# The Sorption of Polyalcohols from Aqueous Alcohol by Cation Exchange Resins

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The rate of sorption and the equilibrium distribution of glycol, glycerol, sorbitol and mannitol between aqueous alcohol and cation exchange resins has been studied. It has been found that the alcohol concentration has a predominating influence upon the rate of uptake. The equilibrium uptake increases considerably for an increase in alcohol concentration, but also the counter ions and the degree of cross-linking have an effect.

In| earlier papers [1-3] it has been shown that sugars, dissolved in a mixture of water and ethyl alcohol, can be taken up by means of ion exchange resins. It was found that considerable amounts could be sorbed especially at low water concentrations in the solution. In the present work these investigations have been extended to include another group of polar non-electrolytes, namely polyalcohols, and it is shown that these behave in a similar manner. Because of the poor solubility of sugars in ethyl alcohol the earlier investigations were restricted to systems with a considerable water content. The higher solubility of certain polyalcohols has made it possible to study the uptake also from an almost water-free medium. As mentioned in a preliminary report, the sorption of polyalcohols is much larger in nearly water-free solutions than in solutions more rich in water [4]. Also, the rate of sorption is highly dependent on the water concentration.

## EXPERIMENTAL PART

*Preparation of ion exchange resins.* The experiments were performed with the cation exchanger Dowex 50. The normally cross-linked resin (X8) with 8 % divinylbenzene as well as a resin (X2) with 2 % divinylbenzene were used. Most experiments were made with Dowex 50 X8 with a particle size of 0.2—0.4 mm obtained by grinding and screening in an air-dried condition (sodium form). In one experimental series (Table 1) the influence of the particle size upon the rate of sorption has been studied and in this case spherical beads of both types of resin have been used.

Before the experiments the resin was immersed in water and very fine particles removed by decantation. The resin was washed with hydrochloric acid and sodium hydr-

oxide solutions several times. The sodium state of the resin was air-dried and stored in tight bottles. When other ionic forms were needed the sodium form of the resin was weighed out and subsequently converted into the desired ionic form.

The exchange capacity was determined titrimetrically by treating the hydrogen form of the resin with potassium chloride solution and subsequently titrating with alkali [5].

In the experiments, samples of the air-dried ion exchanger (usually 7.80 mequiv.) were brought into equilibrium with aqueous alcohol of the same composition as that used as solvent. This equilibration was performed in columns of about 5 ml volume, by passing the aqueous alcohol through the resin. The apparatus used in the experiments with absolute ethanol permitted the ethanol to be supplied intermittently and the eluate collected without contamination by atmospheric humidity. Once or twice every day about 5 ml of ethanol was fed to each column until 100 ml effluent had been collected. Analysis of the effluent showed that its water content was about 3 % higher than it should be when calculated from the water content of the resin as determined by drying the resin over magnesium perchlorate at 60°C in vacuum. This would indicate that the last traces of moisture are not removed during the drying but there is also a possibility that — despite the precautions taken — water has been taken up from the atmosphere.

In the experiments presented in Table 1 the technique was altered in some respects. The ion exchangers were converted into the potassium form and air-dried samples weighed out in this state. Also in this series 7.8 mequiv. were transferred to each column, but all columns were treated simultaneously with absolute alcohol in a special apparatus. The time required to remove the water was around 40 days, but the treatment was continued for 60 days in order to make sure that all the samples were in equilibrium with the solvent.

Absolute alcohol was prepared from 99.5 % ethanol by treatment with magnesium powder [6].

*The sorption of polyalcohol.* After equilibration with the solvent, dried air was sucked gently through the columns at 30 — 40°C in order to remove the interstitial solution and to make it possible to empty the columns. The resin was transferred into 50 ml test tubes fitted with ground in stoppers. The empty columns were also placed in the test tubes in order to avoid any loss of resin. Into each test tube 40 ml of polyalcohol solutions were pipetted. The tubes were closed and rotated slowly in an air thermostat at 25.0 ± 0.1°C. After the desired contact time, the test tubes were taken out of the thermostat, and the solution was passed through a fritted glass filter, which had previously been dried.

