Chemistry. — *"The hydration of dissolved saccharose and the expression of the concentration in measuring the activity of ions."* By I. M. KOLTHOFF. (Communicated by Prof. H. R. KRUYT.)

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1. In an investigation on the influence of neutral salts on the concentration of hydrogen ions of dilute hydrochloric acid, of which a later communication will follow, the difficulty was how to express the concentration of the substances dissolved. This concentration is often measured in grams or mols of dissolved substance per liter of solution; others express it in grams or mols of dissolved substance per 1000 gms. of solution. In the measurements of osmotic pressure and related quantities the concentration is expressed in grammes of substance per 100 gms. of solvent, or in mols dissolved in a constant number of mols of solvent. When n mols of substance are dissolved in N mols of solvent the concentration is

$$x = \frac{n}{N}.$$

Finally the concentration can also be expressed in mols of dissolved substance in mols of solution, in other words, the concentration is

$$x = \frac{n}{n+N}.$$

In interpreting the influence of the concentration in measurements of osmotic pressure A. FINDLAY [1]) prefers the latter way of expression, and N. BJERRUM [1]) too uses it in calculating the activities of ions.

When experimenting with dilute solutions, it is immaterial which way of expressing the concentration is preferred. When, however, we experiment with liquids, in which the number of mols of dissolved substance is of importance with respect to the number of mols of solvent, the way how the concentration is expressed is of great importance.

2. In order to find out what way of expression is the most rational in my investigation, I have studied the influence of non-electrolytes on the concentration of hydrogen ions in 0.01 mol of hydrochloric-acid per liter of solution. The influence of saccharose was more particularly investigated.

As will be seen from what follows, saccharose practically does not influence the activity of hydrogen ions at this dilution of acid.

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[1]) A. FINDLAY, "The osmotic pressure" cited from N. BJERRUM, Z. anorgan. allgem. Chem. **109**, 275 (1920).

In the first place a series of experiments was made in which the concentration of the hydrogen ions is measured in 0.01 N hydrochloric acid, with and without the presence of saccharose. The measurements have been made with the hydrogen-electrode in the Physiological Laboratory of the University. The n calomel-electrode was used as standard half cell. The results obtained are given in the following table. 1.75 N as well as 3.5 N potassium chloride was used as a salt-bridge between the hydrogen- and calomel-electrode. By applying the extrapolation method of BJERRUM the diffusion potential could in this way be more or less eliminated. It is to be noted that this method could not be applied in solutions which contain more than 1 mol of saccharose per liter. The concentrations are expressed in mols per liter.

Concentration of hydrogen ions in 0.01 N HCl in a solution of saccharose.

Composition of the liquid	E. M. F. at 18° against N. C. E.	p_H	$[H^+]$
0 01 mol HCl p. liter	0.4041	2.040	0.91×10^{-2}
0.01 mol HCl + 0.5 mol of saccharose p. l.	0.3924	1.838	$1.45 \times$ —
0.01 „ „ + 1 „ „ „ „	0.387	1.744	$1.80 \times$ —
0.01 „ „ + 1.5 „ „ „ „	0.380	1.623	$2.4 \times$ —

These experiments show that the concentration of hydrogen ions of a solution of hydrochloric-acid apparently increases very much when saccharose is present. I have been able to confirm this result also with colourindicators. Of the liquids mentioned in the table above, $[H^+]$ was also colorimetrically determined with thymolblue and tropaeoline 00 respectively as indicator. The colour was compared with freshly prepared solutions of hydrochloric-acid, which were obtained by diluting 0.1 N HCl.

Colorimetrically determined $[H^+]$ of 0.01 N HCl in solution of saccharose.

