

Chemistry. — *Wateradsorption on silicagel.* By P. KOETS. (Communicated by Prof. H. R. KRUYT.)

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1. *Introduction.*

During work on reactions in systems containing a considerable quantity of a hydrophilic colloid (starch, cellulose or gelatin) besides the reacting components, the question was met in which way the velocity of a reaction would be influenced by the presence of the hydrophilic surface, and whether the course of a reaction taking place at the surface or in the capillaries of a hydrophilic gel would differ from that in pure water.

Different authors, starting from considerations of heterogeneous catalysis, have already studied these problems in the case of a hydrophobic gel such as carbon or SnO_2 , and here it was found that a reaction may be accelerated or retarded by the addition of the carbon. These phenomena have been explained either by a molecular orientation in the adsorption layer¹), or as resulting from a change in concentration due to the preferential adsorption of one of the reacting components, or of the reaction products²).

It has been suggested that on account of the characteristic difference in wetting properties between a hydrophobic substance such as carbon and a hydrophilic one such as silicagel, a repetition of these experiments in the case of silicagel might be advantageous for our knowledge of heterogeneous catalysis.

It may indeed at first sight seem plausible to apply similar considerations of molecular orientation or preferential adsorption to a system containing silicagel, but further consideration shows that these influences will probably be entirely superseded by another phenomenon, viz. the adsorption of water itself and the formation of a hydration layer. This water layer may to a considerable extent inhibit the adsorption of other substances on the hydrophilic surface, perhaps even prevent it completely. In that case the result of the addition of silicagel to a reacting aqueous system will only be an acceleration of the reaction, due to the increase in concentration of all components.

1) KRUYT and VAN DUIN, *Rec.* **40**, 249 (1921).
VAN DUIN, *Rec.* **47**, 715 (1928).

cf. KRUYT, *Zt. Elektrochemie* **35**, 539 (1929).

2) FREUNDLICH, *Kapillarchemie*, IV Aufl., I, 324, 447
KOLTHOFF, *Rec.* **48**, 298 (1929).

3) NEWTON and GORTNER, *Bot. Gaz.* **74**, 422 (1922)
GORTNER, *Coll. Symp.* **1**, 392 (1923).

NEWTON and GORTNER³) have accepted the formation of the hydration layer in explaining the increment in the depression of the freezing point which they observed on the addition of a hydrophilic colloid to a solution of canesugar. KRUYT and WINKLER¹) have tested this explanation and by means of a dehydrating agent, viz. tannin, they were able to take away the waterlayer and at the same time the increment of the freezing point depression.

It should however be possible to place the correctness of this explanation, viz. the adsorption of water to the exclusion of other dissolved substances, beyond a doubt by simple analysis. This way has been chosen in the following preliminary investigation.

2. *The adsorption from canesugar solutions.*

For this purpose we studied the change in concentration of canesugar solutions in contact with a hydrophilic *gel*, the analysis of the intermicellary liquid of a sol still being rather doubtful.

In a well stoppered bottle a weighed amount of silicagel²), generally 5 gr., was added to 50 cc. of a sugar solution. The whole was placed in a thermostat at 25° for 2 hours, together with a similar bottle, containing the same solution as a blank. The concentration of the sugar was measured by means of a polarimeter in a 20 cm tube. In each case the blank was corrected for the original watercontent of the silicagel, varying from 5% to 25% in different samples.

A definite increase in concentration was always observed for the solution in contact with the silicagel. From this increase the amount of water was calculated which should be withdrawn from the blank in order to obtain the same change in concentration and this amount expressed per gram dry silicagel employed.

The results are tabulated here: (See table following page.)

From this we see that under varying circumstances of sugar concentration and of water content of the gel in every case so much water is adsorbed (or rather so much more water than sugar) till an amount of 0.30 gr. of water per gram silicagel is reached. In other words the mean concentration change of the sugar from the gelsurface to the bulk of the outer liquid is such as if a water layer amounting to 0.30 gr. H₂O per gram SiO₂ and impenetrable for the sugar were present next to the surface.

Now it is interesting to note here that the so-called second transition point, which VAN BEMMELEN³) observed, when studying the equilibrium watervapour-silicagel, is also found in most of his preparations at a water-

¹) KRUYT and WINKLER, *Zt. anorg. Chem.* **188**, 200 (1930).

²) Procured from N. V. Chemische Fabriek Gembo, in coarse bits. The original product was washed free from iron with hot hydrochloric acid, then washed repeatedly with boiling distilled water, till the p_H of pure water was not changed in contact with the gel.

