[CONTRIBUTION FROM THE GRADUATE SCHOOL AND THE DEPARTMENT OF PHYSIOLOGY OF THE UNIVERSITY OF MINNESOTA]

The Influence of Salts on the Adsorption of Strong Acids

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The adsorption of strong electrolytes in aqueous solution on charcoal is not very well known. It is complicated particularly owing to the fact that we are always dealing with the adsorption in a mixture of solutes, the single ions having their own characteristic adsorbability, although influencing each other markedly. The presence of the strongly adsorbable hydrogen and hydroxyl ion also causes special effects, first investigated thoroughly by Bartell and Miller (hydrolytic adsorption). The correlation of these effects to small amounts of adsorbed gases such as oxygen and hydrogen was studied extensively by Frumkin and his collaborators.

Another exceptional feature of electrolyte adsorption was discussed some years ago by Rona and Michaelis[1]: although acids and alkalies are, as a very general rule, much more strongly adsorbed than their salts, the presence of salt may change the adsorption of hydrogen and hydroxyl ion pronouncedly, increasing it up to 50% and more. These authors observed this behavior for adsorption by "animal charcoal" in solutions of hydrochloric acid + potassium chloride; nitric acid + potassium chloride; sulfuric acid + potassium sulfate; sulfuric acid + cadmium sulfate; sodium hydroxide + sodium chloride; potassium hydroxide + potassium chloride. In most cases the range of concentration of the salt added was varied.

Rona and Michaelis consider this effect to be an electrical one. In a pure solution of hydrochloric acid hydrogen ion is prevented from being adsorbed according to its natural adsorbability, because the weakly adsorbable chlorine ion tends to remain in solution. Thus the actual adsorption is a compromise between the higher natural adsorption of the hydrogen ion and the smaller natural adsorption of the chlorine ion. A separation of hydrogen and chlorine ion can occur only to an infinitesimal amount, producing a potential drop at the surface of the charcoal. It was assumed by the authors that in a sufficient excess of potassium chloride there is enough chlorine ion at the surface to neutralize electrically any adsorbed hydrogen ion; hence the latter can be adsorbed more strongly according to its natural adsorbability. We would be dealing again with a so-called "swamping" effect[2] of an excess of neutral electrolyte, found to be most important in many phenomena (the "swamping" of diffusion potentials, the determination of diffusion coefficients of ions and colloidal ions, the ultracentrifuging of colloidal electrolytes, etc.).

It seemed worth while to test whether this influence of salts on the adsorption of acids and alkalies could be correlated quantitatively to other swamping effects and whether a similar interaction occurred between other ions in adsorption.

Our experiments were done in part with fairly pure sugar charcoal (obtained from E. H. Sargent, Chicago, Ill.; the ash content was 0.3%) which had not been markedly activated. Generally 3 g. of charcoal was shaken with 50 ml. of the solution for two hours; after that in all acid solutions a well-defined equilibrium was reached. The solutions were all analyzed previous to the adsorption. After the adsorbent had been separated by contrifuging, the solution was analyzed again; in some cases the concentration of all ions in question was determined. With this charcoal the adsorption of hydrochloric acid was so weak that it seemed desirable to use a more strongly adsorbable substance, although the increase in the adsorption of hydrochloric acid by adding potassium chloride was quite distinct. Experiments, therefore, were done with solutions of thiocyanic acid which is much more adsorbable than hydrochloric acid, but is practically quite as strong an electrolyte.[3] It was prepared by precipitating a solution of barium thiocyanate with an equivalent amount of sulfuric acid. Figure 1 represents the adsorption isotherms of the acid in pure solution and in presence of a 0.5 N solution of potassium thiocyanate; a is the amount adsorbed in milliequivalent per gram charcoal, c the equilibrium concentration in moles per liter. The increase in adsorption of the hydrogen ion is very distinct. The adsorption of potassium

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(1) P. Rona and L. Michaelis, *Biochem. Z.*, **97**, 85 (1919); *cf.* also I. M. Kolthoff, *Proc. Koninkl. Akad. Wetenschappen Amsterdam*, **27**, 742 (1924), and *Rec. trav. chim.*, **46**, 549 (1927).

(2) S. Arrhenius, *Z. physik. Chem.*, **10**, 51 (1892), and particularly R. Abegg and E. Bose, *ibid.*, **30**, 545 (1899).

