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PREPARATION, CHARACTERIZATION AND APPLICATION OF ION EXCHANGERS WITH CYCLIC POLYETHER ANCHOR GROUPS

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SUMMARY

By introducing cyclic polyethers of different ring size in polymer matrixes special exchangers are obtained. They bind a certain scale of inorganic salts and organic compounds. The exchangers can be applied in many cases; in particular the ion chromatography for fast separations of cations and anions in analytical chemistry as well as salt conversions and phase-transfer catalysis in preparative chemistry can be mentioned.

INTRODUCTION

Ion exchangers are high-molecular-weight, nearly insoluble polyelectrolytes containing various ionic groups attached to the matrix. They are able to exchange the counter ions connected with these groups. From a synthetic point of view there are two different types: condensation resins and polymerization resins. Both types include cation exchangers, anion exchangers and chelating exchangers. Polymerization resins gradually came in the place of polycondensation resins, and styrene cross-linked with divinylbenzene is the skeletal framework of the most important of these resins.

Commercially available strong acidic cation and strong basic anion exchangers are generally non-specific, which has resulted in a wide field of application and the acquirement of considerable importance in the last 35 years.

Numerous publications have appeared concerning selective chelating resins. Only exchangers with iminodiacetic acid anchor groups attached to a polystyrene matrix are commercially available.

In this paper new exchangers that we have prepared in recent years¹⁻¹¹, in which polyethers are the anchor groups, are reviewed.

Fig. 1 shows the most important representatives of three different types of polyethers. In these crown ethers, cryptates and non-cyclic polyethers, the O atoms may be substituted by S or N. The binding forces of the complexes formed by the

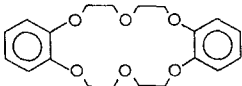
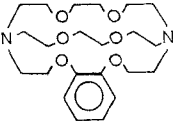
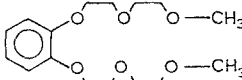
Type of compound	Example	Structure
Monocyclic polyethers or crown ethers	 Dibenzo-18-crown-6	2 Benzene rings, 18-membered ring, including 6O atoms
Bicyclic polyethers or cryptates	 Monobenzo Cryptate [2 _B 2 2]	2 N Atoms; 3 bridges each with 2O atoms; _B is the symbol for an additional benzene ring in a bridge
Non-cyclic polyethers	 —CH ₃	No abbreviated names are commonly used

Fig. 1. Examples of crown ethers, cryptates and non-cyclic ethers.

polyethers are those between the cations and the C—O dipoles of the polyether, and the polyethers are therefore neutral ligands. In order to maintain electrical neutrality anions are bound simultaneously.

Considering these facts, the definition given at the beginning of this Introduction is not acceptable, and there are restrictions.

PREPARATION OF EXCHANGERS

Special exchangers are prepared by condensation, substitution and copolymerisation reactions with polyethers. The procedures used for their synthesis are summarized in Table I.

Dibenzo crown ethers are condensed with formaldehyde in formic acid, and are cross-linked with methylene bridges. Auxiliary cross-linkers, such as toluene, xylene, phenol or resorcinol, are used in condensations of monobenzo crown ethers and monobenzo cryptates. Monobenzo crown ethers and dibenzo crown ethers can be attached to the surface of polystyrene with methylene bridges directly by condensation with formaldehyde.

Matrices similar to polystyrene are formed by the polymerization of monovinylmonobenzo crown ethers with divinyl-dibenzo crown ethers or divinylbenzene as cross-linker.

Substitution reactions can be carried out with chloromethylated polystyrene as well as with silica gel. Using monobenzo crown ethers with amino, hydroxymethyl or bromoalkane groups as substituents they will be fixed to the matrix by —C—NH—C—, —C—O—C—, —C—C—C—, or —Si—O—C— and —Si—C—C— links. It is possible to attach non-cyclic ethers to chloromethylated polystyrene by the same processes.

The monomeric polyethers shown in Figs. 2–5 form an integral part of the polymer matrix when the procedures described are used.

Fig. 2 shows crown ethers with O as the heteroatom. Benzo-15-crown-5 and

TABLE I

PROCEDURES FOR SYNTHESIS OF EXCHANGERS WITH CYCLIC POLYETHERS AND NON-CYCLIC ETHERS AS ANCHOR GROUPS

<i>Procedure</i>	<i>Matrix</i>	<i>Starting materials for exchangers</i>	
		<i>Anchor group</i>	<i>Structural framework, cross-linking agents for exchangers</i>
Condensation	Methylene bridges	Dibenzo crown ether Dibenzo cryptates	Formaldehyde
	Methylene bridges, additional cross-linking agent	Monobenzo crown ether Monobenzo cryptates	Formaldehyde, toluene (xylene, phenol, resorcinol)
	Methylene bridges, polystyrene	Monobenzo crown ether Dibenzo crown ether Phenyl crown ether	
Polymerization	Polystyrene	Monovinylmonobenzo crown ether	Divinyldibenzo crown ether Divinylbenzene
Substitution	Polystyrene, amino bridges	Aminomonobenzo crown ether Monocyclic cryptates	
	Polystyrene, ether bridges	Hydroxymethylmonobenzo crown ether Non-cyclic ethers	Chlormethylated polystyrene
	Silica gel, methoxy bridges, methoxy bridges Silica gel, alkane bridges	Hydroxymethylmonobenzo crown ether ω -Bromoalkanemonobenzo crown ether	Silica gel

benzo-18-crown-6 or dibenzo-18-crown-6 can be attached to polymer matrices according to any syntheses shown. Attachment to silica gels is important for application in high-performance liquid chromatography. Of the exchangers prepared, those with dibenzo-18-crown-6 as the anchor group are the most thoroughly investigated.

Crown ethers with O and N or O and S as the heteroatom are shown in Fig. 3. The relative complex stabilities of these anchor groups and also the sequences of selectivity are similar to those of benzo-15-crown-5 and dibenzo-18-crown-6.

Fig. 4 shows crown ethers, cryptates or urea analogues with O and N as the heteroatom. With the exception of cryptate [2.2] and cryptate [2_B.2] the anchor groups shown are bicyclic aminopolyethers.

Fig. 5 shows non-cyclic ethers. These compounds are mentioned in order to have a complete list of anchor groups, but they have no analytical or preparative importance.

The preparation of crown ethers according to the Williamson ether synthesis is relatively easy. The cryptates and some crown ethers with O and N as heteroatoms are considerably more difficult to prepare. Non-cyclic ethers with 2-11 O atoms are commercially available as mixtures.

