

NEW ION EXCHANGERS, PREPARATION, PROPERTIES AND APPLICATION

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Summary - Properties of various polystyrene/divinyl benzene resins are discussed. Rigidity and porosity are investigated by radiochemical methods, also the kinetic behaviour of macromolecular resins and those of normal porosity. Kinetic properties of superficially and of thoroughly sulfonated resins are compared. The synthesis of resins with tetraphenyl borate as anchor group is described.

Cellulose as a natural macromolecular matrix can also be used for synthesis of ion exchangers. New ways of synthesis are described. Capacity and kinetic properties are determined and discussed. Comparison of distribution coefficients serves as a measure of selectivity. Selectivity of the new ion exchangers is demonstrated. Examples of application are described.

1. INTRODUCTION

Organic ion exchangers are used for many years in laboratory and industry. They consist of a network or matrix carrying functional groups or anchor groups which are responsible for the ion exchange properties. The network may be an artificial one obtained from monomers by polymerisation or copolymerisation or by polycondensation. Products of this kind are called resins. On the other hand natural macromolecules like cellulose may be used as matrices.

The functional groups or anchor groups which are used in organic ion exchangers vary widely. In resins like polystyrene, copolymerized with divinyl benzene mainly sulfonic acid groups are introduced as acidic groups or amino groups as basic groups. These resins are applied in many fields for separation of cations and anions from solutions. They have many advantages and can easily be produced. The two main disadvantages are low selectivity and relatively slow attainment of equilibrium.

Selectivity is given by the difference in distribution coefficients for different ions, elements or compounds and defined by the following equation (1)

$$S = \log K_d(1) - \log K_d(2), \quad (1)$$

wherein $K_d(1)$ is the distribution coefficient of the element, ion or compound considered and $K_d(2)$ the highest value of the distribution coefficient of all other species which may be present. If the selectivity is low as in the case of normal ion exchange resins described above it is not possible to separate one or a few elements from a solution containing high concentrations of other elements. Separations of this kind are the scope of recycling processes when valuable cations or anions are to be separated from a bulk of other salts and of environmental techniques where small amounts of toxic metals have to be isolated from an excess of other ions. The tendency, therefore, is to provide ion exchangers containing anchor groups of high selectivity for special cations or anions. Chelating groups are of great interest for this purpose.

The time necessary to obtain equilibrium is of importance for fast separations. The influence of the kinetic properties of ion exchangers are clearly seen from Fig. 1 in which elution curves from the same column at different flow rates are shown (2). In most practical cases gel diffusion, that is diffusion within the grains of the particles of the resin, is responsible for attainment of equilibrium.

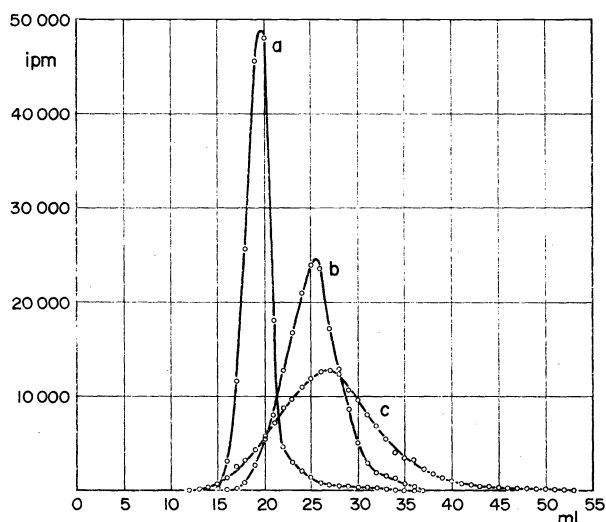


Fig. 1. Elution curves at different flow rates
Dowex-50X8 (100-200 mesh), diameter 0.6 cm, height of filling 11 cm
a) 0.01 ml/m, b) 0.1 ml/m, c) 1 ml/m

In the following sections two matrices will be discussed in more detail: polystyrene copolymerized with divinyl benzene as an artificial macromolecule (resin) and cellulose as representative of a natural macromolecule. The preparation and the properties of resins and of cellulose exchangers containing a broad variety of new anchor groups will be described. Special attention will be given to the kinetic behaviour.

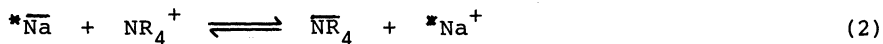
2. POLYSTYRENE

2.1. Rigidity and porosity of polystyrene resins

The free space in the resin beads between the network of the macromolecules is a system of small channels. These channels represent the normal porosity of the resins. By application of special techniques other resins are prepared which contain big pores in addition to the system of small channels. The products are called macroporous resins. The macropores are hollow spaces of the order of 10 nm surrounded by the network of the polymer.

In dry condition the resin matrix is rather compact, the system of channels between the polymer network is shrunk so that these channels almost disappear. But the macropores in macroporous resins can still be observed if the polymers are dry. When the resins beads are contacted with water or another solvent the channels and the pores are filled with liquid phase and the resin beads as a whole expand. Information about porosity is of great interest with respect to ion exchange properties. Most methods used, like electron microscopy, mercury porosimetry and surface determination by the BET method are based on solvent-free materials. Thus they do not give information on the properties of the resins under proper conditions. BET measurements according to Martinola (3) after modified pretreatment of ion exchange resins give the internal surface area of the macropores of macroporous resins. Sometimes attempts were made to use the exclusion of larger ions as a measure for pore size distribution in ion exchange resins (4)-(8). But the results of these experiments are not plain and unequivocal.