*Analyses.* The water concentration in the solution was determined according to a modified Karl-Fischer method [7]. The concentration is expressed in weight per cent and all data given below refer to the solution after the contact with the resin.

The concentration of polyalcohol in the solution, before and after the experiments, was determined by oxidation with periodic acid [8]. The amount of sorbed polyalcohol was calculated from the decrease in solution concentration. No correction was applied for the change in volume of the solution.


### RESULTS AND DISCUSSION

The sorption is characterized by the ratio $m_r/m$, where $m_r$ is the amount of polyalcohol in the resin phase expressed in mmoles per equiv. ion exchanger and $m$ is the concentration of polyalcohol in the solution in mmoles per 1 000 g solvent. Where equilibrium has been established, this ratio, which will be called the sorption coefficient ($K_e$), can be used to characterize the equilibrium distribution. The original concentration of the solution is denoted by $m_o$.

*Rate of sorption.* In order to establish the time required for obtaining equilibrium some kinetic experiments have been carried out. Fig. 1 demonstrates the rate of uptake of glycerol using the lithium form of Dowex 50. Similar curves for the potassium form of the resin are shown in Fig. 2. The glycerol concentration in the original solutions (20 mmole/1 000 g solvent) was the same in all experiments incorporated in Figs. 1 and 2. It may be seen that the rate of uptake depends markedly on the alcohol concentration. This is in
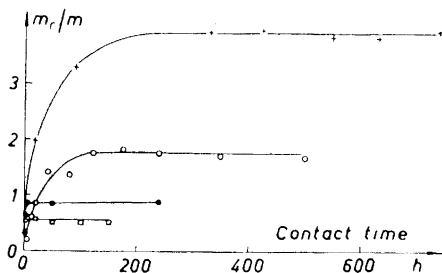
*Fig. 1.* The rate of glycerol sorption by the Li+-form of Dowex 50 from various ethanol-water mixtures. % water at equilibrium 0.06  0.6  7.5  12.6
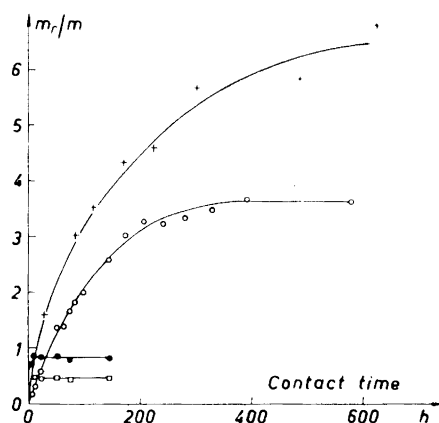       +   O   ●   □

*Fig. 2.* The rate of glycerol sorption on the K+-form of Dowex 50 from various ethanol-water mixtures. % water at equilibrium 0.06  0.6  7.5  12.6
       +   O   ●   □

agreement with earlier observations on the sorption of sugars [2]. At the highest water concentration in the solution (12.6 %) equilibrium is reached within one hour, whereas several hundred hours are required in the experiments at the lowest water concentration. A comparison between Figs. 1 and 2 shows that the lithium form of the resin reacts more rapidly than the potassium form. In ethyl alcohol, as well as in water, lithium ions cause a higher swelling of the resin than potassium ions [9], and in general ion exchange reactions occur at a faster rate the higher the swelling. This is ascribed to differences in diffusion velocity inside the particles. If the particle diffusion is the rate determining step, this explains the difference between the two forms of the resin. Experiments with solutions of glycerol in alcohol containing 7.5 % water showed that within wide limits (20—1 200 mmole/1 000 g solvent) the concentration of glycerol had only slight influence upon the time required for equilibrium. This is an indication that the influence of the film diffusion step can be neglected in these systems.

It is interesting to note that the rate of glycerol uptake decreases to a marked extent when the water content of the solution is lowered from 0.6 % to 0.06 %. For this reason it was deemed to be of interest to study in more detail the rate of uptake in an almost water-free system. The results obtained with a resin in the potassium form are presented in Table 1. In agreement with the results presented in Fig. 2 it has been found that the time required to reach equilibrium is extremely long. This is true not only for the normal cation exchanger but also for the weakly cross-linked resin (X2). The uptake obtained after 1 198 h has been considered as the equilibrium uptake. As the rate of uptake is extremely slow the film diffusion step cannot be rate determining.

