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DESIGN OF ION-EXCHANGE RESINS SELECTIVE OF CAESIUM. SYNERGISTIC EFFECT OF MACROCYCLE IN PHENOLIC RESINS

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ABSTRACT

The extraction of caesium by resorcinol based resins was investigated. At high hydroxide concentration ($[OH^-] = 0.15$ M), the alkali-metal cations' sorption selectivity (determined in competitive extraction system) for resorcinol resins was found to be $Cs^+ > Li^+ > Rb^+ > K^+ > Na^+$, whereas at pH 7 this selectivity was found to be $Cs^+ > Rb^+ > K^+ >> Na^+ \approx Li^+$. Different mechanisms of ion exchange occurring in these phenolic resins can explain this selectivity series. Then different macrocycles were incorporated in the resins. The ionoselective properties of these new ion-exchange resins are strongly influenced by the nature of the crosslinker. The presence of macrocycles lead to an improvement of selectivity towards caesium in relation with the size of the macrocycles introduced.

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INTRODUCTION

Selective complexation and ion exchange of a targeted metal ion by a given polymeric reagent is an important objective for many applications such as water treatment, hydrometallurgy, and chromatography. The methods have found widespread applicability owing to their selectivity (1). The ion-exchange reaction is an extremely versatile process and is well suited to the complexation of cations or anions through electrostatic binding. Cation-exchange resins have a wide application in industry and in environmental remediation. However, common cation-exchange resins with carboxylic acid, sulfonic acid, or phosphonic acid groups usually provide only poor differentiation of a given ion from ions with the same charge (2). This obviates their use for practical recovery processes, which require the selective sorption of valuable or toxic metal cations from a background of useless innocuous ions that are present at much higher concentrations. Therefore, the preparation of new chelating polymers bearing ion-exchange groups would lead to ion-exchange resins with superior selectivity (1,3).

Early works have shown that phenolic ion-exchange resins may be highly selective for the recovery of Cs^+, even in the presence of large excess of Na^+ (4). To further increase the Cs^+ selectivity, resorcinol rather than phenol was used to form condensation polymers with formaldehyde (5,6). We have recently reported the successful extraction of Cs^+ from an alkaline leaching solution of spent catalysts (7).

In order to improve the ionoselective properties shown by resorcinol-formaldehyde resins, different macrocycles have been incorporated in those ion-exchange resins. The influence of the pH during resin synthesis and the nature of crosslinker on the ionoselective properties of resins were also evaluated by using a competitive test that involved five alkali metal ions.

EXPERIMENTAL

Reagents

1,3-Benzenediol (resorcinol), Sigma, dibenzo-18-crown-6 (DB18C6) and dibenzo-24-crown-8 (DB24C8), Merck, formaldehyde (37% aqueous solution) and acetaldehyde, Acros, and sodium hydroxide and hydrochloric acid, Aldrich, were used as received. The alkali metal hydroxide solutions were prepared by dissolving alkali hydroxides, Aldrich, in the form of monohydrate for caesium and lithium, in bidistilled water (Büchi Fontavapor 285).

Resins Synthesis

The condensation reactions used to synthesize resorcinol formaldehyde resins **1** to **6** are shown in Fig. 1. Resorcinol-formaldehyde resin **1** was synthe-