We studied the exchange reaction



by radiochemical methods in various resins (9). The bar indicates that the ions are bound in the resin. Na⁻ ions were labelled with ²²Na, R was varied: R = -H, -CH₃, -C₂H₅ or -C₄H₉. Results are presented in Fig. 2. All resins contain the same functional groups. It was proved that the distribution coefficients for all kinds of NR₄⁺ ions used can be assumed to be nearly equal. The different results shown in Fig. 2 must therefore be due to other factors. The drop in capacity found for the macroporous resin Bio-Rad AGMP50 and the

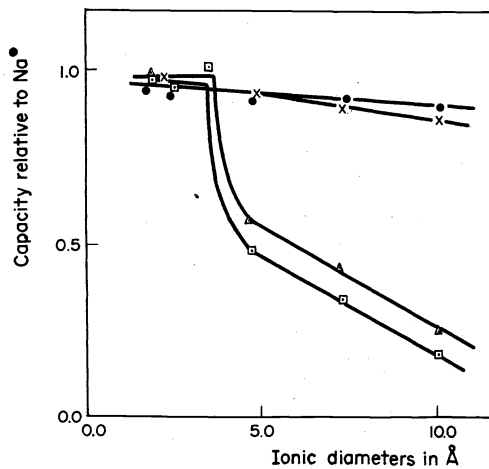


Fig. 2. Relative capacity as function of ionic diameters

- Bio-Rad AG 50 WX2 (2% cross-linking)
- △- Bio-Rad AG 50 WX16 (16% cross-linking)
- Bio-Rad AG MP 50 (macroporous, 20% cross-linking)
- x- Dowex 50 WX4 (4% cross-linking)

resin Bio-Rad AG 50 WX16 at ionic diameters above 0.4 nm can not be caused by the different porosity alone or pore size distribution of these resins. Fig. 2 clearly indicates that cross-linking is the most important parameter. As higher the cross-linking as lower is the capacity at higher ionic diameters. Higher cross-linking makes the resins more rigid. Rigid networks are less able to accommodate larger ions. Thus it is not the porosity but rather the rigidity which limits the uptake of larger ions. This situation makes it difficult to describe the properties of ion exchange resins by porosity or pore size distribution alone as it is done in the case of rigid structures like silica gel. The ability to swell which is directly related to cross-linking is more important. This is shown in Table 1. The rigidity of the matrix structure is

TABLE 1. Properties related to swelling

| Sample | matrix volume | volume of | Swelling = (matrix volume + pore volume)/ matrix volume % |
|--------------------|--------------------------|------------------------|---|
| | mol/g dry | pore water ml/g dry | |
| Bio-Rad AG 50 WX2 | 0.615 [±] 0.002 | 4.82 [±] 0.04 | 884 |
| Bio-Rad AG 50 WX16 | 0.653 [±] 0.007 | 0.63 [±] 0.04 | 196 |
| Bio-Rad AG MP 50 | 0.649 [±] 0.006 | 1.03 [±] 0.02 | 259 |
| Dowex 50 WX4 | 0.627 [±] 0.006 | 2.00 [±] 0.05 | 419 |

primarily responsible for exclusion of larger ions. Rigidity of the structure prohibits swelling necessary to accommodate the ions and also prohibits twisting of the carbon atom chain of the structure which is necessary in order to increase the distances of the exchange sites.

2.2. Kinetic properties of macroporous and other resins (10)

The rate of exchange in ion exchange resins depends on the grain size, the porosity and the ions which are exchanged. Generally gel diffusion is responsible for the rate of exchange if the grain size of the resin is greater than 0.1 mm. Macroporous resins contain pores with diameters of the order of 10 nm in addition to the porosity which is given by the space between the network of the polymer. The transport of the ions in these macropores is expected to be faster than the transport through the polymer network itself. In order to measure the kinetic properties of macroporous resins and other resins of normal porosity two series of radiochemical experiments were carried out.

In one group of experiments the loading of the resins according to the equation



was measured as a function of time. This reaction can be followed easily if the amount of \bar{M}^{n+} offered is less than the amount of exchanging sites which is given by \bar{H} and corresponds to the capacity. In the experiments the amount of $^*M^{n+}$ offered was chosen to be about 2% of the capacity. Under these conditions a distinct drop in $^*M^{n+}$ concentration in the solution takes place which can be measured quite well, but equilibration in the interior of the grains can not be seen in detail. Solutions of Sr^{2+} ions, labelled with ^{85}Sr were used for these investigations.

In the second group of experiments the unloading of the resins according to the equation



was measured as a function of time. This is an isotopic exchange reaction. In order to be able to measure reaction (4) with high sensitivity an excess of unlabelled ions M^{n+} was used. The amount of M^{n+} was chosen to be the 20-fold of the capacity. These experiments are more instructive because equilibration within the resin beads is seen in detail and because enthalpy changes are negligible for isotopic exchange reactions. The resins loaded according to eq. (3) were used in order to study unloading according to eq. (4). The unoccupied sites in the resins are also loaded in the second series of experiments according to the equation



Because only the outcoming labelled $^*M^{n+}$ ions are measured this reaction is not observed. Due to further loading by reaction (5) swelling of the resin beads may increase, but as a first approximation it is assumed that the kinetic properties are not changed appreciably by this change in swelling.

Experimental results are shown in Fig. 3 and 4. In Fig. 3 the half-time of ex-

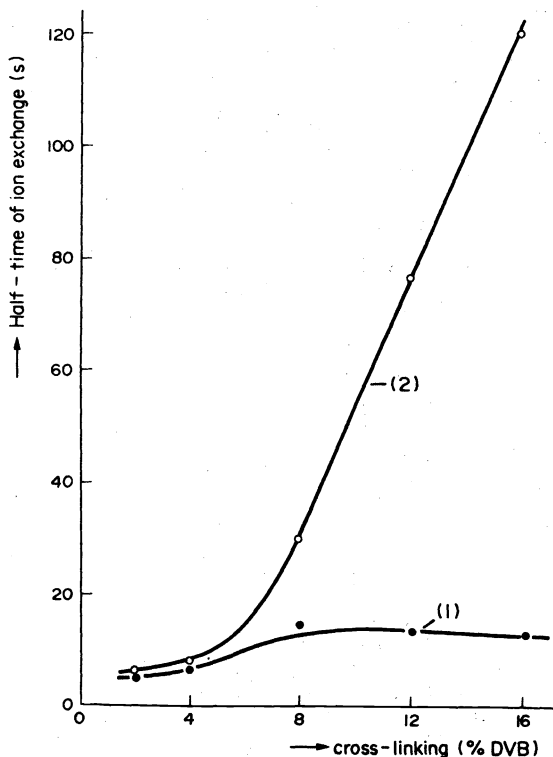


Fig. 3. Half-time of ion exchange with Sr^{2+} ions as function of cross-linking for Dowex ion exchange resins, 100-200 mesh, normal porosity
 (1) Exchange according to eq. (3)
 (2) Exchange according to eq. (4)