Table 1. The rate of glycerol sorption by the K+-form of Dowex 50.
7.80 mequiv. resin + 40 ml alcohol (0.02 % water).
Initial concentration: 2.018 mg glycerol per g solution.

| Time of reaction h | Glycerol uptake, mg per 7.80 mequiv. resin | | | |
| | X2 0.037—0.074 mm | X2 0.14—0.29 mm | X8 0.300—0.385 mm | X8 0.75—1.02 mm |
| --- | --- | --- | --- | --- |
| 1 | 22.12 | 3.21 | 2.65 | 1.50 |
| 5 | 33.73 | 7.65 | 6.49 | 5.55 |
| 12 | 34.22 | 12.35 | 9.51 | 8.70 |
| 25 | 36.35 | 15.77 | 12.73 | 11.69 |
| 45 | 36.90 | 20.29 | 16.07 | 14.71 |
| 70 | 36.56 | 23.11 | 18.35 | 16.66 |
| 110 | 36.90 | 25.00 | 22.58 | 20.28 |
| 185 | 36.94 | 28.72 | 25.09 | 24.08 |
| 1 198 | 37.10 | 38.68 | 37.74 | 37.17 |
| 1 198 | 37.21 | 39.64 | 36.59 | 37.07 |

Consequently, either the diffusion within the particle or the sorption mecha-
nism or these two factors together must determine the rate of uptake. From
Table 1 it is evident that the particle size has a marked influence upon the
rate of uptake, which excludes the possibility that the sorption mechanism
is the rate determining step. This effect is most clearly demonstrated by the
results obtained with the weakly cross-linked resin (X2), whereas with the
normal resin (X8) this effect is surprisingly small. The explanation for the
different behavior of the two types of resin is given by the micrographs pre-
sented in Fig. 3. It may be seen that the weakly cross-linked resin consists
of intact spheres, whereas the normal resin contains a large number of cracked
particles. Consequently, the sorbed molecules may have about the same way
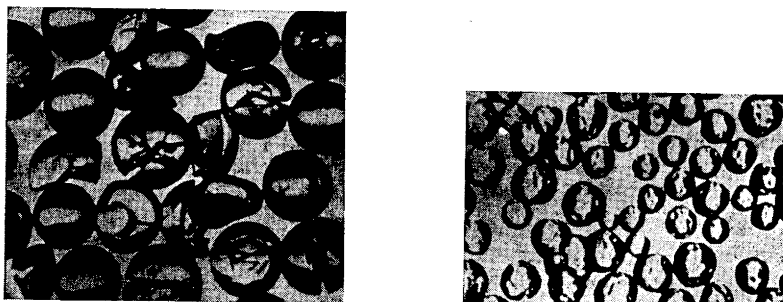to diffuse within the particles of the two samples of the X8 resin.



Fig. 3. Micrographs of the resins used in the kinetic experiment reported in Table 1.
Magnification 25 times.
A: Normally cross-linked resin.
B: Weakly cross-linked resin.

An attempt has been made to apply the theory of particle diffusion according to Boyd, Adamson and Myers [10]. In the present case the solute concentration was not constant throughout the experiment, therefore it may be expected that the equation given by these authors can be applied only to the first part of the reaction. The particle size was not uniform, which has made it necessary to make the calculation for small fractions of each sample. The particle size distribution of the samples has been determined microscopically and the weight distribution curve has been calculated. The diffusion coefficient obtained in this way is around $10^{-10} - 10^{-11}$ cm$^2$/sec for both samples of the X2 resin. For a comparison it may be mentioned that the diffusion constant for glycerol in 96 % ethyl alcohol [11] is $5.3 . 10^{-6}$ cm$^2$/sec. The results support the conclusion that the particle diffusion is the rate determining step.

