

Ion Exchange Behavior of Alkali and Alkaline Earth Metal Ions with a Sulfonated Polystyrene and a Novel Triazacrown Cation Exchanger

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A Merrifield-based triazacrown ion exchanger, [1,7-dioxa-4,10,13-triazacyclopentadecane (N_3O_2) ion exchanger] was synthesized. The ion exchange behaviors of alkali and alkaline earth metal ions on a strongly acidic cation exchange resin, Dowex 50W-X8, 200-400 mesh and on N_3O_2 ion exchange resin, in water and HCl-water solutions were investigated. The distribution coefficients, K_d of alkali and alkaline earth metal ions on Dowex 50W-X8 resin increased with decreasing HCl concentration. On the other hand, HCl concentrations influenced little on the distribution coefficient of the metal ions for N_3O_2 resin, but the distribution coefficient was slightly increased with decreasing HCl concentration, in general. The distribution coefficients of the metal ions in water are larger than those in various HCl concentrations. Of the distribution coefficients of the alkali metal ions on Dowex 50W-X8, in the range of moderate HCl concentrations, the slope, $d \log K_d / d \log M_{HCl}$ was about -1 , while the slope for the alkaline earth metal ions was about -2 . However, at very low HCl concentrations, the linear relation between K_d and HCl concentration was not maintained and the slope was deviated from the above values. The distribution coefficients of the metal ions on N_3O_2 resin increased in a linear manner with decreasing HCl concentration, and had the slope of about -0.1 .

Introduction

The distribution coefficient is equal to the concentration of a cation in the ion exchange resin phase divided by its concentration in the liquid phase,¹ but changes with compositions and concentrations of the reagents in the water phase, the amount of cation to amount of ion exchanger ratio in the exchange system, and the nature of the ion exchange resin. But temperature and pressure have a lesser influence.² An investigation of the cation exchange behavior on Dowex 50W and Bio-Rex 70 ion exchange resins of Na, Rb, and Cs tracers in 0.1 M to saturated solutions of $LiClO_4$, LiCl, $LiNO_3$, $LiC_2H_3O_2$, and of the corresponding acids and of CsCl on Dowex 50W has been carried out by Whitney and Diamond.³ They showed that, as the aqueous phase concentration rises, deviations from the simple mass-action law behavior occur; these deviations are explained in terms of the decreasing water activity, increasing cation-anion interactions in both the exchanger and aqueous phases, and exchanger invasion by nonexchange aqueous electrolyte. The distribution coefficients for 43 cations in various concentrations of hydrochloric acid using the cation exchange sulfonated polystyrene AG 50W-X8 resin were determined.² A comparative study of the adsorbability of alkali metals, lithium to francium, in HCl-water and HCl-methanol-water solutions has been carried out with polystyrene-divinylbenzene-sulfonic acid resin, Dowex 50W-X8 and phenol-formaldehyde-sulfonic acid resin, Duolite C-3.⁴ Separability of K, Rb, and Cs has also been investigated with a zirconium phosphate cation exchanger, Bio-Rad ZP-1.⁴ Fritz and Rettig,⁵ and Korkisch and Ahluwalia⁶ have investigated the ion exchange behavior

of elements in HCl-organic solvent media. Strelow *et al.*⁷ also reported the distribution coefficients for 45 elements in HCl-ethanol media with Bio-Rad AG 50W-X8, a sulfonated polystyrene resin. In their experiments, the acid concentration range 0.1-3.0 M and the ethanol concentration range 0-95% are covered.

Pedersen reported in 1967 that crown ethers can complex alkali, alkaline earth and other cations.⁸⁻¹⁰ Pedersen showed that the complexing ability of the crown compounds could be correlated with the cavity diameter of the macrocyclic polyethers and the relative sizes of the cation. Lehn *et al.*¹¹⁻¹³ have first synthesized cryptands, which are capable of binding alkali and alkaline earth metal ions. Solvent dependence of the stability of cryptates¹⁴ and the characteristics of ion exchangers with azacrown ether and cryptands to alkali and alkaline earth metal ion separation¹⁵ have also been studied. The stoichiometry and stability of the Na^+ and K^+ complexes with noncyclic crown-type polyethers and pyridinophane cryptands were determined, and the kinetic of complex formation was investigated by Tümmeler *et al.*¹⁶ They found that the pyridinophane cryptand compounds and diamide form stable 1:1 complexes with Na^+ and K^+ in aqueous solutions.