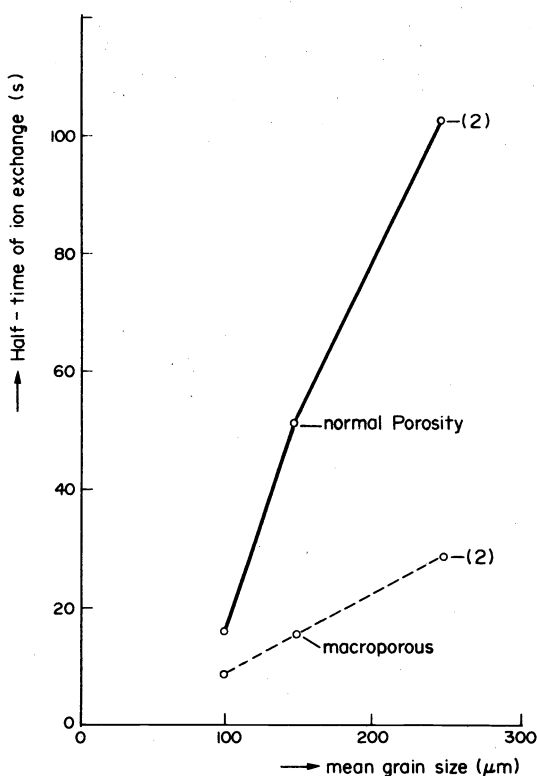


Fig. 4. Half-time of ion exchange with Sr^{2+} -ions as function of grain size for the ion-exchange resins Lewatite S 1080 and SP 1080 (macroporous), cross-linking 8% DVB, (2) Exchange according to eq. (4)

change is plotted as a function of cross-linking for Dowex ion exchange resins. The influence of cross-linking is not seen from the first series of experiments but it is pronounced in the second. High cross-linking increases the half-time of attaining the exchange equilibrium by a factor of about 20. The advantages of macroporous ion exchange resins become evident from Fig. 4. Whereas resins of normal porosity exhibit a sharp increase of the half-time of exchange with grain size, this increase is much smaller for macroporous resins due to the macropores which facilitate the transport within the resins appreciably.

2.3. Superficially sulfonated resins (11)-(13)

The rate of separation by ion exchange is, in general, limited by gel diffusion in the resin beads. Fast attainment of ion exchange equilibrium can be achieved in two ways:

- By use of very small particles (diameter $\leq 10 \mu\text{m}$) in order to make gel diffusion faster. The disadvantage is the very low flow rate which, however, may be overcome by application of pressure (high pressure liquid chromatography).
- By restricting the functional groups to the surface of the solid particles so that the interior of the particles is not accessible to the species to be separated. The thickness of the layer containing the functional groups should again be of the order of $10 \mu\text{m}$ or less. In this case the disadvantage is the low capacity per total mass unit.

The use of very thin layers with functional groups raises another question of theoretical interest: Is the selectivity in those layers the same as in compact ion exchange resins? The answer should be no, if the Gibbs-Donnan model is valid, that is if the pressure caused by swelling of the resin is responsible for the selectivity.

In Fig. 5 the exchange capacity is plotted as a function of the radius R of the grains for different thicknesses r of the sulfonated layer. Sulfonation

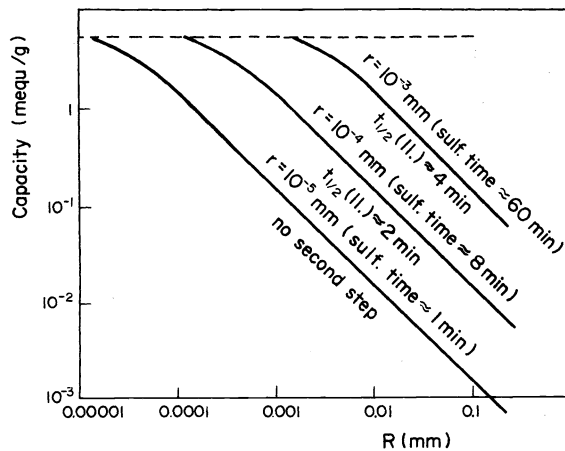


Fig. 5. Exchange capacity of superficially sulfonated resins as a function of the radius R of the beads for different thicknesses r of the sulfonated layer.

time was varied between 1 and 60 m. The polystyrene beads were prepared by pearl polymerization. The radius was of the order of 0.1 mm. Low capacity is tolerable if small quantities are to be separated, for instance in radiochemistry.

The differences in kinetic behaviour between superficially and thoroughly sulfonated resins are demonstrated in Fig. 6. In the superficially sulfonated

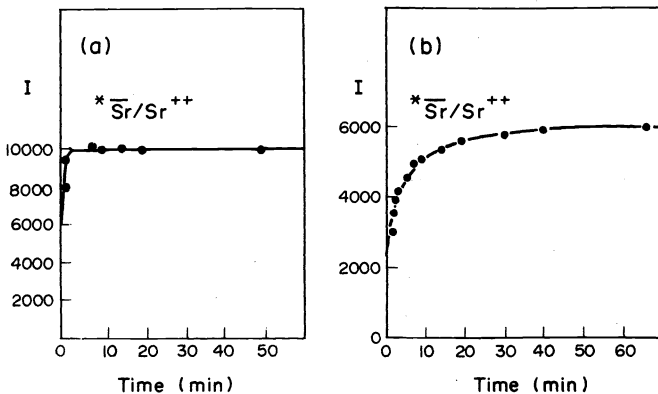


Fig. 6. Comparison of kinetic properties of superficially (a) and of thoroughly (b) sulfonated resins (both 100-200 mesh)

resin equilibrium is attained faster by a factor of more than 10.

