On the Adsorption of a NaCl-Solution by Sand

By

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I. Introduction

In our previous paper[1] on the contact surface of fresh- and salt-water under the ground near a sandy coast, we noticed that for the model experiments on the subject, the adsorption of salt water by sand may be an important factor which we must take into account. For, if salt water changed its concentration considerably by passing through a sand stratum, our theory on the problem might have greatly to be modified; and so it was quite necessary to decide the effect of adsorption experimentally.

In order to acquaint ourselves with the former investigations into this subject, we first looked into the literature of hydrology and water-supply engineering, but unfortunately we could no such reports as we had looked for. Accordingly, we were obliged to begin our own experiments upon the adsorption of NaCl aq. by sand, without any preliminary knowledge and only with the expectation that there would probably be some decrease in the concentration of the solution, going by the analogy of the effective action of a simple sand-filter to render even somewhat bad water drinkable. Contrary to our expectation, however, the result of the experiments showed that salt-water generally became more concentrated after percolating through the sand. Doubting whether this might be due to the evaporation of the water itself, we repeated the experiments thoroughly preventing evaporation, but the result was the same. Thus, we happened to think of the phenomenon

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1 These Memoirs A, **10**, 279 (1927)

of the so-called " negative adsorption," and for our further information we tried to learn, in magazines and in books on chemistry, of as many as possible similar investigations.

Here also, however, the studies on the adsorption of strong electrolytes were comparatively few, and especially for NaCl aq. We could find only the investigations with blood-charcoal by Lagergren,[1] Y. Osaka,[2] and Rona & L. Michaelis,[3] and with asbestos by N. Ishizaka,[4] but none with sand.

The nature of the adsorption was negative in the case of Lagergren and Osaka with a fairly concentrated solution, and positive with Rona & Michaelis and Ishizaka using very dilute solutions ; but the amount of adsorption was very small in every instance.

Now since the chief object of our experiments was to know what change in concentration would occur when NaCl aq. was passed through *sand in the natural state* whatever the cause might be, so we used the samples of sand mostly after mere drying. In such cases, of course, the change of concentration would involve the influence of the preexisting salt in the sand itself besides the adsorption-origin. Hence, in order to separate the adsorption-effect only, some of the samples were washed with pure running water for several days before the test.

From the geophysical stand-point, it is desirable to know not only the total amount of adsorption (or capacity for adsorption) by the sand ; but also the difference of adsorption according to the priority of the parts of salt-water which percolated through the same stratum of sand, the difference being again a function of the velocity of adsorption and the time required to pass through the sand stratum.

The capacity of adsorption is commonly represented by the well-known formula of Freundlich, namely

$$A = A_1 C^a, \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(1).$$

where A = the capacity of adsorption per unit quantity of adsorbent,

C = the initial concentration of the adsorbed material,

$A_1 \& a$ = characteristic constants concerning the nature of the two materials in contact.

But the mode of reaching the final state with time, especially the

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1   Freundlich, Kapillarchemie (1909), s. 165

2   These Memoirs 1, 257 (1915)

3   Biochem. Zeitschr, **94**, 240 (1919)

4   Zeitschr. f. Physik. Chemie, **73**, 385 (1910)

equational rule to represent it, is not yet well determined, so we propose the formula given below :

Let A be the capacity of adsorption as before and a the amount of adsorption at a time t after the two materials have come in contact, then the velocity of adsorption da/dt will obviously be a function of $A-a$, perhaps a linear approximately. Thus we may put

$$da/dt=f(A-a)=\beta(A-a) \text{ say,}$$

which gives

$$a=A(1-e^{-\beta t})$$
$$\text{and} \quad da/dt=\beta A e^{-\beta t}, \qquad \rbrace \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(2)$$

where β and A are constants characteristic of the system of adsorption.

In the experiments described below we carried them out in such a way that we could touch the adsorption-velocity as well as the adsorption-capacity.

II. Experiments

1. Samples of sand

The samples of sand used in the experiments were taken from the following six places :

Sample	Place	Remark
I	Drain near the dormitory of Kyoto Imp. University.	Much probability of containing salt of artificial origin.
II	4 meters below the ground near the office of the Science Department, Kyoto Univ.	Clean alluvial sand.
III	Slope of the hill, Kamigamo.	Containing some humus.
IV	A small branch of the rivulet, Shirakawa.	Clean river sand.
V	Rice-field at Shimogamo.	Black muddy soil.
VI	Top of the hill, Kamigamo.	Clean sand.