We report in this paper, a study of two different types of ion exchange behavior of alkali and alkaline earth metal ions with a sulfonated polystyrene and a novel triazacrown cation exchanger in water and HCl-water solutions. This involves the distribution coefficients of the metal ions between Dowex 50W-X8 and a novel triazacrown ion exchanger. Effect of solvent, the relative sizes of the cation, and of the cavity diameter of the triazacrown on the distribution coefficients

are also discussed.

Experimental

Apparatus. The triazacrown compound, 1,7-dioxa-4,10,13-triazacyclopentadecane trihydrobromide salt ($N_3O_2 \cdot 3HBr$), was prepared according to the procedures of Sun *et al.*,¹⁷ Lehn *et al.*,¹⁸ and Martell and Delgado and their coworkers.¹⁹ The novel triazacrown ion exchange resin (N_3O_2 ion exchanger) was synthesized according to published procedures.²⁰⁻²² Elementary analyses were performed by using Perkin-Elmer 240A. Infrared spectra (IR) were recorded on a FTIR spectrophotometer (Bomem Hartmann & Braun SPG 5200G). Proton nuclear magnetic resonance (1H NMR) spectra were obtained on a Varian T-60 spectrometer. Mass spectra were obtained with the GC-Mass HP 5890, II-VG Trio II. Thermobalance and differential calorimeter were used for the determination of rate of weight change and amount of heat transmitted to the sample by DTG and DSC.²³ The structural formulas proposed for the triazacrown compound and corresponding ion exchange resin are consistent with data derived from IR, 1H NMR, mass spectra, and elementary analysis.²³ Synthesized N_3O_2 azacrown and corresponding ion exchanger were identified with data in reference.²³ A polarized Zeeman AA-spectrophotometer, Z-2000, Hitachi, Japan, and shaker, Edmund Bücher, Germany, have also been used.

Reagents. All chemicals were of the analytical and reagent grade commercially available, and used without further purification. All solvents were distilled and stored over molecular sieves. The cation exchange resins were Dowex 50W-X8, 200-400 mesh, a styrene-based sulfonic acid ion exchanger (Dow Chemical Comp., U.S.A.), and a Merrifield-based triazacrown ion exchanger (N_3O_2 resin), prepared in our laboratory. The capacity of the Dowex 50W-X8 was 4.8 meq/g dry resin.²⁴ On the other hand, the novel N_3O_2 ion exchange resin had a capacity of 3.2 meq/g dry resin.²³ The alkali and alkaline earth metal salts and hydrochloric acid solutions were prepared by volumetric dilution of accurately analyzed concentrated solutions of reagent grade chemicals with bidistilled water.

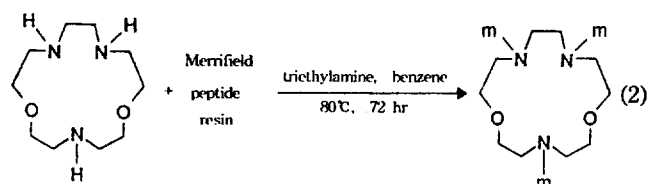
Distribution Coefficients. For the determination of the distribution coefficients, Batch method was employed.²³ Each portion of 0.2 g of Dowex 50W-X8, 200-400 mesh resin in the hydrogen form which has been dried to constant weight at 60 °C, was weighed out accurately and transferred into a 100 mL polyethylene vial with a polyethylene screw top. Then 1.0 mL of 0.01 M metal chloride solution was added, followed by 49 mL of hydrochloric acid solution of the desired concentration to give a final volume of 50 mL. The vials were stoppered and shaken in a shaker for 24 hours at room temperature. Sample of 1.0 mL was removed through fritted glass filter and determined the amount of the element using an AA-spectrophotometer. In the case of the triazacrown resin, the distribution coefficient determination was all done with Batch method, similar to a Dowex 50W-X8 described above. The distribution coefficient, K_d was calculated as

$$K_d = \frac{(C_{st} - C_{eq})V_{soln}}{C_{eq} \times M_p} \quad (1)$$

where C_{st} is the metal ion concentration of the standard solution, C_{eq} the concentration after equilibrium, V_{soln} the total volume of the solution, and M_p is the weight of the dry resin indicated.