Furthermore superficially sulfonated resins have at least the same selectivity as normal resins. From this result it must be concluded that the theory of Gregor (14) which is based on the Gibbs-Donnan (15) model can not be valid. The selectivity may be explained by other theories, for instance by the model of ion pair formation (16) (17).

As an example of application the fast separation of alkali ions is shown in Fig. 7. In order to obtain elution curves of the same sharpness with thoroughly sulfonated resins of the same grain size the flow rate has to be reduced by a factor of about 1000. In other words, by use of superficially sulfonated resins column separations can be carried out by a factor of about 1000 faster whereby the elution curves are not broadened. Fig. 7 also demonstrates the good selectivity of the superficially sulfonated resins.

2.4. Tetraphenylborate as anchor group

Instead of sulfonic acid groups various other groups have been introduced as functional groups or anchor groups into the macromolecular network of polystyrene/divinyl benzene copolymers. The first example was reported by Skogseid (18) who prepared a resin containing dipicryl amine as anchor group. This compound is selective for K. Other examples are resins with -SH groups (19)

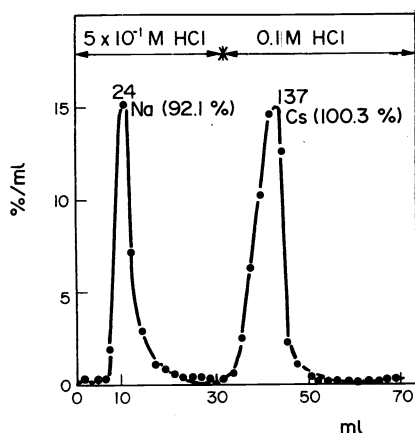
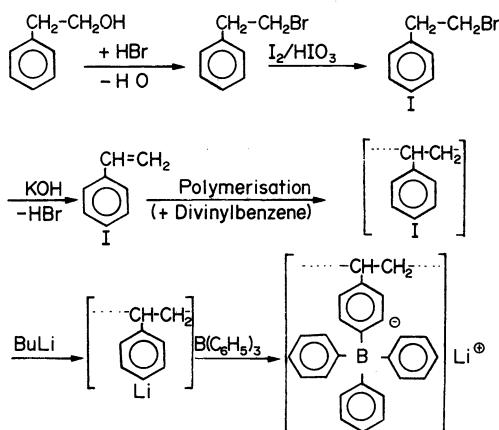


Fig. 7. Application of superficially sulfonated resins - Fast separation of ^{24}Na and ^{137}Cs in a separation column (inner diameter 1 cm, height of the filling 15 cm, flow rate $13 \text{ ml cm}^{-2} \text{ s}^{-1}$)

(20) which are selective for Hg^{2+} or those with N-carboxy-methylen-phenyl-diamine which are selective for Ni^{2+} . Ion exchange resins containing complexons as anchor groups (21) are on the market.

We prepared a resin containing lithium tetraphenylborate as anchor group. The way of synthesis is indicated in the following reaction scheme. The preparation



starts from the monomeric compound and ends up with the polymeric compound in which about one half of the phenyl groups of the polystyrene are part of the tetraphenylborate groups. The capacity varies between 1 and 2 mmoles/g. The resin is highly selective for alkali ions including Tl^+ . It does not react with ions of higher oxidation state. Distribution coefficients and selectivity as defined by eq. (1) are given in Table 2. Even within the group of the alkali

TABLE 2. Distribution coefficients and selectivity of a tetraphenylborate resin

| Distribution Coefficients | | Selectivity |
|---|----------|---|
| $\text{Na}^+ / \overline{\text{Li}}$ | 0.14 | $\text{M}^+ / \text{M}^{2+}, \text{M}^{3+}: S > 3$ |
| $\text{K}^+ / \overline{\text{Li}}$ | 5.8 | $\text{M}^+ \text{ (except } \text{Na}^+) / \text{M}^{2+}, \text{M}^{3+}: S \geq 4$ |
| $\text{NH}_4^+ / \overline{\text{Li}}$ | 10.8 | $\text{K}^+ / \text{Na}^+: S = 1.62$ |
| $\text{Rb}^+ / \overline{\text{Li}}$ | 38.0 | $\text{Cs}^+ / \text{K}^+: S = 0.96$ |
| $\text{Cs}^+ / \overline{\text{Li}}$ | 53.3 | |
| $\text{Tl}^+ / \overline{\text{Li}}$ | 25.8 | |
| $\text{Cu}^{2+} / \overline{\text{Li}}$ | < 0.0002 | |
| $\text{Ce}^{3+} / \overline{\text{Li}}$ | < 0.0002 | |
| $\text{Mg}^{2+}, \text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+}, \text{Mn}^{2+}$ | | |
| $\text{Ni}^{2+}, \text{Zn}^{2+}, \text{Pb}^{2+}, \text{La}^{3+} / \overline{\text{Li}}$ | < 0.0001 | |

ions rather high differences between the distribution coefficients are found. Separation of the alkali ions is shown in Fig. 8. The resin may be used to separate the alkali ions as a group from other ions or to separate the alkali ions from each other.

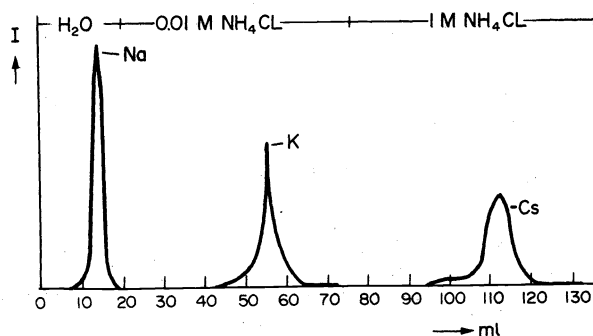


Fig. 8. Separation of the alkali ions by use of a resin containing tetraphenylborate as anchor group. (Inner diameter of the separation column 1 cm, height of the filling 15 cm, flow rate $0,1 \text{ ml cm}^{-2} \text{ s}^{-1}$)

The resin, however, has two disadvantages which restrict its practical use: The long way of synthesis and the instability below pH 4 and above pH 9.