According to the diameters of the sand-grains we adopt the symbols below :

Diam. of grains		Sort of sand	Symbol
3-1	mm	coarse sand	a
1-0 5	,,	intermediate sand	b
0.5-0.2	,,	fine sand	c
0.2-0.05	,,	very fine sand	d
less than 0.05	,,	mud	e

For instance, sample I_b means the intermediate sand (1–0.5 mm) of sample I, and I_c the fine sand (0.5–0.2 mm) of the same sample. Moreover, I_c means that it contains from fine sand to mud (c, d, e,) of the sample I.

2. Method of experiment

Construct a filter as shown in Fig. 1. G is a open glass tube, W a sheet of wire-gauze applied to its lower end, and C a cork which holds two small pipes : one (T) for introducing salt water, and the other (T′) for communicating the atmosphere, to the interior of the main tube.

Fig. 1

Fill a portion of the glass tube with sand for the test, and introduce NaCl aq. of a known concentration through T.

It is desirable to keep the head of water in the tube always at as constant a level as possible, so that the water may percolate through the sand quite steadily.

R is a receiver for the water dropping from the lower end of the tube. Every time a certain amount of water (20 or 50 cc) has percolated into a receiver we change it for another, and titrate the chlorine in the water obtained with a solution of silver nitrate.

The cork C′ is for preventing evaporation of the drip water.

Now, in order to get a conspicuous change in the salinity of the water, it is obvious that the longer we make the tube for the sand, the better it may be. But too long a tube is inconvenient for treatment. After a number of trials, we learned that tubes of 50 to 100 cms. long are appropriate for both management and titration.

Thus the dimensions of the tubes finally adopted are as follows :

Tube	A	B
Whole length	100.0 cms.	65.0 cms.
Diameter	2.0 „	1.2 „
Height (h) of the stratum of sand	75.0 „	50.0 „
Height (h′) of the water column above the sand	25.0 „	15.0 „
Cross-section (S) of the stratum of sand	3.14 cm^2	1.13 cm^2
Volume of the stratum of sand	235.5 cm^3	56.5 cm^3

Tube A is for sand of coarse grains, and B for the fine qualities.
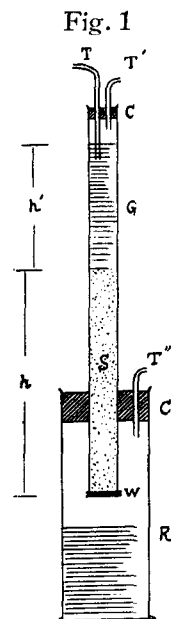
Next, as to the concentration of the NaCl solution, it will be, on the one hand, desirable to test with a solution similar to actual sea-water (mean salinity 35‰), but it is, on the other hand, not convenient for accurate titration. For with such a concentration, the precipitation of AgCl will be so great that, even when well stirred, a part of the indicator is apt to be occluded by it and consequently the end-point of titration is somewhat difficult to discern and the experimental error may be larger. Hence for a special sample (I_b) we examined the adsorption at various concentrations from 1/2 normal (very near to mean sea-water) to 1/100 normal, and determined the main features of the relation between adsorption and concentration. For all the other samples, however, we experimented only with a solution of 1/100 normal which is most adequate for titration, and we were satisfied to know the relative capacity and velocity of adsorption among all the sample of sand.

3. Result of experiments
(A) Relation of adsorption-concentration

In this group of experiments, the sand used was from just one kind of sample, I_b, which is the same as that employed in our previous model-experiment for the contact surface of fresh- and salt-groundwater. It is well washed with pure running water for several days before the test in order to remove the pre-existing salt in the sand. The tube employed was always of the type A.

We experimented on with the NaCl solution of various concentrations from $\dfrac{1}{100}$ to $\dfrac{1}{2}$ N.

But here we show the result of the measurments of only one case in detail, just as an illustration.

$$\text{Exps. with NaCl aq.} = \frac{1}{100}\text{N}, \quad \text{NO}_3\text{Ag aq.} = \frac{1}{100}\text{N}.$$
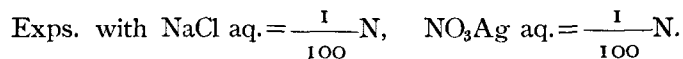
Titrating 10 cc. of the given solution of NaCl without passing the sand five times, we got

No.	AgNO$_3$ required to neutralise 10 cc. of NaCl aq.
1	10.01 cc.
2	10.00 ,,
3	10.00 ,,
4	10.01 ,,
5	10.00 ,,
mean	10.00 cc.