Results and Discussion

The reaction of 1,7-dioxa-4,10,13-triazacyclopentadecane with Merrifield peptide resin in the presence of triethylamine and benzene gave a white powder of N_3O_2 ion exchange resin according to the Equation (2).²³ In the structure of the resin, m indicates the Merrifield peptide matrix.



The Equation for the ion exchange reaction of an alkali ion, M^+ , with a monovalent cation, H^+ , on an ion exchange resin in the hydrochloric acid may be written as



where R is the resin anion indicated.

The corresponding equilibrium constant is

$$K = \frac{(MR)(HCl)}{(MCl)(HR)} = \frac{[MR][HCl]}{[MCl][HR]} \frac{\gamma_{MR}\gamma_{HCl}}{\gamma_{MCl}\gamma_{HR}} \quad (4)$$

where parentheses denote activity, brackets indicate molar concentration units, and γ is the corresponding species activity coefficient. For dilute aqueous solutions and when the alkali ion, M^+ , is present in only tracer quantities, it is possible to write Equation (4) in the form:³

$$K = \frac{[MR][HCl]}{[MCl][HR]} = K_d \frac{[HCl]}{[HR]} \quad (5)$$

Therefore, the distribution coefficient, K_d , may also be written as

$$K_d = k_1 [HCl]^{-1} \quad (6)$$

where $k_1 = K[HR]$, the term $[HR]$ being stood for the product of K and $[HR]$ from the numerator and absorbed into the constant k_1 , since it is constant for a given condition, and taking logarithms and rearranging:

$$\log K_d = \log k_1 - \log [HCl] \quad (7)$$

This Equation states that the distribution coefficient can be related to the hydrochloric acid concentration. A plot of $\log K_d$ versus $\log [HCl]$ gives a straight line of slope -1 and intercept $\log k_1$. The constant, k_1 , may be defined as the K_d at which the concentration of HCl is unity. By analogy, the relation between the distribution coefficient and the hydrochloric acid concentration for the alkaline earth metal ion can be written as

$$\log K_d = \log k_2 - 2 \log [HCl] \quad (8)$$

where k_2 is a constant for the alkaline earth metal ion. The constant, k_2 is equal to $K[HR]^2$ and the term $[HR]^2$ being

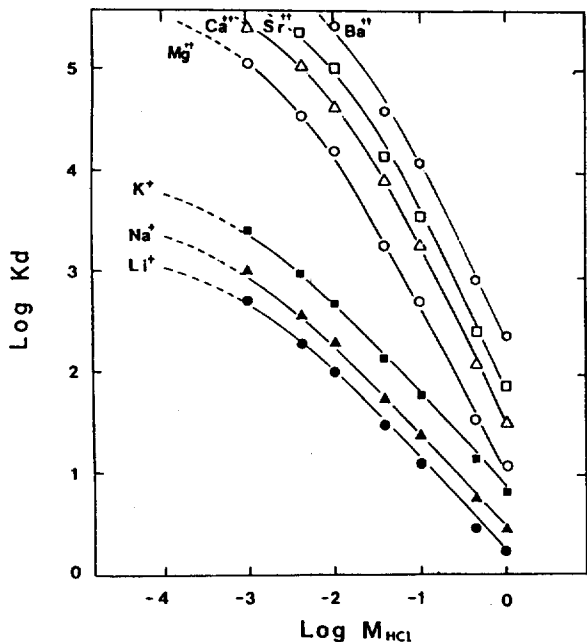


Figure 1. Plot of $\log K_d$ for alkali and alkaline earth metal ions on Dowex 50W-X8 resin versus $\log M_{\text{HCl}}$.

