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Modification of phenolic resins containing crown ether units

J. Bartulín, M. Parra*, A. Ramírez, and H. Zunza

Departamento de Química, Facultad de Ciencias, Universidad de Concepción, Casilla 3-C, Concepción, Chile

SUMMARY

Phenolic resins containing 13-crown-4 and 9-crown-3 units (1) were modified by coupling and nitration in heterogeneous phase. The chromogenic resins extract Li^+ selectively and efficiently, and no extractions of Na^+ were found. The extractions were carried out with aqueous solutions of lithium and aqueous solutions of sodium chloride at pH = 7 and 11. Finally, re-extraction analysis of lithium in methanol and water were made. Resins release partially the cation. Major re-extraction was obtained with methanol.

INTRODUCTION

Pioneering work with chromogenic crown ethers has been made by Vögtle (2) and Takagi (3), who have extensively synthesized uncharged and charged (or proton dissociable) chromogenic crown ethers, respectively. Specifically, the proton-dissociable chromogenic crown ethers are quite attractive for selective cation determination in aqueous solutions.

Crown ethers with proton-dissociable chromophores are capable of extracting certain cations selectively from a basic aqueous phase.

This paper reports the modification of phenolic resins containing crown ethers units (**1-4**) by coupling and nitration in heterogeneous phase and their extraction and re-extraction behavior toward Li^+ and Na^+ ions.

EXPERIMENTAL PART

General Procedure for Diazo Coupling to Crown-Azo-Phenolic Resins (4):

A suspension of 0.027 mol (3.71 g) of p-nitroaniline in THF-H_2O (160/160 ml) containing HCl (6 ml), was cooled in an ice bath. To the mixture was added 0.027 mol (1.85 g) of $NaNO_2$ while stirring. The stirring was continued until the mixture turned clear. To the resulted diazonium salt solutions was quickly added a precooled THF-H_2O (30/30 ml) suspension of a crown phenolic resin (1.2 g) and $NaHCO_3$ (0.077 mol, 6.45 g) while stirring. The stirring was continued for 8 h. at room temperature. The solid was filtered and was washed successively by 10% K_2CO_3 and 0,2% CH_3COOH aqueous solutions. The resin was dried under vacuum at 100°C.

*To whom offprint requests should be sent

All resins (**5-8**) are red solids and were obtained in 100% yield.

General Procedure for Nitration to Crown-Nitro-Phenolic Resins (4):

To 1.26 g of crown phenolic resin suspended in chloroform (100 ml) was added concentrated HNO_3 (200 ml) while stirring and the mixture was cooled in an ice bath. The stirring and cooling was continued for 8 h. Water (200 ml) was added, the mixture was stirred vigorously and the solid was filtered and washed with water. The resin was dried under vacuum at 100°C.

All resins (**9-12**) are yellow solids and were obtained in 100% yield.

Cation Binding Ability (1):

The extraction of lithium and sodium was carried out in a solid-liquid system. The resins (100 mg) were contacted with solutions of lithium and sodium chloride (10 ppm) at pH = 7 and 11. The mixture was shaken vigorously at room temperature for 8 h. The pH was controlled by tetramethylammonium hydroxide (TMAOH).

Re-extraction Ability (1):

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.