As mentioned above, the differences in the rate of uptake between resins in different ionic forms can be explained by differences in swelling. The lowered swelling, which occurs when the water concentration is lowered, may to some extent explain the decrease in rate for a decrease in water concentration. However, the decrease in swelling corresponding to a change in the water concentration from 0.6 % to 0.06 % is so small that it can hardly be determined experimentally (less than 2 %). Consequently, the influence of the water concentration upon the swelling does not give the whole explanation of the differences in the rate of sorption in different solvent mixtures. It must be observed that the water content given in Figs. 1 and 2 refers to the outer solution. Within this range of concentration the water content in the resin phase is considerably higher [9]. From available data it can be roughly estimated that, at an outer concentration of 0.6 % water, the inside concentration is about 13 %, whereas for 0.06 % in the outer solution, the corresponding inside concentration is around 4 %. It is likely that this change in composition of the inside solution may also contribute to a decrease in the rate of diffusion inside the resin particles. A change in composition may have a considerable effect upon the structure of the inside solution. According to Sutra [12,13] the radii of the solvated alkali metal ions in ethyl alcohol are more than twice their size in water. It is known that in a mixture of alcohol and water the solvate sheaths of the alkali metal cations consist of both water and alcohol, water being held preferentially in the solvate sheath. When the alcohol concentration is increased a resolvation must occur, which in the case of ion exchange resins must result in a considerable decrease in the volume of the "free" inner solution. Probably this factor may contribute to a decrease in the rate of diffusion inside the resin particles, which would explain the lowered rate of sorption at extremely low water contents in the solution. It may also be pointed out that some of the glycerol molecules which diffuse into the resin phase must enter the solvate sheath, and that this resolvation may in some way have an influence upon the rate of uptake.

*Equilibrium distribution.* From Figs. 1 and 2 it is obvious that the solvent composition has a large effect upon the equilibrium. In agreement with earlier observations for sugar [2,3], the uptake of glycerol is found to increase when the relative amount of water in the solvent is decreased. It is interesting to note that the uptake is changed by a factor of about two, when the water content in the solvent is lowered from 0.6 % to 0.06 %. Also with glycol and sorbitol

*Table 2.* The effect of the counter ions and the degree of cross-linking upon the distribution equilibrium.

| Polyalcohol | Water conc. % | $m_o$ | %DVB in the resin | $K_e$ | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | H+ | Li+ | Na+ | K+ | Rb+ | Cs+ | NH₄+ |
| Sorbitol | 0.03—0.06 | 7.65 | 8 | 1.17 | 87 | 83 | 169 | 221 | 222 | 30.1 |
| Glycerol | 0.06 | 21.12 | 8 | 0.28 | 3.4 | 10.5 | 6.85 | 5.97 | 4.86 | 1.39 |
| Glycerol | 0.03—0.04 | 20.57 | 2 | 0.40 | 1.37 | 8.51 | 5.80 | 4.92 | 4.13 | 1.12 |
| Glycol | 0.04—0.08 | 13.87 | 8 | 0.23 | 1.32 | 2.35 | 1.36 | 0.84 | 0.86 | 0.51 |
| Glycerol | 7.5 | 12.00 | 8 | 0.24 | 0.89 | 1.11 | 0.95 | 0.87 | 0.79 | 0.62 |

it has been found that the uptake increases considerably for a decrease in water concentration in the solvent (*cf.* Tables 2 and 3). In pure water the net effect is a salting out, *i.e.* the concentration of polyalcohol in the resin phase is lower than in the outer solution [8].

The influence of the solute concentration upon the equilibrium distribution for glycerol in solutions with 7.7 % water is shown in Figs. 4 and 5. Fig. 4 also illustrates the uptake of glycerol from an almost water-free medium. All isotherms are convex, *i.e.* the sorption coefficient decreases for an increase in concentration. The effect of the solute concentration upon the sorption coefficient is largest in almost water-free solutions. This dependence on concentration must be remembered when comparing the sorption by different ionic states of a resin or by resins of different degrees of cross-linking. The rigorous method would be to make the comparison at constant equilibrium concentration in the outer solution. This would require measurements at different concentrations and such measurements have only been made in a few systems. Measurements are available, which permit a comparison between the effects of Li+, Na+ and K+ upon the uptake of glycerol from a solution containing 7.7 % water. The data given in Fig. 4 show that at low solute concentrations the highest sorption is obtained with the Na+-resin and the least sorption with the K+-resin, whereas the Li+-resin takes an intermediate

*Table 3.* The sorption of various polyalcohols on the K+-form of Dowex 50.