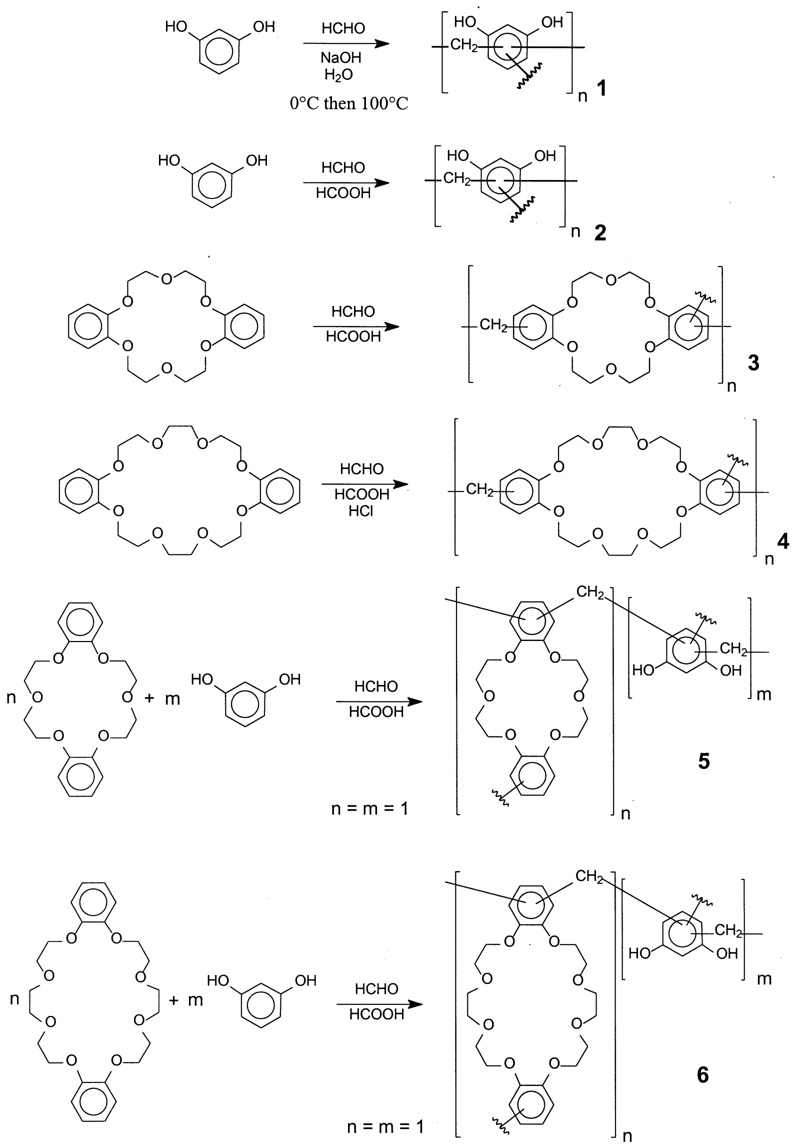

Figure 1. Condensation polymerization and hypothetical structure of resins **1** to **6**.

sized by alkaline polycondensation of formaldehyde with resorcinol. A resorcinol/formaldehyde/NaOH/H_2O mole ratio of 1:2.5:1.5:50 was used (6,7). During formaldehyde addition, the solution was cooled to 0°C and then stirred at room temperature for 1 h. After curing, the polymers were crushed, sieved to −80

+200 ASTM mesh size particles, washed, and conditioned by subjecting them to two 1 N HC1/0.1 N NaOH cycles. The resins were finally converted to acid form and washed thoroughly with water until neutral.

Resins **2–6** were synthesized by condensation polymerization of the corresponding monomers with formaldehyde in formic acid according to a procedure previously described for dibenzo crown ether (8). Although resin **3** was commercially available, the synthesis was done in order to compare resin synthesized in the same conditions. Slight modification was used to synthesize insoluble resin **4**. Dibenzo-24-crown-8 (45 mmol) was dissolved in a solution of formic acid (100 mL) and formaldehyde (100 mL). The mixture was refluxed for 2 h and allowed to cool at room temperature. Then, 10 mL of concentrated hydrochloric acid was added and the mixture was refluxed for 2 h. The precipitate was collected, washed, and conditioned as previously.

