

Strong Absorption of Cations into a Cation Exchange Resin in Concentrated HClO₄

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The absorptions of Fe(III), Tb(III), Tl(I), Ce(III), Th(IV), and UO₂²⁺ ions into the Dowex 50W-X2, 100-200 mesh resin were investigated by spectrophotometry to understand the abnormal strong absorption behavior of cations to cation exchange resins in concentrated HClO₄. The distribution coefficients increase in the order: Tl(I) < Fe(III) < Tb(III) ~ Ce(III) < UO₂²⁺ < Th(IV) and the order is interpreted in terms of the ratio of charge-to-ionic radius. The mole ratios of increment of ClO₄⁻ ion absorption to metal ion absorption showed the same order as the distribution coefficients, which indicates that the electrostatic association between ClO₄⁻ ion and metal ion plays a major role in the strong absorption.

Introduction

The distribution coefficients of trivalent lanthanides and americium into Dowex 50 cation exchange resins show minima around 4 to 4.5M HClO₄ followed by pronounced increase at higher acidities^{1,2}. This anomalous behaviour is not limited to those ions, but fairly uniform to many other cations. An explanation of the strong absorption was suggested involving the extraction of metal ion-perchlorate ion-pairs in resin phase,¹ which was based on the result that the absorption behaviors of trivalent lanthanide and actinide ions in hydrochloric acid solution by Dowex 50 were differentiated by the differences in complex forming abilities in the aqueous phase³. Forming complexes with sulfonate groups of a resin at high acidities where coordinating power of water is decreased may be a factor to cause the strong absorption⁴. Although possible explanations have been suggested, no mechanism for the strong absorption in concentrated HClO₄ is proven. Probably the correct explanation may not be the same for all metal ions and that more than one factor is involved.

Recent studies⁵ on the absorption behaviors of Ce(III) and Tb(III) in hydrochloric-perchloric acid mixed solutions indicated that the absorbabilities were not due to formation of chloride complexes and that perchlorate ion played a more important role in the strong absorption of rare earths than chloride ion. In this work we investigated the effect of perchlorate ion on the absorption of a variety of cations into Dowex 50W-X2, 100-200 mesh resin and correlated the absorption of perchlorate ion with that of metal ions to elucidate that the strong absorption would be caused by the electrostatic association between perchlorate and metal ions in the resin phase.

Experimental

Chemicals. A strong cation exchange resin, Dowex 50W-X2, 100-200 mesh, was freed of metal impurities by washing with distilled water, 3N HCl, 0.2N HCl, and finally distilled water until no Cl⁻ ion was detected by an AgNO₃ solution test. The resin was dried for 12hr at 80°C. The reagent grade of iron powder (Shinyo), Tb₄O₇ (Aldrich), TlNO₃ (Merck), Th(NO₃)₄·5H₂O (Merck), UO₂(NO₃)₂·6H₂O (Merck) were used without further purification. Eu₂O₃ (Merck) was dissolved in concentrated HNO₃ to convert to Eu(NO₃)₃.

Instruments. The quantitative analyses were made by a Cary

17D and Beckman DU-2 spectrophotometers on Fe(III)⁶, Ce(III) and Tb(III)⁷, Th(IV)⁸, Tl(I)⁹, UO₂²⁺¹⁰, ClO₄⁻¹¹ ions by the procedures described in the literatures.

Distribution measurements. Each metal ion was added to a polyethylene bottle containing 30ml of HClO₄ solution followed by 0.5g of resin and then equilibrated for 24 hours by a shaker at room temperature. The solution was filtered through a glass filter. The filtrate was analyzed for metal ion and the filtered resin for ClO₄⁻ ion.

Absorbed ClO₄⁻. The filtered resin on a glass filter was washed 5 times with 20ml of toluene, dried 48 hours at 85-90°C in an oven, put in a beaker containing 250ml of distilled water, and then shaken for 24 hours. All ClO₄⁻ ions absorbed into the resin on contacting with a concentrated HClO₄ solution were leached into distilled water because negative ions negligibly distribute to cation exchange resins in very dilute acid solutions. The leached ClO₄⁻ ions were determined spectrophotometrically¹¹ and compared with the metal ion absorption to elucidate the mechanism of the absorption behavior of metal ions in a cation exchange resin from concentrated HClO₄ solutions. Blank determinations in the absence of metal ions were made by exactly the same procedure.