(3) *Cf.* Wilhelm Ostwald, *J. prakt. Chem.*, **32**, 305 (1885).

thiocyanate in pure 0.5 *N* solution is much weaker than that of the acid as will be discussed more fully later.

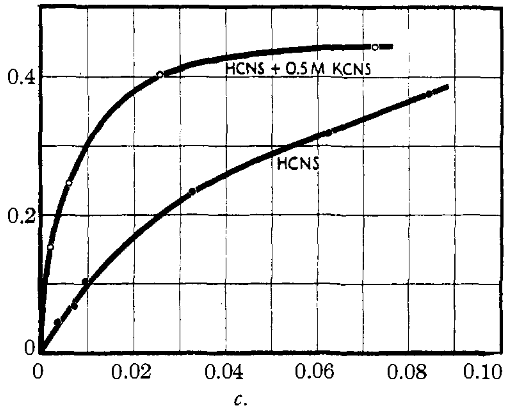

Fig. 1.—Adsorption of thiocyanic acid on unactivated sugar charcoal alone and in the presence of 0.5 *M* potassium thiocyanate.

If the effect shown in Fig. 1 were an electrical one, any other strongly dissociated salt added ought to exert more or less the same influence as the thiocyanate. This is not so: the addition to 0.01 *N* solution of thiocyanic acid of potassium chloride in amounts sufficient to give 0.1, 0.5 and 1.0 *M* solutions lowered the adsorption of hydrogen ion from 0.066 to 0.061, 0.055 and 0.056 milliequivalent per gram of charcoal, respectively; while the addition of equivalent amounts of potassium thiocyanate raised the adsorption of hydrogen ion from 0.066 to 0.136, 0.154 and 0.155 milliequivalent per gram of charcoal, respectively.

On the other hand, the addition of potassium thiocyanate in similar amounts to a 0.01 *N* hydrochloric acid solution raised the adsorption of hydrogen ion from 0.006 to 0.108 and 0.158 milliequivalent per gram of charcoal, respectively.

The objection might be raised that the experiments by Rona and Michaelis were done with an activated charcoal, ours not. We, therefore, repeated and extended these experiments after having activated the sugar charcoal mentioned by heating it for fifteen hours to about 900° in a covered porcelain crucible. The results are given in Table I.

On comparing this table with the values just mentioned it is seen that the adsorption of hydrogen ion is markedly greater than that caused by the non-activated charcoal. In all other respects the behavior is substantially unchanged: the adsorption of hydrogen ion in thiocyanic acid is increased strongly by thiocyanate, decreased by the chloride and the sulfate—the sulfate ion is also weakly adsorbed by charcoal; the adsorption of hydrogen ion in hydrochloric acid is increased weakly by the chloride, markedly by the thiocyanate, decreased weakly by the sulfate, etc.

TABLE I

ADSORPTION OF H^+-ION IN MIXTURES OF ACIDS AND EXCESSES OF SALT

Salt added	a_{H^+} HCNS 0.00936 *N*	a_{H^+} HCl 0.00956 *N*	a_{H^+} H_2SO_4 0.00912 *N*
No salt	0.478	0.260	0.084
KCNS (0.5 *N*)	.684	.705	.708
KCl (0.5 *N*)	.444	.303	.337
K_2SO_4 (0.5 *N*)	.380	.228	.099

We are obviously obliged to give up the explanation proposed by Rona and Michaelis, for this reason: these authors assume explicitly that the amount of chlorine ion adsorbed in a solution containing 0.01 *N* hydrochloric acid + 1 *N* potassium chloride does not differ essentially from that adsorbed in a pure 1 *N* solution of potassium chloride (there is then, as was said above, enough chlorine ion in the adsorption layer to allow the presence of hydrogen ion at the surface according to its natural adsorbability). The assumption made concerning the adsorption in the two solutions is actually not true. The amount of anion adsorbed in a concentrated pure salt solution is much smaller than the amount adsorbed when a small concentration of hydrogen ion is present. Using the unactivated charcoal the amount of thiocyanate ion adsorbed from a pure 0.5 *N* solution of potassium thiocyanate was 0.07 milliequivalent/gram charcoal in two independent experiments. The concentration of the potassium ion, determined by treating 5 ml. of the solution with an excess of sulfuric acid, evaporating to dryness and weighing as potassium sulfate, did not change in the limits of analytical error. The solution became in one case very slightly alkaline, in the other a change in *p*H was not perceptible. In a solution containing at the outset 0.01 *N* thiocyanic acid + 0.5 *N* potassium thiocyanate the amount adsorbed of hydrogen ion and accordingly of thiocyanate ion was 0.15 milliequivalent/gram charcoal as was calculated from the results given in the upper curve of Fig. 1.

