

# Synthesis of Formaldehyde-Dibenzo-18-Crown-6 Condensation Resins Containing Phosphonic Acid Groups and Their Alkali-Metal Cation Sorption

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## SYNOPSIS

Ion-exchange resins are prepared by introducing phosphonic acid monoethyl ester or phosphonic acid groups into formaldehyde condensation poly(dibenzo-18-crown-6) resin. The phosphonic acid ion-exchange groups provide accessibility for metal cations, while the ion-selective cyclic polyether binding site influences the selectivity. The selectivities and efficiencies for competitive alkali-metal cation sorption from aqueous solutions by these crown ether-containing phosphonic acid resins are strongly influenced by the pH of the aqueous solution, the identity of the phosphonic acid groups, and the molar ratio of ion-exchange groups to crown ether units. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Selective complexation and ion exchange of a targeted metal ion by a given polymeric reagent is an important objective for many applications, including catalytic, chromatographic, and metal ion recovery processes.<sup>1-5</sup> The advantages of polymeric reagents include their ease of recovery and reuse, adaptability to continuous processes, and reduced toxicity compared with that of the corresponding monomers.

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, phosphonic acid, or sulfonic acid groups usually provide only poor differentiation of a given ion from ions with the same charge. This obviates their use for practical recovery processes, which require the selective sorption of valued or toxic metal cations from a background of innocuous ions that are present at much higher concentrations. This disadvantage for common ion-exchange resins is attributed to the small free energy differences among

the ion-exchange reactions with the different metal cations.<sup>6</sup>

Ion-selective ligands can selectively complex with specific cations. This complexation can be quite selective for certain metal cations. Therefore, the introduction of significant selectivity into ion-exchange resins might result when a highly ion-selective ligand is incorporated in the vicinity of the ion-exchange site. The ion-exchange site would provide accessibility for the metal cation, while the ion-selective ligand would provide a degree of selectivity. This type of resin, which contains two types of functional moieties, ion-exchange sites and ion-selective ligand sites, is termed a dual mechanism ion-exchange resin. Some of the dual-mechanism ion-exchange resins that have been reported include a copper-selective resin based on hydroxyoxime and carboxylic acid groups<sup>7</sup> and cadmium-selective resins that contain both quinoline and carboxylic acid groups.<sup>8</sup>

Bartsch and co-workers have synthesized a series of crown ether and acyclic polyether carboxylic acid resins by formaldehyde polycondensation reactions of dibenzo polyether monomers.<sup>9</sup> The selectivity and efficiency for competitive alkali-metal cation sorption from aqueous solution exhibited by these polyether carboxylic acid resins were found to be strongly influenced by the acyclic or cyclic nature of the

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polyether units and the conformational positioning of the carboxylic acid group relative to the polyether cavity. Good sorption selectivity for sodium cations from a mixture of the alkali-metal cations was observed for a dibenzo-16-crown-5 resin with a pendent carboxylic acid group oriented over the crown ether cavity.

The metal cation sorption behavior of ion-exchange resins is influenced by the identity of the ion-exchange group. Phosphonic acid groups, including phosphonic acid monoalkyl ester and phosphonic acid functions, are moderately strong acidic ion-exchange groups. This feature gives them a higher sorption capacity than weaker carboxylic acid groups at low pH and a higher selectivity than the strongly acidic sulfonic acid groups. In the present research, phosphonic acid monoethyl ester and phosphonic acid groups were introduced into pre-formed formaldehyde condensation poly(dibenzo-18-crown-6) resin, and the alkali-metal cation sorption behavior of the resultant resins was investigated. The effect of the identity and substitution degree of the phosphonic acid groups on alkali-metal cation sorption by the resins was also studied.

## EXPERIMENTAL

### Materials

Dibenzo-18-crown-6 was purchased from Aldrich Chemical Co. and used as received. All of the alkali-metal hydroxides and chlorides were obtained from Alfa Products and had purities of 99+%. Other inorganic and organic compounds were reagent grade commercial products and were used as received. Purified deionized water was prepared by passing distilled water through three Barnstead D8922 combination cartridges in series.