The condensation reactions used to synthesize resorcinarene-acetaldehyde and resorcinol acetaldehyde resins **8** and **9** are shown in Fig. 2. Resorcinarene **7** was synthesized according to a procedure previously described (9). Resins **8–9** were synthesized by alkaline polycondensation of acetaldehyde with resorcinol or resorcinarene **7**. A phenolic compounds/acetaldehyde/NaOH/H_2O mole ratio of 1/2.5/1.5/50 was used. Control of the temperature of the solution was not necessary, as the polymerization process was not exothermic unlike polycondensation

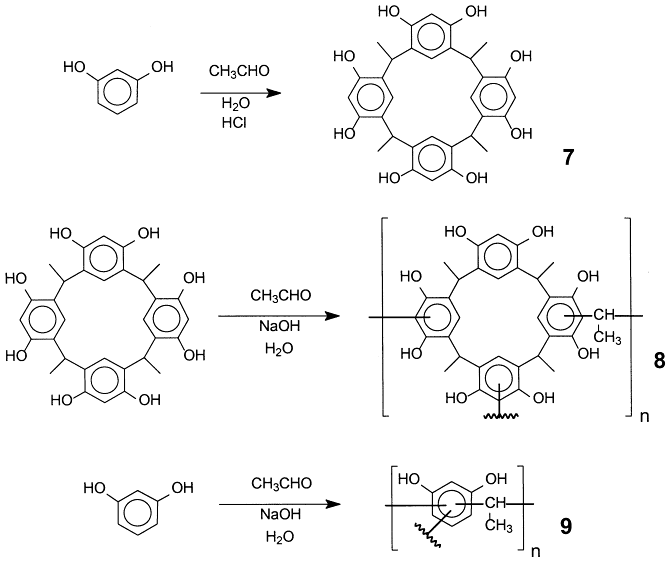

Figure 2. Synthesis of resorcinarene **7**, condensation polymerization, and hypothetical structure of resins **8** and **9**.

with formaldehyde. The resins were then collected, washed, and conditioned as previously. For all synthesis the chemical yield was quantitative.

Metal Extraction and Analytical Procedure

Competitive alkali metal sorption by resins was performed according to a method previously described (7). A known amount of resin was shaken for 8 h with the solution of the five alkaline salts. The distribution coefficient was calculated as follows:

$$D = \frac{[M^+]_i - [M^+]}{[M^+]} \times \frac{V}{m}$$

The concentration of the metal cations before and after adsorption was determined by atomic emission spectroscopy (Perkin-Elmer type 1100 M: air-acetylene flame). The subscript i refers to initial conditions, V (mL) to volume of solution, and m (g) to mass of resin (dry). After 8 h of contact, no variation of distribution coefficient of alkali metal or pH were noticed. Standard deviations were determined from six independent ion-exchange experiments.

The selectivity M_1/M_2 was calculated as follows:

$$S_{M_1/M_2} = \frac{D_{M_1}}{D_{M_2}}$$

The pH of the solutions was determined before and after extraction using a Suntex 2000 A pH meter.

RESULTS AND DISCUSSION

Phenolic resins have been thoroughly studied and the effect of numbers of synthesis variables on the Cs^+ affinity of those resins has been studied: phenolic compounds, temperature reaction, ratio of reactant, and choice of catalyst (6,7,10). The high selectivity toward Cs^+ was explained by hydration energy of the different alkali metal ions (11), but this could not explain the difference of selectivity towards Cs^+ between different substituted phenol (7). To improve the selectivity for Cs^+ in those resins, new starting materials and new experimental procedures were used and an original competitive extraction test was used to compare their ionoselectivity.

Batch Competitive Extraction of Alkali-Metal Cations

Methods previously described for the evaluation of ionoselective properties with multicomponent solutions determine the efficiency of sorption using a stripping method (8, 12, 13). The stripping is performed with an aqueous HCl solution. In those cases, for the correct evaluation of ionoselective properties the stripping step should be completed. Nevertheless, it has been shown that the efficiency of the back-extraction step was dependent on the type of alkali-metal cations and anions involved (8). In those cases, extraction efficiencies were the result of a two-step process (sorbtion/stripping). Furthermore, uncomplexed alkali-metal salts from the resin bed could alter the result.

Evaluation was performed by using a solution of the alkali-metal hydroxides (7). The concentration of the salts and the ratio between the volume of solution and mass of polymer were modified in order to improve extraction and precision, thus margin of error was minimized.

