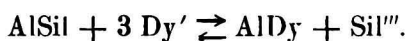


**Chemistry.** — “*The adsorption of electrolytes on charcoal.*” By I. M. KOLTHOFF. (Communicated by Prof. H. R. KRUYT.)

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1. Though numerous investigations have been described in the literature about the adsorption of electrolytes on charcoal, the explanation of this process still escapes us. On the whole electrolytes do not change the surface tension of water with regard to air — nor probably to charcoal either — or very slightly at most, so that it is not rational to explain their adsorbability by making use of the well-known theorem of GIBBS.

Another phenomenon often appears in the adsorption of electrolytes which is called “selective adsorption of ions.” Charcoal often shows a preference for a particular anion or kation, if e.g. a dye-solution is shaken with charcoal, much more of the dye ion is absorbed than of the anion — or kation — with which the dye was combined<sup>1)</sup>. In this so-called selective adsorption of ions the coal must send so many ions into the solution as corresponds with the difference between the quantity of adsorbed dye ion, and the other ion with which the dye ion was combined. If this were not the case the liquid would not remain electrically neutral. So we must imagine that the coal contains electrolytes as impurities, which are not easily removed, and the ions of which are able to react with other ions. Suppose e.g. a charcoal containing aluminium-silicate as an impurity we may represent the adsorption of a dye anion approximately by the following process:



The amount of dye ions taken away is replaced by an equivalent amount of silicate ions in the solution. According to this suggestion the adsorption of electrolytes is a purely chemical phenomenon, and by means of the laws of stoichiometry it is possible to deduce the formula of the adsorption isotherm, which, generally speaking, is also applicable in the adsorption of strong electrolytes.

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<sup>1)</sup> See i.a. L. MICHAËLIS and P. RONA, *Biochem. Z.* 97, 85 (1919); summary in L. MICHAËLIS: „Die Wasserstoffionenkonzentration”, 2e Aufl. 1922, p. 200 and following. HARTLEBEN: *Biochem. Z.* 115, 46 (1921).

A few years ago<sup>1)</sup> I tried to explain the phenomena in the adsorption of electrolytes on coal from a chemical standpoint. I started from the assumption that molecular adsorption of the electrolyte does not take place as such, but that the decomposition adsorption is the only phenomenon that plays a part. As, in the course of a continued investigation different facts were found which could not easily be explained from previous theories, we thought it necessary to investigate if molecular adsorption is not found with electrolytes.

2. In order to exclude decomposition adsorption it was necessary to start with charcoal of the highest purity possible, and practically free from electrolytes. It was prepared in more or less the same way as F. E. BARTELL and E. J. MILLER<sup>2)</sup> had obtained this prepartate. I started from cane sugar with 0,005 % of ash. It was carefully carbonised in a platinum dish. Then the coal was heated for some days in a silica crucible, over a gasoline burner, until its appearance was no longer bright black but more or less dull. At first we admitted some air during the process of heating, which was discontinued later on. The coal thus obtained had a percentage of ash varying between 0,08 % and 0,09 %. I call attention to the fact that BARTELL and MILLER's charcoal was better, as it contained only 0,01 % of ash or even less. At any rate my charcoal was sufficiently pure for my investigation, and the conclusion which we shall discuss in the following pages — viz. that a molecular adsorption of electrolytes on charcoal is taking place — is decidedly justified.

3. When it was seen that acids were appreciably absorbed on the pure charcoal we thought it necessary to demonstrate that practically speaking as much of the kation as of the anion was withdrawn from the solution. The charcoal used in these investigations had an ash content of 0,09 %; the ash of one gram of charcoal neutralized 0,15 cc. of 0,1 N. acid (indicator methylorange); this corresponds therefore with an alcalinity of 0,015 milli-equivalents per one gr. of coal.