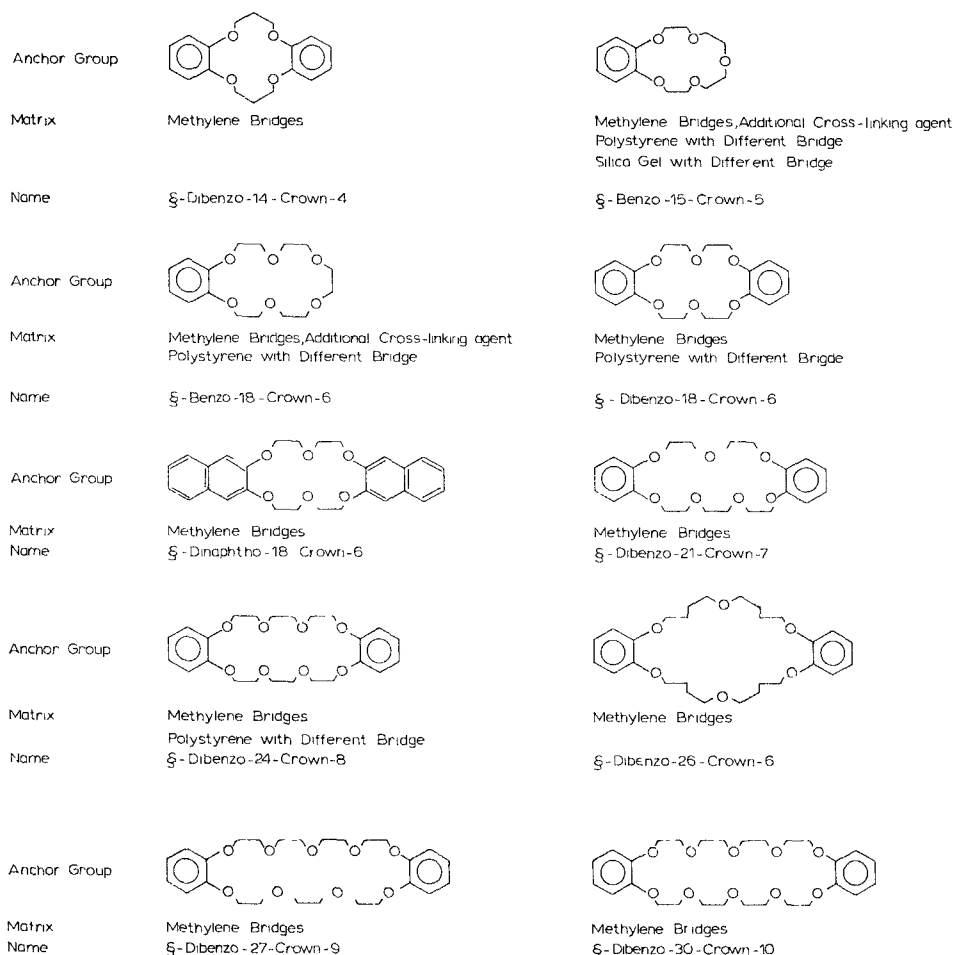


Fig. 2. Exchangers with cyclic polyethers as anchor groups: crown ethers with O as heteroatom.

PROPERTIES AND APPLICATIONS

By incorporating cyclic polyethers with different ring diameters, special exchangers can be prepared that form complexes with particular ranges of inorganic and organic compounds. The characteristic properties of these new exchangers open up new possibilities in ion-exchange applications.

Table II lists the most important properties in comparison with those of commercially available exchangers.

The uptake of exchangers containing only O as the heteroatom is independent of pH. Protonation of the N atoms occurs in exchangers with O and N atoms in the anchor groups, the complexation of salts is diminished and with the presence of quaternary ammonium groups the exchangers have become partially anion exchangers.

Exchangers with cyclic polyethers as anchor groups have a wide range of

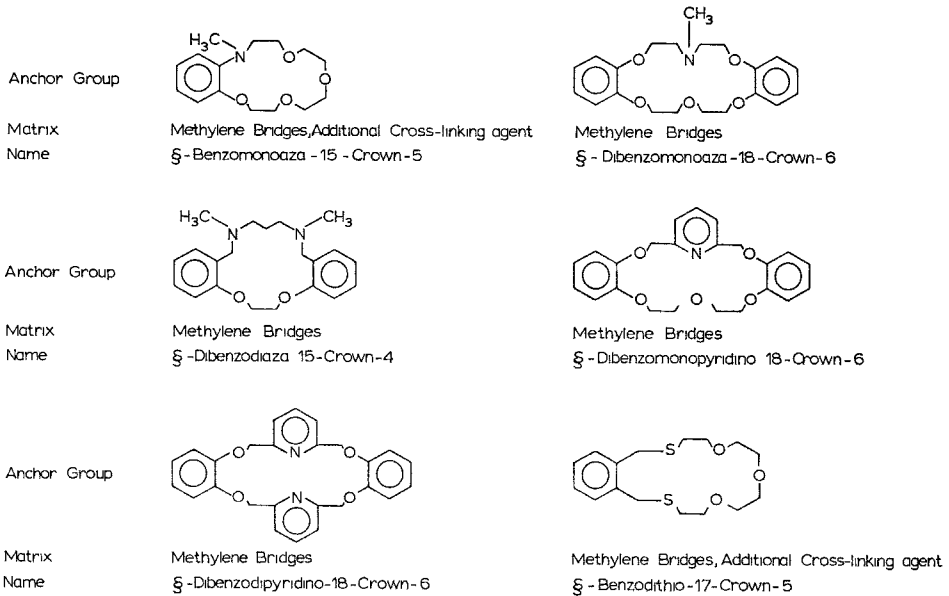


Fig. 3. Exchangers with cyclic polyethers as anchor groups: crown ethers with O and N or O and S as heteroatoms.

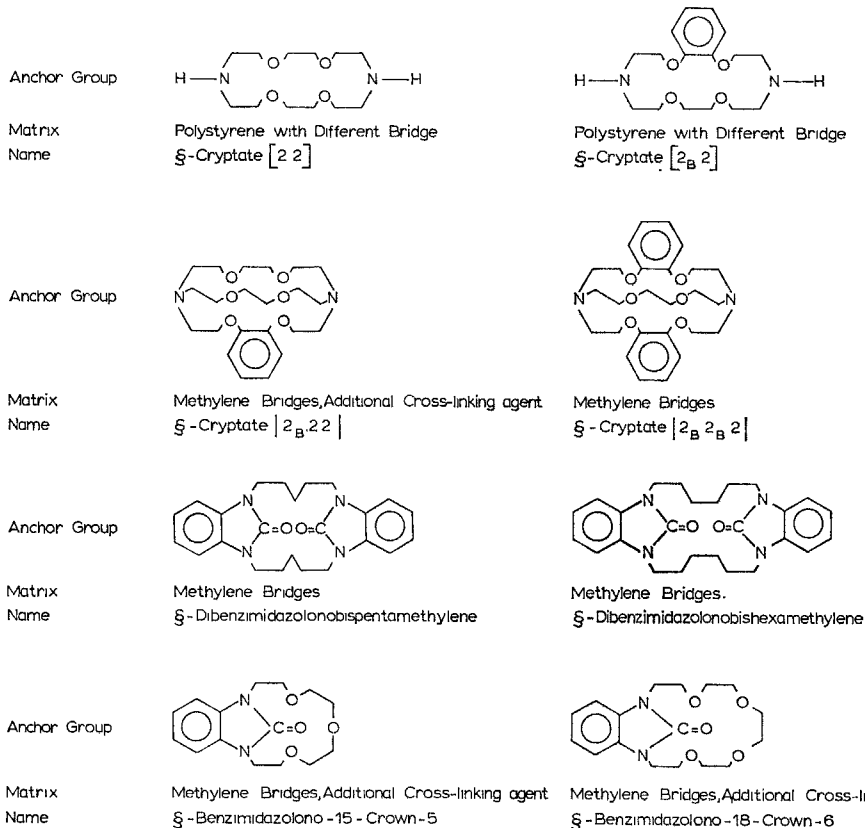


Fig. 4. Exchangers with cyclic polyethers as anchor groups: crown ethers, cryptates and urea analogues with O and N as heteroatoms.