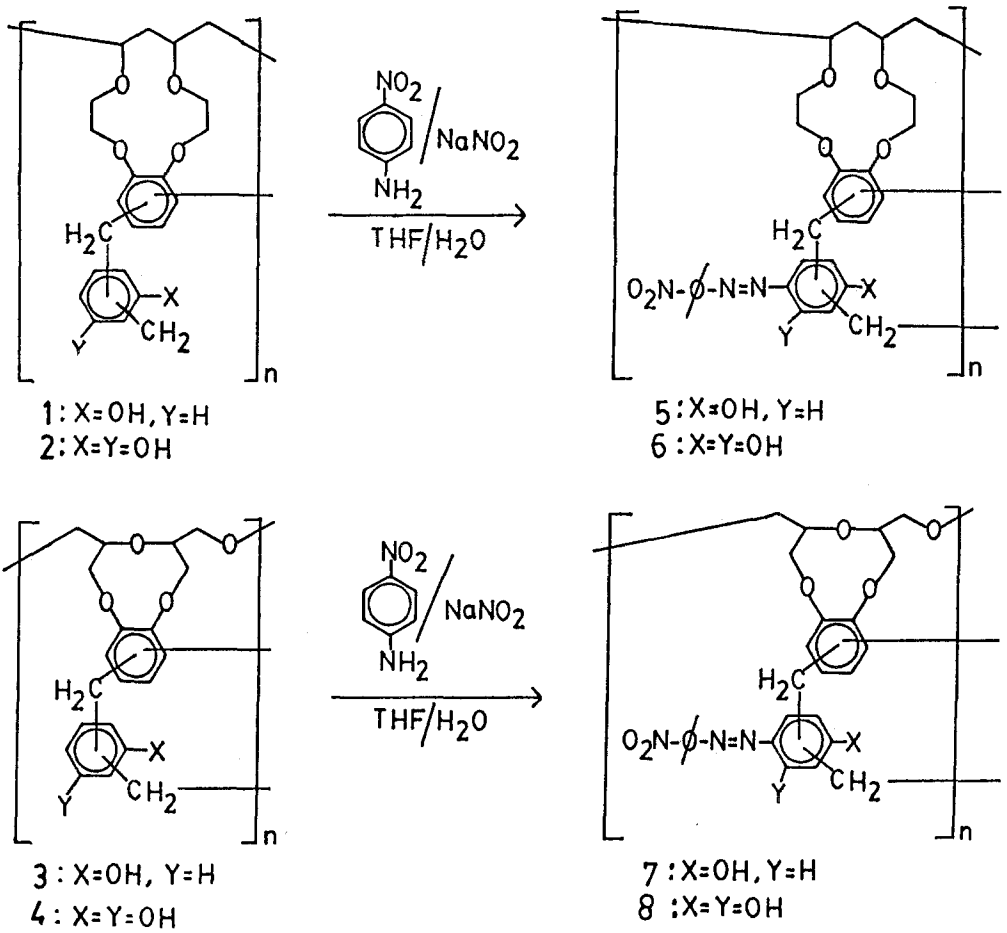
Measurements:

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

RESULTS AND DISCUSSION

The resins (**1-4**), previously reported (1), have phenolic hydroxyl groups **1** and **3** from phenol, **2** and **4** from resorcin. These resins were modified by coupling and nitration reactions in heterogeneous phase, obtaining crown phenolic resins with azo and nitro groups as chromophores, respectively.

The crown-azo-phenolic resins were synthesized by conventional diazo coupling using p-nitroaniline as the diazo component to obtain **5-8** in good yields.