2.5. Other anchor groups

As in the previous example the synthesis of macromolecular compounds carrying selective anchor groups is in most cases very laborious and troublesome. Many macromolecular compounds with ion exchange properties have been synthesized by polycondensation (23) (24) instead of polymerization or copolymerization. Not all examples described in literature can be reported here. Generally, the most promising way to prepare ion exchange resins with selective groups is to use a given macromolecular resin and to introduce the anchor groups later by simple reactions. Styrene divinyl benzene copolymers with chlorine or amino groups are appropriate starting materials. The resin Dowex A-1 which contains iminodiacetic acid as anchor group is also prepared in this manner.

In Darmstadt we are studying several methods to introduce various chelating reagents into macromolecular networks by simple reactions. I will explain the methods of synthesis in more detail for the preparation of various chelating ion exchangers on the basis of cellulose. Ion exchange resins with specific properties can be obtained by similar methods.

3. CELLULOSE

3.1. Properties of cellulose

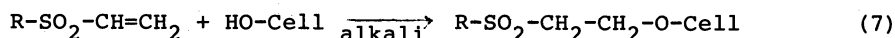
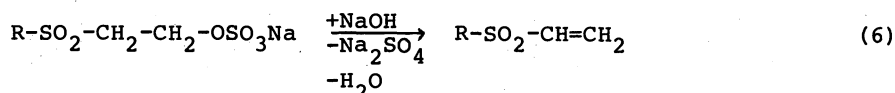
Whereas the copolymerisates of styrene and divinyl benzene are synthetic macromolecules, cellulose is a natural product. In general, the macromolecular resins are used in form of beads of varying diameters and with varying cross-linking. Cellulose, on the other hand, is applied in different forms:

- microcrystalline cellulose (e.g. Avicel, Merck Darmstadt)
- amorphous cellulose (e.g. Schleicher & Schüll 123/45)
- bead cellulose (e.g. after J. Stamberg (25))
- short-fibred cellulose (e.g. Schleicher & Schüll 123/3)
- long-fibred cellulose (e.g. cotton-wool)
- cotton fabric

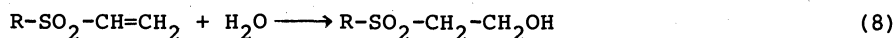
Amorphous cellulose can be stabilized by cross-linking with formaldehyde (26). The hydroxyl groups in positions 2, 3 and 6 are able to react with suitable groups by formation of ethers or esters. In most cases these groups are introduced in form of halogenated compounds (27). But the preparation of suitable compounds is difficult and the application of the method is restricted. Furthermore esters of cellulose are not stable in acidic or alkaline solutions.

3.2. New synthesis of cellulose exchangers

Reactive dyestuffs are bound on cellulose fibres by various methods. Compared with other products "Remazol" dyestuffs (28) developed by Hoechst, Frankfurt, have outstanding qualities with respect to stability against hydrolysis. We extended the principle of "Remazol" dyestuffs to the synthesis of cellulose ion exchangers. The way of preparation can be described by the following equations



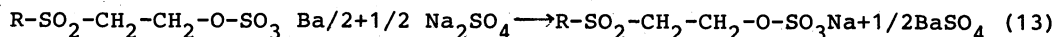
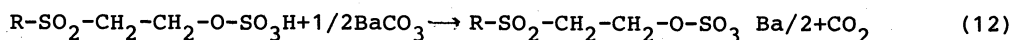
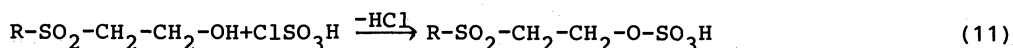
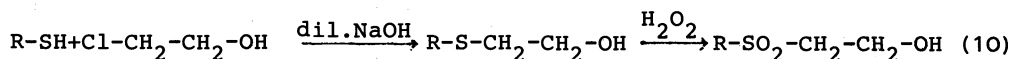
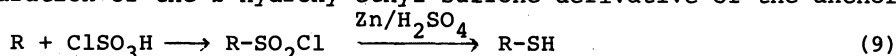
The vinyl sulfone $\text{R-SO}_2\text{-CH=CH}_2$ is formed as an intermediate. It reacts with water according to the equation



Reaction (8) is predominant in aqueous systems. It is the reason why in the process of dyeing in aqueous alkaline media only small amounts of dyestuffs are bound on cellulose, generally less than 0.05 mmoles per g of cellulose (28) (29). By use of non-aqueous solvents like dimethyl sulfoxide reaction (8) can be suppressed and the yield for reaction (7) considerably be increased. Two main reaction paths are possible which can be described here only very briefly (30).

