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Synthesis of resins with crown ethers units as anchor groups

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SUMMARY

Polymers containing benzo-13-crown-4 (**1**) and benzo-9-crown-3 (**2**) units (1) were crosslinked with formaldehyde, phenol/formaldehyde, and resorcin/formaldehyde (2,3). Resins (**3-8**) were contacted with aqueous solutions of lithium and aqueous solutions of sodium chloride at pH = 7 and pH = 11. Finally, re-extraction analysis were carried out by two systems, in methanol and in water. The extraction and re-extraction results were analyzed by atomic absorption.

INTRODUCTION

Macroheterocyclic ligands immobilized on insoluble supports offer distinct advantages over soluble compounds. In catalytic applications the ease of recovery of the insoluble ligands by filtration facilitates product purification and prevents their contamination with toxic macrocycles. It also permits recycling of the rather expensive ligands and the use of continuous flow reactors. These compounds have chiefly been applied for analytical purposes as chromatographic stationary phases in the separation of ionic and neutral inorganic and organic substances and in preparative chemistry as heterogeneous phase-transfer catalysts.

Because of their selective complexation of ions, macroheterocyclic ligands have been extensively investigated for applications in chemical analysis (4).

It was especially Blasius and his coworkers who explored in depth the analytical use of exchange resins with crown ethers as anchor groups (5,6-9).

This paper reports the synthesis of resins with crown ethers units as anchor groups by crosslinking of soluble polymers (**1** and **2**) with formaldehyde, phenol/formaldehyde and resorcin/formaldehyde and their lithium extraction and re-extraction properties.

EXPERIMENTAL PART

Synthesis of resins by crosslinking with formaldehyde.

General Method (2): 2 g of poly(crown ether) (**1** or **2**) were dissolved in 25 ml formic acid at boiling temperature. To this solution, 0.94 g formaldehyde 35% were added. The reaction mixture was stirred and refluxed for 5 h. It was poured on water-ice. The resin was purified in a Soxhlet with methanol for 8 h and dried under vacuum at 100°C.

Resin **3** is a brown solid and it was obtained in 90.6% yield; **4** is a yellow solid and it was obtained in 64% yield.

Synthesis of resins by crosslinking with phenol/formaldehyde and resorcin/formaldehyde.

General Method (3): 2.5 g of poly(crown ether) (**1** or **2**) were dissolved in 72 ml sulphuric acid 15%. To this solution 3 g formaldehyde 35% were added. The reaction mixture was stirred and heated for 8 h at 95-100°C. Then phenol or resorcin, 2.5 g were added. The reaction was kept for 8 h and after 3 g formaldehyde were added and heated at 100°C for 24 h with vigorously stirring.

The mixture was neutralized with $NaHCO_3$ 10%, and the solid was filtered and purified in a Soxhlet with methanol and water for 20 h. After, the product was dried under vacuum at 100°C.

Resins containing phenol (**5** and **7**) are yellow solids. **5** was obtained in 64% yield and **7** in 73% yield.

Resins containing resorcin (**6** and **8**) are orange solids. **6** and **8** were obtained in 99% yield.

Cation binding ability: The extraction of lithium and sodium was carried out in a solid-liquid system. The resins were contacted for 8 h with solutions of lithium and sodium chloride at pH = 7 and pH = 11. Tetramethylammonium hydroxide (TMAOH) was used as base for controlling pH, in order to eliminate any effect of metal ion binding by the crown ether moiety on the proton dissociation.