Evaluation of Resorcinol-Formaldehyde Resin

Resorcinol-formaldehyde resin **1** was synthesized according to the procedure previously described (7). The control of the temperature during formaldehyde addition improves the reproducibility as well as the ion-exchange capacity (7).

The resin **1** was tested with a solution of the five alkali-metal salts (Fig. 3). At high hydroxide concentration ($[OH^-] = 0.15$ M), the alkali-metal cations sorption selectivity was found to be $Cs^+ > Li^+ > Rb^+ > K^+ > Na^+$. The resorcinol-

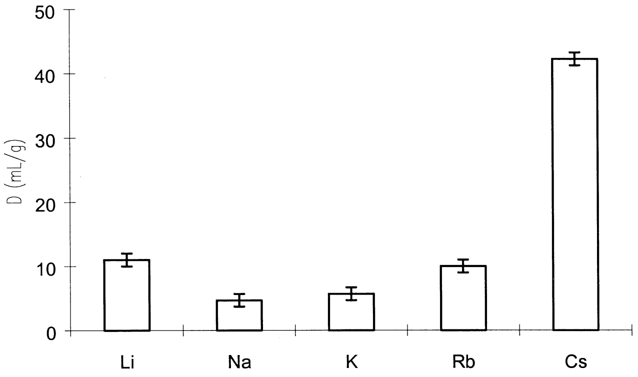

Figure 3. Distribution coefficient of alkali metal cations from 4 mL aqueous solution containing [LiOH] = [NaOH] = [KOH] = 0.5 M, and $[RbNO_3] = [CsNO_3] = 0.25$ M by 0.2 mmol (27 mg) of resin **1** after 8 h of contact at high hydroxide concentration, $[OH^-] =$ 0.15M.

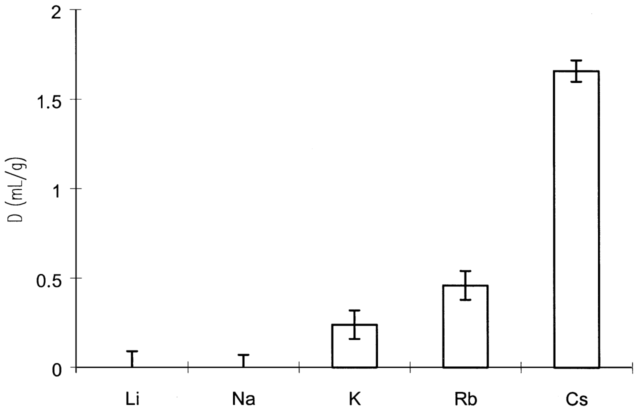

Figure 4. Distribution coefficient of alkali metal cations from 4 mL aqueous solution containing $[LiNO_3] = [KNO_3] = [RbNO_3] = [CsNO_3] = 0.25$ M, $[NaNO_3] = 0.15$ M, and $[NaOH] = 0.15$ M by 0.2 mmol (27 mg) of resin **1** after 8 h of contact at low hydroxide concentration (equilibrium pH = 7). The pH of the solution varies from 13 to 7 due to ion-exchange process.

formaldehyde resin strips Cs^+ off with Cs^+/Na^+ selectivity of 9. This resin shows also a high selectivity for Li^+ with a Li^+/Na^+ selectivity greater than 4.

The extraction of Cs^+ by phenolic resins is believed to involve cation exchange with a phenolic proton to form Cs^+ phenolate. The present result suggests different mechanisms of ion exchange in the resorcinol-formaldehyde resins. The first process involved the acid strength of phenolic-OH groups. The selectivity order for alkali-metal cations on weakly acidic cation-exchange resins, like phenolic resins, follows the inverse lyotropic series $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$ (14). The second process involved the stabilization of the complex alkali-metal cation/phenolate. This higher stabilization could be explained by interaction of Cs^+ ions with lower hydration energy compared to the other alkali-metal ions. In addition, benzene rings could participate as π-donor in the complexation of metal cations (15,16). The hydroxy group of resorcinol could also be involved in non-covalent bonding interaction with cations (11).