Reaction path A consists of the following steps:

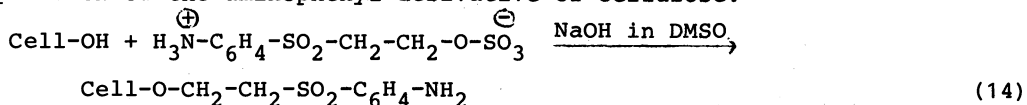
A1 Preparation of the β -hydroxy ethyl sulfone derivative of the anchor group R:



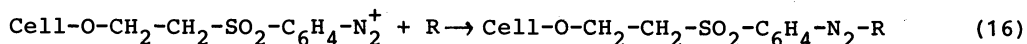
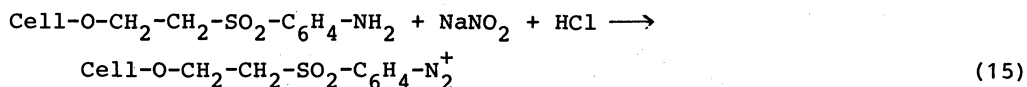
A2 The product obtained by reaction (13) is used for the synthesis according to eq. (6) and (7)

Reaction path B comprises the following steps:

B1 Preparation of the aminophenyl derivative of cellulose:



B2 Diazotation of the product obtained by reaction (14) and coupling with suitable anchor groups R



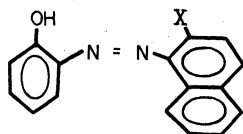
Variations of these main reaction paths are possible. Diazotation and coupling have also been used in order to introduce functional groups into other compounds (31)-(34). Synthesis according to reaction path B is rather simple and variable. We have been able to bind many different anchor groups on cellulose by reaction path B, for example

- alizarin
- alizarin-S
- arsenic azo III
- 4,4'-bis-(dimethylamino)-thiobenzophenone
- bis-(salicylaldehyde)-ethylenediimine (Salen)
- bis-(salicylaldehyde)-phenylenediimine (Salphen)
- diamino-dibenzene-18-crown-6

- 1,2-dihydroxy-benzene
- 1,2-dihydroxy-benzene-3,5-disulfonic acid (Tiron)
- 1,8-dihydroxy-naphthalene-3,5-disulfonic acid
- 5-(4-dimethylamino-benzylidene)-rhodanine
- diphenylcarbazide
- dithizone
- eriochrome black T
- ethylenediamine-N,N'-bis-(o-hydroxyphenyl-acetic acid)
- glyoxal-bis-(2-hydroxyanile)
- 1-(2-hydroxyphenylazo)-2-naphthol (Hyphan [®])
- 1-(2-hydroxyphenylazo)-2,4-phenylenediamine-N,N,N',N'-tetraacetic acid
- 8-hydroxy-quinoline
- 2,2'-imino-benzoic acid
- morin
- 4-[pyridyl-(2)-azo]-naphthol-2 (PAN)
- 4-[pyridyl-(2)-azo]-resorcin (PAR)
- pyrogallol
- quinalizarine
- salicylaldehyde
- salicylic acid
- 1-[thenoyl-(2')] -3,3,3-trifluoroacetone (TTA)
- 2-[thiazolyl-(2)-azo]-4-methoxyphenol (TAM)

Many of these groups are chelating groups with 3 to 6 coordination sites.

Very favorable is the inclusion of the diazo group into complex formation. This can be accomplished by diazotation and coupling of the o-aminophenyl cellulose prepared according to reaction (14) with 2-naphthol or 2-naphthylamine derivatives (35). In this way anchor groups with the formula



are obtained. Cellulose ion exchangers with X = -OH, -NH₂, and -N(CH₂COOH)₂ have been prepared. Resins containing o-(2-hydroxyphenylazo)-benzoic acid and -arsonic acid as anchor groups are described in literature (36).

Table 3 gives a survey of cellulose ion exchangers with 1-(2-hydroxyphenylazo)-2-naphthol (Hyphan) as anchor group on different kinds of cellulose. Other groups can be introduced into these various forms of cellulose in the same way (37). Matrices different from cellulose may be used as well for synthesis

TABLE 3. Hyphan 1-(2-hydroxyphenylazo)-2-naphthol on different kinds of cellulose

| Cellulose | Origin | Particle size | Ion exchange capacity (mmoles/g) | Use |
|---------------------------|--------------------------------|--------------------|----------------------------------|---|
| microcrystalline | Avicel (Merck, Darmstadt) | 20-100 μ m | 0.5-1.0 | separation columns or batch experiments |
| amorphous | Schleicher & Schüll 123/45 | 20-150 μ m | 0.5-1.0 | separation columns or batch experiments |
| bead cellulose | After J. Stamborg (25) | 200-400 mesh | 0.5 | separation columns |
| short-fibred | Schleicher & Schüll 123/3 | 400-600 μ m | 0.4-0.6 | separation columns or filters |
| long-fibred (cotton-wool) | Dr. Hartmann (for medical use) | for several cm | 0.8 | filters |
| cotton fabric | - | 25 cm ² | 0.3 | filters |

analogous to those reported in this section.

3.3. Capacity of the cellulose exchangers

The capacity of ion exchangers can be determined by two different methods, determination of the number of anchor groups per mass unit by analysis or of the maximum number of ions which are bound per mass unit. The first value may

in some cases be somewhat higher if anchor groups are inaccessible. For the cellulose ion exchangers described in the previous section both values were in agreement within the limits of error. The capacity was of the order of 1 mmole/g.

The number of anchor groups per mass unit (capacity) can be varied within certain limits by the method of preparation. Long reaction times lead to higher capacities. This is shown in Fig. 9 for the first step of the synthesis (B1, eq. (14)) of the cellulose exchanger with Hyphan as anchor group. The content of aminophenol groups increases appreciably with reaction time for many hours. It depends also on the cross-linking of the cellulose. In cellulose with higher cross-linking reaction (14) proceeds more slowly. The second step of the synthesis (B2, eq.(15) and (16)) is rather fast and comes to an end within a very short time. This can be seen from Fig. 10. Practically all o-amino-

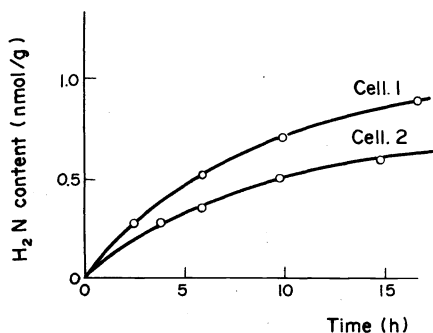


Fig. 9. o-aminophenol content in cellulose as a function of reaction time (Eq. (14)).
Cell 1 : time of cross-linking of the cellulose powder Avicel, Merck, 10 m. Cell 2 : time of cross-linking of the same cellulose powder 60 m.