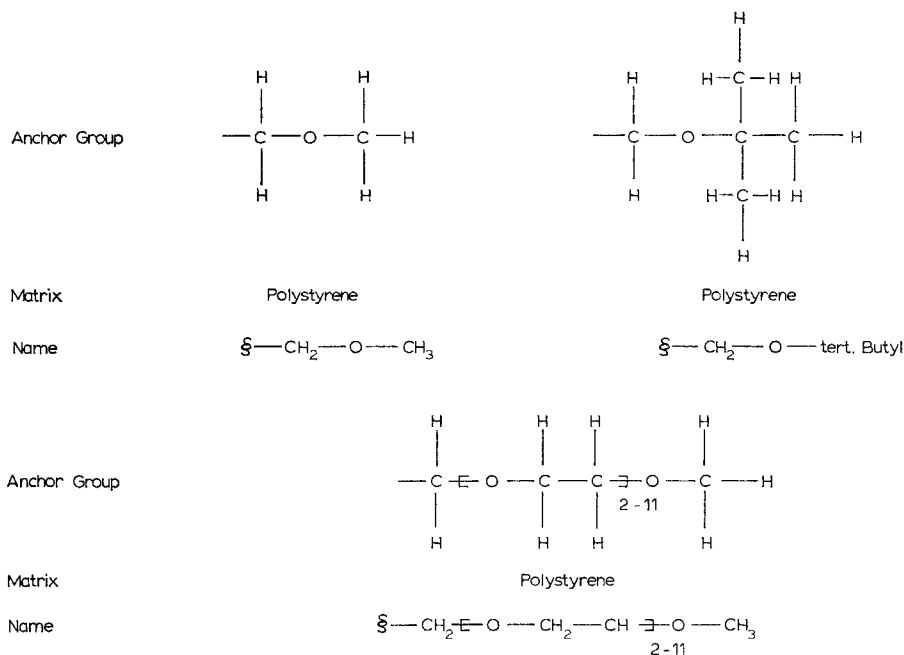


Fig. 5. Exchangers with non-cyclic ethers as anchor groups.

TABLE II

IMPORTANT PROPERTIES OF EXCHANGERS WITH CYCLIC POLYETHERS AS ANCHOR GROUPS COMPARED WITH COMMERCIAL CATION AND ANION EXCHANGERS

High resistance to chemicals, temperature and radiolysis
Neutral ligands as anchor groups
Simultaneous uptake of cations and anions in order to preserve electroneutrality
Loosening or complete stripping of the shell of solvent molecules from the cations and anions
Binding of ions is facilitated in less polar solvents than water, <i>e.g.</i> methanol
Stability of the polyether complexes depends on the cation, anion, solvent and size of the ring as well as on the type and basicity of the heteroatom (O, N, S)
Complexation with alkali metal cations
Salt uptake increases in the sequence of polarizability of the anions by unchanged cation
Activation of anions, also of C-H acid compounds
Salt uptake { independent of pH if only O is heteroatom in the anchor groups dependent on pH for pH < 3 if O and N are heteroatoms in the anchor groups
Elution with pure solvents (<i>e.g.</i> , water or methanol), no contamination of the eluate

applications (Table III). The application of crown ethers attached to silica gel or polystyrene in ion-chromatography is of particular interest.

PERFORMANCE OF COLUMN EXPERIMENTS

As always in column chromatography, very carefully packed columns are a prerequisite for good separations (Fig. 6).

TABLE III

APPLICATIONS OF EXCHANGERS WITH CYCLIC POLYETHERS AS ANCHOR GROUPS

Analytical chemistry	Preparative chemistry
Separation of cations (e.g., alkaline earth metals, heavy and precious metals)	Salt conversions (e.g., iodides, thiocyanates)
Separation of anions (e.g., halides, pseudohalides, isopolyacids, heteropolyacids)	
Separation of uncharged organic compounds	Purification or isolation of organic compounds
Trace enrichment (e.g., radionuclides)	
Determination of water in inorganic and organic compounds	Anion activation in organic reactions (e.g., nucleophilic substitutions, polymerizations)
Column chromatography (low-pressure liquid chromatography, high-performance liquid chromatography, ion chromatography, column electrophoresis)	
Thin-layer chromatography, thin-layer electrophoresis	
Ion-sensitive membranes	

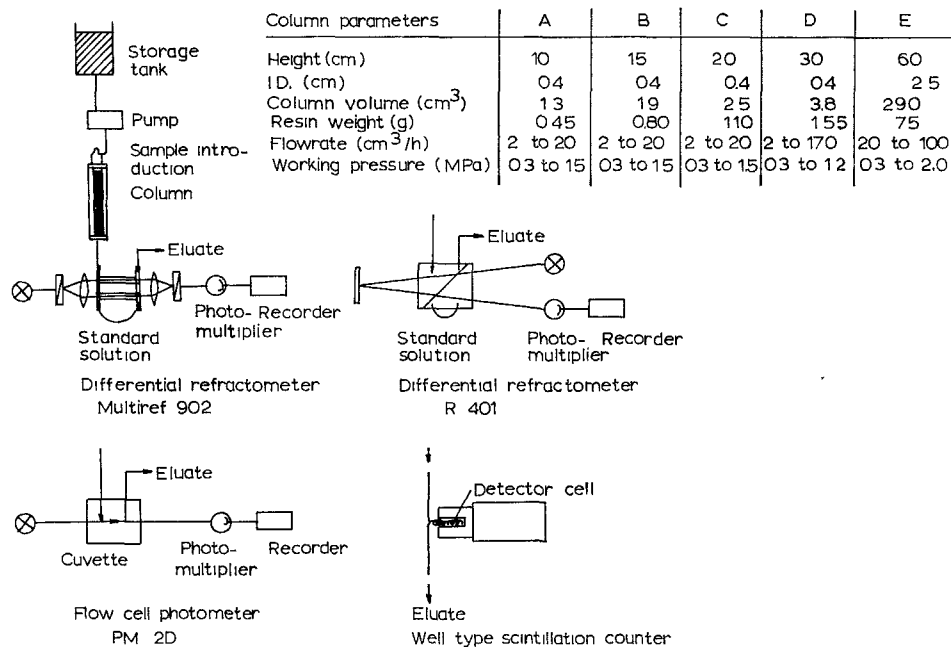


Fig. 6. Exchangers with cyclic polyethers as anchor groups: procedure for elution chromatography with different detectors.