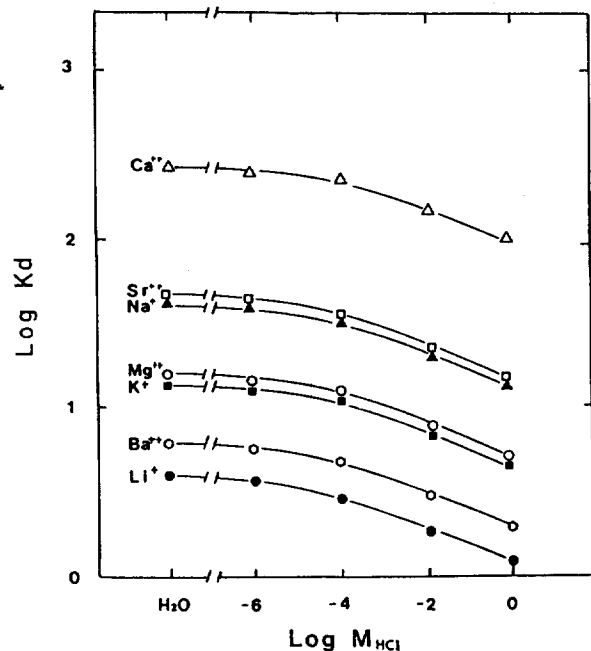


Figure 2. Plot of $\log K_d$ for alkali and alkaline earth metal ions on N_3O_2 resin versus $\log M_{\text{HCl}}$.

stood and absorbed into the constant k_2 , since it is constant for a given condition. The constant, k_2 , may again be defined as the K_d at which the concentration of HCl is unity. A plot of $\log K_d$ versus $\log[\text{HCl}]$ gives a straight line of intercept $\log k_2$ and slope -2 . The distribution coefficients of alkali and alkaline earth metal ions on Dowex 50W-X8, 200-400 mesh in HCl-water solutions are shown in Figure 1 as log-log plot of K_d versus M_{HCl} . The slope, $d\log K_d/d\log M_{\text{HCl}}$ is about -1 for the alkali metal ions at the moderate HCl

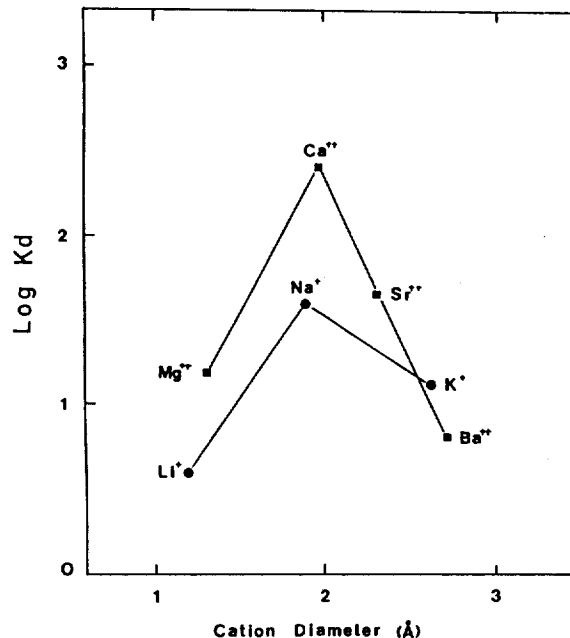


Figure 3. Plot of $\log K_d$ versus cation diameter. Ion exchange resin: N_3O_2 resin; Solvent: Water; Temperature: 25°C ; ●, Alkali metal ion; ■, Alkaline earth metal ion.

concentration as expected for ideal 1:1 exchange. But, in the case of the alkaline earth metal ions, the slope is about -2 as expected for ideal 1:2 exchange. Experimental evidence indicates that Equations, 7 and 8 are valid for alkali and alkaline earth metal ions. Deviations from the corresponding slopes occur slightly at very low HCl concentration. The selectivity of a moderately cross-linked strong sulfonic acid type cation exchange resin, Dowex 50W-X8 for alkali, hydrogen, and alkaline earth metal ions, in dilute water solution is in the order of $\text{Li}^+ < \text{H}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+ < \text{Mg}^{++} < \text{Ca}^{++} < \text{Sr}^{++} < \text{Ba}^{++}$.²⁵⁻²⁶ As shown in Figure 1, the distribution coefficients increase with increasing selectivity at the same hydrochloric acid concentration.