### Equipment

IR spectra were measured with a Perkin-Elmer Model 1600 FT-IR spectrophotometer. Concentrations of alkali-metal cations in the aqueous phases were determined with a Dionex Model 2000i ion chromatograph. pH measurements were made with a Fisher Scientific Accumet Model 825MP pH meter and a Corning 7605 glass body combination electrode. A Burrell Model 25 wrist action shaker was used to shake the aqueous solution-resin mixtures. To prevent metal contamination, all glassware was soaked in 5% HNO<sub>3</sub>

solution for 24 h and rinsed with deionized water before use. Elemental analysis was performed by Desert Analytics (Tucson, AZ).

### Preparation of Poly(dibenzo-18-crown-6) Resin (1)

Dibenzo-18-crown-6 (2.16 g, 6.0 mmol) was dissolved in a solution of formic acid (100 mL) and formaldehyde (37% aqueous solution, 50 mL). The solution was refluxed in a 115°C oil bath for 24 h, and the resultant mixture was cooled to room temperature. The precipitate was collected on a sintered glass funnel and washed with formic acid (2 × 25 mL), 0.1 N HCl (4 × 25 mL), and deionized water (10 × 50 mL). After drying in a vacuum oven at 100°C for 1 day, 1.47 g (68%) of light brown solid was obtained. The resin was ground to finer than 100 mesh for use in the next step of the synthesis. IR (KBr): 3448 (O—H), 1269, 1053 (C—O) cm<sup>-1</sup>.

### Preparation of Chloromethylated Poly(dibenzo-18-crown-6) Resins (2)

Dry poly(dibenzo-18-crown-6) resin (2.00 g) was added to a 50 mL ampoule and further dried in a vacuum oven at 100°C for 4 h. After cooling to room temperature, 10.0 mL (113 mmol) of methylal and 8.5 mL (116 mmol) of thionyl chloride were added to the ampoule by syringe and the ampoule was cooled in an acetone-dry ice bath. To the ampoule was added 0.20 mL (1.7 mmol) of SnCl<sub>4</sub> and the ampoule was sealed immediately with a torch. The sealed ampoule was gently rotated for 3 days at room temperature by connection to a stirring motor. The ampoule was opened carefully and the reaction mixture was poured into 150 mL of vigorously stirred carbon tetrachloride and filtered with a sintered glass funnel. The resin was washed on the funnel with carbon tetrachloride (5 × 50 mL), acetone (5 × 50 mL), 1 N HCl (5 × 50 mL) and then with deionized water until the pH of the washing water was about 5. After drying in a vacuum oven at 100°C for 2 days, 2.15 g of product was obtained. IR (KBr): 1250 (C—H in CH<sub>2</sub>Cl), 680 (C—Cl) cm<sup>-1</sup>. Elemental analysis; Found Cl, 3.29% (36% chloromethylation). When the reaction scale was increased by five times and the same reaction conditions and work-up procedure were used, 11.93 g of chloromethylated poly(dibenzo-18-crown-6) product was obtained from 10.00 g of poly(dibenzo-18-crown-6) resin (1). Elemental analysis; Found Cl, 5.66%

(65% chloromethylation). IR (KBr): 1250 (C—H in CH<sub>2</sub>Cl), 680 (C—Cl) cm<sup>-1</sup>.

#### Preparation of Poly(dibenzo-18-crown-6) Resins Containing Phosphonic Acid Diethyl Ester Groups (3)

Dry chloromethylated poly(dibenzo-18-crown-6) resin (2.00 g) and 20.0 mL (117 mmol) of triethylphosphite were added to a 50-mL flask. The mixture was refluxed with stirring under nitrogen for 24 h and filtered with a sintered glass funnel. The resin was washed on the funnel with acetone (10 × 50 mL) and dried in a vacuum oven at 100°C for 2 days. From 2.00 g of the lower and higher chloromethylated resins **2**, 2.08 g and 2.15 g of products were obtained, respectively. IR (KBr): 2972 (C—H in CH<sub>3</sub>), 1247 (P=O), 1023, 1180 (P—O) cm<sup>-1</sup>.

