

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE PENNSYLVANIA STATE COLLEGE]

## THE EFFECT OF INORGANIC SALTS ON THE ADSORPTION OF INORGANIC ACIDS AND BASES

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RECEIVED<sup>1</sup> MAY 4, 1927

PUBLISHED JULY 5, 1927

It is the generally accepted idea that the stability of colloidal dispersions is dependent upon the presence of an electrical charge on the dispersed particle.<sup>2</sup> This electrical charge is generally conceded to be due to the adsorption of an ion.<sup>3</sup> However, the actual mechanism of such adsorption is by no means completely understood. Many investigations have been performed in order to furnish data by means of which some general theory of adsorption could be formulated. Thus far the work done has yielded results which vary widely. Consequently, it has been impossible to formulate any one theory of adsorption which will fit the known facts in all cases. Probably the most important reason for the wide variation in the results published is the use of complex and impure adsorbents. Chemical reactions with impurities would appear as adsorption. Relatively few attempts have been made to purify the adsorbent so that only adsorption would take place.

The investigations on the adsorption of acids and bases by charcoal in the presence of a salt with a common ion, as performed by Michaelis and Rona,<sup>4</sup> are considered in practically all theoretical discussions pertaining to adsorption. However, Miller's work<sup>5</sup> has demonstrated that the former investigation is open to criticism. Therefore, for these experiments charcoal was chosen as the adsorbent because it could be prepared in a very pure state.

Some of the experiments of Michaelis and Rona have been repeated, using Merck's blood charcoal as reported by them, as well as a pure form of charcoal.

### Preparation and Activation of the Charcoal

Many different methods of purifying charcoal have been published.<sup>6</sup>

<sup>1</sup> A preliminary version of this manuscript was submitted on June 11, 1926.

<sup>2</sup> Hardy, *J. Physiol.*, **24**, 288 (1899); *Z. physik. Chem.*, **33**, 385 (1900); Zsigmondy and Spear, "Chemistry of Colloids," chap. 3, John Wiley and Sons, Inc., New York, 1917.

<sup>3</sup> Nernst, "Theoretische Chemie," Ferdinand Enke, Stuttgart, 1921, p. 367. Freundlich, "Kapillarchemie," Akademische Verlagsgesellschaft, Leipzig, 1923. Northrop, Bogue's "Colloidal Behavior," McGraw-Hill Book Co., New York, 1924, p. 77. Burton, *ibid.*, p. 139.

<sup>4</sup> Michaelis and Rona, *Biochem. Z.*, **94**, 240 (1919); **97**, 268 (1919); **102**, 85 (1920).

<sup>5</sup> Miller, *THIS JOURNAL*, **44**, 1866 (1922); **45**, 1106 (1923); **46**, 1150 (1924); **47**, 1270 (1925).

<sup>6</sup> Odén and Andersson, *J. phys. Chem.*, **25**, 311 (1921). Firth and Watson, *J. Chem. Soc.*, **123**, 1750 (1923). Watson, *J. Soc. Chem. Ind.*, **38**, 998 (1919). Herbst, *Biochem. Z.*, **115**, 204 (1921).

Use of commercial charcoals is not satisfactory, since all contain large amounts of impurities. Blood and bone charcoal are known to be of a very complex nature. Even a sample of supposedly pure commercial activated sugar charcoal was found to contain 28% ash. Although the ash from this charcoal was largely soluble in hydrochloric acid, it has been shown that boiling with concentrated acids is inadequate in removing the impurities from the charcoal.<sup>7</sup> Other suggested methods present similar difficulties. Consequently it was considered necessary to use specially prepared charcoal.

In preparing the charcoal, the best obtainable commercial cane sugar was recrystallized three times from conductivity water. In preparing the conductivity water the same method as that adopted by Harkins was used.<sup>8</sup> The recrystallized sugar, dried by suction on a Büchner funnel, was then charred at a low temperature in a platinum dish and ignited in order to burn off the adsorbed hydrocarbons.