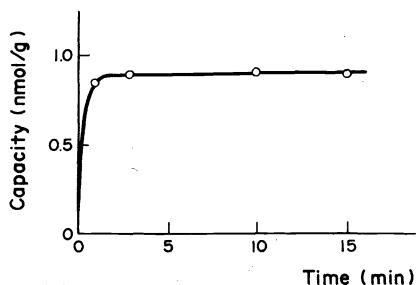


Fig. 10. Diazotation and coupling of o-aminophenol in cellulose as a function of time (Eq.(15) and (16)).

phenol groups introduced in reaction step 1 are diazotated and coupled within a few minutes.

On the other hand, reaction time has a pronounced effect on the kinetic properties. During long reaction times an increasing amount of anchor groups is introduced in remote sites of the matrix which are less easily accessible. Equilibrium with anchor groups at these less easily accessible sites is attained more slowly. The kinetic properties of the cellulose ion exchangers are described in more detail in the following section. In practice it is favorable to find an appropriate compromise between capacity and kinetic behaviour.

3.4. Kinetic properties

The kinetic properties of the cellulose ion exchangers were determined by the methods described in section 2.2. The attainment of equilibrium according to eq. (3) and (4) was measured as a function of time by application of radio-nuclides and by taking samples as a function of time. In general, it was observed that exchange was rather fast with half-times of the order of 20 s for microcrystalline cellulose, cross-linked by treatment with formaldehyde, as well as for powdered cellulose. As an example attainment of equilibrium is shown as a function of time for the exchange reaction



on a cellulose exchanger with Tiron (1,2-dihydroxy-benzene-3,5-disulfonic acid) as anchor group in Fig. 11. This rather high rate of exchange is a distinct

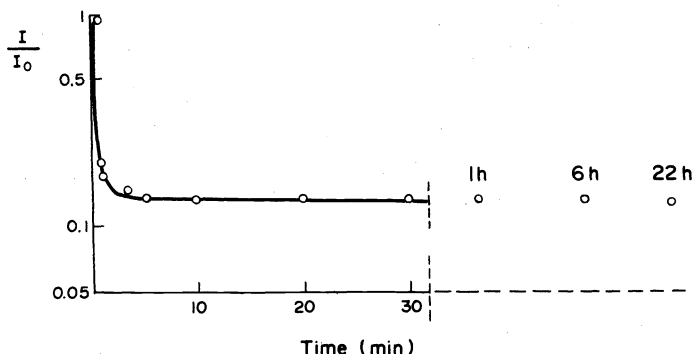


Fig. 11. Exchange $n \bar{H} + \text{Fe}^{3+} \rightleftharpoons \bar{\text{Fe}} + n \text{H}^+$ as a function of time on a cellulose exchanger with Tiron as anchor group (matrix: microcrystalline cellulose cross-linked with formaldehyde, capacity 0.2 mmoles/g).

advantage of these new ion exchangers.

The kinetic behaviour illustrated in Fig. 11 was observed for all ion exchangers obtained by restricted reaction times of several hours. Extended reaction times of the order of one day lead to higher capacities as discussed in the previous section. But at the same time a second slower step in the exchange reaction is observed with half-times of several minutes. Thus by longer reaction times the advantage of very fast attainment of equilibrium which is a characteristic feature of the cellulose ion exchangers is partially lost.

Only in one case a slow reaction was observed, namely for 8-hydroxy-quinoline as anchor group. For 8-hydroxy-quinoline slow complex formation is already reported in literature (38). For this group the rate of complex formation itself seems to be the rate determining step and not the transport within the matrix. Further investigation of this finding is under progress.

3.5. Distribution coefficients and selectivity

Distribution coefficients have been measured as function of pH for many of the new cellulose exchangers listed in section 3.2. Only a few examples can be presented here.

In Fig. 12 distribution coefficients are plotted as function of pH for Fe^{3+} and Sr^{2+} on a cellulose exchanger with Tiron as anchor group in presence of different salt concentrations (39). In absence of salt the difference in K_d

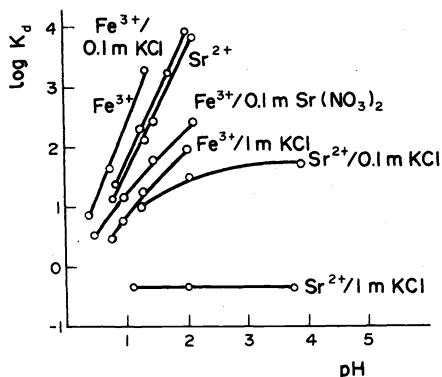


Fig. 12. Distribution coefficients for Fe^{3+} and Sr^{2+} at different salt concentrations as function of pH for a cellulose exchanger with Tiron as anchor group.

for Fe^{3+} and Sr^{2+} is about one order of magnitude. That means according to eq. (1) selectivity $S \approx 1$. In 0.1 M KCl and in 1 M KCl solutions selectivity is found to be $S > 2$ at pH 2. S increases with pH, specifically at higher salt concentrations. The curves in Fig. 12 demonstrate the high selectivity of Tiron for Fe^{3+} . Separation of Fe^{3+} from solutions containing high salt concentrations is rather easy.

In Fig. 13 distribution coefficients for a cellulose exchanger with Hyphan as anchor group are plotted as function of pH for various metal ions. The differences in $\log K_d$ are very high and illustrate the selectivity of this material. Cu^{2+} ions can be separated from all other ions at pH 3 - 5 with $S > 1.5$. The preference of this ion exchanger for some transition elements is very pronounced. Non-transition elements like Ca^{2+} , La^{3+} and Zn^{2+} have relatively low K_d values. Thus Cu^{2+} or Fe^{3+} can easily be separated from Ca^{2+} , La^{3+} , Zn^{2+} and others.