#### Preparation of Poly(dibenzo-18-crown-6) Resins Containing Phosphonic Acid Monoethyl Ester Groups (4)

Poly(dibenzo-18-crown-6) resin with pendent phosphonic acid diethyl ester groups **3** (1.00 g) was added to 25 mL of 8% NaOH in water-ethanol (95 : 5) in a 50-mL flask. The mixture was refluxed for 24 h and filtered with a sintered glass funnel. The resin was washed on the funnel with 1 N HCl solution (3 × 50 mL) and then with deionized water until the pH of the washing water was about 5. The resin was dried in a vacuum oven at 100°C for 2 days. From 1.00 g of the lower and higher substituted **3** resins, 0.95 g and 0.92 g of product resins **4** were obtained, respectively. Elemental analysis; Found for the lower substituted **4**: C, 60.77, H, 5.76, P, 2.67. Found for the higher substituted **4**: C, 58.90, H, 5.43, P, 4.28.

#### Preparation of Poly(dibenzo-18-crown-6) Resins Containing Phosphonic Acid Groups (5)

Poly(dibenzo-18-crown-6) resin with pendent phosphonic acid diethyl ester groups **3** (1.00 g) was added to 25 mL of 15% HCl solution in a 50-mL flask. The mixture was refluxed for 24 h and filtered with a sintered glass funnel. The resin was washed on the funnel with deionized water until the pH of washing water was about 5. The resin was dried in a vacuum oven at 100°C for 2 days. From 1.00 g of the lower and higher substituted **3** resins, 0.88 g and 0.79 g of product resins **5** were obtained, respectively. Elemental analysis; Found for the lower sub-

stituted **5**: C, 58.98, H, 5.40, P, 2.97. Found for the higher substituted **5**: C, 57.38, H, 5.10, P, 3.84.

#### Competitive Alkali-Metal Cation Sorption by Dibenzo Polyether Phosphonic Acid Resins

A mixture of 5.00 mL of an aqueous solution of LiOH, NaCl, KCl, RbCl, and CsCl (0.10M in each, pH about 12.8) and 40.0 mg of the crown ether phosphonic acid resin was shaken for 2 h in a 30-mL, pear-shaped flask at room temperature with a Burrell wrist-action shaker. The mixture was filtered with a sintered glass funnel and the resin was washed on the filter with 100 mL of deionized water and dried at 100°C in an oven for 1 day. Of the dried resin, a 20.0 mg of sample was shaken with a 5.00 mL of 0.10M HCl for 1 h to strip the alkali-metal cations from the resin into the aqueous acidic solution. The concentrations of alkali-metal cations in the aqueous stripping solution were determined by ion chromatography after a 20-fold dilution with deionized water.