³) VAN BEMMELEN, *Die Adsorption* (Dresden, 1910).

cf. e.g. KRUYT, *Colloids*, 2nd Ed., p. 237 ff.

	gr. gel		rotation (α_D)			Δ	gr. H ₂ O withdrawn per gr. gel
	wet	dry	blank	blank corr.	after ads.		
SiO ₂ 21 % H ₂ O	5.00	3.95	3.92	3.84	3.93	0.09	0.30
	5.00	3.95	48.61	47.61	48.99	1.38	0.36
	10.00	7.90	48.82	46.86	49.12	2.26	0.30
	5.00	3.95	65.77	64.66	65.96	1.30	0.30
	5.00	3.95	65.06	63.95	65.35	1.40	0.33
	25.00	19.75 ¹⁾	3.92	3.24	3.92	0.84	0.31
SiO ₂ 25.4 % H ₂ O	5.00	3.73	41.97	40.93	41.87	0.94	0.31
	10.00	7.46	41.97	39.94	41.75	1.81	0.30
SiO ₂ 5.7 % H ₂ O	4.18	3.94	37.61	37.40	38.30	0.90	0.30
	8.29	7.82	37.61	37.19	39.00	1.81	0.30
	4.22	3.98	42.14	41.90	42.92	1.02	0.30
	8.19	7.72	42.14	41.66	43.66	2.00	0.30

content of 1 mol H₂O to 1 mol SiO₂, that is of 0.30 gr. water per gram dry silicagel. It is assumed that at this point, where the gel becomes transparent once more, the capillaries of the gel are empty save for a waterlayer adsorbed on their walls, a view which is confirmed by the fact that beyond this point the dehydration of the gel follows a reversible adsorption isotherm.

If a correlation with our measurements in aqueous solution might be accepted, it would mean that the observed negative adsorption of the sugar is not so much due to the preponderance of the adsorbed water molecules over the sugar molecules, both being adsorbed next to each other, but rather to the adsorption of water alone, the sugar being practically entirely excluded. The orientation of the water molecules, becoming more rigid the nearer they are to the gelsurface, must then be taken to offer an increasing resistance to the penetration of the sugar molecules.

3. The adsorption from solutions of electrolytes.

When we add silicagel to a solution of an electrolyte such as KCl instead of to a solution of sugar, we shall meet with the keener competition between the gelsurface and the ions in solution for the possession of the water molecules. Especially those ions will exert their influence on the formation of the hydration layer of the gel which orientate the water mole-

¹⁾ In this case 25 gr. SiO₂ were added to 25 cc. solution instead of to 50 cc.

cules in the same way as does the gelsurface, that is, the negative ones in the case of silicagel.

The procedure was the same as in paragraph 2. As a rule 5 gr. of silicagel were added to a weighed quantity of solution and left in a thermostate at 25° for 2 hours next to a blank. The change in concentration of both ions was determined in the two solutions. Cl' and CNS' were found volumetrically by VOLHARD's method, K[•] and Li[•] gravimetrically as sulphates after evaporation of the solution and subsequent treatment with concentrated sulphuric acid.

n KCl.

5 gr. SiO ₂ (5.7 % H ₂ O) added to 25 cc. (26.162 gr.)	
mgr Cl' found per gr. solution	
in blank :	33.83, 34.02, 33.90 mean 33.92
after ads. :	34.45, 34.36, 34.40 mean 34.40
mgr K [•] found per gr. solution	
in blank :	38.39, 38.34, 38.45 mean 38.39
after ads. :	38.05, 38.02, 38.02 mean 38.03

Assuming again that only H₂O is adsorbed and eventually K[•] but no Cl' at all, we may calculate the amount of water withdrawn per gram dry silicagel to be 0.14 gr., instead of 0.30 gr. found for canesugar ¹⁾.

For KCNS, the anion of which is assumed to have a lower waterbinding capacity than the Cl-ion, we found :

n KCNS.

5 gr. SiO ₂ (5.7 % H ₂ O) added to 25 cc. (26.187 gr.)	
mgr CNS' found per gr. solution	
in blank :	54.35, 54.30, 54.31 mean 54.32
after ads. :	55.91, 55.77, 55.85 mean 55.84
mgr K [•] found per gr. solution	
in blank :	37.30, 37.05 mean 37.17
after ads. :	35.36, 35.43, 35.32 mean 35.37

From this 0.21 gr. water are found to be adsorbed per gram dry silicagel, which would mean that indeed the counteracting of the waterbinding by the silicagel is less in the case of KCNS than of KCl.

Using LiCl as the electrolyte in solution, we found :

n LiCl.

5 gr. SiO ₂ (5.7 % H ₂ O) added to 25 cc. (26.401 gr.)	
mgr Cl' found per gr. solution	
in blank :	63.73, 63.65 mean 63.69
after ads. :	65.10, 65.76 mean 65.43
mgr Li [•] found per gr. solution	
in blank :	12.63, 12.50 mean 12.56
after ads. :	12.75, 12.72 mean 12.73

¹⁾ The unequal adsorption of the two ions causes the solution to shift slightly to higher acidity.

Water adsorbed per gram dry silicagel is calculated to be 0.18 gr . The positive Li-ion is probably adsorbed on the gelsurface, and its waterbinding capacity being higher than that of the K-ion, the wateradsorption is higher than in the case of KCl.

The influence of other ions will probably also be in accordance with their place in the lyotropic series.

4. The adsorption from water-alcohol solutions.

It may be observed from paragraph 2 that the wateradsorption by silicagel is independent of the concentration of the sugar solutions. This fact becomes clear when we realize that even in the highest concentrations used, we are still far from any appreciable preponderance of the sugar molecules over those of the solvent, a 50 vol % sugar solution representing only a molar concentration of about 2.5 %.