2 grs. of the coal was shaken with 50 cc. of solutions of hydrochloric acid of different concentrations. In the filtrate I determined by titration the concentration of the hydrogen ions, as well as of the chlorine ions; I moreover calculated from the conductivity of the filtrate the corresponding concentration of the hydrochloric acid.

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<sup>1)</sup> I. M. KOLTHOFF, Koll. Z. **30**, 35 (1922).

<sup>2)</sup> F. E. BARTELL and E. J. MILLER, J. Am. Chem. Soc., **44**, 1865 (1922).

The final concentrations of hydrogen ions  $[H^+]$ , chlorine ions  $[Cl']$ , and  $[HCl]$  thus found, are seen in the following table:

Experiments with 2 gr. of charcoal and 50 cc. of solution.

Conc. of hydrochloric acid	Final conc. $[H^+]$	$[Cl']$	$[HCl]$ from $K_{18}$
0.0504 N	0.0436	0.0448	0.0440
0.0201 „	0.015	0.0159	0.0153
0.0100 „	0.0057	0.0069	0.0059
0.0050 „	0.00122	0.0022	0.00153

As is seen from the figures but little more hydrogen ions than chlorine ions are withdrawn from the solution by the charcoal. This was to be expected as the charcoal still contained some substance with an alkaline reaction (see above) which can react with the hydrogen ions, in consequence of which less mobile ions pass into the solution. In agreement with this fact we also find a value for the final concentration of the hydrochloric acid, calculated from the conductivity, which lies between the values of  $[H^+]$  and  $[Cl']$ .

From the above data we have also deduced how much  $H^+$  and  $Cl'$  were adsorbed in the different final concentrations. It was seen that in both cases the formula of the adsorption isotherm holds good:

$$\frac{x}{m} = \alpha c \frac{1}{n}$$

in which  $\frac{x}{m}$  represents the number of milli-equivalents adsorbed per one gr. of charcoal,  $c$  is the final concentration, and  $\alpha$  and  $\frac{1}{n}$  are constants.

In order to obtain further evidence of the fact that almost all the hydrochloric acid as such is adsorbed, and that there is no decomposition adsorption, I have made the following experiment. 2 grs. of charcoal was boiled for five minutes with 50 cc of 0,05 N. hydrochloric acid, during which time the water evaporated was continually replenished.

The charcoal was filtered off and washed with boiling water until the filtrate did not give any acid reaction with litmus paper. From the titration of the filtrate it was seen that in this case 1 gr. of charcoal had adsorbed 0,075 milli-equivalents of HCl (compare with the table above, referring to room temperature). This adsorbed quantity of hydrochloric acid passes but slowly into water. The charcoal was

Isotherm of [H<sup>+</sup>]

C	$\frac{x}{m}$ found	$\frac{x}{m}$ calculated	
0.0436	0.17	0.17	
0.015	0.13	0.13	$1/n = 0.25$
0.0057	0.109	0.102	$\alpha = 0.37$
0.00122	0.095	0.070	

Isotherm of Cl<sup>-</sup>

C	$\frac{x}{m}$ found	$\frac{x}{m}$ calculated	
0.0448	0.14	0.137	
0.0159	0.108	0.107	$1/n = 0.24$
0.0069	0.084	0.0874	$\alpha = 0.29$
0.0022	0.0735	0.0663	

washed again several times with small quantities of boiling water, until we had obtained a filtrate of 100 cc. After cooling it had a faint acid reaction on methylorange; it was seen that one gr. of charcoal had given off 0,015 to 0,02 milli-equivalents of HCl. In order to make the charcoal quite free from hydrochloric acid, we washed it with 5 cc of 0,02 N. sodium hydroxide and afterwards with boiling water. Acid- and chloride-determination indicated that all the hydrochloric acid had been removed.

From these experiments results that the molecularly adsorbed hydrochloric acid cannot be completely removed by washing with water. This fact is of importance, as most of the investigations, described in the literature, have been made with impure charcoals which had been treated with acid. All these charcoals probably contain a certain amount of molecularly adsorbed hydrochloric acid, so that it is likely that with these charcoals results are obtained totally different from those with the pure charcoal which I used in my investigations.