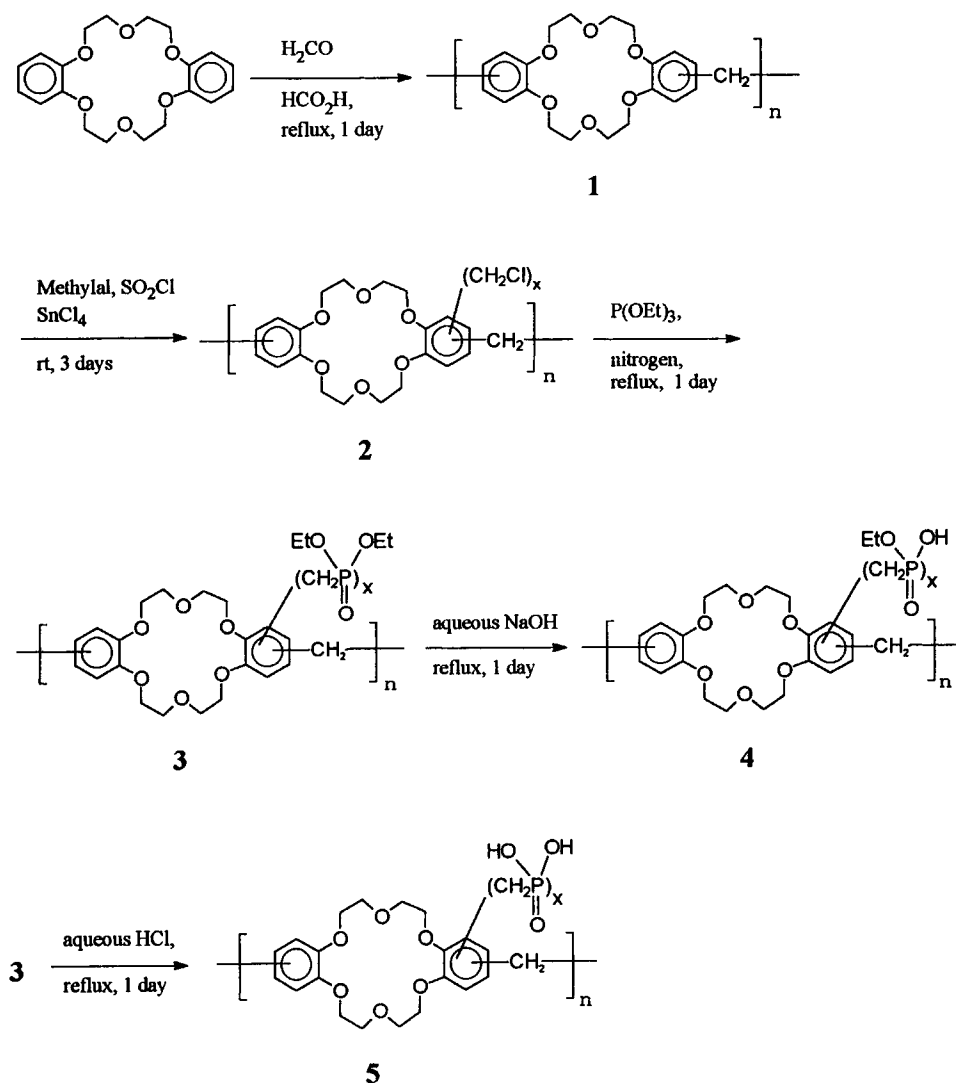
Alkali-metal cation sorption by crown ether phosphonic acid resins at different equilibrium pH values for the aqueous phase was carried out by adding varying amounts of LiOH solution to the aqueous solution of the other alkali-metal salts. The total lithium ion concentration was then adjusted to 0.10M by addition of 0.50M LiCl solution. The equilibrium pH of the aqueous phase following the sorption step was determined after filtration of the resin.

## RESULTS AND DISCUSSION

### Resin Synthesis and Characterization

Formaldehyde-dibenzo-18-crown-6 condensation resins with phosphonic acid monoethyl ester or phosphonic acid groups on the aromatic rings were synthesized according to the scheme shown in Figure 1. The first step was the introduction of a precursor group into resin **1** for subsequent modification. Resin **1** was synthesized by refluxing dibenzo-18-crown-6 in a mixture of aqueous formaldehyde and formic acid.<sup>10-14</sup>

Chloromethylation of the aromatic rings with methylal and thionyl chloride catalyzed by SnCl<sub>4</sub> is a procedure that has been used widely to prepare precursors for crosslinked polystyrene anion exchange resins.<sup>15</sup> It is a mild chloromethylation procedure that may be used with crosslinked polystyrene beads. Over 90% of the polystyrene beads remained unbroken after the chloromethylation reaction.<sup>16</sup>



**Figure 1** Synthesis of poly(dibenzo-18-crown-6) resins 4 and 5 with phosphonic acid monoethyl ester and phosphonic acid groups, respectively.

Chloromethyl groups were introduced into poly(dibenzo-18-crown-6) resin (1) by reaction with methylal and thionyl chloride catalyzed by  $\text{SnCl}_4$  at room temperature in a sealed tube. The chlorine content of the resultant chloromethylated resin 2 obtained from 2.00 g of resin 1 was determined to be 3.29% by elemental analysis and a chloromethylation degree of 36% for each dibenzocrown ether unit of the resin was calculated.

The chloromethylation reaction was found to be very sensitive to changes in reaction conditions. With a fivefold enhancement in the reaction scale, the chlorine content of resin 2 increased to 5.66%, and a chloromethylation degree of 65% was calculated. The higher level of chloromethylation is probably due to a higher temperature, which was

caused by the larger scale of the reaction. By this method, lower (36%) and higher (65%) chloromethylated poly(dibenzo-18-crown-6) resin 2 samples were prepared. Compared with resin 1, the IR spectra of chloromethylated resin 2 samples showed a new shoulder at  $1250\text{ cm}^{-1}$  assigned to  $-\text{CH}_2-$  (in  $-\text{CH}_2\text{Cl}$ ) and another new weak peak at  $680\text{ cm}^{-1}$  attributed to the  $\text{C}-\text{Cl}$  bond.