In trace and micro analysis, columns A–D with a differential refractometer or a flow-cell UV detector are used. Investigations in radiochemistry are carried out with a well-type scintillation detector. As in all the other chromatographic methods, the detection and determination limits depend on the detector used in the separation, and range from micrograms to picograms. The sample volume is 1–200 μ l.

EXAMPLES OF APPLICATIONS

The application of some exchangers that have been thoroughly investigated (Fig. 7) is dependent on the following considerations.

(a) ξ -Benzo-15-crown-5 (matrix: silica gel); ξ -Dibenzo-18-crown-6 (matrix: methylene bridges). The two exchangers have comparable properties and prefer K^+ among the alkali elements. ξ -Dibenzo-18-crown-6 is the most versatile exchanger, and its synthesis is simple.

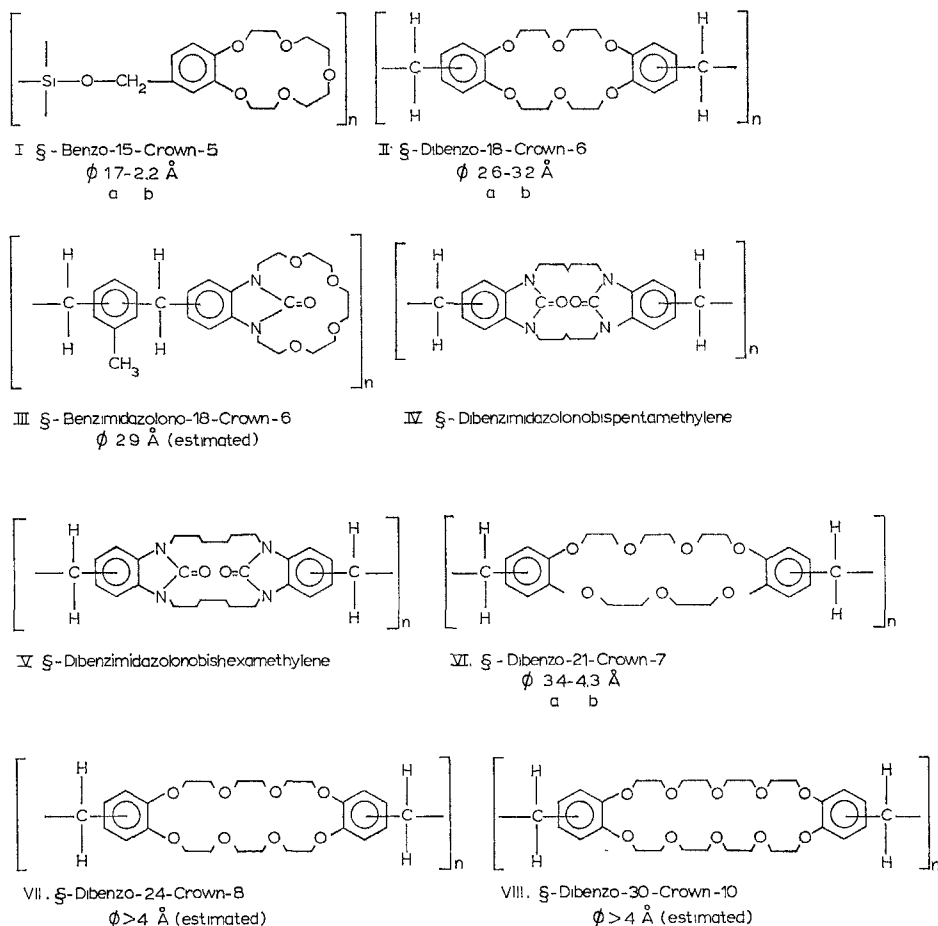


Fig. 7. Exchangers with cyclic polyethers as anchor groups, with O and N as heteroatoms. Ring diameter in accordance with the atomic models of (a) Corey-Pauling-Koltun and (b) Fisher-Hirschfelder-Taylor.

(b) ξ -Benzimidazolono-18-crown-6; ξ -dibenzenimidazonobispentamethylene; ξ -dibenzenimidazonobishexamethylene. Their complexing abilities for Rb^+ and Cs^+ are the same. In the sequence of increasing atomic number the alkaline earth cations are complexed more strongly. ξ -Benzimidazolono-18-crown-6 binds Ra^{2+} considerably more strongly than Ba^{2+} .

(c) β -Dibenzo-21-crown-7. This exchanger is selective for Rb^+ .

(d) β -Dibenzo-24-crown-8. This exchanger is selective for Cs^+ and very suitable for the separation of the heavier alkali metals such as K^+ , Rb^+ and Cs^+ .

(e) β -Dibenzo-30-crown-10. This large polyether ring shows little tendency to form complexes with metal cations. However, it can be used for the separation of uncharged organic molecules.

Analytical chemistry

The exchangers have numerous fields of application, including the separation of cations with a common anion, the separation of anions with a common cation, the separation of uncharged organic compounds and the determination of water.

Separation of cations with a common anion. Examples of some separations of the alkali elements in water or methanol are depicted in Figs. 8–12.

The separation of a salt (sodium chloride) from the corresponding acid (hydrochloric acid) is shown in Fig. 8. The ether ring also complexes the proton.

The separation of two strong bases is shown in Fig. 9. The exchanger charged with alkali metal hydroxide is of great value as a solid base in phase-transfer catalysis.

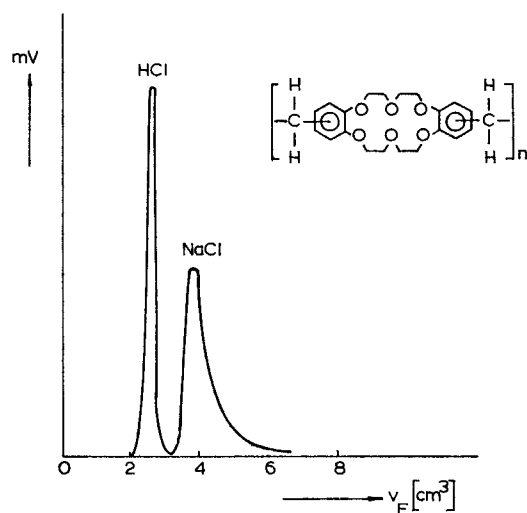


Fig. 8. Exchangers with cyclic polyethers as anchor groups: separation of 0.09 mg of HCl and 0.30 mg of NaCl by elution with water.

Fig. 10 shows the complete separation of the alkali metal halides by means of high-performance liquid chromatography (ion chromatography). The eluent is methanol. Using a pressure of 24 MPa (240 bar) at the top of the column, the separation is completed in 18 min. The exchanger with dibenzo-24-crown-8 as anchor group is especially selective for Cs^+ , and is of great value for the separation of Cs from medium-active waste solutions.

