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

Dong Won Kim\\*, Chang Suk Kim\\*, Ki Young Choi\\*.
Yong Il Lee\\*, Choon Pyo Hong\\*, and Hyo Shik Kwon\\*

Department of Chemistry, College of Natural Sciences, Chungbuk National University, Cheongju 360-763, Korea
\\*Department of Chemistry Education, College of Education, Chungbuk National University, Cheongju 360-763, Korea
\\*Department of –Chemistry, College of Natural Sciences, Mokwon University, Daejeon 301-729, Korea
\\*Department of Chemistry, College of Natural Sciences, Kyungpook National University, Nonsan 320-800, Korea

Received January 23, 1995

A Merrifield-based triazacrown ion exchanger, \([\text{1,7-dioxa-4,10,13- triazacyclopentadecane (N}_4\text{O}_2\text{)}\text{ ion exchanger}]\) 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\(_4\)O\(_2\) 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\(_4\)O\(_2\) 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, \(\log K_d/\log M_{\text{ionic}}\), 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\(_4\)O\(_2\) 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\(_2\)H\(_5\)O\(_2\), 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.\(^4\) 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.\(^5\) Fritz and Rettig,\(^6\) and Korkisch and Ahluwalia\(^7\) have investigated the ion exchange behavior of elements in HCl-organic solvent media. Strelow \textit{et al.}\(^8\) 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 \textit{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 cryptates\(^14\) and the characteristics of ion exchangers with azacrown ether and cryptands to alkali and alkaline earth metal ion separation\(^15\) 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 Tümmler \textit{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
Ion Exchange Behavior of Alkali and Alkaline Earth Metal Ions

are also discussed.

Experimental

Apparatus. The triazacrown compound, 1,7-dioxo-4,10,13-triazacryptandecane trihydrobromide salt (N₂O₃·3HBr), 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 (N₂O₃ 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.²² Synthesized N₂O₃ azacrown and corresponding ion exchanger were identified with data in reference.²² 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 (N₂O₃ 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 N₂O₃ ion exchange resin had a capacity of 3.2 meq/g dry resin.²⁵ 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.²⁶ 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, Kₑ, was calculated as

\[ Kₑ = \frac{(Cₑ - Cₑp)V_{soln}}{Cₑp \times Mₑ} \]  

(1)

where Cₑ is the metal ion concentration of the standard solution, Cₑp the concentration after equilibrium, V_{soln} the total volume of the solution, and Mₑ is the weight of the dry resin indicated.

Results and Discussion

The reaction of 1,7-dioxo-4,10,13-triazacryptandecane with Merrifield peptide resin in the presence of triethylamine and benzene gave an white powder of N₂O₃ ion exchange resin according to the Equation (2).²³ In the structure of the resin, m indicates the Merrifield peptide matrix.

\[ \text{MCl} + \text{HR} \rightleftharpoons \text{MR} + \text{HCl} \]  

(3)

where R is the resin anion indicated.

The corresponding equilibrium constant is

\[ K = \frac{(MR)(HC1)}{(MC1)(HR)} = \frac{[MR][HCl]}{[MC1][HR]} \frac{Y_{MC1}Y_{HCl}}{Y_{MC1}Y_{HR}} \]  

(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:²⁷

\[ K = \frac{[MR][HCl]}{[MC1][HR]} = K₀[HCl] \]  

(5)

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

\[ Kₑ = k₁[HCl]^{-1} \]  

(6)

where k₁ = K[HR], the term [HR] being stood for the product of K and [HR] from the numerator and absorbed into the constant k₀, since it is constant for a given condition, and taking logarithms and rearranging:

\[ \log Kₑ = \log k₁ - \log [HCl] \]  

(7)

This Equation states that the distribution coefficient can be related to the hydrochloric acid concentration. A plot of logKₑ versus log[HCl] gives a straight line of slope -1 and intercept \log k₁. The constant, k₁, may be defined as the Kₑ 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

\[ \log Kₑ = \log k₂ - 2\log[HCl] \]  

(8)

where k₂ is a constant for the alkaline earth metal ion. The constant, k₂ 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\(_2\)O\(_5\) resin versus log\(M_{\text{HCl}}\).

Figure 3. Plot of log\(K_d\) versus cation diameter. Ion exchange resin: N\(_2\)O\(_5\) resin; Solvent: Water; Temperature: 25 °C; ●, Alkali metal ion; ■, Alkaline earth metal ion.