The distribution coefficients of alkali and alkaline earth metal ions on N_3O_2 resin in HCl-water solution are given in Figure 2, a log-log plot of K_d versus M_{HCl} . The functions are not similar to that for Dowex 50W-X8 resin. The slope, $d\log K_d/d\log M_{\text{HCl}}$ is about -0.1 for both alkali and alkaline earth metal ions. These results indicate that in N_3O_2 resin-HCl-water solution system, the ideal exchange does not occur and the concentration of hydrochloric acid weakly affect to the distribution coefficients. As can be seen in Figure 2, the distribution coefficients increase in the order of $\text{Li}^+ < \text{Ba}^{++} < \text{K}^+ < \text{Mg}^{++} < \text{Na}^+ < \text{Sr}^{++} < \text{Ca}^{++}$. These phenomena suggested that the cation diameter strongly affected to the distribution coefficients on N_3O_2 resin rather than that of the selectivity. The Pauling ionic radii are of 0.6 for Li^+ , 0.95 for Na^+ , 1.33 for K^+ , 0.65 for Mg^{++} , 0.99 for Ca^{++} , 1.13 for Sr^{++} , and 1.35 for Ba^{++} in Å, respectively.²⁷ Pedersen²⁸ listed the several factors that affect the stability of the crown ether complexes; these include the cavity size of the ligand, cation diameter, spatial distribution of ring binding sites, the character of the hetero atoms, the presence of additional binding sites and the type of solvent used. The

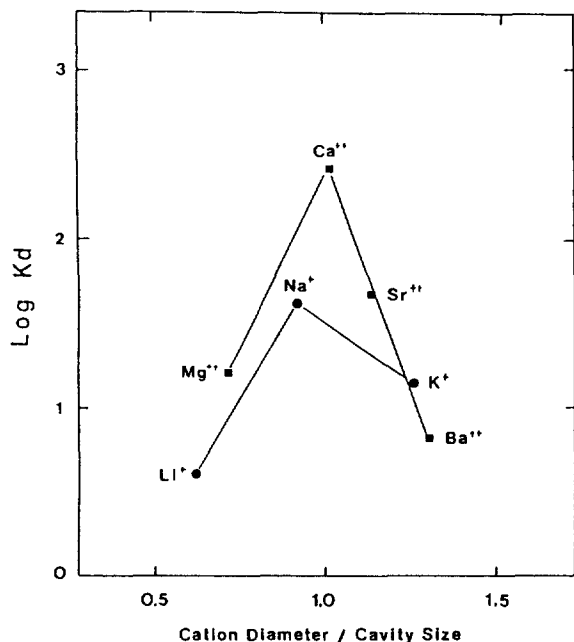


Figure 4. Relation between $\log K_d$ and the ratio of cation diameter to cavity size for N_3O_2 -15-crown-5 in water at 25 °C. Ionic diameters taken from Cotton and Wilkinson.²⁷

more closely the size of the cation and the cavity of the crown ether match, the more stable is the complex formed.²⁸ Cavity diameter of N_3O_2 (15-crown-5) crown is 1.7-2.2 Å.²⁹⁻³⁰ Our findings for aqueous and HCl-aqueous solutions of N_3O_2 ion exchanger with alkali and alkaline earth metal ions are shown in Figure 3 as plot of $\log K_d$ versus cation diameter. Figure 3 indicates that, for mono and divalent cations, the values of $\log K_d$ depend on the cation diameter. The maximum value is found with Ca^{++} .

In general, large differences are not observed between the $\log K_d$ values of the alkali and alkaline earth metal ions, though relatively high values are observed for Ca^{++} , Sr^{++} , and Na^+ , whose ionic diameters approximate the cavity diameter of N_3O_2 -15-crown. As shown in Figures 2 and 3, the K_d values for alkaline earth metal ions are larger than those for alkali metal ions, in general. A comparison of Na^+ and Ca^{++} , whose ionic diameters are nearly the same, shows that the K_d value for Ca^{++} is much larger than that for Na^+ . For ions with smaller diameters, however, the difference in the K_d value between Li^+ and Mg^{++} , is not as great. The low value of K_d for Li^+ with a small ionic diameter, is due to a large hydration energy for the ion having a high electron density.^{28,31} The adsorption of alkali and alkaline earth metal ions in water on N_3O_2 -15-crown ion exchange resin is shown in Figure 4. The larger values of K_d are obtained, when the ratio of the relative sizes of the cation and the cavity of the crown is close to unity. This result well agrees with Pedersen's conclusion.²⁸ However, little work has been reported so far on the ion exchange behavior of the crown ion exchanger,^{15,32-33} the thermodynamics,³⁴ chromatography,^{15,32} and the formation and dissociation kinetics of the crown complexes.³⁵⁻³⁶

