobility which they possess in ordinary aqueous solution. Since these salt solutions in equilibrium with the adsorbed substances on the charcoal are alkaline, any inversion produced would necessarily have to be attributed to the adsorbed acid on the charcoal or in the film immediately surrounding the charcoal. The procedure in this case was as follows. The charcoal (2 g.) was added to the salt solution or to the acid-salt mixtures and allowed to stand overnight. Sufficient sugar and water were then added to make 100 cc. of a 5% sucrose solution and the

TABLE XIV

RESULTS WITH SALT SOLUTIONS AND ACID-SALT SOLUTIONS

Activated sugar charcoal

Solution	0.02 N KOH in soln. at 80°. cc.	0.02 N acid on charcoal at 80°. cc.	Invert sugar found. g.
50 cc. 4 N KCl	2.96	2.96	0.000
50 cc. 4 N KCl + 4 cc. 0.02 N HCl	1.87	5.87	.000
50 cc. 4 N KCl + 8 cc. 0.02 N HCl	0.86	8.86	.000
50 cc. 4 N KCl + 12 cc. 0.02 N HCl	0.05	12.05	.000
50 cc. 0.1 N sodium benzoate	9.34	9.34	.000
50 cc. 4 N KCl + 10 cc. 0.02 N H₂SO₄	0.63	10.63	.000

Purified blood charcoal

50 cc. 4 N KCl	6.95	6.95	.000
50 cc. 4 N KCl + 10 cc. 0.02 N HCl	2.43	12.43	.000
50 cc. 4 N KCl + 20 cc. 0.02 N HCl	0.60	20.60	.000

[8] Bartell and Miller, THIS JOURNAL, **45**, 1106 (1923).

suspension was digested at 80° for one and a half hours as usual. The total quantity of adsorbed acid on the charcoal was the sum of the added acid and the acid hydrolytically adsorbed from the salt solution. The latter was, of course, equivalent to the amount of alkali found in the solution at 80°. The data for sugar charcoal and purified blood charcoal with potassium chloride and sodium benzoate are presented in Table XIV. These data show definitely that there was no inversion under these conditions or even when the quantity of adsorbed acid was augmented by the addition of small quantities of acid to the salt solution. Similar results were obtained when other types of salts, such as methylene blue chloride, were used.

Adsorption of Glucose from Solution

Negative catalysis has sometimes been explained on the theory that the products of reaction are adsorbed so strongly by the catalyst that a coating of the reaction products is formed, through which the reactants cannot diffuse, thereby stopping or slowing down the reaction. The possibility that such conditions might be operative in the present work was investigated. The adsorption of glucose alone and in mixtures with sucrose was determined, as well as the displacement of adsorbed glucose by sucrose. The data in Tables XV and XVI show that the presence of sucrose in the usual 5% solution cut down greatly the adsorption of glucose. It is also evident that the glucose, if formed even in minute quantity on the charcoal, would be largely displaced and would appear in solution where it could be detected. When as little as 5 mg. of glucose was adsorbed on 2 g. of charcoal, more than half of it was displaced when the charcoal was suspended in the usual 100 cc. of 5% sucrose solution at 80°. There is evidence that fructose is even less adsorbed than glucose. It is certain, therefore, that strong adsorption of the products of reaction is not the cause of the negative catalysis in this case.

TABLE XV

ADSORPTION OF GLUCOSE FROM SOLUTION

2 g. of charcoal + 100 cc. of solution at 80°

Before adsorption		After adsorption	Amount adsorbed
Sucrose. g.	Glucose. g.	Glucose, g.	Glucose, g.
....	4.78	4.30	0.48
5.00	0.99	0.91	.08
5.00	.50	.47	.03

TABLE XVI

DISPLACEMENT OF ADSORBED GLUCOSE BY SUCROSE

2 g. charcoal carrying adsorbed glucose digested with 100 cc. of 5% sugar solution for 1.5 hours at 80°

Adsorbed glucose, g.	0.020	0.010	0.005
Glucose displaced, g.	.015	.006	.003

Discussion

The results of this investigation show conclusively that acids when adsorbed on charcoal are incapable of inverting sucrose. The fact that the inversion process is not merely slowed up but completely stopped by adsorption is of importance for certain theories of adsorption and contact catalysis.