Another portion of the sugar was charred by treating it with concd. sulfuric acid, and washing until the water showed no acidity when treated with methyl orange.

Freshly charred charcoal is not adsorptive. It must first be activated. Of the various methods suggested for activation, that used by Miller seemed to offer the best source of pure active amorphous carbon. However, steam activation gives a more active carbon, but hydrogen is liberated which is strongly adsorbed and very difficult to remove. For this reason steam activation was avoided except for a few preliminary experiments. Treatment with iodine, sodium carbonate or other reagents presents similar difficulties. Some sugar was charred in platinum dishes, and ground but not passed through a sieve, heated in a quartz tube for 24 hours at about 950° and then activated by steam for 30 minutes. The charcoal was then heated for one hour more in an atmosphere of nitrogen, and allowed to cool under the same conditions. After cooling, the sample was used at once in order to avoid carbon dioxide.

Samples of this produced about the same amount of adsorption of hydrochloric acid and sodium hydroxide. The presence of sodium chloride increased the amount of each adsorbed. Since this is not in agreement with the experiments of Miller, other experiments with alkalis are being conducted and will be given in a later paper. The filtrate from sodium hydroxide solutions was slightly clouded unless a little sodium chloride was added before filtration, in which case a perfectly clear filtrate resulted. The adsorption of pure hydrochloric acid by the steam-activated charcoal was checked by titrating the chlorides according to the method of Volhard. The unactivated charcoals showed no adsorptive power. The results are given in Table I.

<sup>7</sup> Miller, *Mich. State College Expt. Sta. Tech. Bull.*, No. 73, 1926.

<sup>8</sup> Harkins, *THIS JOURNAL*, 48, 943 (1926).

TABLE I  
 ADSORPTION BY STEAM-ACTIVATED CHARCOAL

Material used	Concd. NaCl N. F.	0.01 <i>N</i> HCl adsorbed per g. of charcoal per 100 cc. of soln.		0.01 <i>N</i> NaOH adsorbed per g. of charcoal per 100 cc. of soln. cc.
		Titration of acid, cc.	Titration of chlorides, cc.	
Unactivated	0.0	None	None	None
Activated	.0	20.20	20.50	18.95
Activated	1.0	27.10		25.90

The charcoal used for the greater part of this work was prepared by heating the sugar which had been charred in platinum dishes to a temperature of 950° in 2 × 61 cm. quartz tubes for 24 hours. The quartz tubes were enclosed in an asbestos box and heated by five Méker burners. The tubes were packed tightly with charcoal and the ends left open until the maximum temperature was reached. This assisted in driving off any remaining adsorbed hydrocarbons. Then the ends of the tubes were fitted with glazed porcelain stoppers, and so remained until the heating was completed. The final heating was carried out in covered porcelain crucibles in an electric furnace which was kept at 1000° for 48 hours. This charcoal was then ground in an agate mortar to pass through a 200-mesh sieve, and thoroughly mixed. Charcoal prepared in this way is an active adsorbent and contains less than 0.2% of ash. A 10g. sample shaken with conductivity water and allowed to stand for 24 hours and then filtered, left a filtrate which was neutral to the common indicators.

The charcoal which had been charred with sulfuric acid was activated by heating for 24 hours in closed quartz tubes, and for 24 hours more, during which time a measured amount of air was forced through the tube, the amount of air being sufficient to burn about two-thirds of the original charge. This charcoal was also ground in an agate mortar to pass through a 200-mesh sieve. It contained less than 0.05% of ash, and also left a neutral filtrate when shaken with water and filtered.