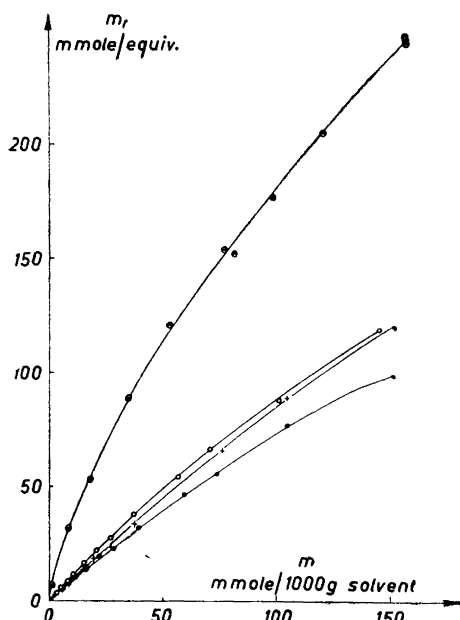| Polyalcohol | $m_o$ | m | $m_r$ | % sorbed | $K_e$ |
|---|---|---|---|---|---|
| Glycol | 9.18 | 8.64 | 2.10 | 5.9 | 0.24 |
| | | 8.76 | 1.83 | 4.6 | 0.21 |
| Glycerol | 9.05 | 8.06 | 4.18 | 12.3 | 0.52 |
| Mannitol | 9.29 | 4.84 | 19.64 | 47.9 | 4.06 |
| | | 4.82 | 19.56 | 48.1 | 4.06 |
| Sorbitol | 9.30 | 3.90 | 23.71 | 58.1 | 6.08 |
| | | 3.93 | 23.72 | 57.7 | 6.04 |

*Fig. 4.* The glycerol sorption by alkali
metal forms of Dowex 50.

⊖ Li⁺,    0.02—0.06 % water, 720 h
○ Li⁺
+ Na⁺ } 7.7 % water, 170 h
● K⁺

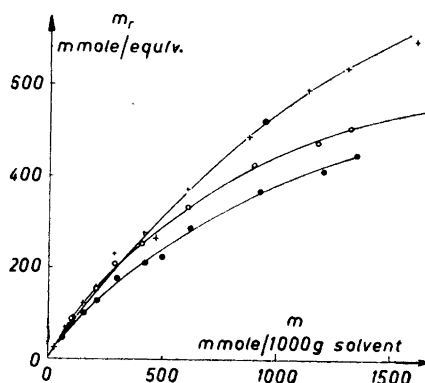*Fig. 5.* The glycerol sorption by alkali
metal forms of Dowex 50 from solutions
with 7.7 % water. Contact time 170 h.
+ Li⁺
○ Na⁺
● K⁺

position. From Fig. 5 it may be seen that the order of the $Li^+$-resin and the $Na^+$-resin is reversed, *i.e.* the sorption isotherms for these two forms of the resin cross each other.

A reversed order of the effects of different counter ions can be obtained also when the relative amount of water in the solvent is changed. A comparison between Fig. 1 and Fig. 2 confirms that at higher water concentrations (7.5 and 12.6 %) the lithium form is a more effective sorbent than the potassium form. At low water concentrations (0.06 and 0.6 %) the order is reversed and the sorption is much higher for the potassium form.