The chloromethyl groups of resin 2 were transformed into phosphonic acid diethyl ester functions by an Arbuzov reaction. The chloromethylated resin 2 was refluxed with an excess of triethylphosphite for 24 h under nitrogen. The IR spectra of the product resins 3 showed a significant decrease in the  $680\text{ cm}^{-1}$  absorption assigned to the  $\text{C}-\text{Cl}$  bond. New peaks attributed to the phosphonic acid diethyl ester

**Table I Infrared Spectral Features of Resins 3, 4, and 5**

Wavelength ( $\text{cm}^{-1}$ )	3	4	5
2973 ( $-\text{CH}_3$ )	shoulder	small shoulder	none
1023 ( $\text{P}-\text{OR}$ )	significant peak	hard to see	hard to see
991 ( $\text{P}-\text{OH}$ )	none	hard to see	small shoulder

group at  $2972\text{ cm}^{-1}$  ( $\text{CH}_3-$ ),  $1247\text{ cm}^{-1}$  ( $\text{P}=\text{O}$ ) and  $1023\text{ cm}^{-1}$  ( $\text{P}-\text{O}$ ) appeared. These IR spectral features of the product resins are consistent with the transformation of the chloromethyl groups into phosphonic acid diethyl ester groups by the Arbuzov reaction. However, this transformation was probably not complete, because the weight gain of the resins during the reaction was somewhat smaller than the theoretical value which was calculated from the level of chloromethylation as determined by elemental analysis.

Hydrolysis of the phosphonic acid diethyl ester groups under strongly basic and acidic conditions provided the phosphonic acid monoethyl ester and phosphonic acid resins, respectively. Resins **3** were refluxed in 8% aqueous sodium hydroxide for 24 h to provide the poly(dibenzo-18-crown-6) phosphonic acid monoethyl ester resin **4** and in 15% hydrochloric acid for 24 h to produce poly(dibenzo-18-crown-6) phosphonic acid resin **5**. The resultant resins were characterized by IR spectroscopy, with the results presented in Table I. It should be noted that serious overlap and broad peaks were observed in the IR spectra of these crosslinked resins. The IR absorptions attributed to the diethyl esters were observed to decrease after hydrolysis under the strongly basic conditions and diminish even more after hydrolysis under the strongly acidic conditions, as shown in Table I. Meanwhile, the peak at  $991\text{ cm}^{-1}$  assigned to the phosphonic acid ( $\text{P}-\text{OH}$ ) group was found to increase upon hydrolysis of the phosphonic acid diethyl ester. Another phosphonic acid peak at about  $2700\text{ cm}^{-1}$  for the  $\text{PO}-\text{H}$  stretch was not observed due to its overlap with the absorption of residual water in the resins. Significant water peaks were observed in IR spectra for resins that had been dried in vacuum oven at  $100^\circ\text{C}$  for 2 days. The high hydrophilicity of resins **4** and **5** made them very difficult to dry.

The presence of phosphonic acid monoethyl ester and phosphonic acid groups in resins **4** and **5**, respectively, was further verified by determining their ion-exchange capacities. This involved measuring their sodium ion sorption from  $0.20\text{M}$  aqueous  $\text{NaOH}$ . The sorption results of the lower and higher

substituted **4** and **5** resins are given in Table II. Both the lower and higher substituted phosphonic acid resins produced by hydrolysis under strongly acidic conditions have almost twice the sodium ion sorption levels of the resins produced by hydrolysis under basic conditions. This verifies that the basic hydrolysis conditions provided the phosphonic acid monoethyl ester resins **4** and the strongly acidic hydrolysis conditions afforded the phosphonic acid resins **5**.

### Alkali-Metal Cation Sorption

Competitive alkali-metal sorption by resins **1-5** was investigated using the procedure that is described in the Experimental section. Control experiments showed that a shaking time of 2.0 h in the metal cation sorption step and 1.0 h in the metal cation stripping process were sufficient to produce equilibrium sorption results.

