

Adsorption of carbohydrates on anion exchangers

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ADSORPTION OF CARBOHYDRATES ON ANION EXCHANGERS

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ABSTRACT

Anion exchangers can be used for the conversion of glucose and lactose to mixtures of glucose and fructose and of lactose and lactulose respectively.

In this paper adsorption of these sugars on several ion exchangers is described. Experiments have been carried out for different sugar concentration levels at 278, 298 and 308 K. Three adsorption models are tested. Together with ionization data, the adsorption constants and heats of adsorption could be calculated.

INTRODUCTION

Ion exchangers can be used as catalysts for the conversion of carbohydrates. The various reactions occurring with ion exchangers have been discussed in a survey by Kunin [1]. One of these reactions, the isomerization of glucose and lactose has been studied by us [2].

These heterogeneous catalytic reactions, on strongly basic ion exchangers, are described as taking place in a pseudo-homogeneous solution within the catalysts. The amount of glucose, adsorbed within the ion exchanger, combined with the degree of ionization [3] determines the driving force for the chemical reactions. Expressions for these quantities are the basis of a mathematical model for the catalyzed isomerization of the carbohydrates mentioned.

Only a small number of authors have studied the adsorption of sugars on ion exchangers. Fujji et al. [5,6] measured the adsorption of sucrose, glucose and fructose on Amberlite IRA 900 and IRA 401. The result of the adsorption experiments with sucrose, carried out with concentrations between 2 and 60 mol m⁻³, could be described with a Freundlich relation [9]. Adsorption on IRA 900, increased in the order sucrose, glucose, fructose, while the adsorption of sucrose on IRA 401 was somewhat less than on IRA 900. Addition of KCl decreased the adsorption of sucrose linearly because the Cl⁻ adsorbed on the resin. Further there are the exploratory measurements by London et al. [7] and by Turton [8] and the reports by Shaw and Tsao [10,11] on the adsorption of glucose and fructose on a resin in the aluminate-form.

For our kinetic study we need a description of the adsorption of the different types of sugar on various types of ion exchangers as a function of the temperature and the concentration of the sugar in the solution outside the ion exchangers.

ADSORPTION MODELS

The commercially available anion exchangers are generally in the chloride form and are activated by the replacement of the strongly adsorbing Cl^- by the less strongly adsorbing OH^- [1,12].



The dissociation of the adsorbed sugar (S_{ie}^-) is enhanced by the presence of these hydroxyl ions. The sugar ion (S_{ie}^-) is more or less immobilized on the active sites. The adsorption of sugar anions can be described as:



with

$$C_{\text{OH}_{\text{ie}}^-} = C_{\text{OH}_{\text{ie}}^-, t=0} - C_{\text{G}_{\text{ie}}^-} \quad (3)$$

As the hydration of the different ions is supposed to be only a function of the temperature, no solvation water has to be taken into account to define the exchange equilibrium constant:

$$K_{\text{ES}} = y_{\text{S}_{\text{ie}}^-} \cdot C_{\text{S}_{\text{ie}}^-} / (y_{\text{S}_{\text{sol}}^-} \cdot C_{\text{S}_{\text{sol}}^-}) \cdot y_{\text{OH}_{\text{sol}}^-} \cdot C_{\text{OH}_{\text{sol}}^-} / (y_{\text{OH}_{\text{ie}}^-} \cdot C_{\text{OH}_{\text{ie}}^-}) \quad (4)$$

with y_i = activity coefficient of component i .

In the solution outside the resin the total ionic concentration is very low ($\text{pH} \sim 7$). According to the Debye-Hückel expression [3,13], combined with a molality molarity conversion, we can conclude:

$$y_{\text{S}_{\text{sol}}^-} \sim y_{\text{OH}_{\text{sol}}^-} \sim 1.00 \quad (5)$$

Inside the ion exchanger the total ionic concentration (I) for gel-type resins is about 4 mol kg^{-1} (see below), and is about equal to the concentration of the active groups. The ionic strength I is dependent on the amount of sugar adsorbed. For glucose, for example, I increases from 4.0 to 7.5 mol kg^{-1} when the coverage of glucose $\theta_{\text{G}} (= \theta_{\text{GH}} + \theta_{\text{G}^-})$ increases from 0 to 2 .