### Procedure

The balance, weights, flask, pipets and burets were calibrated according to the usual methods. Pyrex glassware was used throughout. All solutions were prepared with conductivity water. The acids and bases used were Baker's "Analyzed," and the neutral salts were Merck's "Reagent" products. All of the experiments were performed with 0.0100 *N* acid or base, prepared as follows: 50 cc. of the 0.1000 *N* solution was mixed with a definite amount of salt solution in a 500cc. graduated flask, and diluted to volume. This method gave solutions of the desired neutral salt concentration, which were 0.0100 *N* with respect to the acid or base present. For example, with hydrochloric acid, the acid in each sample was 0.01 *N*, but the concentration of the sodium chloride was increased in successive samples from 0 to 4.5 *N*; 4.5 *N* is the closest normality to the

saturation point with which it is practical to work. Before treating the charcoal these solutions were titrated with 0.01 *N* standard solution, as an assurance that the prepared solutions were exactly 0.0100 *N*.

Phenol red (phenolsulfonephthalein) was the indicator used.<sup>9</sup> It was prepared from the dye according to Clark's directions.<sup>10</sup> This indicator is extremely sensitive to carbon dioxide; consequently the solutions were all boiled before and during the titration. When dealing with alkaline solutions it was particularly necessary to boil the solutions after each addition of acid in order to determine the true end-point, since during the process of filtration they adsorb carbon dioxide.

From each solution two 125cc. portions were taken. Each portion was shaken with 1.2500 g. of charcoal in a 500cc. Erlenmeyer flask. The flasks were placed in a constant-temperature bath and kept at 25° for 24 hours. This gave ample time for equilibrium to be reached. The charcoal was then removed by filtering. A blank determination showed that the concentration of a solution was unchanged by a possible selective adsorption of the filter paper. Fifty-cc. portions were titrated again, using the 0.01 *N* standard solutions. The difference in the concentrations before and after treatment with charcoal indicated the amount adsorbed. According to this method two 50cc. portions were titrated from each sample and two samples were taken for each salt concentration. This gave four measurements for each result obtained. When unexpected results were obtained, extra samples were prepared and titrated.

### Experimental Results

The results for the adsorption of hydrochloric acid are tabulated below

TABLE II  
ADSORPTION OF 0.01 *N* HYDROCHLORIC ACID IN THE PRESENCE OF INCREASING CONCENTRATIONS OF SODIUM CHLORIDE

NaCl, <i>N</i>	Mg. equiv. adsorbed per g. of charcoal per 100 cc. of solution		
	Av. from each sample		Final av.
0.00	0.0530	0.0545	0.0537
.10	.0564	.0560	.0562
.20	.0744	.0626	.0685
.30	.0780	.0780	.0780
.50	.0880	.0944	.0912
.75	.1078	.1080	.1079
1.00	.1158	.1142	.1150
1.50	.1254	.1236	.1245
2.00	.1386	.1404	.1395
2.50	.1444	.1456	.1450
3.50	.1702	.1720	.1711
4.50	.1925	.1910	.1917

<sup>9</sup> Chesney, *J. Exptl. Med.*, **35**, 181 (1922).

<sup>10</sup> Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, 1923, p. 80.

in milligram equivalents adsorbed per gram of charcoal per 100 cc. of 0.01 *N* solution. The amount of hydrochloric acid adsorbed increases rapidly with increased concentration of the sodium chloride up to 0.5 to 0.75 *N* concentration of sodium chloride. With more concentrated solutions, in respect to the salt, the increase in adsorption of the acid approaches a linear function of the increase in the salt concentration. This fact is shown graphically in Fig. 1. The milligram equivalents adsorbed are plotted as ordinates, and the concentrations of a salt, expressed in terms of normality, are taken as abscissas.

TABLE III

ADSORPTION OF 0.01 *N* NITRIC ACID IN THE PRESENCE OF INCREASING CONCENTRATIONS OF SODIUM NITRATE

NaNO <sub>3</sub> , <i>N</i>	Mg. equiv. adsorbed per g. of charcoal per 100 cc. of solution		
	Av. from each sample		Final av.
0.00	0.1450	0.1480	0.1465
.10	.1830	.1860	.1845
.20	.2052	.2026	.2039
.30	.2094	.2092	.2093
.50	.2202	.2210	.2206
.75	.2334	.2310	.2322
1.00	.2458	.2466	.2462
1.50	.2550	.2598	.2574
2.50	.2912	.2972	.2942
3.50	.3058	.3170	.3124
4.50	.3306	.3336	.3321
5.50	.3670	.3612	.3641

The presence of sodium nitrate affects the adsorption of nitric acid in the same manner. The nitric acid is adsorbed to a greater extent than the hydrochloric acid.