Results and Discussion

Percent on Resin, %S. The distribution coefficients, $K_d = (\text{mg metal/g resin})/(\text{mg metal/ml solution})$, characterize the differences in absorbabilities of various elements. However, when ionic concentration is very low or very high corresponding to very large or very small absorption, respectively, analyses of the solution after batch contact are not highly accurate. Thus reporting batch data in units of K_d can be misleading. Instead of K_d values distribution data were presented by the percent of absorbed element, %S, defined as¹²

$$\text{percent on resin} \equiv \%S = 100 (S_{\text{pre}} - S_{\text{post}}) / S_{\text{pre}} \quad (1)$$

where S_{pre} and S_{post} are the ionic concentrations in a solution before and after the contact of resin with the solution, respectively. The %S data can be converted to K_d values by using the relation, $K_d = (\%S)R / (100 - \%S)$ where R is the ratio of solution volume (ml) to resin weight (g). In this work $R = 60$.

The %S values are plotted against the corresponding HClO₄ concentration in Figure 1 for Fe(III), Tb(III), Tl(I), and UO₂²⁺,

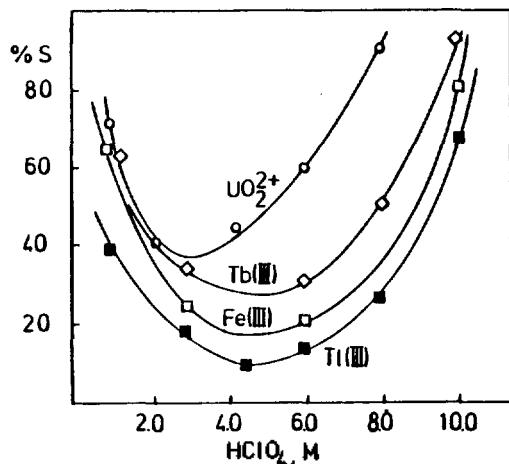


Figure 1. Percent on resin, %S of Tl(I), Fe(III), Tb(III), UO_2^{2+} ions into Dowex 50W-X2 in $HClO_4$.

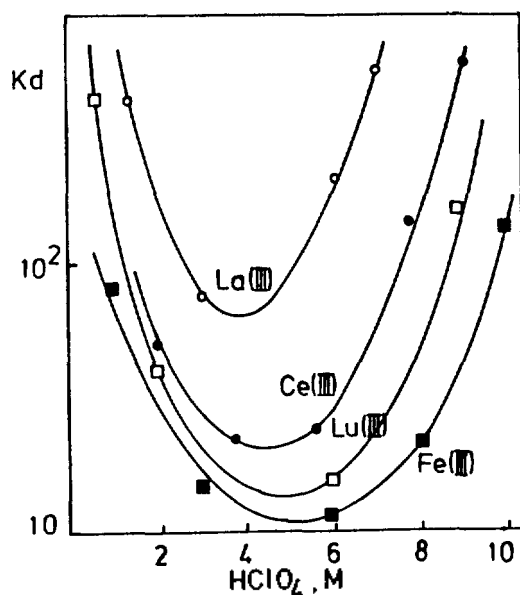


Figure 2. Distribution coefficients of Ce(III) and Fe(III) ions into Dowex 50W-X2 in $HClO_4$. Data for La(III) and Lu(III) ions are from reference 2.

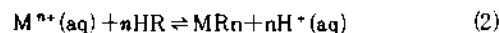
and in Figure 2 for comparison with trivalent cations, Fe(III), Ce(III), La(III), and Lu(III) among which data for La(III) and Lu(III) are from the reference 2. Essentially all Th(IV) ions are absorbed in the resin over all the range of $HClO_4$ concentration studied except at 3M $HClO_4$ where %S was about 90%. Cerium exists as Ce(III) in the presence of resin^{12,13} and the oxidation state of uranium is UO_2^{2+} in all $HClO_4$ solutions employed here¹².

The results of equilibrium distribution show very well the minima in %S for Fe(III), Tb(III), Ce(III), La(III), Tl(I), Lu(III) around 4-6M $HClO_4$, and for UO_2^{2+} near 2M $HClO_4$, and the continuous increase with further increasing $HClO_4$ concentrations. These results are generally in good agreements with those reported^{1,2}, particularly when we consider that the previous investigations were made by radioanalytical methods with different resins.