Results for competitive sorption of alkali-metal cation from basic aqueous solutions by resin **1** and the higher substituted resins **2** and **3** are presented in Table III. Alkali-metal cation sorption was very low for all the three neutral resins. However, a sorption selectivity for potassium ion by the dibenzo-18-crown-6 moieties in all three resins is noted. Also, the introduction of polar groups, such as chloromethyl and phosphonic acid diethyl ester groups, onto the poly(dibenzo-18-crown-6) resin should increase the hydrophilicity of the resins and appears to slightly enhance the sorption ability for alkali-metal salts.

**Table II Sodium Cation Sorption by Phosphonic Acid Monoethyl Ester and Phosphonic Acid Group-Containing Poly(dibenzo-18-crown-6) Resins 4 and 5**

Resin	Lower- 4	Lower- 5	Higher- 4	Higher- 5
$\text{Na}^+$ sorption (mmol/g)	0.76	1.41	0.89	1.84

**Table III Alkali-Metal Sorption by the Neutral Poly(dibenzo-18-crown-6) Resins 1-3**

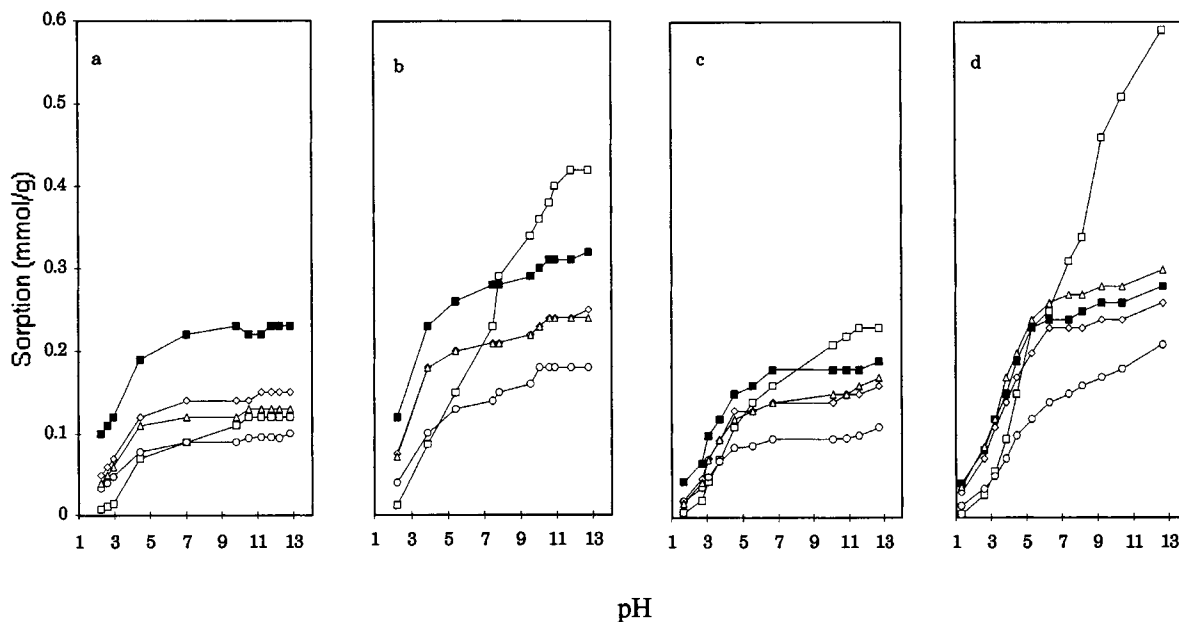
Resin	Sorption (mmol/g)				
	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>
<b>1</b>	< 0.01	0.01	0.03	< 0.01	< 0.01
Higher-2	0.01	0.04	0.07	0.05	0.06
Higher-3	0.02	0.04	0.09	0.06	0.05

The alkali-metal cation sorption profiles for the lower and higher substituted resins **4** and **5** from aqueous solutions with varying equilibrium pH values are presented in Figure 2. Compared with the sorption results for crown ether carboxylic acid ion-exchange resins in the low pH range,<sup>9</sup> the phosphonic acid poly(dibenzo-18-crown-6) resins **4** and **5** provide higher sorption for alkali-metal cations. For the carboxylic acid resins, no significant sorption was observed when the pH was less than 3 with the sorption reaching and maintaining maximal levels when the pH was greater than 7. Ion-exchange sorption of the alkali-metal cations is controlled by deprotonation of the acidic groups in the resins. Phosphonic acid monoethyl ester and phosphonic acid groups are stronger acids than the carboxylic acid function and can be deprotonated at a lower pH.