The presence of a certain amount of hydrogen ion is always of paramount importance for the adsorption, even if the salt is very strongly in excess. The adsorbed hydrogen ion is neutralized at the surface by an equivalent amount of anion; in a mixture that anion is preferred which is more strongly adsorbable.

This is demonstrated by the data on the adsorption of various ions as given in Tables II and III, where c_a is the original concentration and c the equivalent concentration of a given ion in the solution, a being the amount adsorbed per gram of activated sugar charcoal. The chlorine ion was determined by the Volhard method after the thiocyanate ion had been removed by oxidizing it with concentrated nitric acid; the potassium ion by the method previously mentioned.

TABLE II

ADSORPTION OF IONS IN HYDROCHLORIC ACID SOLUTIONS

Ion	c_a	c	a
H^+	0.0102	0.0073	0.193
Cl^-	.0102	.0074	.186
KCl added in excess (0.0517 N)			
H^+	0.0102	0.0070	0.210
Cl^-	.0619	.0584	.230
K^+	.0517	.0519	.00
KCNS added in excess (0.1000 N)			
H^+	0.0102	0.0031	0.48
Cl^-	.0102	.0102	.00
K^+	.1001	.0999	.00
CNS^-	.0996	.0920	.51

TABLE III

ADSORPTION OF IONS IN THIOCYANIC ACID SOLUTIONS

Ion	c_a	c	a
H^+	0.0103	0.0054	0.33
KCl added in excess (0.1039 N)			
H^+	0.0103	0.0059	0.29
CNS^-	.0104	.0060	.29
K^+	.1039	.1039	.00
Cl^-	.1038	.1037	.00

Tables II and III show that the hydrogen ion is adsorbed pronouncedly together with about an equivalent amount of thiocyanate ion, while the potassium and the chlorine ion remain practically quantitatively in solution. This holds both when the thiocyanate ion in excess causes an increased adsorption of the hydrogen ion (Table II) and when the chlorine ion in excess causes a decrease in the adsorption of the hydrogen ion (Table III).

The discrepancy as to equivalence in the adsorption of cations and anions in Table II is just on the border-line of the accuracy of the analyses.

The essential difference between the influence of salts upon the adsorption of acids and the swamping effects quoted above consists in the fact that in swamping we are actually able to produce at will the higher concentration of anion in the space where we need it. This is not so, however, in these adsorption experiments, where the concentration of the different ions in the adsorption layer is, as it were, outside our sphere of influence; it may remain very small, even when the concentrations in solution are large. Hence the influence of added salt on the adsorption of hydrogen ion would be explained by the influence of the adsorbability of the anion added: the adsorbed amount of hydrogen ion increases, if in presence of one kind of anion the concentration of the latter increases and particularly if on adding a second kind of anion, the latter is more strongly adsorbable; it may decrease, if this second anion is weakly adsorbable.

We are dealing with a more involved phenomenon than would have been the case, if the explanation of Rona and Michaelis had been true.[4] Our explanation where mainly the ions and their specific adsorbabilities[5] are taken into account, may still be too simple, and we may have to consider the influence of "non-dissociated" electrolyte, of the so-called "pairs of ions." The presence of such ion pairs is widely supposed to change in a remarkable way the behavior of more concentrated electrolyte solutions.[6] We think they might become conspicuous in adsorption layers even at moderate concentrations in the solution.

An influence of the latter kind is perhaps indicated by the fact that lithium and sodium thiocyanate differ appreciably from potassium thiocyanate in the way they change the adsorption of thiocyanic acid, as is shown by Fig. 2. The experiments were done with the non-activated sugar charcoal. The abscissas are the concentrations of the salt added, the ordinates the amount of hydrogen ion adsorbed in a solution which always was 0.01 N at the outset. Up to about 0.25 N the three salts do not differ essentially. At higher concentrations the potassium salt behaves as would be expected from the data given above, whereas the lithium salt and still

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(4) We have discussed this question by letter with Dr. L. Michaelis. He would not like to repudiate the "swamping effect" entirely, but believes it may also come into play particularly when we are dealing with a very weakly adsorbable anion in absence of any foreign anion.