Composition of the liquid	$[H^+]$ on thymolblue	$[H^+]$ on tropaeoline 00
0.01 mol HCl per liter	1×10^{-2}	1×10^{-2}
0.01 mol HCl + 0.5 mol of saccharose p. l.	$1.4 \times$ —	$1.32 \times$ —
0.01 „ „ + 1 „ „ „ „	$1.8 \times$ —	$1.75 \times$ —
0.01 „ „ + 1.5 „ „ „ „	$2.5 \times$ —	$2.1 \times$ —
0.01 „ „ + 2 „ „ „ „	5—$5.5 \times$—	

As is well known, thymolblue is an indicator which behaves as an acid, tropaeoline 00, on the contrary, as a very weak base. Yet, in the saccharose solution their indication of the concentration of the hydrogen ions is almost identical. Generally the values found with thymolblue are a little higher than those with the other indicator. This is explained by the fact that the dissociation constant of either indicator is very little diminished by the saccharose. The result is that thymolblue indicates a reaction which is a little too acidic, tropaeoline 00, on the contrary, a reaction slightly less acidic than is actually the case.

We may further observe that the agreement between the electrometric and colorimetric determinations is very satisfactory. It is seen that the concentration of hydrogen ions regularly increases with increasing concentration of saccharose. In a solution, containing 2.5 mols of saccharose and 0.01 N of hydrochloric-acid, I found, with thymolblue, a concentration of hydrogen ions of even $\pm 1.5 \times 10^{-1}$, consequently 15 times greater than might be expected according to the concentration of hydrochloric-acid (expressed per liter).

There is a great element of uncertainty in electrometric determinations. In liquids, containing hydrochloric-acid only, the diffusion potential, against potassium-chloride solutions, is rather large, so that the extrapolated value of the E.M.F. is at least 1 millivolt inaccurate. It is very difficult to find, when repeating the experiments, an agreement of 1 millivolt with the solutions mentioned.

Therefore another series of measurements has been made under the same circumstances; the difference is that all the liquids also contain 0.09 mol of potassium chloride per liter. A liquid containing 0.01 N HCl and 0.09 N potassium chloride is recommended by S. P. L. SÖRENSEN as standard in electrometric determinations of hydrogen ions. In agreement with SÖRENSEN we found that, in such a liquid at 18°, a hydrogen electrode has a potential against the N calomel-electrode of 0.4040 ± 0.0001 Volt.

I have made the measurements not only with the hydrogen electrode but also with the quinhydron electrode at 18°, using the quinhydron electrode in the standard hydrochloric-acid mixture as reference electrode. In this case the measurements could be reproduced to 0.0001 Volt.

When we refer the E.M.F. to the standard hydrochloric mixture the calculation of the change of p_H and $[H^+]$ is very simple, for the saccharose solutions contain the same quantity of hydrochloric acid and potassium chloride as the standard mixture. When π is the E.M.F. measured, the change of p_H is equal to

$$\triangle\, p_H = \frac{\pi}{0{,}0577}\,(18^\circ).$$

Moreover I have colorimetrically determined $[H^+]$ in the mixtures, by comparing them with solutions of hydrochloric-acid in 0.09 N potassium-chloride. The addition of the latter salt is absolutely necessary, as otherwise greatly divergent values are found. The presence of a minute quantity of salt has a rather great influence on the intensity and the tint of the indicators. I hope to return to this part of the subject in a future paper.

Measurements with the hydrogenelectrode in 0.01 N HCl, 0.09 N KCl and saccharose.

Composition of the liquid	π with resp. to 0.01 N HCl + 0.09 N KCl	Decrease of p_H by sacch.	Increase of the [H+] by sacch.
0.01 N HCl + 0.09 N KCl + 0.5 mol of sacch.	6.1 ± 0.4 m. Volt	0.104 ± 0.01	$1.27 \times \pm 0.03$
0.01 „ „ + 0.09 „ „ + 1 „ „ „	11.6 ± 0.4 „ „	0.201	$1.59 \times \pm 0.03$
0.01 „ „ + 0.09 „ „ + 1.5 „ „ „	18.4 ± 0.4 „ „	0.319	$2.08 \times \pm 0.03$
The same with the quinhydronelectrode.			
0.01 N HCl + 0.09 N KCl + 0.5 mol of sacch.	5.8 ± 0.1 m. Volt	0.101	1.26 times
0.01 „ „ + 0.09 „ „ + 1 „ „ „	12.5 ± 0.1 „ „	0.217	1.65 „
0.01 „ „ + 0.09 „ „ + 1.5 „ „ „	19.2 ± 0.1 „ „	0.334	2.16 „

Below are given the values which are found colorimetrically.