4. The charcoal which I used also showed good results in the adsorption of bases. I investigated the adsorption of sodium hydroxide and of baryta.

The table given below illustrates the results obtained with sodium hydroxide:

Experiments with 2 grs. of charcoal and 50 cc. of sodium hydroxide.

Initial concentration	C	$\frac{x}{m}$ found	$\frac{x}{m}$ calculated
0.05 N	0.044	0.15	0.187
0.02 ..	0.015	0.125	0.129
0.01 ..	0.0067	0.082	0.080
0.005 ..	0.003	0.05	0.032

$$1/n = 0.58$$

$$z = 1.45$$

We see that the adsorption-isotherm is rather unsatisfactory.

On the whole there is much less adsorption of salts than of acids or bases. From the determination of the concentration of the kation and of the anion in the filtrate, and usually also of the conductivity, was shown that we have here molecular adsorption of the electrolyte, and that there is no decomposition adsorption of ions.

Contrary to the results of E. J. MILLER<sup>1)</sup>, I have never observed a marked hydrolytic adsorption, not even with salts as ammonium chloride, metheleneblue chloride, and salicilate of sodium.

In the adsorption of the strongly hydrolysed sodium salt of veronal (medinal) I found that the hydroxyl ion concentration of the solution was strongly reduced after the adsorption. In this case there was a simultaneous adsorption of the salt itself, and of the sodium hydroxide which was set free by hydrolysis.

Finally I wish to call attention to the fact that the charcoal which was used, lent itself readily to the adsorption of non electrolytes, as iodine and phenol.

5. Without speculating on the nature of molecular-adsorption of electrolytes we must assume that the electrolyte is adsorbed by the charcoal as an undissociated molecule or, according to the modern views of N. BJERRUM and others as associated ions. It is to be expected that neutral salts which diminish the electrolytic dissociation of the electrolyte, will increase the adsorbability.

It is also to be expected that the amount of adsorption is a specific property of every electrolyte. When we compare the adsorbability of two strong acids under the same circumstances the result may be totally different. From the data in the following table we

<sup>1)</sup> E. J. MILLER. J. Am. Chem. Soc., 46, 1150 (1924).

see that these views are indeed correct. In the tests I used a sugar-charcoal with 0,08 % of ash. 2 grs. of charcoal were shaken with 50 cc of 0,05 N. solution of the acid, with the neutral salt of the acid, as well as without, after which the concentration in the filtrate was determined. In the table is noted the amount of acid in milli-equivalents per one gr. of charcoal adsorbed.

The specific character of the adsorbability is seen very clearly when we compare the behaviour of nitric acid and perchloric acid. Under the same conditions the adsorbability of the former is 4 times as strong as of perchloric acid, and trichloroacetic acid has a degree of adsorbability 7 times smaller than nitric acid. Phosphoric acid is practically speaking, not absorbed at all. Further we see that

2 grs. of charcoal with 50 cc. of 0.05 N. acid.

Acid used	Addition of salt	$\frac{x}{m}$ p. 1 g.
Hydrochloric acid	—	0.16
„	in 2 N KCl	0.29
Hydrobromic acid	—	0.16
„	„ 1 N KBr	0.26
Hydroiodic acid	—	0.27
„	„ 1 N KI	0.42
Nitric acid	—	0.28
„	„ 2 N KNO <sub>3</sub>	0.53
Perchloric acid	—	0.072
Trichloroacetic acid	—	0.042
Sulphuric acid	—	0.048
Phosphoric acid	—	0.02
Oxalic acid	—	0.46
Acetic acid	—	0.51
„	„ 2 N NaAc	0.55

neutral salts markedly increase the adsorbability of strong acids. In contrast with this the presence of acetate of sodium does not influence the adsorption of acetic acid. This was to be expected as the acid in 0.05 N. solution is for the greater part present in the undissociated state, so that the acetate of sodium raises the concen-

tration of the undissociated acid to a very small extent only. Finally I wish to observe that neutral salts on the whole have no influence on the adsorbability of non-electrolytes; on the contrary the adsorbability of sodium hydroxide and of salicylate of sodium is increased by the addition of neutral salts.