Sulfuric acid in the presence of sodium sulfate exhibits the same general type of curve. However, the amount adsorbed decreases as the amount of sodium sulfate increases. This was contrary to the expected results, and contrary to the results obtained by Michaelis and Rona. Conse-

TABLE IV

ADSORPTION OF 0.01 *N* SULFURIC ACID IN THE PRESENCE OF INCREASING CONCENTRATIONS OF SODIUM SULFATE

Na <sub>2</sub> SO <sub>4</sub> , <i>N</i>	Mg. equiv. adsorbed per g. of charcoal per 100 cc. of solution		
	Av. from each sample		Final av.
0.00	0.0776	0.0810	0.0793
.10	.0608	.0510	.0559
.20	.0272	.0398	.0335
.30	.0252	.0240	.0246
.50	.0170	.0220	.0195
.75	.0142	.0156	.0149
.90	.0140	.0118	.0129
1.00	.0060	.0098	.0079

quently, this work was repeated and the same results were obtained the second time. Also this part of the experiment was repeated with a different type of charcoal, as will be discussed in detail later.

However, the results again showed a decrease in the adsorption of sulfuric acid, upon increasing the concentration of sodium sulfate.

The results of these experiments on the adsorption of acids in the presence of a common ion are shown in graphic form in Fig. 1.

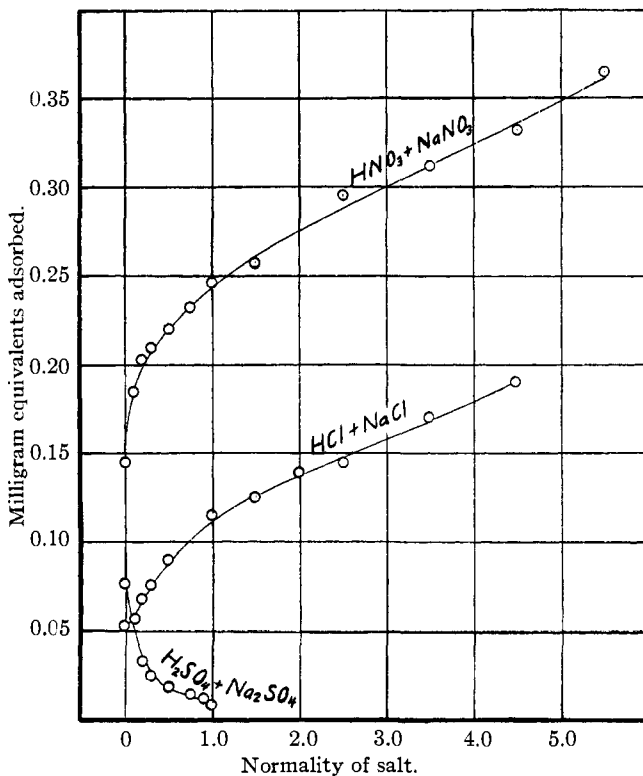


Fig. 1.—Adsorption of acids in the presence of a common ion by sugar charcoal—heat charred.

In order to show more clearly the difference in the adsorption of the acid further determinations were made. The charcoal prepared by treating with sulfuric acid was used for these determinations. It was more active in adsorbing acids and, therefore, accentuates their differences.

