研究論文

153. *Extraction Studies on Dimethyl-benzyl-phenyl-ammonium Chloride-hydrochloric Acid System*

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Extraction behaviors of some sixty elements, from sodium to neptunium, in the dimethyl-benzyl-phenyl-ammonium chloride (DMBPAC)-hydrochloric acid system have been studied. The radionuclide used as tracers were either imported or irradiated in the JRR-1 reactor. Distribution ratios were obtained for the hydrochloric acid concentrations of 0.5, 1, 2, 4, 6, 8, 10 and 12 N.

Considerable regularities are found with respect to the corresponding congeners. The outcomes are compared with those of the hydrochloric acid-anion exchange resin and thiocyanate-triethyl benzyl ammonium chloride systems. Similarities among these systems are observed, however, for the present system the distribution ratios are in most cases smaller. Dependence of extractability upon ion concentrations were also investigated for iron.

Aliphatic and Aryl quaternary ammonium salts have been employed in the detection, colorimetric and gravimetric determination of metallic ions such as Bi, Hg, Cd, etc. A few works⁽¹⁾⁻⁽⁵⁾ have also been carried out in which these compounds were used as extractants for the investigation of metallic ions in heterogeneous systems⁽⁶⁾. However, it seems that their extraction behavior in the hydrochloric acid system is still little known.

In the present paper an extensive study of the extraction behavior of about sixty chemical elements in 0.1M dimethyl-benzyl-phenyl-ammonium chloride-hydrochloric acid system has been performed. Results on some elements are compared with those on triethyl-benzyl-ammonium chloride-hydrochloric acid and triethyl-benzyl-ammonium chloride-thiocyanate systems.

I. EXPERIMENTAL

1. Reagents

Dimethyl-benzyl-phenyl-ammonium chloride was synthesized by mixing together equimolar benzyl-chloride and dimethyl-aniline in a vessel. After laying aside for a week in a refrigerator, the white crystalline product was filtered, washed thoroughly with ether to

remove nonreacted benzyl chloride and dimethyl-aniline and then dried⁽⁷⁾. Stock solution was prepared by dissolving 0.1 M reagent in distilled chloroform, and standardised with 0.1M silver nitrate conductometrically. No appreciable decomposition could be seen over a period of weeks if the solution was stored in a brown colored bottle.

Hydrochloric acid solution was prepared by diluting analytical grade hydrochloric acid, and checked volumetrically whenever necessary.

2. Radioisotopes

Radioisotopes used in this experiment were either obtained by irradiation of highly pure targets in JRR-1 reactor or imported from Oak Ridge National Laboratory, U.S.A. or Radiochemical Centre of the U. K. The radiochemical purities were checked with γ -spectrometer, tracing the decay or β -absorption curves. In Table 1, the radioisotopes used were shown together with their characteristics.

As for the oxidation state the commonest of each element was used.

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Table 1 Sources of radioactive tracers used

Nuclide	Half life	Target material	Radio-chemical purity M_{as} checked by	Remarks
^{24}Na	15.0 hr	NaNO_3	γ -spectrum, decay	
^{27}Mg	9.4 min	Mg metal	γ -decay	
^{32}P	14.5 d		β -decay, absorption	
^{35}S	87 d		β -decay, absorption	
^{38}Cl	37.3 min	NH_4Cl	β -decay	
^{42}K	12.51 hr	KNO_3	γ -spectrum, decay	
^{45}Ca	164 d			Imported
^{48}Sc	85 d			Imported
^{51}Ti	5.80 min	$\text{Ti}(\text{OH})_4$	γ -decay	
^{52}V	3.76 min	NH_4VO_3	γ -decay	
^{51}Cr	27.8 d			Imported
^{58}Mn	2.58 hr	MnO_2	γ -decay	
$^{55,59}\text{Fe}$	3.0 y 45.1 d			Imported
^{60}Co	5.2 y			Imported
^{65}Ni	2.56 hr	$\text{Ni}(\text{NO}_3)_2$	γ -decay	
^{64}Cu	12.8 hr	Cu-metal	γ -decay, spectrum	
^{65}Zn	245 d			Imported
^{72}Ga	14.2 hr	Ga_2O_3	γ -decay, spectrum	
^{76}As	26.5 hr	As_2O_3	γ -decay, spectrum	
^{80}Br	4.5 hr	NH_4Br	γ -decay	
^{82}Br	35.9 hr			
^{86}Rb	19 d			Imported
^{90}Sr	28 y			Imported
^{90}Y	64 hr		β -decay, absorption	Milked from imported ^{90}Sr
^{99}Mo	67 hr	$(\text{NH}_4)_2\text{MoO}_4$	β -decay	
^{99}Tc	2.12+ 10^5y			Imported
^{106}Ru	10 y			Imported
^{108}Ag	2.3 min	AgNO_3	γ -decay	
^{115}Cd	53 hr	Cd metal	γ -decay	Imported
$^{115\text{m}}\text{Cd}$	43 d			
$^{116\text{m}}\text{In}$	540 min	In metal	γ -spectrum, decay	