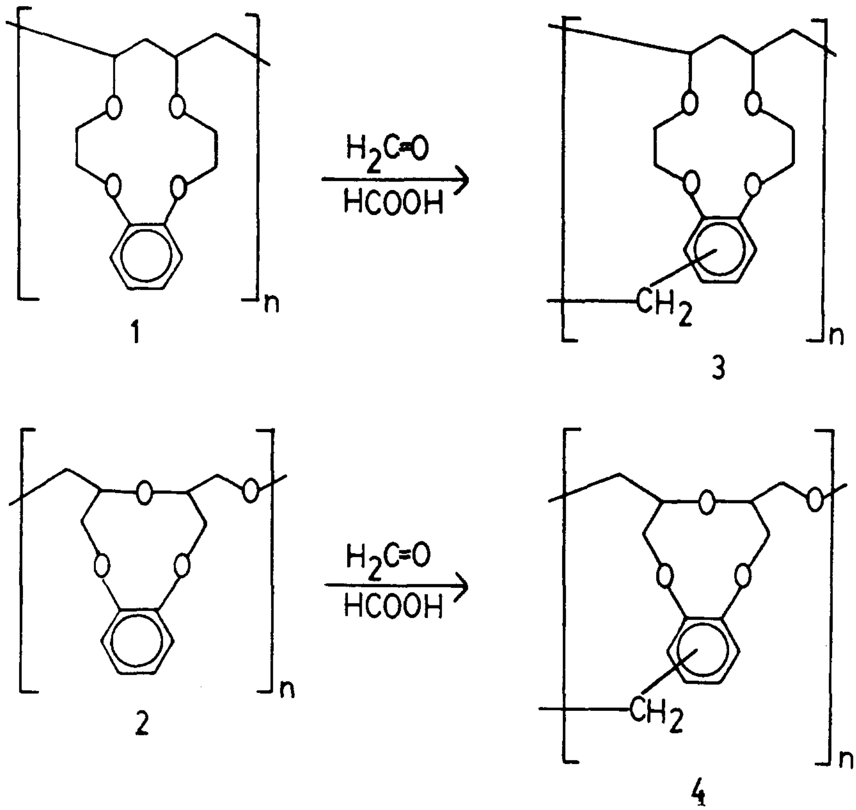
Re-extraction ability: The re-extraction of lithium was carried out in methanol and in water. The resins containing lithium were contacted for 8 h with methanol and with water. The best results were obtained in methanol.

Measurements: IR spectra were recorded on a Perkin Elmer 577 spectrophotometer. Lithium and sodium were analyzed on a Perkin Elmer 306 Atomic Absorption Spectrometer.

RESULTS AND DISCUSSION

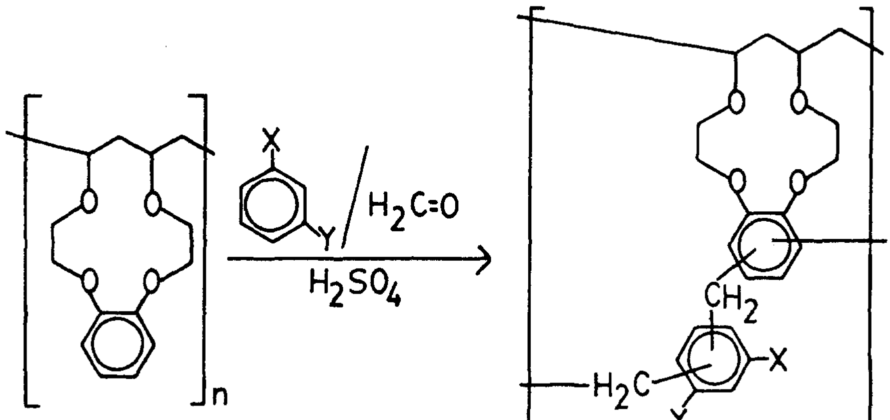
The resins were synthesized from soluble poly(crown ether)s **1** and **2**, formaldehyde, phenol/formaldehyde and resorcin/formaldehyde.

3 and **4** were prepared by reaction of **1** and **2** with formaldehyde in formic acid, yielding a network structure with methylene bridges in 90.6 and 64% yield, respectively.