When the concentration of hydroxide was lower than ion-exchange capacities, pH varies from 13 to 7 due to ion-exchange process. The alkali-metal cation sorption selectivity was found to be $Cs^+ > Rb^+ > K^+ >> Na^+ \approx Li^+$ (Fig. 4). Under those conditions, the acid strength of the phenolic groups couldn't play a part, and the ion-exchange capacity was lower. Consequently, the second process was the only one effective, so very high selectivity for Cs^+ toward Li^+ and Na^+ was observed.

Improvement of Phenolic Resin Selectivity Towards Caesium by Acid Catalyzed Copolymerization of Crown Ether

Specific interaction of weakly hydrated Cs^+ ions with neutral oxygen and aromatic groups could explain the selective extraction of this ion by resorcinol-formaldehyde resins. To further probe this hypothesis, different macrocycles with neutral oxygen and aromatic groups were introduced in the resins and their influence on the selectivity towards Cs^+ was then checked. These macrocycles, like crown ether and resorcinarene, have cavities of various diameter and shape and could form stable complexes by coordination of metal cations within their cavities (17,18). Introduction of these macrocycles in the bulk of resorcinol-based resins could modulate the selectivity toward alkali-metal cation as the function of type and cavity diameter.

Influence of Type of Catalysis on Ionoselectivity

Dibenzo crown ether doesn't react with aldehyde and sodium hydroxide. Conversely, it can be polymerized with formaldehyde with formic acid. It is known that the yield and composition of crosslinked phenol-formaldehyde resins are strongly influenced by the polymerization reaction conditions, such as the ratio of the formaldehyde to phenol monomer, pH, and reaction temperature (10). For the correct evaluation of the ion exchange polymers, the ionoselective properties of resin **1** were compared to resorcinol-formaldehyde synthesized in acid media, resin **2**.

The physical form of the resins was strongly different depending on kind of catalysis used. Acid catalyzed resins were in the form of a pulverulent brown solid, although base synthesized resins were in the form of hard solid that could be hardly crushed. Physical properties were different, but they could be evaluated in the same conditions. The ionoselective properties of resin **1** and **2** were comparable, but acid catalyzed resins (i.e., **2**) tend to form slurry. This property could limit their use, but their evaluation at laboratory scale remain possible.

Synergistic Effect of Crown Ether on Caesium Selectivity

The copolymerization of resorcinol and dibenzo crown ether under acidic conditions was then carried out. The condensation of dibenzo crown compounds with formaldehyde in formic acid occurs with crosslinking by methylene group (19). Under those conditions, no preorganization of resorcinol and crown ether could be obtained, which limits the control of the structure of the resultant copolymer. We arbitrarily set the ratio of crown ether/resorcinol to 1.

Table 1. Distribution Coefficient of Alkali-Metal Cations with Resin **3** and **4** from 4 mL Aqueous Solution Containing [LiOH] = [NaOH] = [KOH] = 0.5 M and [$RbNO_3$] = [$CsNO_3$] = 0.25 M by 0.2 mmol (77 and 95 mg, respectively) of Resin **3** and **4** after 8 h of Contact at High Hydroxide Concentration ([OH] = 0.15 M).

	D (mL/g)				
Resins	Li^+	Na^+	K^+	Rb^+	Cs^+
3	0 ± 1.2	0 ± 1.1	4.5 ± 1.2	1.9 ± 1.2	0 ± 1.2
4	0 ± 1.3	0 ± 1.5	0 ± 1.3	0.7 ± 1.3	1 ± 1.3

Acid synthesized poly(dibenzo crown ether-co-formaldehyde), resins **3** and **4**, were stable at pH 14. Although, those resins at pH 7 and in the presence of nitrate ions show high extraction of alkali-metal cations (8), distribution coefficients at pH > 14 were found to be lower (Table 1). Those low capacities were explained by the formation of strong complexes between alkali-metal cations and hydroxide ions.