Mixtures of two acids, containing 0.005 *N* solutions in respect to each acid, or of a total acidity of 0.01 *N*, show an adsorption less than that of the more active acid alone, but more than that of the less adsorbed acid. One g. of this charcoal adsorbs from 100 cc. of 0.01 *N* solution 0.1696 mg. equiv. of sulfuric acid, 0.2549 mg. equiv. of hydrochloric acid and 0.3232

TABLE V  
 ADSORPTION EXPERIMENTS WITH ACID CHARRED CHARCOAL

Original solution	Mg. equiv. adsorbed per g. of charcoal per 100 cc. of solution		Final av.
	Av. from each sample		
0.01 N H <sub>2</sub> SO <sub>4</sub>	0.1656	0.1636	0.1646
.01 N HCl	.2552	.2546	.2549
.01 N HNO <sub>3</sub>	.3226	.3238	.3232
.01 N NaHSO <sub>4</sub>	.1840	.1720	.1780
{ .005 N H <sub>2</sub> SO <sub>4</sub>	.2950	.2968	.2959
{ .005 N H <sub>2</sub> SO <sub>4</sub>	.2530	.2524	.2527
{ .01 N HCl	.5260	.5090	.5175
{ 0.01 N H <sub>2</sub> SO <sub>4</sub>	.5300	.5276	.5288
{ 0.01 N HNO <sub>3</sub>	.3230	.3156	.3193
{ 0.01 N HNO <sub>3</sub>	.2236	.2222	.2229

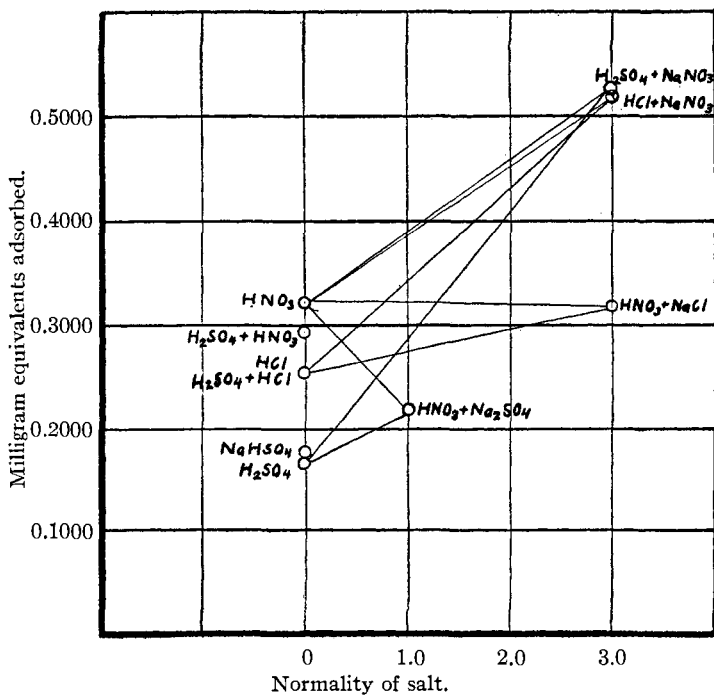


Fig. 2.—Adsorption experiments with mixed acids—sugar charcoal—acid charred.

mg. equiv. of nitric acid. From a mixture of nitric and sulfuric acids, 0.2959 mg. equiv. is adsorbed; from a mixture of sulfuric and hydrochloric acids, 0.2527 mg. equiv. is adsorbed.

Acids in the presence of concentrated solutions of salts without a common ion were also treated, and the amount of adsorption measured. The complete list is tabulated in Table V, and shown in graphic form in Fig. 2.

It was believed that it would be interesting to determine the adsorption of acids and bases in the presence of a common ion, using another type of charcoal. In general the same method was carried out, using Merck's (acid purified) blood charcoal which had been carefully heated to drive off adsorbed gases.

The results are tabulated below, and are shown graphically in Fig. 3.