With the Debye-Hückel expression the activity coefficients at 298 K can be calculated:

TABLE 1

Calculated activity coefficients in a gel-type anion exchanger.

	y_{G^-}	y_{OH^-}	y_{G^-}/y_{OH^-}
$\theta_G = 0; I \sim 4.0$	0.69	0.36	1.9
$\theta_G = 2; I \sim 7.5$	0.68	0.32	2.1

The ratio y_{G^-}/y_{OH^-} hardly varies with the glucose concentration so that an average of 2.0 is used for all concentrations.

By substitution in relation 4 we obtain

$$K_{EG} = 2 \cdot C_{G_{ie}^-} / (C_{G_{sol}^-}) \cdot C_{OH_{sol}^-} / (C_{OH_{ie}^-}) \quad (6)$$

In the ionization model with solvation [3] the equilibria can be described with:

$$K_{G(h)}/K_{H_2O(h)} = \frac{C_{G_{sol}^-} \cdot C_{H_2O_{sol}}^{(1+h_{GH})}}{C_{G_{ie}^-} \cdot C_{H_2O_{ie}}^{(1+h_{GH})}} \cdot \frac{C_{OH_{sol}^-}}{C_{OH_{ie}^-}} = \quad (7)$$

in which

$$C_{H_2O_{sol}}' = C_{H_2O}/C_{H_2O,pure} \quad (8)$$

Substitution in relation 6 yields an exchange equilibrium constant in which the hydration is taken into account:

$$K_{EG(h)} = K_{EG} \cdot K_{H_2O(h)} / (2 \cdot K_{G(h)}) = C_{H_2O_{sol}}^{(1+h_{GH})} \cdot C_{G_{ie}^-} / (C_{G_{sol}^-} \cdot C_{OH_{ie}^-}) \quad (9)$$

As the ion exchange particles have no net overall charge, the electroneutrality requires that:

$$C_{NR_4^+} + C_{H_3O_{ie}^+} = C_{OH_{ie}^-} + C_{G_{ie}^-} \quad (10)$$

As $C_{H_3O^+} \ll C_{NR_4^+}$ the two sides of equation (10) are approximately equal to $C_{NR_4^+}$.

The coverage for component i can now be defined as:

$$\theta_i = C_{ie} / C_{NR4} + \quad (11)$$

Substitution in relation (9) gives for sugar S:

$$K_{ES(h)} = C_{H_2O_{sol}}^{(1+h_{SH})} / C_{SH_{sol}} \cdot \theta_{S^-} / (1 + \theta_{S^-}) \quad (12)$$

This exchange equilibrium model with hydration effects taken into account can be considered as an extension of the Langmuir model [14]. When in diluted solutions ($C_{H_2O_{sol}} \sim 1$) no hydration is assumed ($h_{SH} = 0$), equation 12 becomes the Langmuir equation:

$$K_{AS} = 1/C_{S_{sol}} \cdot \theta_{S^-} / (1 - \theta_{S^-}) \quad (13)$$

Some other adsorption models are:

Linear adsorption, with:

$$K_{Lis} = 1/C_{S_{sol}} \cdot \theta_{S^-} \quad (14)$$

Freundlich adsorption [9,15,16], with:

$$K_{FrS} = 1/C_{S_{sol}}^{\alpha'} \cdot \theta_{S^-} \quad (15)$$

Sips adsorption [17-21], with:

$$K_{SiS} = 1/C_{S_{sol}}^{\alpha} \cdot \theta_{S^-} / (1 - \theta_{S^-}) \quad (16)$$

These models will be discussed below in more detail when the experimental data of the adsorption of sugars on ion exchangers are described.

EXPERIMENTAL

The adsorption experiments were carried out under N_2 in a thermostatted stirred reactor of 200 cm³. A sugar solution was brought into the reactor and recirculated via the measuring and reference cell of a thermostatted refraction meter (Waters, R4). When the system was stable, the reference cell was shortcircuited and an amount of ion exchanger was added. Adsorption caused a decrease of the concentration of the solution. The solution was titrated with a more concentrated sugar solution to maintain the original concentration. In Figure 1 a block diagram is given.