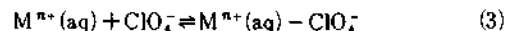
Examination of Figure 1 and 2 reveals that %S values are increasing in the order: Tl(I) < Fe(III) < Tb(III) ~ Ce(III) < UO_2^{2+} < Th(IV). For the case of trivalent cations the increasing order,

Fe < Lu < Tb ~ Ce < La, amounts to an increase with decrease in the ionic radii of bare ions¹⁴, 0.64, 0.92, 1.01, and 1.04Å for Fe(III), Lu(III), Ce(III), La(III), respectively, or presumably decrease in the hydrated ion radius in the resin which is in the direction expected for cation exchange. Absorption of trivalent lanthanides is usually stronger than that of common trivalent cations⁴ such as Al^{3+} , Fe^{3+} , and Cr^{3+} . The %S is also affected by ionic charge. From Figure 1 the increase of %S in the order Tl(I) < Tb(III) < Th(IV) apparently indicates that larger ionic charge is of importance in determining a resin's affinity for the ions of similar ionic radii. More generally the comparison of %S among different ions should take account of ionic radii as well as ionic charge. The larger %S of UO_2^{2+} than that of either Tb(III) or Fe(III) can be explained by the bigger charge-to-ionic radius ratio of UO_2^{2+} . In aqueous solutions the reactivities¹⁵ of uranium are increasing in the order U^{3+} < UO_2^{2+} < U^{4+} , which apparently supports the large %S of UO_2^{2+} in comparison with trivalent Fe or Tb because the interaction between UO_2^{2+} and functional groups within the resin is expected to be greater.

The %S of cations studied in this work decreases at lower acidities up to the concentration where minima occur followed by increase at higher acidities. This anomalous behavior is neither unique to those ions considered here nor universal. There are many elements which do not show minima². Mechanism for this strong absorption in concentrated $HClO_4$ is not proven. There are at least four main factors:³ (a) mass action effect of H^+ in the exchange reaction



where M represents a metal and HR a resin, (b) complex formation with ClO_4^-



(c) dehydration of metal ion, and (d) shrinkage of resin. Although the first factor explains the monotonic decrease before minima, it would not allow for an increase in %S at higher concentrations. This behavior appears to be likely due to factors c and d, i.e., the shrinkage of resin caused by increasing $HClO_4$ concentration results in an increase in the concentration of functional groups within the resin, hence shifting the ion equilibrium favorable to the large %S and the dehydration gives the metal ion a smaller effective radius which should cause the %S to increase. However, these factors would not permit the differences in the distribution behavior of Eu(III) in HCl and $HClO_4$. When a complexing agent is added to a solution of metal cation in equilibrium with a resin, the distribution of metal ion is reduced due to formation of complexes¹⁶ in the aqueous phase

$$K_d^*/K_d = 1 + K_1[L] + K_2K_1[L]^2 + \dots \quad (4)$$

where K_1 and the K_2 are formation constants of ML and ML_2 , K_d^* and K_d the distribution coefficients in the absence and presence of the complexing agent, respectively. Therefore %S should also decrease monotonically with $HClO_4$ concentration because ClO_4^- ion associates to a varying degree with the metal ions studied in the present work¹⁷.

Absorption of ClO_4^- . However, since the environment in a

resin is quite different from that in an aqueous solution the complex formation in the resin phase may be important in enhancing %S at higher acidities contrary to that in the aqueous phase. In fact, for Dowex 50W in 12M HClO₄ there existed approximately equal moles of sulfonate group and ClO₄⁻ ion in the resin phase, and accompanying this invasion by non-exchange electrolyte there was a large decrease in the water content¹. To elucidate the complex formation in the resin phase it seemed necessary to measure ClO₄⁻ ion absorption together with metal ion absorption and to find any correlation between the two absorptions.