1: X=OH, Y=H
2: X=Y=OH

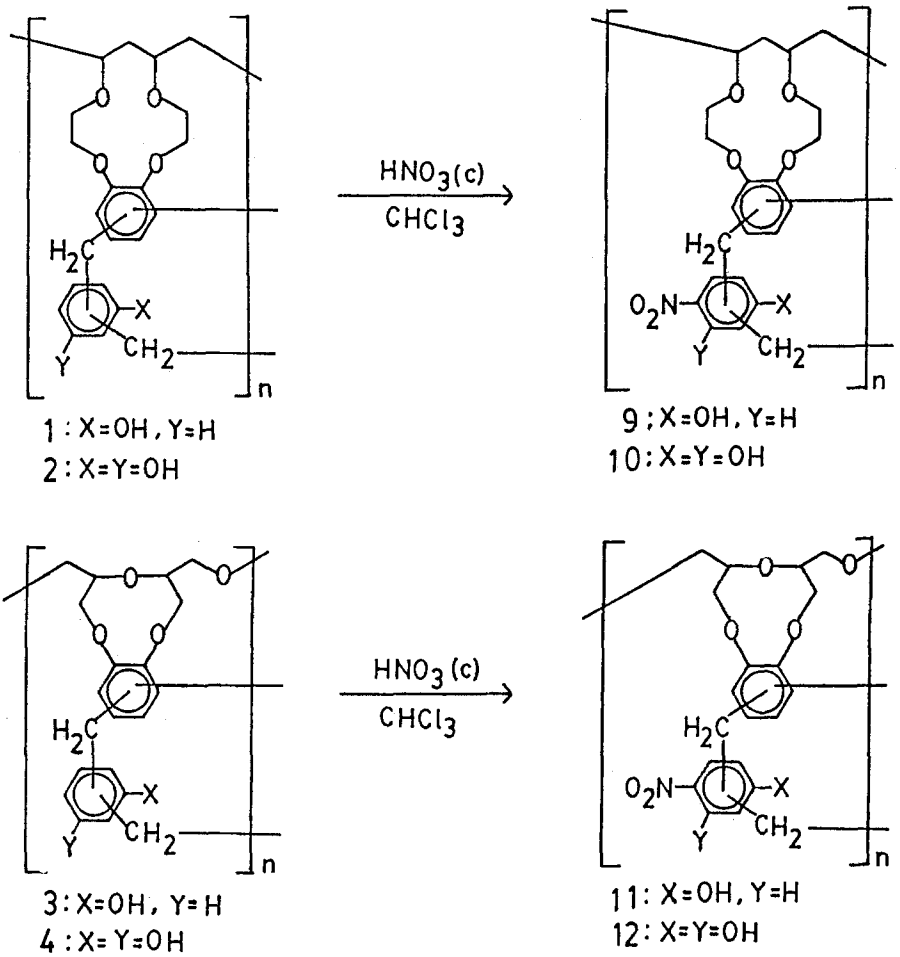
5: X=OH, Y=H
6: X=Y=OH

3: X=OH, Y=H
4: X=Y=OH

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

Both resins containing phenol (**5** and **7**) and those containing resorcin (**6** and **8**) are red solids. The IR spectra present characteristic absorption bands corresponding to νOH at 3400 cm^{-1}, νC=C, and νN=N at 1600 cm^{-1} and νC-O at 1100 cm^{-1}.

Also **1-4** were modified by nitration in heterogeneous phase with concentrated nitric acid, yielding crown phenolic resins, with nitro group in the network.



1 : X=OH, Y=H
2 : X=Y=OH

9 ; X=OH, Y=H
10 : X=Y=OH

3 : X=OH, Y=H
4 : X=Y=OH

11 : X=OH, Y=H
12 : X=Y=OH

These resins are yellow solids and their IR spectra show characteristic absorption bands corresponding to the nitro group at 1330 and 765 cm^{-1}, and absorption bands corresponding to νOH, νC=C and νC-O at 3400, 1600 and 1100 cm^{-1}, respectively.

Extraction Properties of Resins.

Extractions of lithium and sodium were carried out from an aqueous solution. Only lithium can be extracted demonstrating high Li^+ selectivity. Tetramethylammonium hydroxide (TMAOH) was used as the base for controlling pH, to eliminate any effect of metal ion binding by the

crown ether moiety on proton dissociation (5). The results and conditions are given in Table 1.

Table 1. % of extraction of lithium and sodium

Resins	pH = 7		pH = 11		Chromophor and Phenolic moiety	Crown ether unit
	Li^+	Na^+	Li^+	Na^+		
5	1.0	-	4.5	-	N=N-Phenol	13-crown-4
6	21.0	-	60.0	-	N=N-Resorcin	13-crown-4
7	5.4	-	4.5	-	N=N-Phenol	9-crown-3
8	32.0	-	60.5	-	N=N-Resorcin	9-crown-3
9	5.1	-	7.1	-	NO_2-Phenol	13-crown-4
10	17.9	-	49.0	-	NO_2-Resorcin	13-crown-4
11	6.0	-	6.9	-	NO_2-Phenol	9-crown-3
12	29.4	-	50.7	-	NO_2Resorcin	9-crown-3

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

When lithium was extracted into the resins by complex formation, the colour of the resins changed from red to deep brown in the crown azo-phenolic resins (**5-8**) and from yellow to red in the crown nitro-phenolic resins (**9-12**).

Re-extraction Properties of Resins.

Re-extraction analysis of lithium in methanol and water were made. The results are given in Table 2.

Table 2. % of re-extraction of lithium

Resins	Methanol	Water	Chromophor and Phenolic moiety	Crown ether unit
5	26.67	14.68	N=N-Phenol	13-crown-4
6	20.80	8.50	N=N-Resorcin	13-crown-4
7	17.88	12.46	N=N-Phenol	9-crown-3
8	10.51	8.00	N=N-Resorcin	9-crown-3
9	41.21	20.75	NO_2-Phenol	13-crown-4
10	22.45	11.50	NO_2-Resorcin	13-crown-4
11	20.21	13.60	NO_2-Phenol	9-crown-3
12	12.85	8.50	NO_2-Resorcin	9-crown-3

The resins release partially the cation. Major re-extraction was obtained in methanol. In this case, the best results were obtained with resins having nitro-phenol moiety. With respect to crown ether units, the re-extraction of resins containing 13-crown-4 is higher than those having 9-crown-3 units. This is attributed to the stability of the complex formed.

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