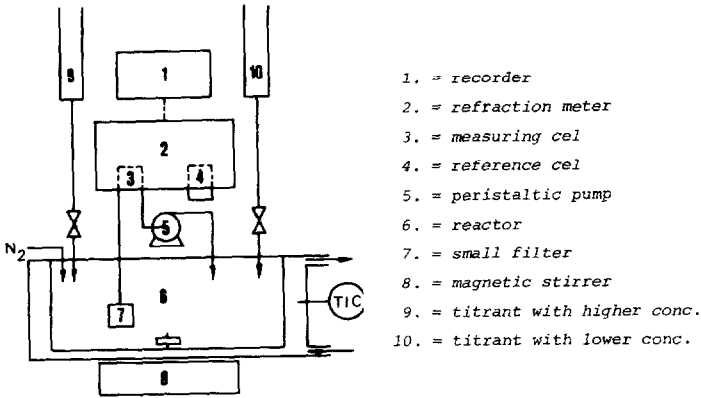


FIGURE 1 Block diagram for adsorption experiments.

To prevent chemical reactions, the experiment started at 273 K. When adsorption equilibrium had been reached, the temperature was raised with increments of 5 K. At these higher temperatures sugar desorbed from the resin, so the solution then had to be titrated with a more dilute solution.

A series of adsorption experiments was carried out covering a concentration range from 0.2 to 2000 mol m⁻³, temperatures between 273 and 313 K and the sugars glucose, fructose, mannose, lactose and lactulose. The exchangers IRA 401, IRA 900, IRA 904, IRA 938 and Lewatit M 504 were studied in this way.

RESULTS AND DISCUSSION

From the results of the adsorption experiments we can calculate the degree of coverage of a sugar (θ_s) and hence the pore volume and $C_{NR_4}^+$ (equation 8 and 9 of our previous paper [4]). The total sugar concentration inside the resin is:

$$C_{S_{ie}} = C_{SH_{ie}} + C_{S_{ie}^-} = (\theta_{SH} + \theta_{S^-}) C_{NR_4}^+ + \theta_{S^-} C_{NR_4}^+ \quad (17)$$

In another paper [3] the ionization of glucose in relation with the hydration has been discussed. To calculate the ionization of other sugars in the ion exchanger, the following assumptions are made:

- for the hydration phenomenon:

$$\begin{aligned} h_{F^-} &= h_{M^-} = h_{G^-} = 0 \\ h_{La^-} &= h_{Lu^-} = h_{FH} = h_{MH} = h_{GH} \\ h_{LaH} &= h_{LuH} = 2 h_{GH} \end{aligned}$$

- The ionization constants of the sugars are estimated from literature data [3]. The activation energies of K_G and K_F , measured by de Wilt [22], are used to estimate the influence of the temperature on the ionization:

$$\begin{aligned} pK_{G,298} &= 12.23 \text{ with } E_{\text{ion},G} = -17 \text{ kJ mol}^{-1} \\ pK_{F,298} &= 11.96 \text{ with } E_{\text{ion},F} = -22 \text{ kJ mol}^{-1} \\ pK_{M,298} &= 11.97 \text{ with } E_{\text{ion},M} = -20 \text{ kJ mol}^{-1} \\ pK_{La,298} &= 12.36 \text{ with } E_{\text{ion},La} = -17 \text{ kJ mol}^{-1} \\ pK_{Lu,298} &= 12.09 \text{ with } E_{\text{ion},Lu} = -22 \text{ kJ mol}^{-1} \end{aligned}$$

As the resin particles are electrically neutral, an electro-neutrality equation equivalent to equation (10) holds, so that it is now possible to calculate C_{SHie} , C_{Sie^-} and C_{H_2Oie} , and from these values, with equation 11, θ_{SH} , and θ_{OH^-} ($= 1 - \theta_S^-$). The actual evaluation of the adsorption data requires several numerical iteration operations.

INFLUENCE OF CONCENTRATION ON ADSORPTION

In Figure 2 the calculated θ_G , θ_{G^-} , θ_{GH} and θ_{OH^-} for the adsorption of glucose on IRA 401 at $278 \pm K$ is given. A concentration axis is added in this figure based on a pore volume of $0.59 \cdot 10^{-3} \text{ m}^3 \text{ eq}^{-1}$. To obtain a high accuracy, 56 experiments have been varied out for this condition.