The determination of ClO₄⁻ ion absorption should be preceded by the removal of HClO₄ adsorbed on resin surface and trapped between resin beads without disturbing the equilibrium established by ClO₄⁻ ion in the resin phase. Since water is not a good solvent for washing the filtered resin in this respect, a suitable organic solvent is selected as follows. The filtered resin previously equilibrated in 10M HClO₄ in the presence and absence of Ce(III) ion was washed 5 times with equal volume of solvent and analyzed for the absorbed ClO₄⁻ ion by the procedure in the Experimental. Among the solvents tested methylene chloride, 1,4-dioxane, toluene, and cyclohexane gave similar increments of ClO₄⁻ ion absorption over the reagent blank, whereas tetrahydrofuran and n-hexane showed lower results. Methylene chloride and 1,4-dioxane were excluded due to their relatively large solubilities in water¹⁸. Toluene was finally selected, however cyclohexane could be equally employed.

The moles of ClO₄⁻ ion absorbed were higher in the presence

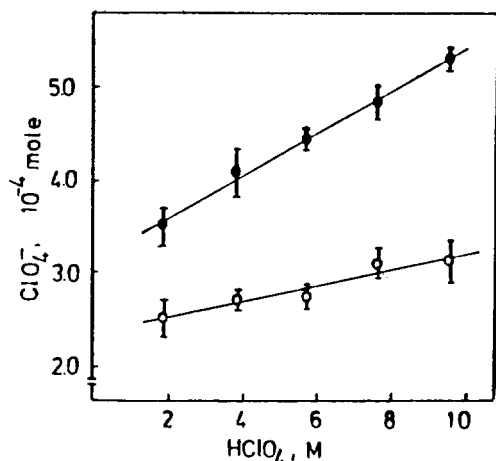


Figure 3. Absorption of ClO₄⁻ ion Dowex 50W-X2 in HClO₄ in the presence (closed circles) and absence (open circles) of Ce(III) ion. The uncertainties represent 1 standard deviation of the mean of three measurements.

TABLE 1: Absorption of Ce(III) and ClO₄⁻ ion into Dowex 50W-X2 in HClO₄ with 3.04 × 10⁻³ Mole of Ce(III)^a R_{ce} is the Absorbed mole Ratio of ClO₄⁻ to Ce(III)

HClO ₄ , M	Ce(III), 10 ⁻⁵ moles	ClO ₄ ⁻ , 10 ⁻⁵ moles	R _{ce}
1.9	0.88	0.95	1.1
3.9	0.76	1.4	1.8
5.8	0.78	1.8	2.3
7.7	1.46	1.7	1.2
9.7	2.03	2.2	1.1

^a acid volume to resin weight = 60.

than in the absence of a metal ion. A typical result is displayed in Figure 3 for Ce(III). Each point represents an average of three measurements. Although the reagent blank is quite high and the data are scattered because of difficulties in removing effectively unwanted HClO₄, Figure 3 clearly shows that the resin absorbs more ClO₄⁻ ions in the presence than in the absence of Ce(III) over the entire range of HClO₄. Similar increments were observed for other metal ions and the data are summarized in Table 1 and 2. In Table 1 the calculated moles of absorbed Ce(III) from the %S data are included.

To find any relationship between the increment of ClO₄⁻ ion absorption and the metal ion absorption the ratio of the former to the latter, R_M are computed and plotted in Figure 4 as a function of HClO₄ concentration. The values for Fe(III) are not included because of unexpectedly high results. Whereas the increment of ClO₄⁻ ion does not very strongly as the concentration of HClO₄, the curves of %S show considerable increase at concentrations outside the region of minima, hence the mole ratios exhibit broad maxima around the concentration where the minima in %S occur. Also from Figure 4 we notice that R_M decreased in the order especially at higher acidities. Th(IV) > UO₂²⁺ > Ce(III) ~ Tb(III) > Tl(I). This order surprisingly coincides with that of %S, that is, the larger the distribution coefficient of a metal ion, the more the ClO₄⁻ ion absorption. The identical sequence of the relative R_M and %S apparently indicates that the electrostatic association between ClO₄⁻ and metal ions plays a significant role in the strong absorption of metal ions into the resin in concentrated HClO₄. This conclusion is supported by the observation⁵ that the %S of rare earth ions increased whereas the ratios of Cl⁻ ion absorption to that of Tb(III) or Ce(III) ion decreased with the increase in the fraction of HClO₄ in HCl-HClO₄ mixed solutions. The magnitude