TABLE VI

ADSORPTION OF 0.01 *N* SULFURIC ACID IN THE PRESENCE OF INCREASING CONCENTRATIONS OF SODIUM SULFATE

$\text{Na}_2\text{SO}_4$ , <i>N</i>	Mg. equiv. adsorbed per g. of charcoal per 100 cc. of solution		
	Av. from each sample		Final av.
0.00	0.2914	0.2976	0.2945
.25	.2790	.2820	.2805
.50	.2696	.2728	.2712
.75	.2664	.2634	.2649
1.00	.2508	.2634	.2571

TABLE VII

ADSORPTION OF 0.01 *N* SODIUM ACID SULFATE IN THE PRESENCE OF INCREASING CONCENTRATIONS OF SODIUM SULFATE

Concn. of <i>N</i> $\text{Na}_2\text{SO}_4$	Mg. equiv. adsorbed per g. of charcoal per 100 cc. of solution		
	Av. from each sample		Final av.
0.00	0.3490	0.3314	0.3352
.25	.2930	.3012	.2971
.50	.2686	.2760	.2723
.75	.2584	.2654	.2619

TABLE VIII

ADSORPTION OF 0.01 *N* HYDROCHLORIC ACID IN THE PRESENCE OF INCREASING CONCENTRATIONS OF SODIUM CHLORIDE

$\text{NaCl}$ , <i>N</i>	Mg. equiv. adsorbed per g. of charcoal per 100 cc. of solution		
	Av. of each sample		Final av.
0.00	0.2904	0.2864	0.2882
.25	.3200	.3220	.3210
.75	.3560	.3570	.3565
1.00	.3620	.3640	.3630
1.50	.3800	.3810	.3805
2.50	.4065	.4055	.4060
3.50	.4304	.4272	.4288
4.00	.4446	.4460	.4452



TABLE IX

ADSORPTION OF 0.01 *N* SODIUM HYDROXIDE IN THE PRESENCE OF INCREASING CONCENTRATIONS OF SODIUM CHLORIDE

NaCl, <i>N</i>	Mg. equiv. adsorbed per g. of charcoal per 100 cc. of solution Av. from each sample		Final av.
0.00	0.2790	0.2830	0.2810
.10	.3238	.3306	.3272
.25	.3388	.3336	.3352
.75	.3467	.3485	.3476
1.00	.3513	.3560	.3536
1.50	.3640	.3620	.3630
2.50	.3733	.3819	.3776
3.50	.3816	.3824	.3820
4.00	.3818	.3838	.3828

In all cases the same relative amounts were adsorbed, which resulted in similar curves to those for pure sugar charcoal. Hydrochloric acid and sodium hydroxide show an increased adsorption as the concentration of the sodium chloride increases. Sulfuric acid shows a decrease as the concentration of the sodium sulfate increases. Sodium acid sulfate shows a rapid decrease with increased concentration of sodium sulfate.

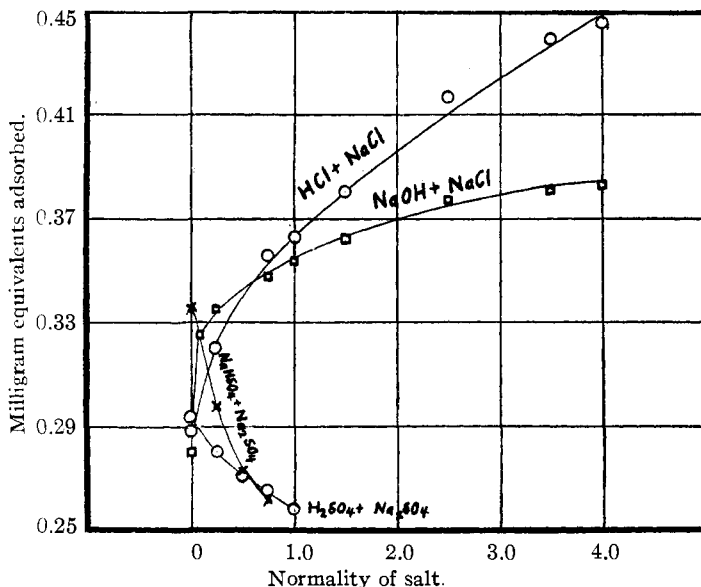


Fig. 3.—Adsorption experiments with blood charcoal.