Fig. 11 shows the separation of all of the alkaline earth metal cations on β -benzimidazolono-18-crown-6. Anchor groups containing only O heteroatoms form

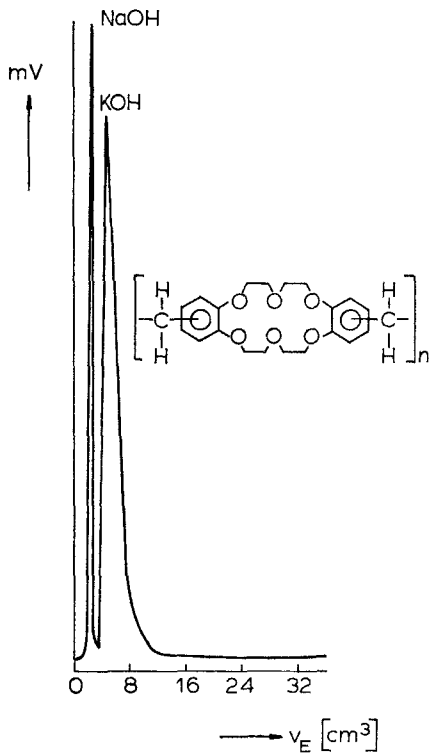


Fig. 9. Exchangers with cyclic polyethers as anchor groups: separation of 1.99 mg of NaOH and 2.80 mg of KOH by elution with water.

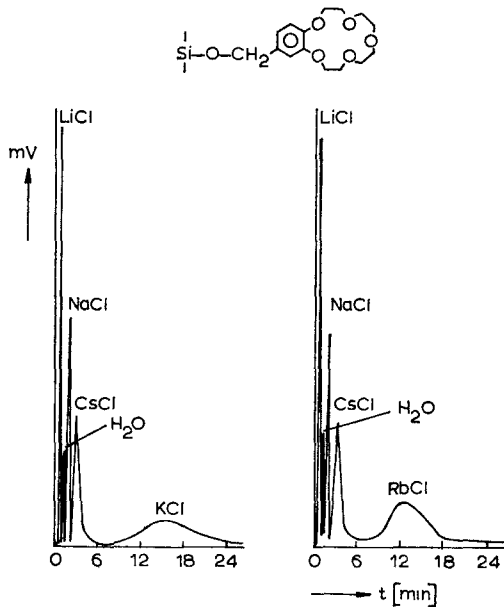


Fig. 10. Exchangers with cyclic polyethers as anchor groups: Separation of alkali metal halides by elution with methanol. Left: 0.020 mg of LiCl, 0.080 mg of NaCl, 0.330 mg of KCl and 0.276 mg of CsCl. Right: 0.020 mg of LiCl, 0.080 mg of NaCl, 0.423 mg of RbCl and 0.276 mg of CsCl. Flow-rate, 5.0 cm³/min; pressure, 24 MPa.

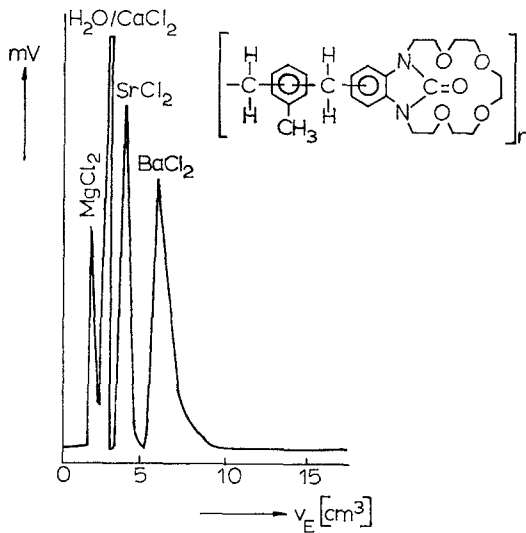


Fig. 11. Exchangers with cyclic polyethers as anchor groups: separation of alkaline earth metal chlorides by elution with methanol; 1.2 mg of MgCl_2 , 0.1 mg of CaCl_2 , 1.3 mg of SrCl_2 and 1.9 mg of BaCl_2 .

very strong complexes with Ba^{2+} salts, and therefore very large elution volumes are necessary. Very small amounts of ^{90}Sr can be separated from a large excess of Ca^{2+} , a problem that is important for the determination of ^{90}Sr in environmental fallout.

The separation of other nuclides, e.g., $^{133}\text{BaCl}_2/^{226}\text{RaCl}_2$, is also possible with these exchangers (Fig. 12). The problem of the separation of Ra^{2+} and Ba^{2+} was of great importance in the discovery of nuclear fission by Hahn and Strassmann. The rapid elution of traces of Ra^{2+} from Ba^{2+} is achieved best with methanol (Fig. 12, centre) or with 0.5 M hydrochloric acid (Fig. 12, bottom). In the latter instance, protonation of the N atoms occurs and an anion exchanger is formed.

The separation of transition metal salts or heavy metal salts can also be carried out easily using water as eluent.

Separation of anions with a common cation. As salts with the same cation but different anions will be separated according to the sequence of polarizability of the anions, anion separations are possible (Figs. 13–17).

The separation of alkali metal halides is illustrated in Fig. 13.

The separation of polyvalent anions is also possible (Fig. 14). The separation of traces of sodium sulphate from concentrated sodium chloride solutions is possible up to a molar ratio of 1:10,000.

Fig. 15 shows the separation of oxoanions of potassium halides. The separation of complex salts is also possible.

Because salt uptake is not dependent on pH, exchangers with no heteroatoms except oxygen are very useful for obtaining information about the composition of iso- and heteropolyacid systems. The aggregates formed on acidification of sodium vanadate are shown in Fig. 16. In alkaline solution (pH 12 or 9) hydrogenvanadate is separated from the slowly decomposing decavanadate ion. At about pH 5 dihydrogenvanadate and hydrogendecavanadate are present. At pH below 3 dihydrogenvanadate

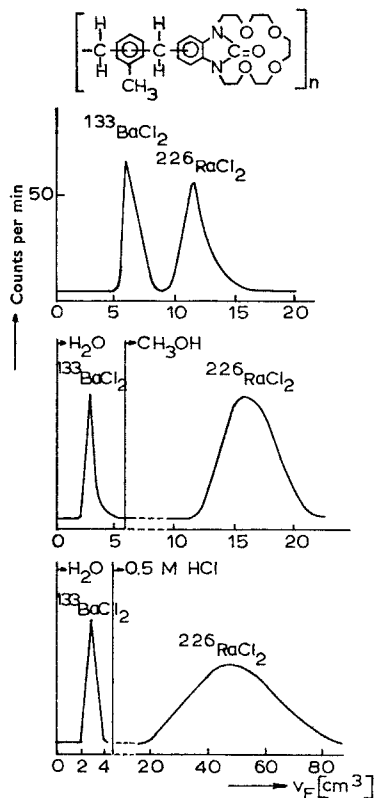


Fig. 12. Exchangers with cyclic polyethers as anchor groups: separation of ^{133}Ba -labelled BaCl_2 and $^{226}\text{RaCl}_2$. Top: 20 ng of BaCl_2 and 25 ng of RaCl_2 (molar ratio 1.5:1) by elution with methanol. Centre: 4 mg of BaCl_2 and 0.6 μg of RaCl_2 (molar ratio $10^4:1$) by elution with water or methanol. Bottom: 4 mg of BaCl_2 and 0.6 μg of RaCl_2 (molar ratio $10^4:1$) by elution with water or 0.5 M HCl.