Introduction of macrocycles in resorcinol-formaldehyde resins strongly modifies the sorption of alkali-metal ions (Fig. 5). For resin **5,** the distribution coefficient of Na^+ and K^+ was improved whereas the distribution coefficient of Rb^+ decreased as expected from the relationship between the crown ether cavity (dibenzo-18-crown-6) and metal ion diameters. The distribution coefficient for Cs^+ was raised. When dibenzo-24-crown-8 was used, resin **6**, improvement of the

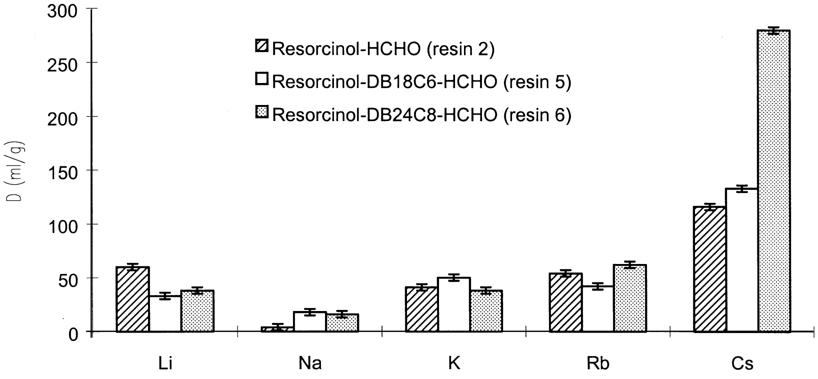

Figure 5. Comparison of the distribution coefficient of alkali-metal cations from 4 mL aqueous solution containing [LiOH] = [NaOH] = [KOH] = 0.5 M, and [$RbNO_3$] = [$CsNO_3$] = 0.25 M by 0.2 mmol (27mg, 105mg and 122 mg respectively) of resins **2**, **5**, and **6** after 8 h of contact at high hydroxide concentration [OH^-] = 0.15 M.

distribution coefficient of Na^+, Rb^+ was observed, but especially an increase of distribution coefficient of Cs^+ by a factor 2 was noticed. The strong improvement of Cs^+ extraction and Cs^+ selectivity could be attributed to a synergy between the two kinds of structure having affinity towards Cs^+. The presence of additional neutral oxygen atoms that could interact with Cs^+ ions leads to resins having a Cs^+/Na^+ selectivity greater than 17.

Copolymerization of Macrocycle in Basic Conditions

Unlike phenol, high reactivity of resorcinol with formaldehyde didn't allow the formation of a well-defined product, calixarenes. Nevertheless, with acetaldehyde, resorcinol forms in high yields via simple, one-step procedures in acidic media and without using templates or high dilution techniques a cyclotetramer (9), resorcinarene **7** (Fig. 2). Furthermore, the selective complexation of Cs^+ by resorcinarene has been described (20), thus the introduction of such macrocycle with acetaldehyde in basic condition was undertaken.

Effect of the Crosslinker on Ionoselective Properties of Phenolic Resins

The result achieved for the resins **1** and **9**, synthesized in the same conditions are given in Fig. 6. Use of acetaldehyde instead of formaldehyde lower the

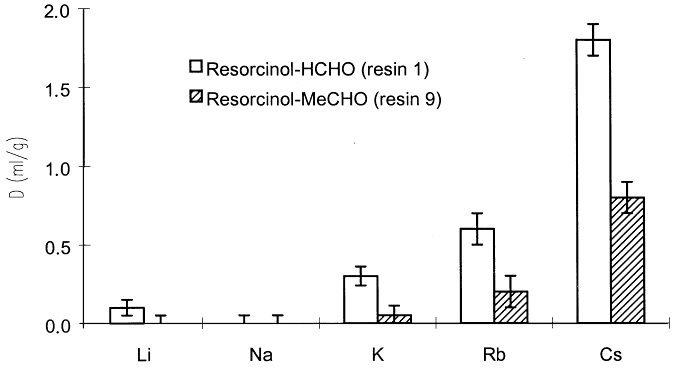

Figure 6. Influence of the crosslinker on ionselective properties of resins **1** and **9.** Distribution coefficient of alkali-metal cations from 4 mL aqueous solution containing $[LiNO_3] = [KNO_3] = [RbNO_3] = [CsNO_3] = 0.25$ M, $[NaNO_3] = 0.15$ M, and $[NaOH] = 0.15$ M by 0.2 mmol (30mg) of resin after 8 h of contact at low hydroxide concentration (equilibrium pH = 7). The pH of the solution varies from 13 to 7 due to ion-exchange process.