In Table 2 further data are collected showing the influence of the counter ions upon the equilibrium uptake of different polyalcohols. The data refer to the solute concentration given in the table and, as already mentioned, the sorption coefficients are affected by changes in the solute concentration. Among the alkali metal resins the sodium form is the most effective sorbent for glycol and glycerol at the concentrations investigated. On the other hand, sorbitol is sorbed more strongly by the resin saturated with potassium ions and particularly with rubidium and cesium ions. In this respect sorbitol behaves like glucose[2]. The hydrogen and ammonium forms of the resin
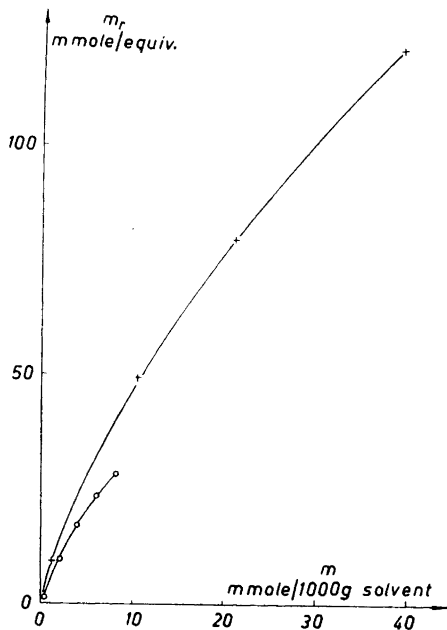
Fig. 6. The sorption of sorbitol and mannitol by the K+-form of Dowex 50 from solutions with 12.5 % water. Contact time 48 h.
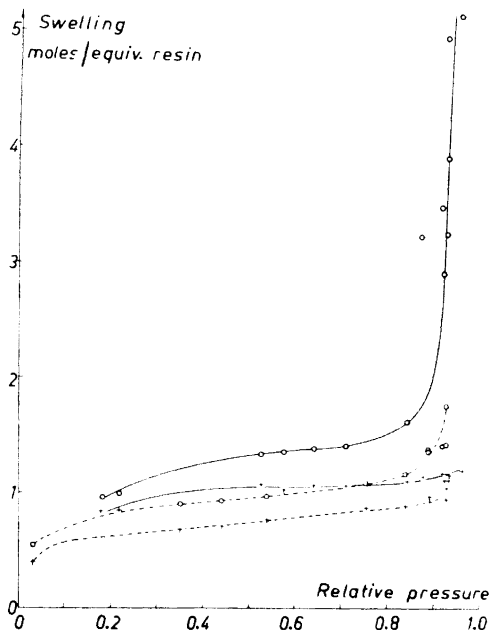+ sorbitol
O mannitol

Fig. 7. Uptake of ethyl alcohol vapor. Continuous lines: desorption. Dotted lines: sorption.
+ Dowex 50 X8
O Dowex 50 X0.5

sorb less than the alkali metal forms, which is in agreement with the results obtained with glucose.

The experiments with glycerol presented in Table 2 indicate that the degree of cross-linking has an influence upon the sorption. However, this factor is less important than the effect of the ionic form of the resin. This is in agreement with the results obtained with glucose [3].

The sorption differs considerably for various polyalcohols. Table 3, which contains data for the sorption from a solution with 12.5 % water shows that the uptake increases according to the following series: glycol < glycerol < mannitol < sorbitol. In an almost water-free medium only glycol, glycerol and sorbitol have been investigated and it has been found that the sorption increases according to this sequence. In water the sequence is reversed [8]. Evidently the number of hydroxyl groups in the sorbed molecule has a marked effect upon the distribution coefficient. The uptake of mannitol and sorbitol at various solute concentrations is demonstrated in Fig. 6. The two polyalcohols have the same number of hydroxyl groups in the molecule, but sorbitol is held more strongly than mannitol. Consequently, small differences in the structure between different solutes may have a considerable influence upon the sorption.

In a previous work on the distribution of polyalcohols between an aqueous solution and an ion exchange resin an attempt was made to split up the distribution coefficient into two parts, a pressure term and an interaction term [8]. The calculation was based upon the Gibbs-Donnan theory. It was found that both terms have a considerable influence upon the distribution. Because of the lack of data, e.g. swelling pressure data, no attempts will be made to perform such calculations for the uptake from the solvents used in the present work. However, some remarks of a qualitative kind may be made.