In this figure we see that the adsorption increases with the concentration in the bulk. When the ionic and molecular adsorption are considered separately, two regions can be distinguished:

$$\text{region 1: } 0 < C_G < 150 \text{ mol m}^{-3}: \theta_{G^-} \sim \theta_G < 0.85; \theta_{GH} \ll \theta_{G^-}$$

Here, almost all of the adsorbed glucose is dissociated and the molecular glucose in the exchanger can thus be neglected.

$$\text{region 2: } C_G > 450 \text{ mol m}^{-3}; \theta_{G^-} \sim 1.0; \theta_{GH} \sim 1.0.$$

The coverage θ_{G^-} is constant and thus independent of the glucose concentration in the bulk. The glucose concentrations inside as well as outside the ion exchanger can be read directly from the figures. Some approximate data are given in Table 2.

When the adsorption is considered as a simple exchange of ions, it has to be described with $K_{ES(h)}$ (relation 12).

In Figure 3 $K_{ES(h)}$ is given as a function of the bulk glucose concentration C_{Gsol} .

It is clear that it is not possible to describe the adsorption over a wide range with the exchange coefficient (with hydration) $K_{ES(h)}$.

Although the Langmuir adsorption model is used in the literature to describe adsorption on resins [11,22,23], for the adsorption of glucose over the total concentration range, K_{AG} is even less valid than $K_{EG(h)}$ (broken line in Figure 3).

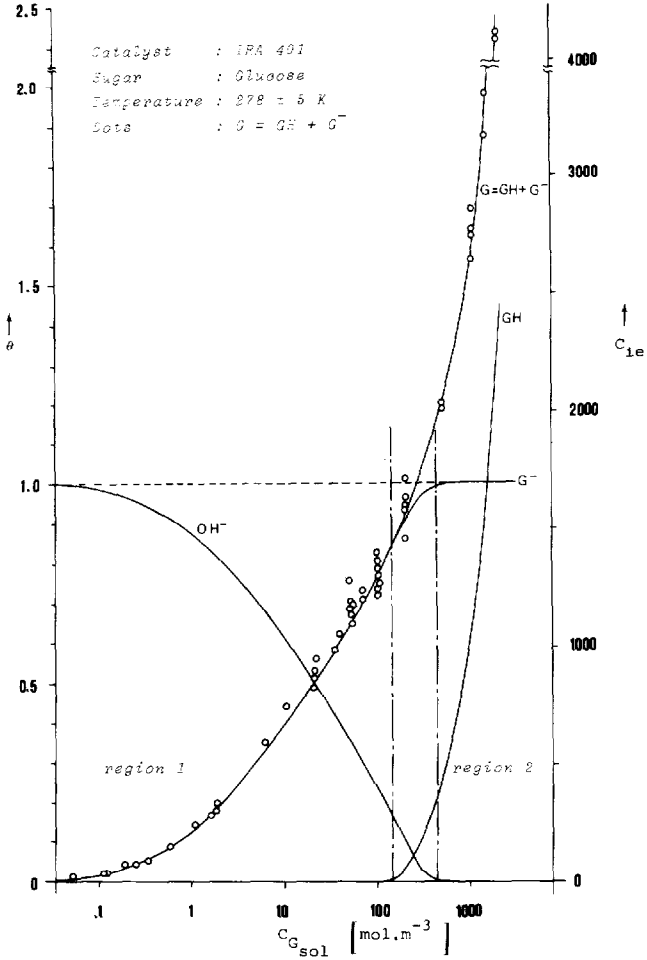


FIGURE 2 Adsorption of glucose on IRA 401 at 278 K.

TABLE 2

Approximate glucose concentrations inside and outside the ion exchanger, IRA 401 at 287 K.

in solution	inside the ion exchanger		
$C_{GH_{sol}} \sim C_{G_{sol}}$	$C_{GH_{ie}}$	$C_{G^-_{ie}}$	$C_{G_{ie}}$
1	~ 0	200	200
10	~ 0	600	600
100	~ 0	1600	1600
1000	900	1700	2600
2200	2500	1700	4200

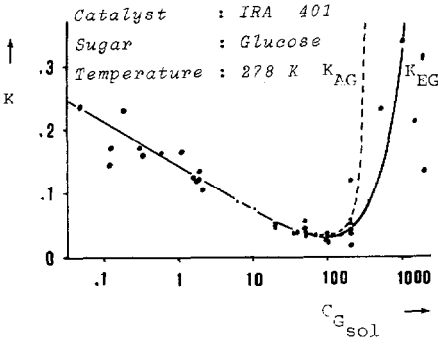


FIGURE 3 K_{AG} and $K_{EG}(h)$ as a function of C_G .