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Effect of Adsorption of Endoglucanase on the Degradation of Microcrystalline Cellulose

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The influence of adsorption of endoglucanases on enzymatic hydrolysis of microcrystalline cellulose was investigated. All the data of adsorption on microcrystalline cellulose were found to obey the Langmuir adsorption isotherm. The values of adsorption affinity for endoglucanases increased in regular sequence of EG IV < EG III < EG I < EG II. It was found that the mechanisms of enzymatic hydrolysis of a crystalline and an amorphous cellulose are different. The hydrolysis of amorphous cellulose with endoglucanase depends on its activity. But the hydrolysis of microcrystalline cellulose with endoglucanase is directly correlated with its adsorption affinity. The major factor related to cellulases that control the difference in the reactivity of the crystalline and amorphous cellulose appears to be the adsorption affinity of endoglucanase on cellulose. From the results of hydrolysis with endoglucanases (EG I, II, III, and IV) in combination with cellobiohydrolase (CBH II), the reducing sugar produced during degradation is increased when the enzyme system contains endoglucanase with high affinity to cellulose.

Introduction

Cellulases are multicomponent enzyme systems which are capable of hydrolyzing cellulose to glucose. Among the best characterized cellulases are those derived from *Trichoderma*.¹⁻⁵ The cellulases of *Trichoderma viride* degrade cellulose in a cooperative manner and consist of two cellobiohydrolases (CBH I and CBH II) and at least four endoglucanases (EG I, EG II, EG III, and EG IV), the former releasing cellobiose from the nonreducing ends of the cellulose chain and the latter cleaving internal glucosidic bonds in native cellulose.⁶⁻⁸ Because of the complex physicochemical properties of the cellulose, the diversity of the enzymes, and the lack of the structure information, the precise mechanism action of those enzymes is not understood.

The cellulases from *T. viride* comprise two or more domains which function independently. A common arrangement is a catalytic domain connected to a cellulose-binding domain (CBD) by a linker.⁹⁻¹¹ This implies that the first step in the enzymatic hydrolysis is adsorption of cellulase binding domain on the surface of the water-insoluble cellulose fibrils. After binding of the enzyme molecules the actual catalytic action, *i.e.*, the hydrolysis of the susceptible glucosidic bonds, takes place. Therefore, the degradation actions of cellulase components can be observed from the viewpoint of adsorption behaviors of cellulase components.

Removal of CBDs reduces the hydrolytic activity of enzymes on microcrystalline cellulose, whereas their activities

on soluble and amorphous celluloses are either unaffected or increased. Binding of the CBDs to cellulose is not affected significantly by removal of their catalytic domains.¹²⁻¹⁶ It was recently reported that CBD of cellulase disrupted the surface of Ramie cotton fibers and that the catalytic core domain had a smoothing or polishing effect on the surface.¹⁴ Klyosov^{17,18} suggested that the defibrillation effect is an inherent property of both CBH and EG, evidenced by their ability to be adsorbed tightly to cellulose. In other words, only those enzymes with high affinity for crystalline cellulose render it susceptible to hydrolysis. Clearly, an understanding of the degradation of cellulose requires an understanding of the roles of the CBDs in the process.

In this study, we investigated the major factor related to cellulases that control the difference in the reactivity of the crystalline and an amorphous cellulose. The influence of adsorption of endoglucanase on the enzymatic degradation of microcrystalline cellulose is also discussed.

Experimental

Enzymes. Major cellulase components, such as endoglucanases (EGs; I, II, III, and IV) and cellobiohydrolase (CBH II), were isolated from a commercial cellulase (Meicelase TP 60, Lot No. CEPB-5291) derived from the fungus *Trichoderma viride* by a series of chromatographic procedures involving Bio-Gel P 10, Bio-Gel P 100, DEAE-Sephadex A-50, SP-Sephadex C 50, and Avicel PH 101.⁵ The purified endogluca-