In aqueous solutions the distribution coefficient ($K^*$) is less than unity, which means that the concentration of polyalcohol is lower in the resin than in the outer solution. This net effect is explained by the contributions of the pressure term and the interaction term, which both have an influence in the same direction. The pressure term will always act in this direction and therefore it may be concluded that for solutions in ethanol, where the net effect is a considerable sorption, the pressure term is small compared with the interaction term. The pressure term has a larger influence upon large molecules than upon small ones, but despite this fact the larger molecules are, in alcohol solution, sorbed more strongly by the resin. This can only be explained if the interaction term has a higher numerical value for the larger molecules.

The interaction term accounts for the interaction between the solute and the ion exchanger and between the solute and the solvent. The interaction between the solute and pure solvent mixtures can be accounted for if the activity coefficients for the solute are known at different solvent compositions. Data, which show the solvent composition inside the resin as a function of the outer concentration, are given in an earlier paper [9]. Within the range of alcohol concentrations studied in the present work the water concentration inside the resin is higher than in the outer solution and therefore the polar solutes, preferring the better solvent, will accumulate in the resin phase. Based upon solubility measurements, an attempt was made in an earlier paper to estimate the relative magnitude of the solute-solvent interaction and the solute-resin interaction for glucose in aqueous alcohol. It was shown that both factors have to be taken into consideration. As to the solute-resin interaction it has been demonstrated that for sugars the interaction between the ions inside the resin and the solute is a more important factor than the interaction between the resin matrix and the solute [2,3]. For less polar solutes, e.g. acetic acid, the latter factor may predominate [5].

As demonstrated in earlier papers the uptake of polar non-electrolytes from aqueous alcohol can be used for analytical separations. Under suitable conditions non-electrolytes can be separated according to the chromatographic technique [4,1]. From the present work it is obvious that the separation factors, i.e. the ratio between the sorption coefficients (or distribution coefficients), differ much more in aqueous alcohol than in pure water [cf. Ref.[8]]. An increase in alcohol concentration causes an increased separation factor. For this reason it is advantageous to use a high alcohol concentration for chromatographic separations of polar non-electrolytes. As observed earlier for sugars [1,2] and confirmed in the present work for polyalcohols, the reaction equilibrium is reached slowly in aqueous alcohol and as demonstrated above the rate of reaction is extremely low in an almost water-free medium. This is a consider-

able disadvantage as far as chromatographic work is concerned, and for practical purposes the concentration cannot be chosen too high.

In this connection it may be mentioned that glycol, glycerol and sorbitol can be easily separated, e.g. by elution with 95 % ethyl alcohol from a column with the sodium form of Dowex 50 [4]. Glycol and glycerol appear as sharp peaks and sorbitol, which is bound much more strongly, appears as a broad band of low concentration. After glycol and glycerol have been eluted, sorbitol can be displaced quickly by means of water. The resin swells much more in water than in aqueous alcohol and so it might be necessary to break up the resin bed after the addition of water. Because of the influence of solvent composition upon the swelling, gradient elution based upon a gradient in solvent composition cannot be used as the changes in swelling causes channelling or even plugging in the column [14].

## APPENDIX

An attempt was made to determine the swelling pressure of Dowex 50 in ethyl alcohol according to the isopiestic method [15,16]. Isotherms of the same shape as for water were obtained. The weakly cross-linked resin X0.5 sorbed considerably more than the normally cross-linked resin. The sequence of the ionic forms of the resin was the same as for water sorption, i. e. the lithium form sorbed more than the sodium form, which showed a stronger sorption than the potassium form. The order is the same as obtained for the swelling in alcohol solutions [9].

Considerable experimental difficulties arose in these experiments and only the results obtained with the sodium form of the resin will be given in the present paper. The isotherms are given in Fig. 7. The time of reaction in these experiments has been 3 — 6 days and no significant differences have been observed for different times of reaction. The isotherms for the sorption and desorption do not coincide, and for this reason it seems improbable that a true equilibrium has been reached. Furthermore, it is very difficult to prevent traces of water vapor from entering the system, so no swelling pressure data will be given here. It may only be mentioned that the lithium resin gave data of the same order of magnitude as for water [15,16], whereas higher pressures were calculated for the sodium and potassium forms of the resin.

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