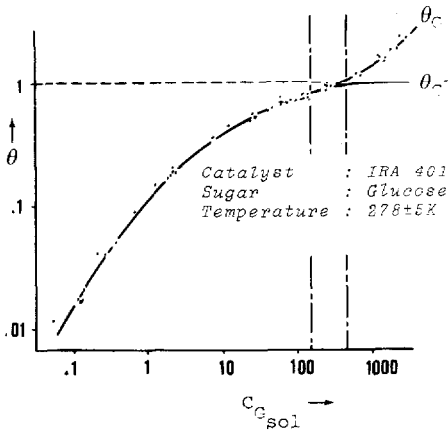


FIGURE 4 Adsorption of glucose on IRA 401 at 278 K according to the relation of Freundlich.

The average $NR_4^+ - NR_4^+$ distance is found [4] to be about 1 nm. Thus, when a glucose ion (molecular diameter about 0.8 nm) adsorbs on a NR_4^+ -site, it might hamper adsorption of G^- on neighbouring sites.

Fujji et al. [5,6] described the adsorption of sugars with a Freundlich relation. In Figure 4 the degree of coverage θ and the concentration in the solution are both plotted on a logarithmic scale, with the purpose to find a straight line in this figure. The figure shows that the linear relation, following from the Freundlich isotherm as found by Fujji, is not present; it can only be obtained for a narrow concentration range.

For the total range of concentrations the relation of Sips gives superior results. This isotherm (equation 15) can be rewritten as:

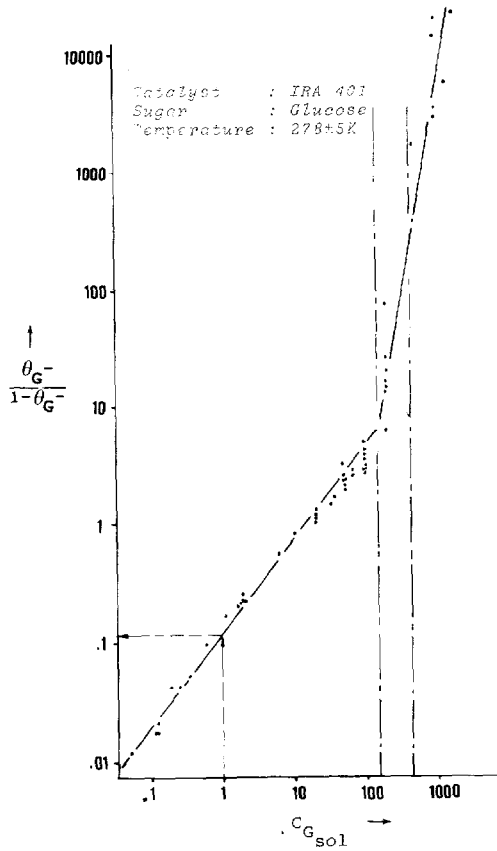


FIGURE 5 Adsorption of glucose on IRA 401 at 278 K according to the relation of Sips.

$$\log \frac{\theta}{1 - \theta} = \alpha \log C_{S_{sol}} + \log K_{SiS} \quad (18)$$

and this relation gives a straight line when $\theta_G/(1 - \theta_G)$ and $C_{G_{sol}}$ are both plotted logarithmically (Figure 5).

In region 1 as well as in region 2 the adsorption can be described with the Sips isotherm. The linear relation in region 2 is only of academic interest, as the coverage is about 1.0. From Figure 5 we read:

$K_{SiS,278} = 0.122$ and $\alpha = 0.67$. The value $(1 - \alpha)$ is a measure of the interference of adsorbed sugar anions with neighbouring sites.

The same type of relation is found for five types of sugars and five types of ion exchangers investigated.

For the isomerization not only the coverage of the resin but also the relative water concentration $C_{H_2O, free}$ and the residual C_{OH^-} are of importance. In Figure 6 the external as well as the internal water concentrations are given as a function of the external glucose concentration. These data were calculated with relation 35 from literature [3].