Compositon of the liquid	Increase of the concentration of the hydrogen ions with	
	Thymolblue	Tropaeoline 00
0.01 N HCl + 0.09 N KCl + 0.5 mol of sacch.	1.29 times	1.25 times (not sharp)
0.01 „ „ + 0.09 „ „ + 1 „ „ „	1.65 „	± 1.5 „ „ „
0.01 „ „ + 0.09 „ „ + 1.5 „ „ „	2.4 „	no accurate determination possible

The values found with thymolblue are probably a little too high. For the rest the agreement between the results is very satisfactory. Summarizing we find that by the presence of the saccharose the activity of the hydrogen ions apparently is increased ; on an average we find :

in a solution with 0.5 mol of saccharose per liter an increase of 1.27 ×
„ „ „ „ 1 „ „ „ „ „ „ „ „ 1.60 ×
„ „ „ „ 1.5 „ „ „ „ „ „ „ „ 2.1 ×

Some objections may be made to these results ; these we shall discuss first :

1°. It is possible that the constants of the hydrogen- and quinhydronelectrode are changed by the saccharose so that the method of calculation is inaccurate. This, however, is beside the truth, for I have also made measurements in buffer-solutions of different composition. In these the concentration of hydrogen ions is fixed, and is controlled by the relations of the undissociated acid and its anion. The total concentration of the two components is of subordinate value. Now I observed that the saccharose in the buffer-mixtures practically has no influence on the concentration of the hydrogen ions; the very small effect that was found points to a minute decrease of the dissociation constant of the acid, which occurs in the buffermixture.

2^0. It is possible that the sensitivity for hydrogen ions of the indicators used is changed by the saccharose. Indeed, the saccharose has a very slight influence on the dissociation constant of the indicators. The change which might be due to this influence, however, is much smaller than the effect we have observed. Moreover, the indicator tropaeoline 00 becomes a little less sensitive, so that in the saccharose mixtures it indicates a $[H^+]$ which is a little too low.

3^0. Saccharose itself is a very weak acid. The dissociation constant, however, is very small, about 2×10^{-13}, and the concentration of hydrogen ions of 1 or 1.5 N saccharose is of the order of only 10^{-6}.

On account of its acid nature the saccharose cannot increase the concentration of hydrogen ions of 0.01 N hydrochloric-acid.

The increase of the activity of the hydrogen ions in the presence of saccharose really exists. In the first instance we can explain this influence in two ways:

1^0. It is admitted that hydrogen ions in aqueous solution are hydrated and that the electrometric determinations give us only the concentration of anhydrous ions.

It would therefore be possible to assume that the dissolved saccharose has a dehydrating influence on the hydrogen-ions, so that more anhydrous ions appear. Then we should also have to admit that the colour indicators are sensitive only for anhydrous hydrogen-ions.

If this explanation were correct we should have to find that the saccharose would increase the concentration of hydrogen-ions in buffer-mixtures as much as in hydrochloric-acid. As is mentioned already this is not the case.

In solutions of organic acids saccharose has another effect than in hydrochloric-acid. We have found that 1 mol saccharose per liter increases the concentration of hydrogen-ions of hydrochloric acid 1.6 ×. In solutions of organic-acids $[H^+]$ also increases, and this not 1.6 ×, but less, namely so much as corresponds with an increase of the total concentration of 1.6 times.