Figure 2 show that resins **4** and **5** have significant alkali-metal cation sorption even when the pH is as low as 2. Compared with the neutral poly(dibenzo-18-crown-6) resins **1-3** (Table III), the phosphonic acid resins **4** and **5** have much higher alkali-metal cation sorption levels.

In Figure 2, significant differences in alkali-metal sorption behavior are observed for phosphonic acid resins **4** and **5**, with different levels of acid substitution. The lower substituted resin **4** with a phosphonic acid monoethyl ester groups has a sorption selectivity for the potassium ion over the entire pH range. The size of potassium ion best matches the cavity of the dibenzo-18-crown-6 units. This demonstrates that the sorption process involves both the ion-exchange phosphonic acid monoethyl ester group and the crown ether cavity. The phosphonic monoacid group provides a cation access site and the crown ether unit, dibenzo-18-crown-6, affords the cation sorption selectivity.

The sorption behavior of the higher substituted resin **4** is shown in Figure 2(c). In the low pH range of less than about 8, slight sorption selectivity for the potassium ion is observed. In the high pH range of greater than 8, weak sorption selectivity for lithium ion is observed. Of the alkali-metal cations, sorption of lithium ion is preferred by most ion-exchange resins due to its high charge density. The



**Figure 2** Alkali-metal cation sorption profiles for the phosphonic acid-containing poly(dibenzo-18-crown-6) resins at different equilibrium pH values for the aqueous phase: (a) lower substituted **4**; (b) lower substituted **5**; (c) higher substituted **4**; and (d) higher substituted **5**. (□) Li<sup>+</sup>, (○) Na<sup>+</sup>, (■) K<sup>+</sup>, (◇) Rb<sup>+</sup>, (△) Cs<sup>+</sup>.

higher substituted resin **4** has an enhanced ratio of phosphonic acid monoethyl ester groups to crown ether units. This causes changes in selectivity for the ion-exchange sorption process. A low molar ratio of phosphonic acid monoethyl ester groups to crown ether units allows the crown ether cavity to exert its cation binding selectivity. When the ratio of phosphonic acid monoethyl ester groups increases, the sorption selectivity becomes controlled to a larger extent by the ion-exchange site, and sorption selectivity for lithium ion is observed.

Similar trends in sorption behavior are also found for the lower substituted resin **5** [Fig. 2(b)], which has phosphonic acid groups. In the low pH range, there is some sorption selectivity for potassium ion. However, this changes to lithium ion selectivity at alkaline pH. It is impossible for each phosphonic acid group to have two crown ether units around it because of the fixed and rigid structure in the solid resins. Therefore, there are not enough crown ether units in the vicinity of the phosphonic acid groups to selectively bind with a second metal cation. This causes the disappearance of sorption selectivity for potassium ion by the lower substituted resin **5** at high pH range.

For the higher substituted resin **5**, whose sorption results are shown in Figure 2(d), no sorption selectivity for potassium ion is observed even in the low pH range, and a high lithium ion sorption selectivity is observed in the high pH range. This is caused by the combined effects of both the high level of phosphonic acid substitution and the second deprotonation of the phosphonic diacid group in the high pH range.

## CONCLUSIONS

Synthetic routes for the incorporation of phosphonic acid monoalkyl ester and phosphonic acid groups into pre-formed formaldehyde-dibenzo-18-crown-6 condensation resins have been established. The presence of ion-exchange groups markedly enhanced the alkali-metal cation sorption. The selectivity of competitive alkali-metal cation sorption was found to be influenced by the identity of the ion-exchange

group, the ratio of ion-exchange to crown ether units, and the pH of the aqueous phase from which the alkali-metal cations are extracted.

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