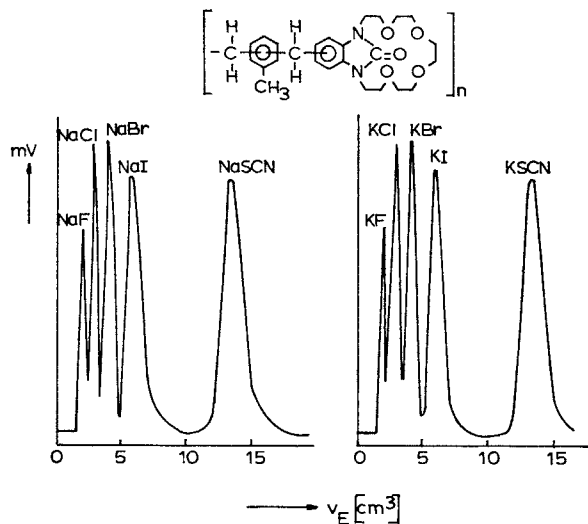


Fig. 13. Exchangers with cyclic polyethers as anchor groups: separation of alkali metal halides and thiocyanates by elution with water. Left: 0.2 mg of NaF, 0.4 mg of NaCl, 0.5 mg of NaBr, 0.5 mg of NaI and 0.7 mg of NaSCN. Right: 0.2 mg of KF, 0.4 mg of KCl, 0.5 mg of KBr, 0.5 mg of KI and 0.9 mg of KSCN.

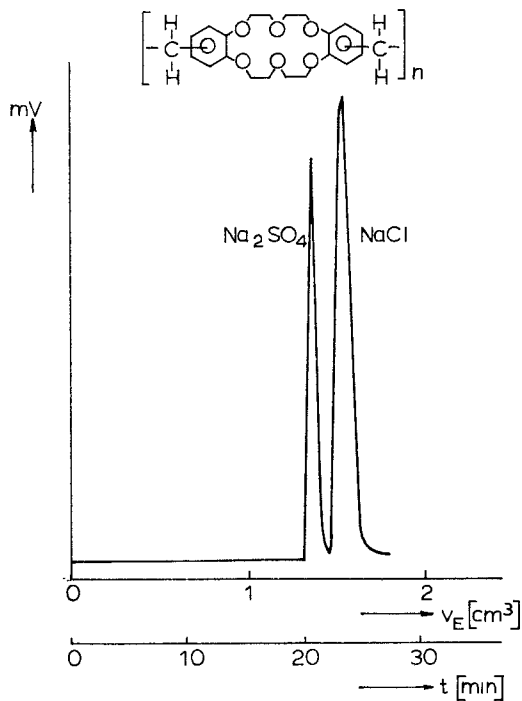


Fig. 14. Exchangers with cyclic polyethers as anchor groups: separation of 0.43 mg of Na_2SO_4 and 0.58 mg of NaCl by elution with water.

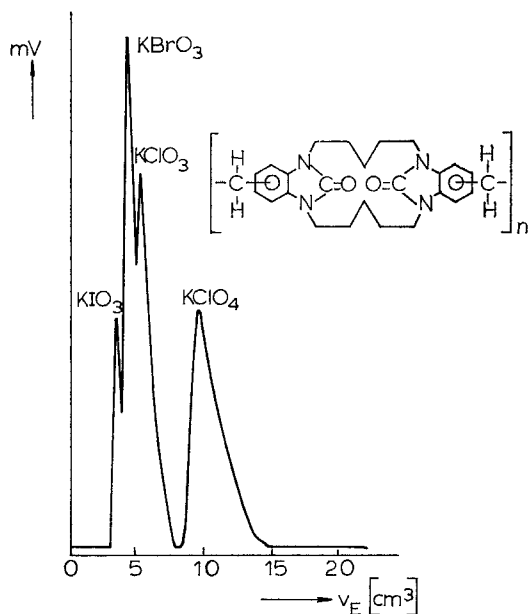


Fig. 15. Exchangers with cyclic polyethers as anchor groups: separation of potassium salts of halogen oxo acids by elution with water; 0.65 mg of KIO_3 , 0.85 mg of KBrO_3 , 0.61 mg of KClO_3 and 0.58 mg of KClO_4 .

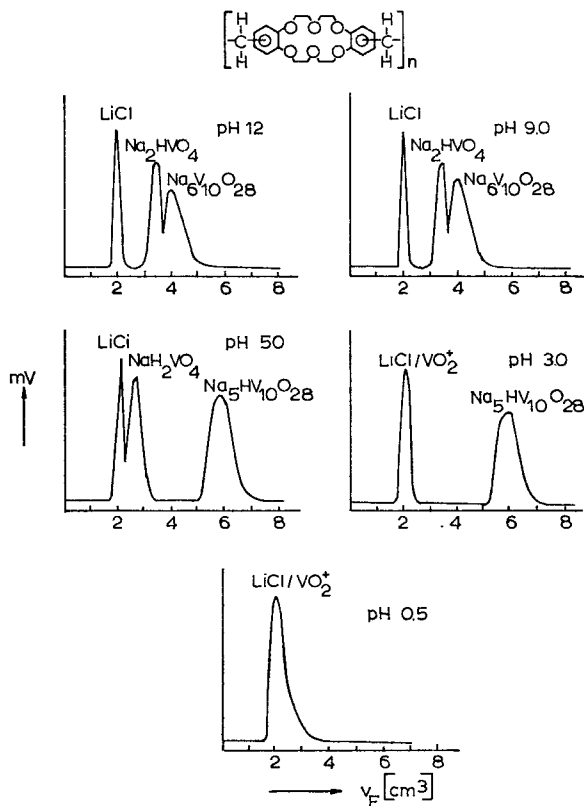


Fig. 16. Exchangers with cyclic polyethers as anchor groups: separation of 0.36 mg of NaH_2VO_4 and 3.4 mg of $\text{Na}_5\text{HV}_{10}\text{O}_{28}$ by elution with water at different pH.

and at pH below 0.5 hydrogendecavanadate are also converted into the vanadyl cation. The vanadyl cation is eluted together with the inert peak of LiCl.

Separation of uncharged organic compounds. Exchangers with cyclic polyethers as anchor groups are able to separate uncharged organic compounds. Separations caused by the matrix are not influenced by the different anchor groups. In the separation of other types of compounds, the properties of the anchor groups dominate. The best exchanger for separations of organic compounds in water or methanol is β -dibenzo-30-crown-10.