2^0. The other explanation which remains is that the saccharose displaces the water in the solution; the concentration of the water, or, the free volume of the water, diminishes, and the concentration of the solute increases. This would lead us to deduce that the concentration of the acid must be expressed in mols of solute, dissolved in mols of solution or mols of solvent. In our case there is little difference between the two modes of expression; experimentally we cannot decide which is the correct one. It is obvious to express the concentration in mols of solution.

I could also prove another way that one of the two modes of expression is correct.

As is said above, saccharose increases the concentration of hydrogen-ions in weak acids. Carbonic-acid, however, behaves differently; saccharose slightly diminishes the concentration of H-ions. The reason is, that in a carbonic-acid solution the greater part of the acid is present in the form of CO_2 (about 99 %), and that a small part is in the acid form as H_2CO_3. The concentration of the latter is also dependent of the concentration of the water:

$$CO_2 + H_2O \rightleftarrows H_2CO_3$$
$$[H_2CO_3] = K\,[CO_2]\,[H_2O].$$

If the concentration of the water becomes a × smaller, $[H_2CO_3]$ also becomes a × smaller. On the other hand the total concentration of the acid becomes as many times greater by the displacement of the water by the saccharose. If therefore the saccharose has no influence on the dissociation constant of carbonic-acid, we should find that the reaction is not changed by the saccharose. We indeed find a slight decrease of the concentration of the hydrogen-ions, corresponding with a slight fall of the constant.

The difference between saccharose and a substance as aethylalcohol is very peculiar as regards their influence on the dissociation constant of weak acids. The latter is strongly diminished by aethylalcohol, but hardly by saccharose. The explanation probably is that solutions of saccharose in water have a rather great dielectric constant [1]). In this respect saccharose, as a solvent, may be compared with water.

3°. If, from what precedes, we conclude that the concentration of the solute must be expressed as $\frac{n}{N}$ (or as $\frac{n}{n+N}$) in which n is the number of mols of solute and N the number of mols of solution, we can calculate from the increase of the concentration of the hydrogen-ions, how great the free volume is of the remaining water.

For, if we find that in 1 liter of solution, containing 0.01 mol of saccharose, the increase is 1.28 ×, this means we have 0.01 mol of HCl in $\frac{1000}{1.28} = 780$ C. of water. According to the specific gravity of a saccharose solution of 0.5 molal (WINDISCH's table) the liquid contains 895 cc of water per liter. From this we may conclude that 0.5 mol of saccharose binds 895—780 = 115 cC of water.

If we consider this water as hydration water, it follows, from what is said above, that in 0.5 molal solution of saccharose 230 gms. of water are bound by 1 mol saccharose, corresponding to a hydration of 12.8 mols of water for 1 mol of saccharose.

On account of the uncertainty in the measurements, mentioned in sub. 2, this last figure is not very certain, and changes between 10 and 14 mols.

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[1]) Compare i. a. THWING, Z. Physik. Chem. **14**, 292 (1894).
DRUDE, Z. Physik. Chem. **23**, 305 (1897).

From the results of the measurements with the other saccharose solutions we can also calculate the hydration, and then we find :

Hydration of saccharose in solution.

Concentration of saccharose per liter	Mols of water per mol. of saccharose
0.5 molal	10 to 11
1 „	6.6 „ 11.2
(1.5 „	9.2 „ 10.8)

As a slight error in the determinations of the concentration of the hydrogen-ions causes a great change in the hydration calculated, the latter cannot be deduced from the measurements with great certainty. We can only give the order of magnitude approximately (about 10 mols of water per mol of saccharose), which of course will diminish in concentrated solutions.

4. If saccharose apparently increases the activity of hydrogen-ions in solutions of hydrochloric acid, this must also manifest itself when the inversion constant in concentrated solutions of saccharose is determined.

Data in the literature prove indeed that the constant increases with increasing saccharose content. J. SPOHR [1]) already gave an explanation for this anomaly, by pointing out that the concentration should not be expressed in gms. of saccharose per liter of acid solution, but per gms. of solution. If this is done we get, according to SPOHR, a constant which is independent of the concentration of the saccharose dissolved.