^{113}Sn	112 d			
^{124}Sb	60 d			Imported
^{131}I	8.06 d			Imported
^{137}Cs	30 y			Imported
^{140}Ba	128 d			Imported
^{140}La	40.2 hr		γ -decay	Prepared by Kimura, Radiochem. Group, JAERI
^{144}Ce	285 d			Imported
^{165}Dy	2.32 hr	Dy metal	γ -decay	
^{181}Hf	46 d			Imported
^{182}Ta	111 d			Imported
^{185}W	73 d			Imported
^{186}Re	3.87 d	Re metal	γ -decay	
^{188}Re	17 hr			
^{191}Os	15 d			Imported
^{192}Ir	74.4 d	Ir metal	γ -decay	
^{194}Ir	19 hr			
^{198}Au	2.69 d	Au metal	γ -decay	
^{203}Hg	48 d			Imported
^{204}Tl	4.0 y			Imported
^{212}Pb	10.6 hr			
^{210}Bi	5.00 d			Kimura, Radiochem. Group
^{234}Th	3.64 d		γ -decay, β -spectrum	
^{233}Pa	27.4 d		γ -decay, spectrum	
^{238}U				
^{239}Up	2.33 d			Nakamura, Radiochem. Group

3. Extraction techniques

The distribution ratio of a specific radio-nuclide in a heterogenous system is defined as the quotient of its activity in the organic phase divided by that in the aqueous phase, as equilibrium is attained. Distribution ratios were determined in hydrochloric acids solution of various concentrations.

Two and half milliliter dimethyl-benzyl-phenyl-ammonium chloride-chloroform solution were added to 2.5 ml hydrochloric acid solution.

After adding a trace quantity of the radioisotope and shaking for 2 min, the organic and aqueous layers were transferred separately into tubes and centrifuged at about 4,000 r.p.m. Aliquots of each phase were taken into a glass stoppered tube or disc for counting.

Most of the data were obtained by γ -counting with a well type scintillation counter, and the rest by measurements of β -activities with GM-counter.

As for the distribution of dimethyl-benzyl-phenyl-ammonium chloride between chloroform

Fig. 1 0.1M dimethyl-benzyl-phenyl-ammonium chloride—Hydrochloric acid system
Acid dependence

and aqueous layers conductometric titrations were carried out. The reagent in the chloroform layer was stripped off with deionised water, and the titration was carried out over aqueous solution. Miscibility of hydrochloric acid into the chloroform was determined beforehand and taken as blank.

II. RESULTS AND DISCUSSION

Figs. 1 and 2 represent the dependence of distribution ratios on hydrochloric acid concentration.

All of the four alkali metals give ex-

tremely small K_d values, which are independent of hydrochloric acid concentration. This is the same for alkaline earth metals, except Ca, whose K_d values increase above 2 N acid.

Among the halides, Cl ion yields small K_d values irrespective of acidity, while those of Br decrease with the increase of acid concentration. The behavior of I is somewhat singular, for even in the absence of the reagent, as shown by the dotted line, it can be extracted into the chloroform layer appreciably. However, in the presence of the reagent it shows maximum extractability at 4 N acid and decreases thenceforth.

Fig. 2 K_d values in 0.1M dimethyl-benzyl-phenyl ammonium chloride—0.5~12 N hydrochloric acid

Sc and rare earths behave similarly, showing always very small K_d values. Within 2 to 10 N hydrochloric acid Ti shows constantly low values while the K_d values of V increase with increasing acidity.

K_d values of Fe (III) depend largely upon acid concentration, especially within the range of 0.5 to 6 N. Cr (III), Mg (II), Co (II) and Ni²⁺ (II) always behave similarly giving smaller K_d values.