Compounds containing sulphur are usually bound very strongly. Fig. 17 shows the separation of urea and thiourea in water. This separation is important in the degradation of proteins, as proteins containing sulphur are identified as thiourea.

Aromatic compounds are probably bound by complexation, and three separations are shown in Fig. 18.

Determination of water. The determination of water in methanol as solvent serves as an example of the quantitative application of the elution chromatography of exchangers with cyclic polyethers as anchor groups. Methanol (Merck, analytically pure) itself contains a maximum of 0.01 % of water. This does not disturb the measurement, however, as a differential refractometer detector is used.

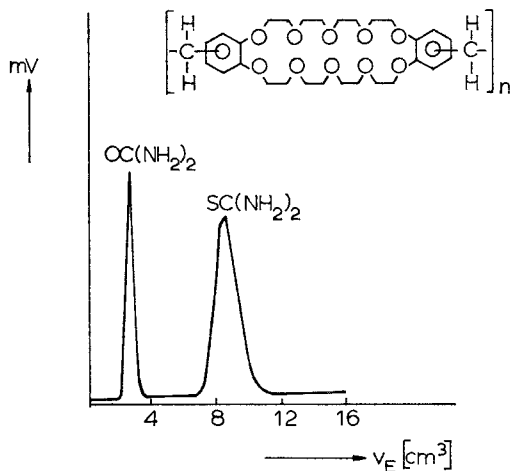


Fig. 17. Exchangers with cyclic polyethers as anchor groups: separation of 0.8 mg of urea and 0.8 mg of thiourea by elution with water.

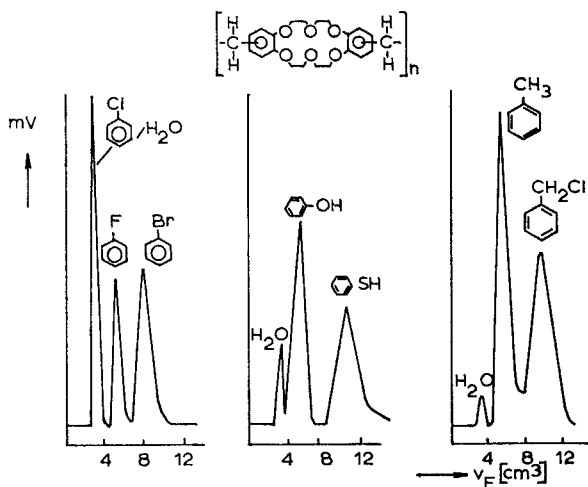


Fig. 18. Exchangers with cyclic polyethers as anchor groups: separation of benzene derivatives by elution with methanol. Left: 1.0 mg of fluorobenzene, 2.0 mg of chlorobenzene and 1.0 mg of bromobenzene. Centre: 0.7 mg of phenol and 0.6 mg of thiophenol. Right: 1.2 mg of toluene and 1.2 mg of benzylchloride.

Additional traces of water in methanol and in other organic solvents lead to a water band. In this way water of crystallization and association in salts and organic compounds can be determined. By quantitative evaluation of the area of the water peak it is now possible to determine concentrations down to 1 ppm.

Fig. 19 illustrates the elution of some salts with different water contents. In the examples shown, the salt appears before the water. In most other instances the salt is complexed more strongly than the water. In addition, it has been shown that the

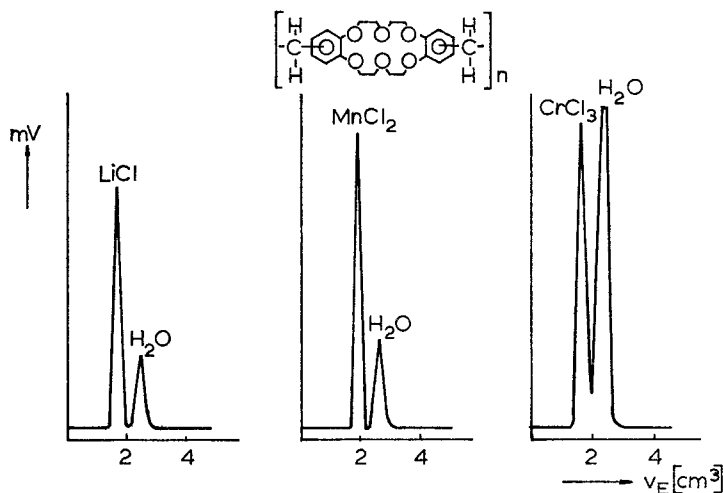


Fig. 19. Exchangers with cyclic polyethers as anchor groups: determination of water by elution with methanol. Left: 0.02 mg of $\text{LiCl} \cdot x\text{H}_2\text{O}$. Centre: 0.09 mg of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$. Right: 0.35 mg of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$.

water of solvation and crystallization in most salts is quantitatively stripped during complexation.

Preparative chemistry

Preparative applications of the exchangers include salt conversions (cations and anions changing partners), purification of organic compounds and anion activation in organic reactions.

Salt conversions. Salt conversions can be carried out easily by means of the exchangers, because their complexing power for cations is governed by the corresponding anion. Fig. 20 shows the conversion of LiSCN and RbCl into LiCl and RbSCN .

Column processing results in reaction yields of 100%, but large elution volumes and long separation times are necessary. The batch process is simpler and, after completion of the batch process the chromatographically and spectroscopically pure salts are washed from the exchanger with a small amount of solvent (Soxhlet apparatus). In this way thiocyanates and iodides, which are difficult to prepare by other methods, are easily produced on a gram scale.

Hence it follows that for the separation of trace amounts of cations from a large amount of other species sometimes the addition of the appropriate counter ion to the solution is necessary.

Anion activation. Numerous reactions can be carried out or improved in anhydrous solutions using anion activation by means of polyethers. This is very important if water interferes in the reaction.

In contrast to the soluble monomeric polyethers and alkylammonium and alkylphosphonium compounds, there is no pollution of the reaction system due to the solid exchanger. It is recovered from the reaction mixture by filtration and often repeated application is possible because of its high thermal and mechanical stability.

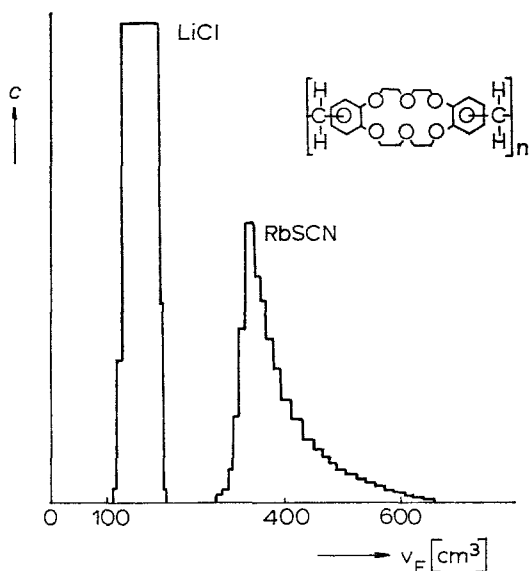


Fig. 20. Exchangers with cyclic polyethers as anchor groups: $\text{LiSCN} + \text{RbCl} \rightarrow \text{LiCl} + \text{RbSCN}$. Salt conversion of 0.520 g of LiSCN and 0.975 g of RbCl by elution with water. c is concentration.