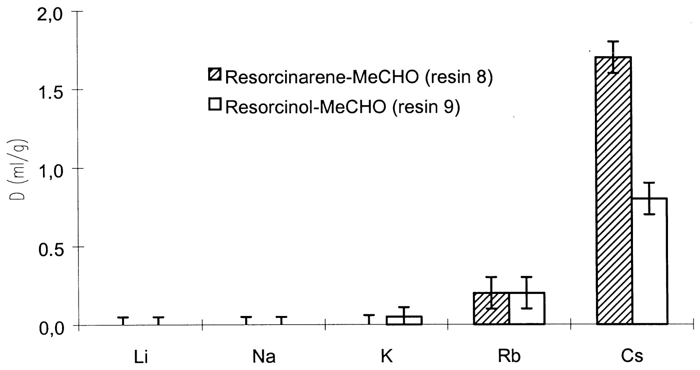

Figure 7. Influence of resorcinarene on ionoselective properties of resins **8** and **9.** Distribution coefficient of alkali-metal cations from 4 mL aqueous solution containing [$LiNO_3$] = [KNO_3] = [$RbNO_3$] = [$CsNO_3$] = 0.25 M, [$NaNO_3$] = 0.15 M, and [NaOH] = 0.15 M by 0.2 mmol (30 mg) of resin after 8 h of contact at low hydroxide concentration (equilibrium pH = 7). The pH of the solution varies from 13 to 7 due to ion-exchange process.

ionoselective properties of the phenolic resins. Steric hindrance and increasing of hydrophobicity could explain this phenomena. Despite the lower capacity, the alkali-metal sorption selectivity was found to be similar.

Influence of Resorcinarene on Ionoselective Properties of Phenolic Resins

The ionoselective properties of resin **8** were compared with resin **9** synthesized in the same conditions (Fig. 7). In both cases, the ratio resorcinol/acetaldehyde was kept constant. Comparison of the ionoselective properties of resins **8** and **9** exhibited the influence of pre-organization on Cs^+ selectivity. Resins **8** and **9** contained the same constituent resorcinol, acetaldehyde, and the initial proportion of these constituents were the same. Introduction of resorcinarene improves the selectivity of the resins for Cs^+ by a factor 2. Thus, a synergy between the macrocycle selective of Cs^+ and resorcinol was clearly brought to the fore. This effect could be explained by the shape of the cavity that fits well with the Cs^+ ion diameter and by the interaction between Cs^+ and the hydrogen-bond network formed by the resorcinol-acetaldehyde cyclotetramer. These results clearly showed the importance of preorganization of phenolic compounds to reach high selectivity toward caesium (21).

CONCLUSION

New phenolic resins were synthesized by polycondensation of resorcinol with formaldehyde or acetaldehyde. The cation-binding properties of the resins were determined via a competitive extraction of five alkali-metal cations. For resorcinol-formaldehyde resins, at $\mathrm{pH} > 14$, the selectivity series for alkali metal ion has been found to be $\mathrm{Cs}^+ > \mathrm{Li}^+ > \mathrm{Rb}^+ > \mathrm{K}^+ > \mathrm{Na}^+$, although at pH 7 it was $\mathrm{Cs}^+ > \mathrm{Rb}^+ > \mathrm{K}^+ > \mathrm{Na}^+ \approx \mathrm{Li}^+$. The acid strength of the functional group alone cannot be considered as the factor governing ion exchange selectivity for alkali-metal cations.

Introduction of macrocycle like crown-ether or resorcinarene in resorcinol based resins improve their selectivity towards Cs^+. A synergy in phenolic resins was demonstrated.

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