(5) The true values of these adsorbabilities can apparently not be determined experimentally. The difficulty may be analogous to the fundamental difficulty of determining absolute single electrode potentials.

(6) K. Fajans, *Naturwissenschaften*, **9**, 729 (1921); **11**, 165 (1923); K. Fajans and G. Karagunis, *Z. angew. Chem.*, **43**, 1046 (1930); K. H. Meyer and M. Dunkel, *Z. physik. Chem.*, Bodenstein-Festband, 553 (1931).

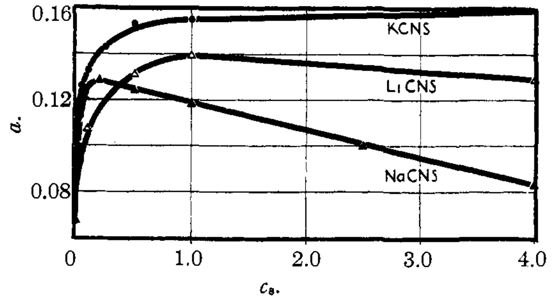

Fig. 2.—Adsorption of thiocyanic acid on unactivated sugar charcoal in the presence of its salts.

more the sodium salt cause a lowering of the maximum value of adsorption reached in moderate concentrations.

At very low concentrations there is no essential difference in the behavior compared to that in moderate concentrations of the salt added: in a pure 0.002 *N* solution of thiocyanic acid the amount adsorbed by the non-activated charcoal was 0.016 millimole/gram of charcoal; it increased to 0.021, if the solution contained also potassium thiocyanate in a concentration of 0.002 *N*.

Our experiments do not solve the complex question of the weak adsorption of a salt in pure solution.

Among our further results some done with alkalies may be mentioned. The adsorption by the non-activated charcoal was marked, but it is doubtful whether we are dealing with a pure case of adsorption: equilibrium was not reached in a short time, but the concentration went on decreasing for hours and days. Some experiments with potassium hydroxide where the solutions were shaken for a short time are given, nevertheless, in Table IV showing again a regular increase of uptake with increasing concentration of potassium chloride.

TABLE IV

ADSORPTION OF OH^--ION IN A MIXTURE OF POTASSIUM HYDROXIDE AND AN EXCESS OF POTASSIUM CHLORIDE

Absorbent: non-activated sugar charcoal

c_s	$a_{OH'(KCl)}$
0.00	0.080
.05	.096
.20	.108
.50	.116

We believe that our conclusions hold good, if all inorganic electrolytes in question are strong. With weak electrolytes, *e. g.*, benzoic acid, the behavior apparently differs in some respects and would need a special investigation. Here the difference in adsorbability between activated and non-activated charcoal was striking; a very strong adsorption by the activated charcoal, a surprisingly weak one by the other. With the non-activated charcoal the addition of sodium benzoate caused a pronounced decrease in the adsorption of benzoic acid.

Summary

1. The change in adsorption of hydrogen (and hydroxyl) ion caused by an excess of other inorganic ions was investigated using both an activated and a non-activated charcoal. The mixtures which were chiefly studied were: thiocyanic acid + potassium (lithium and sodium) thiocyanate; thiocyanic acid + potassium chloride (and sulfate); hydrochloric acid + potassium chloride (thiocyanate and sulfate); sulfuric acid + potassium sulfate (chloride and thiocyanate); potassium hydroxide + potassium chloride.

2. The assumption that the added salt always causes an increase in the adsorption of the hydrogen ion and that this is due to an electrical effect, a kind of "swamping," was found to be not true. Under some conditions the salt added was also able to decrease the adsorption of the hydrogen ion. This was the case, if the anion of the salt added in excess was less adsorbable than the anion of the pure acid which is present in a small amount. In low and moderate concentrations of the salt added the behavior observed could be explained by assuming that the adsorption of the hydrogen (or hydroxyl) ion was of paramount importance and that the latter is electrically neutralized at the surface by an equivalent amount of anion (or cation), the more adsorbable ion of opposite charge being markedly preferred.

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RECEIVED NOVEMBER 12, 1940