In order to study the adsorption over the whole range of molar concentrations we determined the change of ethylalcohol-water solutions in contact with silicagel.

The necessary solutions were made up by weighing together absolute ethylalcohol and water into small flasks with well ground glass covers, 2 gr. of silicagel being added to 20 gr. solution.

The change in concentration relative to the blank was measured by means of a ZEISS interferometer¹⁾. A difficulty presents itself in this method at the higher concentrations of alcohol, the refraction-concentration curve passing through a maximum and therefore the differences in refraction between neighbouring concentrations approaching zero. For this reason we

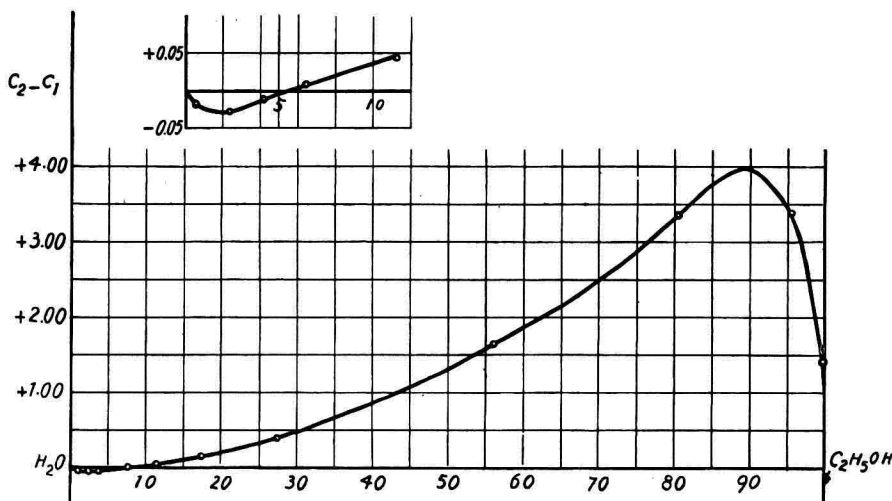


Fig. 1.

¹⁾ Kindly placed at our disposal by Prof. N. SCHOORL. For details of this instrument see: LÖWE, Chem.-Ztg. **45**, 405 (1921). COHEN and BRUINS, Zt. phys. Ch. **103**, 337 (1923).

diluted the solutions above 60 % alcohol by a known weight of water before taking their readings, thus allowing the comparison of the refractions to be made at a steeper part of the refraction-concentration curve.

The concentrations were recalculated and expressed in mole percent. The following changes were observed :

Alcohol conc.		Absolute change $c_2 - c_1$	Relative change $\frac{c_2 - c_1}{c_2}$
Blank c_1	After ads. c_2		
0.57	0.55	— 0.02	— 3.63 %
2.41	2.38	— 0.03	— 1.26 %
4.13	4.12	— 0.01	— 0.24 %
6.33	6.34	0.01	0.16 %
11.20	11.24	0.04	0.36 %
17.21	17.36	0.15	0.86 %
27.39	27.83	0.44	1.58 %
54.39	56.04	1.65	2.94 %
76.86	80.23	3.37	4.20 %
92.00	95.39	3.39	3.55 %
98.19	99.63	1.44	1.47 %

In fig. 1 the absolute changes are plotted against the equilibrium concentrations.

Only at the lower concentrations a positive adsorption of alcohol is found. At a concentration of about 6 mole percent (15 weight percent) no change is observed, alcohol and water being adsorbed in the same ratio in which they are present in solution. From all more concentrated solutions up to practically absolute alcohol a *preferential adsorption of water is found*. This adsorption shows a maximum at about 90 mole percent (95 weight percent) alcohol.

For the higher concentrations the negative adsorption of alcohol was confirmed by measuring the change in density by means of a pycnometer. The maximum was found in the same place as before. A quantity of 10 gr. silicagel to 30 gr. solution was used. (See table following page.)

The general trend of the apparent adsorption curve is in accordance with that found by BARTELL and FU¹⁾ for the adsorption from binary non-

¹⁾ BARTELL and FU, J. Physic. Chem. **33**, 1758 (1929).

aqueous mixtures by carbon, which they studied by measuring the heat of wetting.

These authors, having measured the adhesion tension of water against silica and calculated that of alcohol, state the adhesion tension of alcohol to

Mole percent alcohol		$c_2 - c_1$
Blank c_1	After ads. c_2	
26.33	26.99	0.66
44.58	46.15	1.57
79.50	83.24	3.74
90.36	93.13	2.77

be probably slightly below that of water. In accordance with the general principles developed by these authors we find that the component with the lower adhesion tension (in our case alcohol) is preferentially adsorbed only at low concentrations and then in small amounts. Moreover, the difference in adhesion tension between water and alcohol being small, the preferential adsorption of water, though undoubtedly present, does not give rise to greater changes than of about 4 % of the original concentrations.

I wish to express my indebtedness to Prof. H. R. KRUYT for the hospitality extended to me in his laboratory during the course of this investigation.

Valenciennes, March 1931.