After the solution of NaCl had passed through the sand in tube A, its concentration was changed as follows:

No.	Volume of perco-lated water successively	AgNO$_3$ to neutralise 10 cc. of the percolated water	Change from the initial	1/10 of product of 2nd & 4th columns
1	50 cc.	10.85 cc.	0.85 cc.	4.25 cc.
2	50 ,,	10.41 ,,	0.41 ,,	2.05 ,,
3	50 ,,	10.02 ,,	0.02 ,,	0.10 ,,
4	100 ,,	10.01 ,,	0.01 ,,	0.10 ,,
5	100 ,,	10.00 ,,	0.00 ,,	0.00 ,,
6	100 ,,	10.00 ,,	0.00 ,,	0.00 ,,
				Sum = 6.50 cc.

Thus the total amount of NaCl adsorbed negatively by the sand must be equal to the salt in the initial solution of volume 6.50 cc.

Or, since the solution was $\frac{1}{100}$ N, the amount is 0.065 milli-mol.

Remembering the dimensions of the tube A on p. 268, we calculate the capacity of adsorption per 1 cc. of the sand as

$$0.065 \div 235.5 = 0.000275 \text{ milli-mol.}$$

In like manner we obtained the following table from our observed data:—

| C = Concentration	A = Capacity of negative adsorption per 1 cc. of the sand
0.01N	0.000276 milli-mol
0.02N	0.000469 ,,
0.05N	0.001163 ,,
0.10N	0.002161 ,,
0.20N	0.004529 ,,
0.30N	0.006312 ,,
0.40N	0.010516 ,,
0.50N	0.010423 ,,

Plotting these values as in Fig. 2, we see that the adsorption-capacity of this sand is approximately proportional to the concentration of the NaCl-solution.

Really, if we apply these values in eq. (1), we get

$$A_1 = 0.02154 \text{ milli-mol.}$$
$$a = 0.967$$

Fig. 2
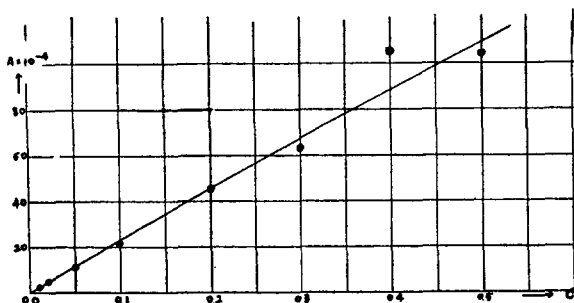
(B) Adsorption capacity of various samples of sand,
and adsorption-time relation

In this group of experiments we examined the various samples of sand with a NaCl-solution of a fixed concentration of $1/100$ normality. The sand taken was not washed with water as before, but was merely dried before the test, with the intention of keeping it in as natural a state as possible.

Exp. for Sample I_c, with Tube B.
Before passing through sand.

AgNO$_3$ aq. required to neutralise 10 cc. of NaCl aq.$=9.90$ cc. After passing through sand.

No.	Quantity of water percolated successively (ΔQ)	Time-interval (Δt)	AgNO$_3$ aq. to neutralise 10 cc of the sol.	Change from the initial (ΔC)
0	First drop.	13^m 35^s $(=t_0)$		
1	20 cc.	16 10	11.90 cc.	2.00 cc.
2	20 ,,	16 10	10.50 ,,	0.60 ,,
3	20 ,,	16 35	10.20 ,,	0.30 ,,
4	20 ,,	16 40	10.10 ,,	0.20 ,,
5	20 ,,	16 28	10.00 ,,	0.10 ,,
6	20 ,,	16 20	9.90 ,,	0.00 ,,
7	20 ,,	16 42	9.90 ,,	0.00 ,,

mean$=16^m$ $26.^s4$

In the table " the time interval for the first drop " means the time interval from the commencement of introducing water in the tube of sand to the instant when the first drop is about to fall into the receiver.