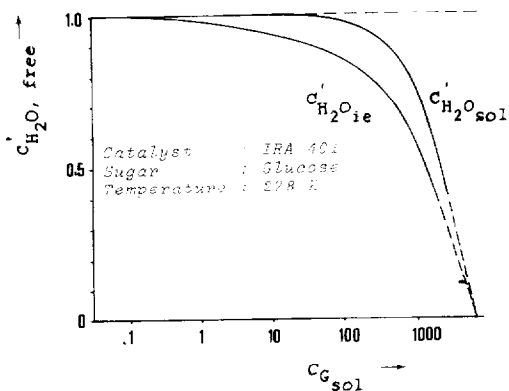


FIGURE 6 $c'_{H_2O, free}$ inside and outside the resin.

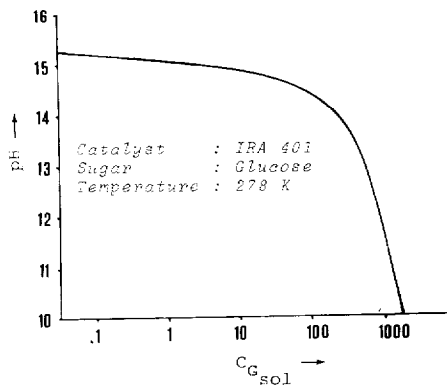


FIGURE 7 pH_{ie} as a function of $c_{G, sol}$.

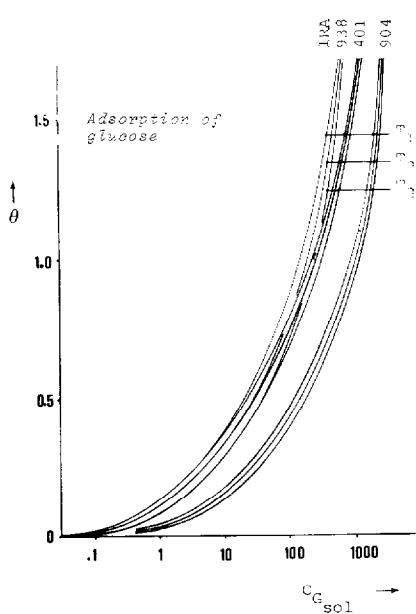


FIGURE 8 Adsorption of glucose.

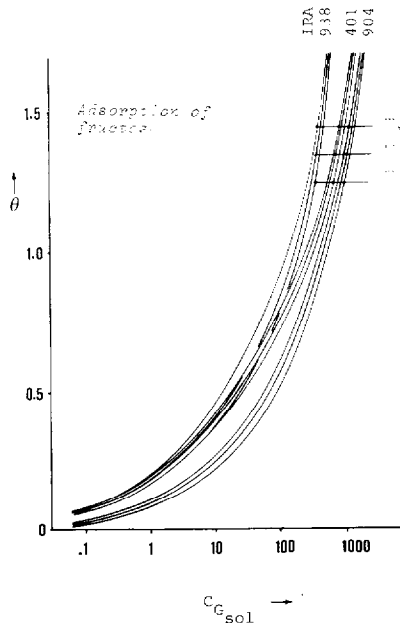


FIGURE 9 Adsorption of fructose.

The lower water concentration inside the resin reflects the sugar concentrating effect of the resins, as was shown in Table 2.

In Figure 7 the pH inside the ion exchanger, as calculated from the different relations, is given as a function of the external sugar concentration. At high concentrations this internal pH decreases strongly.

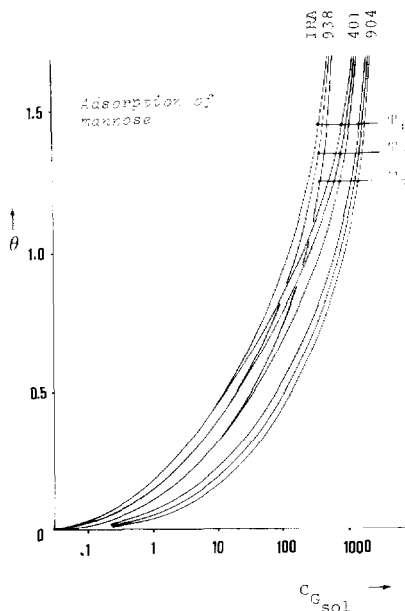


FIGURE 10 Adsorption of mannose.