Application of the exchangers as polymer catalysts in three-phase transfer catalysis (liquid–solid–liquid or solid–solid–liquid) proved to be of great value in the following reactions: (a) nucleophilic substitutions (exchange of halides, formation of nitriles and ethers, esterification, saponification); (b) alkylation reactions; (c) dichlorocarbene reactions; and (d) polymerization reactions. The uncharged exchangers are added to the solid salts or to a solution of them in water and then the mixture is stirred with a solution of the organic reactants in an organic solvent. When the reaction is completed, the exchangers are filtered, regenerated and used for the next reaction.

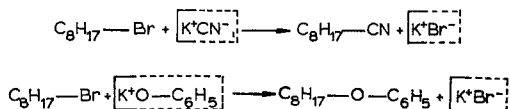
Table IV shows a comparison of the catalytic efficiencies of the exchangers in the formation of nitriles or ethers from the reaction of octyl bromide with activated cyanide or phenolate ions.

After a reaction time of 3 h for the formation of nitriles and 4 h for the formation of ethers, Kryptofix 222 B and ξ -dibenzo-18-crown-6 show the highest yields. Apart from the lower yield in the formation of the nitrile, ξ -dibenzo-18-crown-6 proves to be the best for all of the other reactions. The increase in yield and the shortening of the reaction time compared with the blank experiments shows that the exchanger can be used economically.

The application of ξ -dibenzo-18-crown-6 in the anionic polymerizations is illustrated in Table V. Polymerization of ethylene oxide or propylene sulphide is accomplished by the exchanger charged with carbazolyl potassium in tetrahydrofuran at low temperature. The osmometrically determined relative molecular masses for the two polymers are in good accordance with the theoretically determined values. Hence it follows that the polymerization is based on anionic catalysis. The relative molecular masses increase with increase in the amount of monomeric starting material and the catalyst used in the reaction.

TABLE IV

CATALYTIC EFFICIENCIES OF EXCHANGERS WITH CYCLIC POLYETHERS AND NON-CYCLIC ETHERS AS ANCHOR GROUPS



Reaction of octyl bromide with potassium cyanide or potassium phenolate to give octylcyanide or octyl phenyl ether, respectively.

<i>Exchanger</i>	<i>Formation of nitrile: yield (%)</i>	<i>Formation of ether: yield (%)</i>
Blank experiment without exchanger	0	7
§-Benzo-15-crown-5 (phenol)	1	29
§-Benzo-15-crown-5 (toluene)	0	36
§-Benzo-18-crown-6 (phenol)	10	45
§-Benzo-18-crown-6 (toluene)	7	44
§-Dibenzo-18-crown-6	75	93
§-O-CH ₂ -benzo-18-crown-6 (macroporous)	22	60
§-Dinaphtho-18-crown-6	5	52
§-Dibenzo-21-crown-7	36	89
§-Dibenzo-24-crown-8	37	77
§-Dibenzo-26-crown-6	0	31
§-Dibenzo-27-crown-9	15	56
§-Dibenzo-30-crown-10	53	50
§-Cryptate[2 _B .2]	2	46
§-Cryptate[2 _B .2.2] (resorcinol)	0	38
§-Cryptate[2 _B .2.2] (phenol)	2	35
§-Cryptate[2 _B .2 _B .2]	3	41
Kryptofix 222 B polymer	100	45
§-Benzimidazolono-18-crown-6	8	28
§-Benzomonoaza-15-crown-5	43	53
§-CH ₂ -(O-CH ₂ -CH ₂) ₂₋₁₁ -O-CH ₃ (macroporous)	0	31
§-CH ₂ -O- <i>tert.</i> -butyl (macroporous)	0	14
§-CH ₂ -O-CH ₃ (macroporous)	0	21

A number of applications of propylene oxide depend on the relative molecular mass. Polymers with a relative molecular mass of 5000–6000 are used in pharmaceuticals and cosmetics as protecting colloids and surfactants. Polymers with a relative molecular mass greater than 100,000 serve as lubricants and emulsifiers in photography and as films in packaging materials.

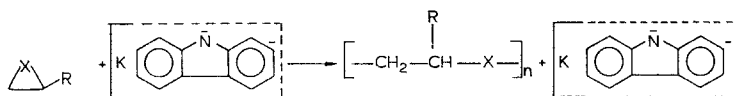
The technical polymerization is carried out using basic catalysts in the temperature range 100–200°C; 20% of the ethylene oxide reacts to give undesirable by-products.

CONCLUSION

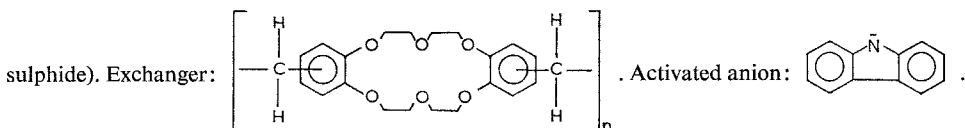
Exchangers with cyclic polyethers as anchor groups have numerous fields of applications. In contrast to conventional exchangers, cations and anions are complexed simultaneously and therefore can be applied as cation and anion exchangers. Differences in the stability constants of polyether complexes are large enough to

TABLE V

APPLICATION OF EXCHANGERS WITH CYCLIC POLYETHERS AS ANCHOR GROUPS IN ANIONIC POLYMERIZATIONS



Polymerization of ethylene oxide or propylene sulphide to poly(ethylene oxide) or poly(propylene



Starting material	Amount	Charged	Reaction	Reaction	Yield	Relative molecular mass		
Compound	Amount (mg)	of exchanger (mg)	with potassium carboxylate (mg)	temperature (°C)	time	(%)	Theoretical	Osmometric
Ethylene oxide	1677	51.2	4.8	25	27 days	53	38,000	35,000
	1170	8.8	2.0	25	14 days	46	—	—
	640	3.8	2.0	37	8 days	37	—	—
Propylene sulphide	950	5.0	3.0	-30	120 min	94	97,000	106,000
	1460	17.8	2.1	25	30 min	89	126,000	208,000
	929	93.0	2.2	25	30 min	65	268,000	209,000

render possible separations of complete sequences of cations and anions. The eluents used are pure solvents, *e.g.*, water or methanol.

The application of the new exchangers might be of great importance in the following two areas:

(a) In analytical chemistry, the most important possibility is in ion chromatography. Using high elution rates, separations with exchangers fixed to silica gel can be carried out easily and rapidly. A disadvantage is the low chemical stability of the stationary phases in alkaline solutions. Polystyrene beads with cyclic polyethers attached to the surface by methylene bridges show more favourable properties.

(b) In preparative chemistry, salt conversions and anion activation are important. For this purpose we are now preparing copolymers from vinyl and divinyl crown ethers and other cross-linkers by grain polymerization.

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