It seems certain that in adsorption of acids (and probably other substances) from solutions by charcoal there is not merely a concentration of the acid in solution at the interface nor in a highly concentrated film of solution on the adsorbent and separate from the equilibrium solution as postulated by Ostwald and Izaguirre.[9] If adsorption of acid and sugar were of this nature, inversion undoubtedly would take place.

The results, likewise, point to a conclusion contrary to that frequently accepted with regard to the adsorption of acids. It is frequently considered that when acids are adsorbed there exists at the interface or around the particles of the adsorbent a higher concentration of hydrogen ions than in the bulk of the solution. The existence of a high concentration of hydrogen ions or indeed of any hydrogen ions on the surface of the charcoal particles carrying adsorbed acids seems absolutely disproved by this work. Since it is fairly certain that the inversion of sucrose by acids is due solely to the hydrogen ion it seems reasonable to conclude that the adsorbed acids on charcoal are in an undissociated state.

The possibility that oriented adsorption of either or both the acid or sucrose molecules might be responsible for the negative catalysis seems precluded, in this case at least, by the fact that the reaction is completely inhibited. If it were merely retarded, orientation, whereby there might arise a tendency to keep the reactive parts of the molecules from coming together, would have to be considered. Furthermore, the orientation of the acids would undoubtedly be with the hydrogen ion away from the charcoal and toward, or in, the water phase for it was shown[8,10] that adsorption by pure charcoal is an oriented adsorption and that the charcoal attracts the hydrocarbon end of the carboxylic acid molecule. The orientation with the carboxyl group and the hydrogen ion toward the water or solution phase should favor inversion, provided, of course, the sucrose molecules were not adversely oriented. According to the "diffuse" double-layer theory of Gouy,[11] the hydrogen ions under these conditions should extend for an appreciable distance into the solution. This should result in inversion. The data in Table XIII show, however, that neither adsorbed inorganic acids nor adsorbed carboxylic acids are able to cause inversion. Thus, considerations of orientation also make it seem rea-

[9] Ostwald and Izaguirre, *Kolloid-Z.*, **30**, 279 (1922).

[10] Bartell and Miller, *J. Phys. Chem.*, **28**, 992 (1924).

[11] Gouy, *J. phys.*, **9**, 457 (1910).

sonable to conclude that the adsorbed acid is in an undissociated state.

It is generally considered[12] that charcoal does not catalyze many reactions. There are, however, a number of instances of heterogeneous contact catalysis in which charcoal acts either as a positive or negative catalyst. As illustrations may be cited the work of Firth and Watson[13] on the catalytic decomposition of hydrogen peroxide and the studies of Kruyt and van Duin[14] on the catalytic effect on the saponification of ethyl acetate, the removal of bromine from α,β-dibromopropionic acid by potassium iodide, and other reactions. The saponification of ethyl acetate was retarded by charcoal while the removal of bromine was accelerated. These authors emphasized the fact that simple adsorption or concentration of the reactants at an interface is not sufficient to catalyze a reaction. They explained the results on the basis of the Langmuir-Harkins theory of oriented adsorption.

Non-inversion of sucrose by adsorbed acids on charcoal is apparently an extreme instance of negative catalysis in which both reactants are adsorbed. As pointed out above, oriented adsorption does not seem to account for the complete inhibition of the reaction. Neither does the theory that the reaction products are so strongly adsorbed that they slow up or stop the reaction seem to offer any possibilities. On the contrary, it appears that the reactants themselves are so strongly adsorbed that they cannot react.

Since the reaction in this instance involves as one of the reactants the hydrogen ion and not the undissociated acid it seems reasonable to conclude that the adsorbed acid on the charcoal is held in the form of undissociated molecules or, possibly, as neutral atoms or groups on the adsorption points of the charcoal lattice. Such an explanation would seem to account satisfactorily for the phenomenon.

Summary

1. Evidence has been submitted to show that adsorbed acids on ash-free charcoals are unable to invert sucrose.

2. It is suggested that adsorbed acids on charcoal are in an undissociated state.

3. Contrary to existing ideas the adsorption of acids does not imply a high concentration of hydrogen ions around the adsorbent.

4. The significance of the non-inversion of sucrose by adsorbed acids for certain theories of adsorption and catalysis has been pointed out.

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[12] Taylor, J. Phys. Chem., 28, 898 (1924).

[13] Firth and Watson, Trans. Faraday Soc., 19, 601 (1924); 20, 370 (1924–1925).

[14] Kruyt and van Duin, Rec. trav. chim., 40, 249 (1921).