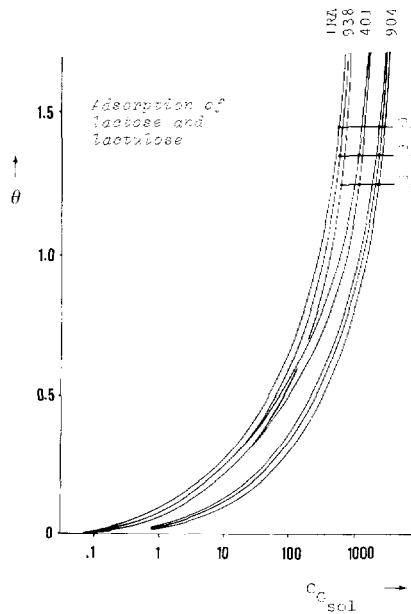


FIGURE 11 Adsorption of lactose and lactulose.

INFLUENCES OF TEMPERATURE ON ADSORPTION

The adsorption experiments have been carried out at temperatures from 273 K till 313 K with intervals of 5 K. As the temperature influence is relatively small, the experiments are lumped into 3 groups: $T_1 = 278 \pm 5$ K, $T_2 = 293 \pm 5$ K and $T_3 = 308 \pm 5$ K.

In the Figures 8-11 the degree of coverage is given for respectively glucose, fructose, mannose and the disaccharides lactose and lactulose. Each figure shows the adsorption on the resins IRA 938, IRA 401 and IRA 904 at the temperatures T_1 , T_2 and T_3 .

From these data the adsorption constant K_{SIS} and the exponent α in the Sips relation can be calculated as shown for glucose on IRA 401 at 278 K in the previous section.

According to Sips [18] the average heat of adsorption can be calculated with:

$$\ln K_{SIS} = \bar{Q}_{ads} \cdot \alpha / R \cdot T - \alpha \cdot \ln a \quad (19)$$

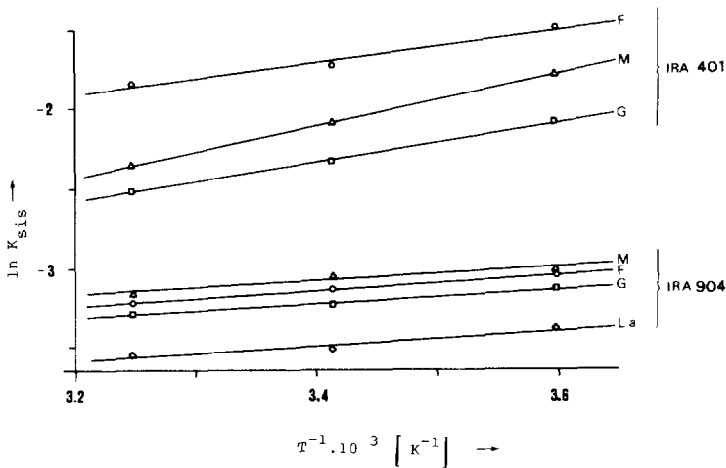
The final results are given in Table 3.

The exponent α tends to decrease slightly with increasing temperature. This means that the influence of an adsorbed sugar anion on surrounding sites increases with temperature, as would be expected.

TABLE 3

Adsorption constants according to the relation of Sips.

resin	sugar	K_{SiS}			Q_{ads}	α		
		278 K	293 K	308 K	$\frac{kJ}{mol}$	278 K	293 K	308 K
IRA 401	glucose	.122	.098	.080	14.7	.67	.64	.62
	fructose	.223	.175	.156	15.7	.52	.53	.53
	mannose	.165	.122	.094	19.5	.70	.68	.63
IRA 904	glucose	.043	.039	.037	6.0	.57	.56	.54
	fructose	.047	.043	.039	6.2	.66	.65	.64
	mannose	.048	.044	.042	5.1	.62	.61	.59
	La, Lu	.034	.031	.029	6.4	.52	.53	.53

FIGURE 12 Temperature dependence of K_{SiS} .

The markedly higher degree of adsorption for fructose, as compared with the other sugars on IRA 401, is reflected in a higher degree of interference as follows from the lower α .