6. Now that we have demonstrated that electrolytes, as such, are adsorbed, and that the amount of adsorbability is a specific property of the electrolyte, it would be interesting to trace the influence of capillary-active substances, as phenol and amyralcohol, on the adsorption of electrolytes. Assuming that the adsorption is generally effected because a chemical affinity <sup>1)</sup> exists between the charcoal and the substance adsorbed, it is to be expected that capillary active substances, which are strongly adsorbed by charcoal, can replace the electrolytes. This indeed proved to be the case. The tests, the results of which are mentioned in the following table, have been made with 2 grs. of charcoal und 50 cc. of 0.05 N. solutions of electrolytes, without and with salt in absence and presence of 5 millimols of phenol or amyralcohol. (See table next page).

These figures prove that the strong electrolytes, to which, in this case also oxalic acid belongs, are practically totally removed from the charcoal by phenol. In this respect amyralcohol is less effective than phenol. The fact that we always find a small quantity of acid adsorbed when phenol is present, is to be attributed to the charcoal having a slight alkalinity. Neutral salts, as potassium, iodide, and salicylate of sodium are completely driven away from the charcoal by capillary active substances. Acetic acid, which also behaves like a capillary active substance is only partially driven away, as to be expected.

7. From the data, given in this preliminary paper, it follows that the adsorption of electrolytes in any commercial charcoal containing many impurities, is a very complex phenomenon. In the first place we have the molecular adsorption of the electrolyte, as described above. But at the same time the so called replacing adsorption appears, in which one ion can react chemically with one of the impurities of the charcoal. As both adsorptions always take place simultaneously, the results can never lead to a general conclusion. If the displacement adsorption alone is to be investigated, a capillary active substance must always be added, in order to repress completely the molecular adsorption of the electrolyte. A further investigation is

<sup>1)</sup> Cf. N. SCHILOW and L. LEPIN, Z. Physik. Chem. **104**, 25, (1920).

Influence of capillary substances on the adsorption of electrolytes.

Electrolyte used	Addition of salt	$\frac{x}{m}$ without capillary active subst.	$\frac{x}{m}$ in presence of	
			phenol	amylalcohol
Hydrochloric acid	—	0.16	0.03	0.04
„	2 N KCl	0.29	0.03	0.04
Hydrobromic acid	—	0.16	0.04	
„	N KBr	0.26	0.04	0.045
Hydroiodic acid	—	0.27	0.02	
Nitric acid	—	0.28	0.015	0.08
„	2 N KNO <sub>3</sub>	0.53	0.05	0.08
Oxalic acid	—	0.51	—	0.01
Acetic acid	—	0.51		0.23
Sodium hydroxide	—	0.035	0.00	0.01
„	2 N KCl	0.08	0.01	0.02
Potassium iodide	—	0.02	0.00	
Salicylate of sodium	—	0.042	—	0.001
„	2 N KCl	0.057	—	0.007

already being made along these lines, and I have already obtained results which clear up former anomalies. A further paper on this subject will treat this matter more exhaustively.

#### S U M M A R Y.

1. A molecular adsorption of electrolytes takes place on pure charcoal.

2. Neutral salts increase the adsorbability of strong electrolytes.

3. Capillary active substances prevent or decrease the adsorption of electrolytes on pure charcoal.

4. A marked, so called "hydrolytic adsorption" on pure charcoal has not been observed.

5. A molecular- and an ion adsorption takes place simultaneously on charcoal with impurities. Both phenomena differ completely in nature. If adsorption of ions alone is to be investigated the addition of some capillary active substance is necessary to prevent molecular adsorption.

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