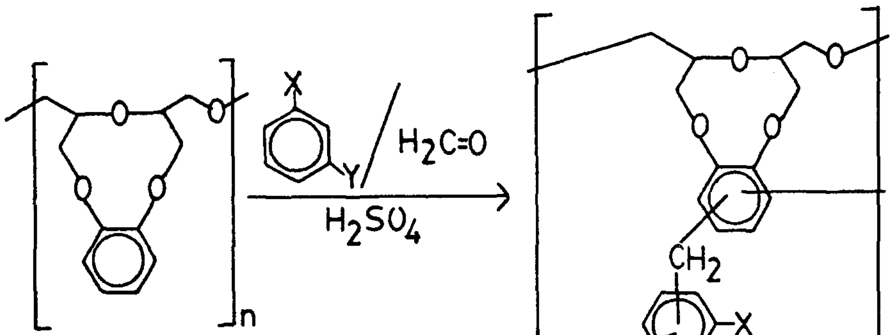
The IR spectra of **3** and **4** present characteristic absorption bands corresponding to $\nu_{C=C}$ at 1590 cm^{-1} and ν_{C-O} at 1100 cm^{-1}.

Also, crosslinked resins were synthesized by reaction of **1** and **2** with formaldehyde and additional crosslinking agents like phenol or resorcin.



1

5 : X = OH, Y = H
6 : X = Y = OH



2

7 : X = OH, Y = H
8 : X = Y = OH

These resins have phenolic hydroxyl groups; **5** and **7** from phenol, **6** and **8** from resorcin.

Resins containing phenol are yellow solids and were obtained in 64% and 73% yield, respectively. Those having resorcin are orange solids and were obtained in 99% yield.

The IR spectra present characteristic absorption bands corresponding to ν_{OH} at 3400 cm^{-1}, $\nu_{C=C}$ at 1590 cm^{-1} and ν_{C-O} at 1100 cm^{-1}.

All resins are insoluble in water and organic solvents.

Extraction properties of resins.

Extraction analysis of lithium and sodium were made. The results and conditions are given in Table 1.

Table 1. % of extraction of lithium and sodium

Resins	pH=7		pH=11		Crosslinking Agent	Crown ether unit
	Li^+	Na^+	Li^+	Na^+		
3	5.6	-	2.8	-	Formaldehyde	13-crown-4
4	5.8	-	2.9	-	Formaldehyde	9-crown-3
5	0.8	-	20.0	-	Phenol/Formald.	13-crown-4
6	1.7	-	70.1	-	Resorc./Formald.	13-crown-4
7	2.6	-	19.8	-	Phenol/Formald.	9-crown-3
8	25.6	-	77.5	-	Resorc./Formald.	9-crown-3

All resins extract lithium and the best results were obtained with those having resorcin and at basic pH. Sodium extraction was not observed under the experimental conditions.

Crown ethers containing phenolic nuclei are able to extract cations by complexation from a basic aqueous phase. On the complex formation the crown ethers undergo proton dissociation on the phenolic moiety to yield an anion, which in turn interacts intramolecularly with a metal ion complexed by the crown ether moiety (10).

Re-extraction properties of resins.

Re-extraction analysis of lithium in methanol and water were made. The resins release partially the cation. Major re-extraction was obtained in methanol. The results are given in Table 2.

Table 2. % of re-extraction of lithium

Resins	Methanol	Water	Crosslinking agent	Crown ether unit
3	11.79	6.09	Formaldehyde	13-crown-4
4	11.37	5.84	Formaldehyde	9-crown-3
5	22.82	13.82	Phenol/Formald.	13-crown-4
6	16.40	7.98	Resorc./Formald.	13-crown-4
7	16.00	11.43	Phenol/Formald.	9-crown-3
8	11.19	7.81	Resorc./Formald.	9-crown-3

In this case, the best results were obtained with resins prepared with phenol. With respect to crown ether units, the re-extraction of resins containing 13-crown-4 units is higher than those having 9-crown-3 units. This is attributed to the stability of the complex formed.

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