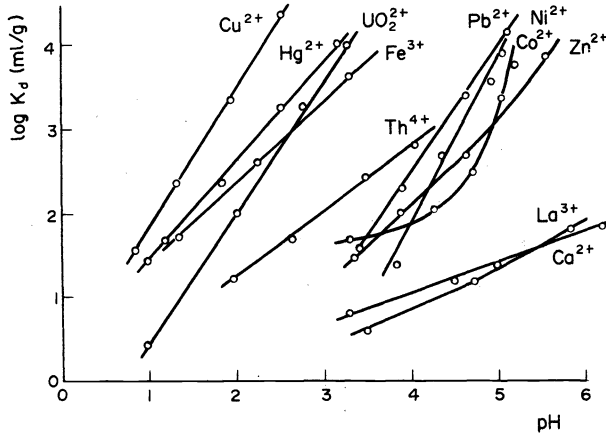


Fig. 13. Distribution coefficients as function of pH for the cellulose exchanger with Hyphan as anchor group in aqueous solutions

The high selectivity is somewhat diminished but not lost in presence of high salt concentrations. Fig. 14 shows distribution coefficients of some ions in 0.5 M NaCl solutions also for the cellulose exchanger with Hyphan as anchor group. In the pH range 3 - 5 the differences between $\log K_d$ for Cu^{2+} or Fe^{3+}

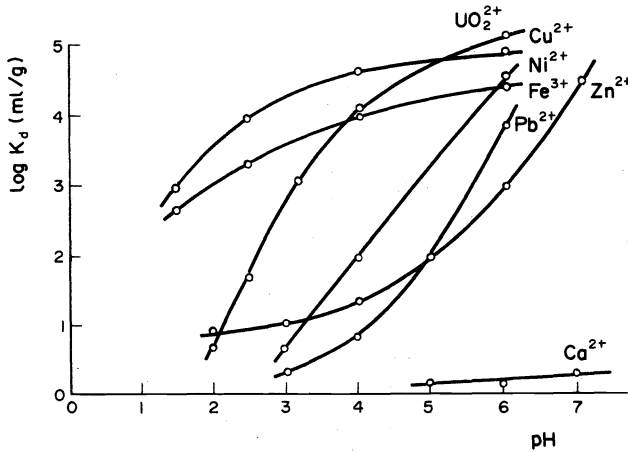


Fig. 14. Distribution coefficients as function of pH for the cellulose exchanger with Hyphan as anchor group in 0.5 M NaCl solutions

and for Zn^{2+} or Pb^{2+} are still $S > 2.3$. The selectivity for the separation of Fe^{3+} from Ca^{2+} is $S \approx 4$ and the selectivity for the separation of Fe^{3+} from Zn^{2+} is > 2.3 in the same range of pH. For comparison distribution coefficients are plotted in Fig. 15 for the resin Dowex A-1 which contains iminodiacetic acid as anchor group. This group is also a chelating agent but it differentiates much less between transition and non-transition elements than the Hyphan group does. Thus the selectivity for the separation of Fe^{3+} from Ca^{2+} is only

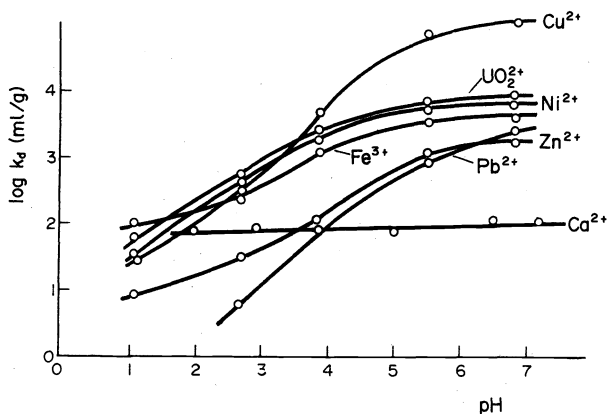


Fig. 15. Distribution coefficients as function of pH for the resin Dowex A-1 (iminodiacetic groups as anchor group) in 0.5 M NaCl solutions.

$S \approx 0.6 - 1.5$ and the selectivity for the separation of Fe^{3+} from Zn^{2+} only $S \approx 0.9 - 0.6$ (all values for pH 3 - 5). At pH 6 or in neutral solutions the selectivity is even less.

Many other examples can be given. In most cases the selectivity can be deduced from the stability constants of the 1:1 complexes which are formed.

3.6. Examples of application

The new ion exchangers have found manifold applications in our laboratory. In the field of analysis they are used for separations of individual elements. Many examples for these separations are evident from the comparison of distribution coefficients and from the previous section. Another application is the separation or preconcentration of trace elements from solutions. Because of the high distribution coefficients and the fast attainment of exchange equilibria separation or preconcentration of trace elements from aqueous solutions by cellulose ion exchangers is very effective, even in presence of high salt concentrations. Thus the ions of many transition metals are separated with high yields from natural water including sea water (40). The elements can then quantitatively be determined by X-ray fluorescence or neutron activation analysis. Three procedures of preconcentration are employed, according to the conditions: Column separation and subsequent elution, separation by a filter or by shaking with a small amount of cellulose exchanger. Filter separation is the simplest procedure. The filters are prepared from cellulose ion exchangers and may directly be used for X-ray fluorescence analysis (41).

In preparative work the cellulose ion exchangers are used for purification of reagents or for separation of trace elements from solvents. Thus the content of heavy metals in salts of alkali metals or alkaline earth metals is diminished by a factor of about $10^2 - 10^3$ by passing a solution of these salts through a column filled with an appropriate cellulose exchanger. In the same way traces of Cu^{2+} or Fe^{3+} are separated from concentrated solutions of ZnSO_4 . Uranium can be separated from water or sea water (42). The cellulose ion exchangers may be regenerated by treatment with diluted acid.

Other applications are seen in the possibility of recycling precious metals from solutions and in the separation of toxic metals from effluents. The most appropriate groups for the special problem may be selected and bound on cellulose or other suitable matrices by reactions of the kind described in section 3.2. Because the synthesis is relatively simple a broad field of application of various groups for selective separations in many fields is open.

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