### Discussion and Interpretation of Results

The adsorption of an ion gives a charge to the colloidal particle which attracts to it, although less strongly, the oppositely charged ion of the electrolyte. The resultant effect is a reversible equilibrium of electrostatic

forces. There is the attraction of the colloidal particle for the ion which it adsorbs. Also there is a tendency for the oppositely charged ion to diffuse through the solution, attracting to it the adsorbed ion. The direction of this last attraction is away from the colloidal particle.

The effect of the attraction away from the colloidal particle will depend upon the degree to which the ion is adsorbed. Langmuir's explanation for the adsorption of gases by charcoal<sup>11</sup> undoubtedly applies here. "Between the atoms of carbon, there must be spaces of all possible sizes and shapes, some just too small to hold a gas molecule, others big enough to hold one but not hold two, etc. There are some spaces in which a molecule would be closely surrounded by carbon atoms on nearly all sides, whereas in other places a molecule would be able to hold on to only a single carbon atom."

There is a stage in adsorption which is approximately irreversible. This has been pointed out by Miller in his description of the difficulty with which part of the adsorbed acid is removed from the charcoal by washing with pure solute. This stage may be pictured as the part of the hydrogen ions which are surrounded on nearly all sides by carbon atoms. Of course if these hydrogen ions cannot be removed by washing, the anions must also remain in the charcoal or in close proximity to it. In the case of hydrochloric acid, for example, when the increased adsorption in the presence of sodium chloride occurs, the same picture is applicable. The excess of chloride ions in the solution decreases the tendency of the chloride ions of the hydrochloric acid to diffuse; consequently, its attraction upon the hydrogen ion away from the particle is lessened. This allows the hydrogen ions adsorbed to become more firmly attached to the carbon, by penetrating further into the spaces between the carbon atoms. This penetration leaves room for more hydrogen ions to be adsorbed, although less firmly, at places nearer the surface of the carbon particle.

In this investigation it was found that 0.01 *N* sodium hydroxide solutions, when filtered, remain cloudy in appearance even after all possible charcoal was filtered out. Evidently the charcoal was peptized by the sodium hydroxide to form a colloidal dispersion. However, when solid sodium chloride was added to this cloudy filtrate, the dispersed charcoal rapidly settled out, and was easily filtered. Evidently the excess of sodium ion decreases the ionization of the sodium hydroxide so that the adsorbed hydroxyl ions are electrically neutralized by the sodium ions, and the colloidal particles are discharged and precipitated. The adsorbed sodium hydroxide remains on the particles when they are precipitated. This is shown by the fact that removing the charcoal decreases the alkalinity of the solution. On this basis the charcoal particles should be dispersed again when the precipitating agent, sodium chloride, is removed by wash-

<sup>11</sup> Langmuir, *THIS JOURNAL*, 38, 2286 (1916).

ing, because of the renewed dissociation of the adsorbed sodium hydroxide. This is indeed the case.

There is no evidence discovered in this work for assuming hydrolysis of the neutral salt. There is, rather, evidence that hydrolytic adsorption does not take place. Sodium chloride increases the adsorption of both the hydrochloric acid and sodium hydroxide. Therefore, if it were due to hydrolytic adsorption we should have hydrochloric acid adsorbed preferentially by charcoal in the case of hydrochloric acid and sodium chloride, and sodium hydroxide in the case of sodium hydroxide and sodium chloride, which would be very mysterious indeed.

Since in a saturated solution of sodium chloride it is not possible to suppress entirely the ionization of 0.01 *N* hydrochloric acid, a continual increase in adsorption with increased concentration of sodium chloride is to be expected. Michaelis states that a maximum adsorption is reached when acid-salt mixtures up to 2 *N* with respect to sodium chloride are used. However, up to and including 4.5 *N* solutions with respect to sodium chloride, no evidence of a maximum adsorption of hydrochloric acid was discovered. The work included not only adsorption by sugar charcoal, but also Merck's blood charcoal, as used by Michaelis.<sup>12</sup> Evidently the thermodynamic basis upon which his theory of adsorption rests does not fit the experimental facts.