The distribution coefficients of alkali and alkaline earth metal ions on N\(_2\)O\(_5\) resin in HCl-water solution are shown in Figure 1 as log-log plot of \(K_d\) versus \(M_{\text{HCl}}\). The slope, dlog\(K_d\)/dlog\(M_{\text{HCl}}\) is about -1 for the alkali metal ions at the moderate HCl 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 Li\(^+\), H\(^+\), Na\(^+\), K\(^+\), Rb\(^+\), Cs\(^+\), Mg\(^{++}\), Ca\(^{++}\), Sr\(^{++}\), Ba\(^{++}\). 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\(_2\)O\(_5\) resin in HCl-water solution are given in Figure 2, a log-log plot of \(K_d\) versus \(M_{\text{HCl}}\). The functions are not similar to that for Dowex 50W-X8 resin. The slope, dlog\(K_d\)/dlog\(M_{\text{HCl}}\) is about -0.1 for both alkali and alkaline earth metal ions. These results indicate that in N\(_2\)O\(_5\) 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 Li\(^+\), Ba\(^{++}\), K\(^+\), Mg\(^{++}\), Na\(^+\), Sr\(^{++}\), Ca\(^{++}\). These phenomena suggested that the cation diameter strongly affected to the distribution coefficients on N\(_2\)O\(_5\) 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. Pedersen 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
more closely the size of the cation and the cavity of the crown ether matrix, the more stable is the complex formed.\textsuperscript{28} Cavity diameter of N\textsubscript{2}O\textsubscript{5} (15-crown-5) is 1.7-2.2 Å.\textsuperscript{29-30} Our findings for aqueous and HCl-aqueous solutions of N\textsubscript{2}O\textsubscript{5} ion exchanger with alkali and alkaline earth metal ions are shown in Figure 3 as plot of logK\textsubscript{d} versus cation diameter. Figure 3 indicates that, for mono and divalent cations, the values of logK\textsubscript{d} depend on the cation diameter. The maximum value is found with Ca\textsuperscript{2+}.

In general, large differences are not observed between the logK\textsubscript{d} values of the alkali and alkaline earth metal ions, though relatively high values are observed for Ca\textsuperscript{2+}, Sr\textsuperscript{2+}, and Na\textsuperscript{+}, whose ionic diameters approximate the cavity diameter of N\textsubscript{2}O\textsubscript{5} crown. As shown in Figures 2 and 3, the K\textsubscript{d} values for alkaline earth metal ions are larger than those for alkali metal ions, in general. A comparison of Na\textsuperscript{+} and Ca\textsuperscript{2+}, whose ionic diameters are nearly the same, shows that the K\textsubscript{d} value for Ca\textsuperscript{2+} is much larger than that for Na\textsuperscript{+}. For ions with smaller diameters, however, the difference in the K\textsubscript{d} value between Li\textsuperscript{+} and Mg\textsuperscript{2+}, is not as great. The low value of K\textsubscript{d} for Li\textsuperscript{+} with a small ionic diameter, is due to a large hydration energy for the ion having a high electron density.\textsuperscript{28,31} The adsorption of alkali and alkaline earth metal ions in water on N\textsubscript{2}O\textsubscript{5} crown ion exchange resin is shown in Figure 4. The larger values of K\textsubscript{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.\textsuperscript{28} However, little work has been reported so far on the ion exchange behavior of the crown ion exchanger,\textsuperscript{12,29-30} the thermodynamics,\textsuperscript{34} chromatography,\textsuperscript{12,32} and the formation and dissociation kinetics of the crown complexes.\textsuperscript{35-36}

Acknowledgment. This Work was Supported by the Basic Science Research Institute Program, Ministry of Edu-

cation, Korea, 1994, Project No. BSRI-94-3435.

References

32. Kim, D. W.; Kim, C. S.; Choi, K. Y.; Jeon, Y. S.; Hong,
Effect of Adsorption of Endoglucanase on the Degradation of Microcrystalline Cellulose

Dong Won Kim*, Yeo Hak Yoon, Young Kyu Jeong, Jae Kuk Lee, and Young Hun Jang

Department of Chemistry, College of Natural Sciences, Chungbuk National University, Chungbuk 360-763, Korea
Received February 14, 1995

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 cellbiohydrolase (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. The cellulases of Trichoderma viride degrade cellulose in a cooperative manner and consist of two cellbiohydrolases (CBH I and CBH II) and at least four endoglucanases (EG I, EG II, EG III, and EG IV), the former releasing cellbiose from the nonreducing ends of the cellulose chain and the latter cleaving internal glucosidic bonds in native cellulose. 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. 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. 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. Kiyosawa 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 cellbiohydrolase (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. The purified endoglucana-