ERNST COHEN [2]) formulated the deviation found more clearly. According to him, the volume of the saccharose in solution should be deducted, in order to calculate the exact concentration of the acid. For, considered kinetically, in a stronger saccharose solution the space, in which hydrochloric-acid and saccharose can collide, is smaller than when the volume of saccharose is small. Therefore the constant found in a stronger saccharose solution will be greater than in a more diluted solution.

M. A. ROSANOFF, R. H. CLARK, and R. L. SIBLEY [3]) demonstrated that the inversion constant really becomes independent of the concentration of the saccharose dissolved, when the concentration of the acid is expressed in the quantity of water present.

ERNST COHEN assumes that the volume of the saccharose dissolved is independent of the solution. In this way he gets the equation :

$$k_{40} : k_{20} = \frac{1}{100-b_{40}} : \frac{1}{100-b_{20}}.$$

Here k_{20} and k_{40} represent the reaction constants in a saccharose solution

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1) J. SPOHR, J. prakt. Chem. **33**, 266 (1886).

2) ERNST COHEN, Z. Physik. Chem. **23**, 442 (1897).

3) ROSANOFF, CLARK and SIBLEY, J. Amer. Chem. Soc. **33**, 1911 (1911).

of 40 %, b_{40} is the volume of the dissolved saccharose in a solution of 40 %, b_{20} in a solution of 20 %.

In this way he calculates that 200 gms. of dissolved saccharose occupy a volume of 177 cc. According to the specific gravity this figure is 123 cc. Hence 200 gms. of saccharose bind 54 gms. of water, or 1 mol of saccharose 5.1 mols of water.

I have compared the values of the inversion constant found by W. OSTWALD [1]) and by J. SPOHR (l.c.) and moreover graphically deduced the value for a solution containing 0 % saccharose.

The figures are found in the following table:

Inversion constant at 25° according to OSTWALD, resp. SPOHR.

Concentration of sacch. p. 100 Cc	Constant of OSTWALD	of SPOHR
0 %	18.25	18.25
2 „	—	(20.47)
4 „	19.19	—
10 „	20.69	21.00
20 „	22.92	24.21
30 „	—	27.21
40	29.20	—

The value found by SPOHR in a solution of 2 % cannot possibly be good. For the rest the agreement between his values and OSTWALD's is not very fine. From the two series of observations I have calculated the inversion constant in a 0.5-, respectively 1 molal saccharose solution. At the same time is indicated how many times the inversion constant is increased, compared with the constant in a solution with 0 % of saccharose. In the two last columns the hydration of the saccharose has been calculated in the way as described above.

Hydration of saccharose according to inversion constant.

Concentration of saccharose	Inversion constant of		Increase of constant of		Hydration of sacchar. according to	
	OSTWALD	SPOHR	OSTWALD	SPOHR	OSTWALD	SPOHR
0.5 molal	22.25	23.4	1.22 ×	1.28 ×	8.3	12
1 „	26.90	28.4	1.47 ×	1.55 ×	6.2	8

In this way we therefore find for the hydration of the saccharose figures of the same order of magnitude as have been deduced from the increase of the concentration of the hydrogen-ions. Further we see from the last table

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[1]) W. OSTWALD, J. prakt. Chem. **31**, 316 (1885).

that the hydration decreases when the concentration of the saccharose increases.

5⁰. *Deduction of the hydration from other physical properties of solutions of saccharose.*

The relative decrease of the osmotic pressure by a dissolved substance is expressed by the equation :

$$\frac{p-p'}{p'}=\frac{n}{N}\left(\text{or }=\frac{n}{n+N}\right),$$

in which p and p' represent the osmotic pressure of the solution, respectively the solvent. From the measurements of the osmotic pressure of solutions of saccharose which have been made by H. N. MORSE and W. W. HOLLAND [1]) we cannot calculate the hydration with sufficient accuracy, as there is some irregularity in their figures. As this is the most accurate investigation on osmotic pressure of solutions of saccharose, we can draw from their figures this qualitative conclusion only, that the saccharose is hydrated.