From the similar experiments we obtained the following table for the adsorption of salt by the various sample of sand. For reference, we give also the soil constant and the voids of each sample.

| Sample	Tube	Voids	Soil const	Capacity of negative adsorption per 1 cc of sand
$I_{\bar{c}}$	B.	46.3%	0.01380 cm/sec	0.001133 milli-mol
$II_{\bar{a}}$	A.	47.0 ,,	0.01848 ,,	−0.000036 ,,
III_c	B.	53.3 ,,	0.02365 ,,	0.000209 ,,
$IV_{\bar{a}}$	A.	50.3 ,,	0.00822 ,,	0.000349 ,,
V_e	B.	50.8 ,,	0.00058 ,,	0.000481 ,,
VI_c	B.	49.5 ,,	0.02178 ,,	−0.000542 ,,

The soil constants were calculated by the equation

$$k = \frac{\Delta Q}{S \cdot \Delta t} \cdot \frac{h}{h + h'}.$$

with the observed values of ΔQ and Δt in the above experiments, but the voids, of course, were found by another and independent method.

Secondly, if we plot the change in salinity with the quantity of percolated water, we get the graphs as Fig. 3, which corresponds to the Exp. with the sample I_e.

Fig. 3
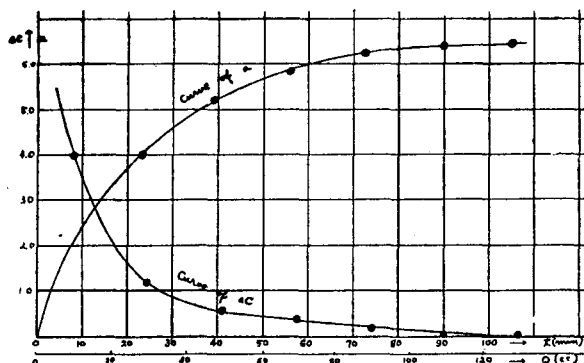
From these we can estimate also the velocity of adsorption as follows :

Let $t_0 =$ the time required from the commencement of introducing water over the sand to the instant at which the first drop of the percolated water is just about to fall the receiver,

$Q=$ the total volume of water filtered in time t' after the first drop.

Then the mean of the time during which the whole amount of sand has been in contact with the salt water may be taken as

$$t=t_0/2+t'$$

and Q must be proportional to time t', i. e.,

$$Q=Q_1 t', \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(3).$$

where Q_1 is a constant corresponding to

$$Q_1=\varDelta Q/\varDelta t=k\cdot S\cdot\frac{h+h'}{h}\dots\dots\dots\dots\dots\dots\dots(4).$$

On the other hand, if we calculate the value

$$\varDelta a=\frac{\varDelta C}{C}\cdot\varDelta Q$$

from the experimental data, it will represent the amount of salt adsorbed from the quantity of water $\varDelta Q$, the unit being taken as the quantity of salt contained in 1 cc. of the initial solution. And the sum of the successive values of $\varDelta a$ up to any instant, of course, gives the value of a at that instant.

Introducing these values of $\varDelta a$ or a into eq. (2), we can determine the value of β which is the measure of the velocity of adsorption.

The following are the results obtained.

Sample	I_c	II_a	III_c	IV_a	V_e	IV_c
β (Min.$^{-1}$)	0.044	0.151	0.045	0.014	0.001	0.094

Hitherto from our special object we passed the NaCl solution through the sand in a natural state without any other treatment except mere drying. Hence the resulting increase of salinity was due both to the effect of adsorption and also to the salt contained originally in the sand itself.

It is, however, sometimes desirable to know these two effects separately and for that purpose we tried the following two series of experiments :

i) Through the sand-tube we pass distilled water, instead of the NaCl solution, at an extraordinarily slow rate for which we close the

communicating holes T′ and T″ in the corks C and C′ of the sand tube (Fig. 1). The salt in the percolated water is measured as before, which, of course, was contained originally in the sand.

ii) On the other hand, we wash an amount of sample-sand with pure running water for several days, and then dry it completely. With this sand we examine the adsorption effect alone by passing the NaCl solution through it.

Sample.	Capacity of pure neg. adsorption (per 1 cc. of sand)	Salt contained originally (per 1 cc. of sand)
I_c	0.000159 milli-mol	0.001004 milli-mol
II_a	0.000032 „	—— „
III_c	0.000178 „	0.000031 „
IV_a	0.000255 „	0.000094 „