In Table 3 and Figure 12 the differences in K_{SiS} (and Q_{ads}) are shown.

INFLUENCE OF TYPE OF SUGAR AND RESIN ON ADSORPTION

Table 3 and Figure 12 show that on IRA 401 mannose adsorbs more weakly than fructose, while on IRA 904 almost no difference is measured. Besides, the heat of adsorption of mannose for IRA 401 is greater than that of glucose and fructose, while for IRA 904 it is smaller. We have no explanation for this discrepancy.

For both ion exchangers, fructose anions adsorb more strongly than glucose anion. This is confirmed by a competition adsorption experiment in which ion exchanger was added to a solution containing equal quantities of glucose and fructose. After adsorption less fructose than glucose was found in the solution while in the exchanger there was more fructose than glucose.

Between the disaccharides lactose and lactulose no significant difference was found, but, as expected, the bigger disaccharides adsorb less well than the monosaccharides. The adsorption decreases with increasing diameter of the adsorbing molecule, at a particular porosity of the gel-phase of the resin.

The total adsorption of sugars on the macroreticular resin IRA 904 is lower than on the gel-type resin IRA 401, while IRA 938 has only a higher molecular adsorption (see Figures 8-11). These differences can be ascribed to differences in gel-phase porosity between the macroreticular resins. It was already concluded in literature [4] that the gel-phase of IRA 904 is less porous than that of IRA 938.

A decreasing porosity relative to the diameter of the adsorbing molecule decreases the adsorption too. This is in agreement with Svetlow and Demenkova [25], who found a decrease of the adsorption with decreasing porosity of gel-type resins, and with Martinola and Siegers [26], who stated that the adsorption in the gel-phase of macroreticular resins is relatively low. The adsorption behaviour of IRA 938 gives the impression that the gel-phase of IRA 938 is the same as the gel-phase of IRA 401. The higher molecular adsorption is apparently realized in the macropores.

The heat of adsorption of IRA 401 is significantly higher than on IRA 904. One would conclude that not only more but also stronger adsorption bonds are formed on IRA 401.

Also the adsorption on the gel-type resin Lewatit M 504 and the macroreticular resin IRA 900 was studied and appeared to be the same as for IRA 401. As the physical properties correspond to those of IRA 401 [4], we may expect that the other type I resins, which have all comparable properties, will show characteristics similar to IRA 401.

LIST OF SYMBOLS

C_i	concentration	mol m^{-3}
C_{NR4}	concentration of sites, related to the volume of the pores	mol m^{-3}
C_{H_2O}	relative water concentration	mol mol^{-1}
E	activation energy	kJ mol^{-1}
F	fructose	
G	glucose	
h_i	hydration number of sugar i	
I	ionic strength	mol kg^{-1}

K_{AS}	Langmuir adsorption constant	$m^3 \text{ mol}^{-1}$
K_{ES}	exchange constant	
$K_{ES(h)}$	exchange constant with hydration taken into account	$m^3 \text{ mol}^{-1}$
K_{FrS}	Freundlich adsorption constant	$m^{3\alpha'} \text{ mol}^{-\alpha'}$
K_i	equilibrium constant	$m^3 \text{ mol}^{-1}$
K_{LiS}	linear adsorption constant	$m^3 \text{ mol}^{-1}$
K_{SiS}	Sips adsorption constant	$m^{3\alpha} \text{ mol}^{-\alpha}$
La	lactose	
Lu	lactulose	
M	mannose	
pH	acidity: $\text{pH} = 3 - \log C_{H^+}$	
\bar{Q}_{ads}	average heat of adsorption	kJ mol^{-1}
R	gas constant	$\text{J mol}^{-1} \text{ K}^{-1}$
S	sugar ($S = SH + S^-$): G, F, M, La, Lu	
S^-	ionized sugar	
SH	molecular sugar	
T	temperature	
y_i	activity coefficient of component i on molarity scale	

GREEK SYMBOLS

α	exponent in the Sips adsorption isotherm	
α'	exponent in the Freundlich adsorption isotherm	
θ_i	coverage of component i	mol eq^{-1}

SUBSCRIPTS

h	hydration
i	component of number
ie	ion exchange resin
sol	solution outside
t=0	initial condition

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