A better result is reached with the data on the lowering of the vapour pressure, respectively the freezing-point of water by saccharose. Direct measurements of the vapour pressure of saccharose solutions have been made by A. SMITS [2]), who found the same figures as DIETERICI [3]).

Whereas the molecular lowering of the vapour pressure of saccharose in a very dilute solution is 0.084, it is 0.0902 in a solution of 1 mol of saccharose in 1000 gms. of water.

Hence the hydration of saccharose in the latter solution corresponds with 6 mols of water.

The most accurate measurements on the lowering of the freezing point of water by saccharose have been made by F. M. RAOULT [4]).

He found :

Grammes of sacch. in 100 g. of water	Molec. freezing-point depression
0	18.72
8.55	19.22
17.292	19.59
34.565	20.79

The molecular freezing-point depression increases with increasing concentration of saccharose ; we therefore get the impression that the

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[1]) H. N. MORSE and W. W. HOLLAND, Amer. Chem. J. **41**, 1 (1909).

[2]) A. SMITS, Z. Physik. Chem. **39**, 385 (1902).

[3]) DIETERICI, Wied. Ann. **62**, 616 (1897).

[4]) F. M. RAOULT, Z. Physik. Chem. **27**, 617 (1898).

concentration of the saccharose increases more strongly than seems to correspond with the figures in the first column. If we assume that this is caused by the hydration of the saccharose, we find in the solution, which contains 34.565 gms. of saccharose, not 100 gms. of free water, but only

$$100 \times \frac{18{,}72}{20{,}79} = 90 \text{ gms.}$$

Hence we deduce a hydration of 5.5 mols of water, and by analogy 5.3 for a solution containing 0.5 mol of saccharose per 1000 gms. of water.

If we express the concentration as $\frac{n}{n+N}$ instead of $\frac{n}{N}$, we find a hydration of 6.4 for a solution of 1 mol of saccharose in 1000 gms. of water, and of 6.0 for a solution of 0.5 mol of saccharose in a similar amount of water.

Viscosity : According to A. EINSTEIN [1]) the relative viscosity of a very dilute solution is :

$$\mu = 1 + 2{,}5\ v.$$

Here v represents the volume of the solute. BURKHARD [2]) has determined the relative viscosity of saccharose at 20° with great accuracy, and has found a value of 1.0245 for a solution of 1 %. By means of EINSTEIN's equation and the specific gravity we calculate a hydration of 6.8 mols of water per 1 mol of saccharose. In this way we find a hydration of 8 for a solution of 2 % ($\mu = 1.0521$).

Lowering of the solubility of substances in water in the presence of saccharose.

According to NERNST [3]) the relative lowering of solubility on account of the presence of a foreign substance is equal to the number of molecules of that substance, divided by the number of molecules of solvent, therefore :

$$\frac{L-L'}{L'} = \frac{n}{N}.$$

So we have here a similar equation as for the lowering of the freezing-point and analogous magnitudes.

However we must apply NERNST's rule with the greatest circumspection, for it is based on the fact that the foreign substance — in our case saccharose — does not function as a solvent.

I have determined at 18° the solubility of different substances in water, and in saccharose solutions, and it appeared indeed, that the rule usually cannot be applied here.

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[1]) A. EINSTEIN, Ann. d. Physik. **24**, 34 (1911); Koll. Z. **27**, 137 (1912).
Originally EINSTEIN (Ann. de Physik. **19**, 301 (1906)) had deduced the equation: $\mu = 1 + v$, which, however, he has corrected later on.

[2]) BURKHARD, Z. des Vereins der Deutschen Zuckerindustrie **24**, 199.

[3]) W. NERNST, Z. Physik. Chem. **6**, 19 (1890).

Here are a few examples :

Solubility of silveracetate.