The adsorption of nitric acid from sodium nitrate solutions is exactly analogous to the case already considered. The fact that nitric acid is more strongly adsorbed than hydrochloric acid shows that although both the nitrate and chloride ions are less strongly attracted to the charcoal than are the hydrogen ions, the nitrate ion is more strongly attracted than the chloride ion.

The decrease in the adsorption of sulfuric acid in the presence of sodium sulfate can be accounted for on the basis of the above theory. The reaction  $\text{H}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 = 2\text{NaHSO}_4$  undoubtedly takes place to some extent. The greater the concentration of the sodium sulfate, the more sodium acid sulfate will be formed. In an excess of sodium sulfate, the sodium acid sulfate will liberate very few free hydrogen ions. Consequently, the higher the concentration of the neutral sulfate, the fewer the hydrogen ions in the solution available for adsorption.

The 0.01 *N* solution of sodium acid sulfate alone is quite noticeably adsorbed. However, when sodium sulfate is added, the decrease in adsorption with increased concentration of added salt is much more rapid than in the case of sulfuric acid. Here again the results obtained are in disagreement with those obtained by Michaelis. His data show an increase in the adsorption of sulfuric acid in the presence of increased concen-

<sup>12</sup> Svedberg, "Colloid Chemistry," Chemical Catalog Co., Inc., New York, 1924, p. 178.

tration of the sulfate ion. Consequently, samples of such mixtures were treated with blood charcoal, as well as with the sugar charcoal, and the decrease in the adsorption was again demonstrated.

Furthermore, dealing with another type of charcoal, that charred with sulfuric acid, it was observed that 1 *N* sodium sulfate decreases the adsorption of nitric acid. One g. of charcoal adsorbed 0.3232 mg. equiv. of nitric acid from 100 cc. of 0.01 *N* solution. With the same acid concentration, containing sodium sulfate, 0.2229 mg. equiv. is adsorbed. Some of the hydrogen ions are tied up with the sodium acid sulfate in the presence of the excess sodium sulfate, according to the reaction  $\text{HNO}_3 + \text{Na}_2\text{SO}_4 = \text{NaHSO}_4 + \text{NaNO}_3$ . Consequently, there is less adsorption than with nitric acid alone.

When the adsorption from a mixture of 3.0 *N* sodium chloride and 0.01 *N* nitric acid is determined, an amount less than the adsorption of free nitric acid is again shown. This is to be expected because of the reaction  $\text{HNO}_3 + \text{NaCl} = \text{HCl} + \text{NaNO}_3$ . Hydrochloric acid is less adsorbed than nitric acid, but the adsorption of the hydrochloric acid formed is augmented by the excess sodium chloride present. The amount adsorbed is, therefore, greater than the adsorption of pure 0.01 *N* hydrochloric acid, but slightly less than that of pure 0.01 *N* nitric acid.

Sodium nitrate, 3.0 *N* with 0.01 *N* solutions of either hydrochloric or sulfuric acid give an adsorption greater than that of any of the pure acids. The results are similar to the adsorption of nitric acid in the presence of concentrated solutions of sodium nitrate.

The results of the adsorptions of mixed acids are not surprising, but give further evidence of the relative adsorbability of the acids considered.

### Summary

1. The phenomena of adsorption are explained on the basis of the attraction of ions by colloidal particles and the effect of mass action upon this attractive force.
2. It has been demonstrated, as has been generally conceded, that the hydrogen ions of inorganic acids and the hydroxyl ions of inorganic bases are the most strongly adsorbed.
3. The nitrate ion is more strongly adsorbed than the chloride ion, and the chloride ion is more strongly adsorbed than the sulfate ion.
4. Relative results can at any time be duplicated, but it is difficult to obtain separately prepared charcoals with the same degree of activation.
5. There is no evidence of hydrolytic adsorption of neutral inorganic salts in the presence of inorganic acids or bases.
6. There is no maximum adsorption of acids in the presence of a salt with a common ion.