TABLE 2: Increment of ClO₄⁻ Ion Absorption in Units of 10⁻⁴ Moles into 0.5g Dowex 50W-X2 in HClO₄ Solutions Containing Cations^a

HClO ₄ , M	Tb(III)	Tl(I)	Th(IV)	UO ₂ ²⁺
1.0	0.43	0.45	0.71	0.8
3.0	0.44	0.40	1.3	1.0
4.5	—	0.40	2.1	1.8
6.0	0.41	0.39	2.0	2.1
8.0	0.42	0.39	1.1	2.2
10.0	0.43	0.38	—	—

^a 7.50 × 10⁻⁵ moles of Tb(III), 2.25 × 10⁻⁴ moles of Tl(I), 5.62 × 10⁻⁵ moles of Th(IV), or 1.13 × 10⁻⁴ moles of UO₂²⁺.

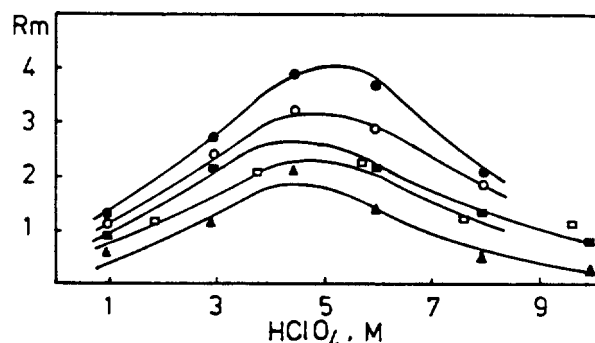


Figure 4. Absorbed mole ratios of ClO₄⁻ ion increment to Th(IV) (●), UO₂²⁺ (○) Tb(III) (■), Ce(III) (□), Tl(I) (▲) ions in HClO₄.

of R_M is likely to reflect qualitatively the relative strength of the interaction between cation and ClO_4^- ion rather than an average number of ClO_4^- ion around the metal ion in the resin phase, since a part of the metal ion absorption is expected to associate with the sulfonate group, which is caused by resin shrinkage and dehydration of the metal ion. In fact, there is appreciable difference between the absorption spectra of either Nd^{3+} or U^{4+} in the resin phase in contact with concentrated HClO_4 and the spectra of those ions in resin in dilute HClO_4 , the latter spectra being the same as those of the ions in the aqueous phase at either high or low acidity⁴. The difference in the absorption spectra additionally supports the conclusion that ClO_4^- ion associates with metal ions in the resin phase. The results observed in this work, however, would not allow for the differentiation whether the association results in a simple ion-pair⁵ as $\text{M}(\text{H}_2\text{O})_n^{2+}-\text{ClO}_4^-$ and/or complex of different kind.

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A Convergent Synthesis of (Z)-13-Octadecen-1-yl acetate, the Pheromone Mimic of the Rice Leaf Folder Moth and Its Biological Activity Test

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(Z)-13-Octadecen-1-yl acetate, the pheromone mimic of the Rice Leaf Folder Moth, *Cnaphalocrosis medinalis*, was synthesized from 1,13-tridecanediol in three steps. Monoacetylation of 1,13-tridecanediol followed by PCC oxidation gave 13-acetoxytridecan-1-ol. Wittig olefination of the 13-acetoxytridecan-1-ol with pentylidenetriphenylphosphonium ylide afforded (Z)-13-octadecen-1-yl acetate, the pheromone mimic of the Rice Leaf Folder.

Introduction

Rice Leaf Folder, *Cnaphalocrosis medinalis*, is an economic pest of the rice in Korea and China. In 1979, Arida¹ reported that (Z)-octadecen-1-yl acetate (1) (Figure 1) is a component of the pheromone mimic of the Rice Leaf Folder, *Cnaphalocrosis medinalis*.

Generally, since pheromonal activity is sensitive to insect

species, place, and climate, Department Entomology, Institute of Agricultural Science in Suwon, Korea needed a fair amount of the pheromone mimic of the Rice Leaf Folder Moth to conduct biological activity test.

Here we wish to report a convergent synthesis of (Z)-13-octadecen-1-yl acetate (1), the pheromone mimic of the Rice Leaf Folder and biological activity test as attractants for males of the Rice Leaf Folder Moth.