Concentration of saccharose per liter	Concentration of silver-acetate per liter	Relative decrease of solubility in %	
0	0.0745 molal		
0.5 molal	0.0745 „	0 %	
1 „	0.0740 „	0.7 „	
	Solubility of sulfanilic-acid.		
0 „	0.0614 molal		
0.5 „	0.0591 „	3.5 „	
1 „	0.0524 „	15 „	
	Solubility of salicylic-acid.		
0 „	0.0125 molal		
0.5 „	0.0131 „	— 4.5 „	
1 „	0.0134 „	— 7 „	
	Solubility of bitartrate of potassium.		
0 „	0.0269 molal		(S. ARRHENIUS)[1]
0.5 „	0.0243 „	10 „	(15 %)
1 „	0.0208 „	22 „	20 „)

In the last table I have also given the figures for the lowering of solubility in potassium-acid-tartrate, which have been deduced from the observations of SV. ARRHENIUS. His results are not in agreement with mine.

From the figures found for the different substances we see that the relative lowering of the solubility on account of the presence of saccharose is not constant, but varies according to the nature of the substance. There is no doubt that the saccharose exercises a specific influence as a solvent.

It is to be expected that saccharose will have a much smaller specific influence on the solubility of gases, as the gases have a much smaller polar character than the substances mentioned in the table above.

In the following table I give a few results on the solubility of hydrogen (deduced from the determinations of P. STEINER[2]), and carbonic-acid (deduced from the determinations of A. CHRISTOFF[3])).

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[1]) SV. ARRHENIUS, Z. Physik. Chem. **31**, 226 (1899).

[2]) P. STEINER, Wied. Ann. **52**, 275 (1894).

[3]) A. CHRISTOFF, Z. Physik. Chem. **53**, 329 (1905).

In the first column the concentration of saccharose is given in mols per liter, in the second column the calculated molecular depression of the solubility by saccharose, and in the third column the hydration derived from it.

Solubility of hydrogen in saccharose solutions (STEINER).

Concentration of sacch. in mols per liter	Molecular depression of the solubility in %	Calculated hydration of saccharose
1 molal	32 %	7 mols of water

Solubility of carbonic-acid in sacch. solutions (CHRISTOFF).

Concentration of sacch. in mols per liter	Molecular depression of the solubility in %	Calculated hydration of saccharose
0.5 molal	42 %	12 mols of water
1 molal	33 %	7 mols of water

So we find here in 1 molal saccharose solution from the solubility of hydrogen, and of carbonic acid the same value for the hydration of saccharose.

6. *Discussion of the results.*

From the figures given for the hydration of saccharose we might suppose that the dissolved cane-sugar binds a certain number of molecules of water. This seems to me to be not the case. It is much better to assume that the saccharose possesses an affinity with respect to the molecules of water, which causes the latter to be "directed" in a certain position, by means of which the activity of the water, or the quantity of free water which remains, is lowered. It is not probable that all the molecules of the hydrate are in the same position ; it is rather to be expected that the molecules of water, nearest to the saccharose, have lost most of their free mobility. The farther they are distant from the molecule of saccharose, the less they have lost of their activity, so that we get a gradual transition of the decrease of the activity of the directed molecules of water, nearest to the molecule of saccharose, to the free water in the solution. The effect which we observe, and which we call hydration, is therefore an expression for the total decrease of the free mobility of the molecules of water. In the preceding paragraphs we have calculated the hydration of the saccharose from different sorts of experiments. A summary has been given in the following table ; here the hydration is given for a solution containing 1 mol of saccharose in 1 liter of solution.