Mo (VI) has maximum distribution ratio at 6 N hydrochloric acid. Tc (VII), Ag and Hg (II) show the same decreasing extraction tendency with respect to increase of acidity. K_d values of Re (VII), Os (III) and Au (III) tend to decrease above 2 N.

However, Au is almost quantitatively extracted in the acidity between 0.5 and 4N. Hf and Ta have small K_d values. Zn and Cd are both similar to Re and have largest K_d values at 2 and 4 N, respectively. Extraction curves for Ga, In and Tl (III) are quite different from each other. The K_d values of Ga change sharply with increasing acid concentration and attain maximum at 6 N, while those of In are almost independent of acidity. Tl (III) has relatively large values and shows decreasing extraction tendency with increase of acidity. Tl (I) exhibits a reverse behavior as compared with Tl (III).

Generally actinide elements are not extractable, but Pa behaves exceptionally and it resembles Fe (III), with much smaller K_d values.

Among nonmetallic elements, As (III) has rather high K_d values at high acid concentration, and the K_d of Se increases above 2 N.

The relationship between distribution ratios and atomic numbers for 6 N hydrochloric acid-DMBPAC and 5 N ammonium thiocyanate-TEBAC (triethyl-benzyl-ammonium chloride) systems are shown in Fig. 3. It can be seen that, in general, K_d values of the corresponding congener are always larger for the latter. Since in this experiment trace amounts of radionuclides were used with relatively high specific activity for the determination of K_d ,

Fig. 3 Relation between K_d values and atomic number

in Fig. 4, a series of extraction with varying Fe (III) concentration was carried out at 6, 8 and 10 N hydrochloric acid solution for comparison. The higher K_d values can be obtained with macro amount of Fe (III).

Fig. 4 Fe (III) concentration dependence of distribution ratios

On comparison, triethyl-benzyl-ammonium chloride-hydrochloric acid systems gives very similar curves.

As compared with the results worked out by Kraus⁽⁷⁾, there are certain similarity between DMBPAC-hydrochloric acid extraction and anion adsorption systems for Fe (III), Zn, Ga, Mo, Ag, Cd, Os, Au, Hg (II) and Tl (III), etc., but relatively large discrepancies of K_d values for Cu, Hf, W, Bi and U were observed. A similar mechanism can be ascribed to the two apparently different systems.

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REFERENCE

- (1) M. ZIEGLER, O. GLEMSER, A. V. BACKMANN: *Angew. Chem.*, **68**, 4411, 436 (1956).
- (2) N. PETRI, M. ZIEGLER, O. GLEMSER: *A. Anal. Chem.*, **154**, 81 (1957).
- (3) M. ZIEGLER, H. G. HORN: *Z. Anal. Chem.*, **166**, 362 (1959).
- (4) T. KARANTASSIS, L. CAPTOS: *Compt. rend.*, **201**, 74 (1935).
- (5) M. ZIEGLER, W. RITTER: *Z. Anal. Chem.*, **164**, 310 (1958).
- (6) J. YOSHIMURA, K. UENO: *Dept. of Chem., Faculty of Sci., Kyushu Univ.*, Ser. C, **4**, No. 1, 63 (1961).

- (7) K. A. KRAUS, F. NELSON: *A/Conf.*, 7, 1837, (1956), United Nations Publication, New York.

0.1M ジメチル-ベンジル-フェニル アンモニウム塩化物-塩酸系にお ける諸元素の行動

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ジメチル-ベンジル-フェニルアンモニウム塩化物の
0.1M クロロホルム溶液と塩酸の系における, ナトリ
ウムよりネプツニウムに至る約60種の元素の行動を輸
入またはJRR-1で照射して作った放射性核種を用いて

調べた。水溶液の塩酸の濃度は0.5, 1, 2, 4, 6, 8, 10およ
び 12N の 8 点を取り, これに対する有機相との間の
分配比を求めた。分配比の測定に用いた放射性核種の
原子価は明瞭でないものもあるが, 最も普通の化学形
を選んだ。酸の濃度に対する分配比は各元素により異
なるが, 周期律表の族についてはかなりの規則性がみ
られた。Fe(III)では特に鉄の量の変化による分配比
の変化を調べた。これらの結果より数種の元素の相互分
離に適した酸の濃度が求められた。

この系で求められた結果を塩酸-陰イオン交換樹脂
系や, チオシアン酸-トリエチル-ベンジルアンモニ
ウム塩化物系と比較しかなりの類似点を見出したが,
一般にこの系では分配比が小さいことがわかった。

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