Summary of the computed values of the hydration of saccharose (1 mol per liter)

Increase of $[H^+]$	Increase of constant of inversion	Lowering of vapour pressure	Lowering of freezing-point	Viscosity	Lowering of solubility of gases
7—11	6—10	6	6.4	6.4	7

This table gives rise to the following observations :

a. The value calculated from the increase of the concentration of the hydrogen-ions of a dilute solution of hydrochloric-acid by saccharose is very uncertain. A small error in the measurement of the E.M.F. causes a great change in the value of the hydration. Moreover we have assumed in the calculation that the saccharose does not change the activity of the hydrogen-ions at all. If this activity should decrease by the influence of the saccharose, the values for the hydration would be too small. The average value of 9 mols of water per mol of saccharose is therefore to be considered as a minimum.

b. In the derivation from the increase of the inversion constant we have assumed that the viscosity of the medium has no influence on the reaction velocity. It may be expected, however, that the greater viscosity diminishes the chance of collision, and that therefore also the reaction velocity is somewhat decreased.

In this connexion I wish to point out that ERNST COHEN [1]) has made very accurate determinations on the inversion constant in solutions of hydrochloric-acid, in 20 % of alcohol. Here the alcohol has no influence as yet on the activity of the hydrogen-ions. Yet COHEN found a decrease of the constant of 4%, with respect to solutions free of alcohol, which perhaps must be attributed to an increase of the viscosity of the medium. However, too little is known of the influence of the viscosity on the reaction velocity to be very certain on this point. The mean value of the hydration of 8 is in any case to be considered as a minimum.

c. As was to be expected, the measurements of the lowering of the vapour pressure, respectively of the freezing-point of water, give the same value for the hydration of saccharose.

The calculation has been made on the assumption that the hydrate water has a vapour tension of 0. This seems improbable to me ; for even in crystallized salts, with water of crystallization, the water has still a vapour pressure. This may also explain why, according to these two methods, we find too low a value for the hydration.

d. Neither is the value for the hydration, calculated from the viscosity, trustworthy. For EINSTEIN's equation, which is true for very dilute solutions only, may be applied only when the dissolved molecules are spheres, which have a large volume with respect to the molecules of the solvent among which they move.

Here too, therefore, we may consider as correct only the order of magnitude of the hydration calculated from the viscosity.

e. It has been observed already, that we have to be very careful with the explanation of the lowering of the solubility, in consequence of the presence of saccharose. Like glycerine, saccharose is also to be considered

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[1]) ERNST COHEN, Z. Physik. Chem. **28**, 144 (1899), where other literature is also referred to.

as a solvent, and from the examples, given sub 5, we see that some substances dissolve better in the presence of saccharose than in pure water (salicylic acid; also benzoic acid, which is not mentioned in the table). Further it is also possible that the water of hydration has a dissolving action.

Determinations of solubility of substances that have little or no polarity, as carbon dioxyde, and hydrogen, are more reliable for this computation. With the data given on this subject in the literature, we find a value for the hydration which agrees with the one found by other methods.

Summarizing we may say, that it is not possible to calculate the hydration accurately from physical data of saccharose solutions. Only the order of magnitude can be approximated, and then we come to the conclusion that a solution of 1 mol of saccharose per liter, contains 8 ± 2 mols of water as water of hydration.

Summary.

1. Sugar increases the concentration of hydrogen-ions of a solution of hydrochloric-acid.

2. This effect is explained by assuming that, when measuring the activity of ions, we must not express the concentration of the solute in mols per liter, but, as BJERRUM does, in mols of solute n per mols of solution $(n + N)$, therefore

$$x = \frac{n}{n + N}.$$

3. If we express the concentration in the way mentioned above, we find a slight increase of the activity of the hydrogen-ions by the presence of saccharose. This is to be attributed to the hydration of the dissolved saccharose.

4. The hydration of 1 mol of saccharose in 1 liter of solution has been calculated in different ways. We find an agreement in the order of magnitude, namely of 8 ± 2 mols of water per mol of saccharose.

5. The hydrate is not to be considered as a stoechiometric component of water and saccharose. It is probable that the molecules of water are directed by the saccharose in a certain position, so that the free mobility decreases. Hence the value which we calculate as hydration is in fact a measure for the decrease of the activity of the water by the dissolved saccharose.

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