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## Extraction of Alkali Metal Tetraphenylborates by Polyurethane Foam

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### Abstract

The extraction of alkali metal tetraphenylborates by polyurethane foam was investigated. The extractability sequences are  $K^+ \approx Rb^+ > Cs^+$  and  $K^+ \approx Rb^+ \approx Cs^+$  for polyether and polyester foams, respectively. The high extraction of  $K^+$  by polyether foam can be explained by the cation chelation mechanism.

### INTRODUCTION

Polyurethane foams have been successfully used for the separation and concentration of a wide variety of organic and inorganic compounds from aqueous solution (1, 2). Many of these previous studies were done without knowledge of the extraction mechanism. It would be advantageous to understand the extraction mechanism to allow developments in useful applications of polyurethane foam more easily.

There are three mechanisms which have been widely used to explain the extraction by polyurethane foam, namely, solvent extraction, anion exchange, and cation chelation. The foam is considered simply as a solid organic sorbent in the solvent extraction mechanism (3, 4). Some functional groups in the foam, such as urea, urethane, ether, and ester, can be protonated in acidic conditions and inorganic complex anions can be extracted by an anion-exchange process (5). According to the cation chelation mechanism (6), many cations including ammonium and alkali metal ions are able to be effectively solvated by a certain portion of the polyether foam. This chelation of the cation facilitates the extraction of anionic metal complexes. The ability of the polyethylene oxide portion of the polyether foam to adopt a helical structure with inwardly directed oxygen atoms is considered to be responsible for the specific interaction between the cation

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and the foam. It was noted that polyether foam exhibits a similar cation selectivity as 18-crown-6, i.e., the highest selectivity for  $K^+$  among alkali metal ions. The inability of polyester foam in the crystalline state to assume the helical structure is accountable for the lower extraction of the anion by polyester foam. This mechanism has been used to explain many extraction systems (7-12).

Much of the work done to study the extraction mechanism by polyurethane foam has involved the sorption of anionic metal complexes, and few reports in the literature have used organic species. Schumack and Chow (13) studied the mechanism of the extraction of simple aromatic compounds by polyurethane foam. The results suggest a solvent extraction mechanism for the extraction of these compounds. In addition, hydrogen bonding between the compound and the foam has a significant effect on the extraction. Compounds able to form hydrogen bonds are more extractable by polyether foam; this has been attributed to stronger hydrogen bonding with polyether foam relative to polyester foam. Recently, Fong and Chow (14) studied the extraction of salicylic acid, 8-hydroxyquinoline, 1-amino-2-naphthol-4-sulfonic acid, and cinnamic acid in the presence of various alkylammoniums, ammonium, and alkali metal cations by polyurethane foam. It was found that these compounds are extracted only in the neutral form by a solvent extraction mechanism. The mechanism was confirmed by the salting-out effect and pH studies. This work also demonstrates that these compounds in the anionic form are too hydrophilic to assist in the extraction of alkali metal cations from aqueous solution.

Tetraphenylborate (TPB) was widely used during 1950-1960 as an analytical reagent to form precipitates with ammonium and alkali metal ions. Fix (15) reported the extraction of rubidium and cesium into nitrobenzene from aqueous 0.1 M sodium TPB solution, and Handley and Burros (16) studied the extraction of cesium TPB into amyl acetate. Sekine and Dyrssen (17) studied the extraction of potassium, rubidium, and cesium from aqueous solutions containing sodium TPB, sodium perchlorate, and perchloric acid into various organic solvents: nitromethane, nitroethane, nitrobenzene, methyl isobutyl ketone, and tributyl phosphate. The highest distribution ratio and separation factor for the TPBs were obtained for extraction into nitrobenzene. The distribution ratio decreases in the order sodium < potassium < rubidium < cesium. Koeva and Hala (18) examined the extraction of potassium, rubidium, and cesium TPBs into nitrobenzene from mixed aqueous-organic solutions. It was found that the extractability of alkali metal TPBs from mixed-organic solutions is always lower than from water irrespective of the nature of the organic component of the polar phase. This effect was ascribed to the increased solubility of TPB salts as well as the possible destruction of water structure in the mixed aqueous-organic phase.

Since polyurethane foam can be regarded as an organic phase for extraction, it is likely that various TPB salts can be extracted from aqueous solution into polyurethane foam. In previous studies of the extraction of anionic metal complexes, a large excess of the chelatable cations was used for the formation of the complexes, and hence only the extraction of the anion was measured. The use of organic anions can eliminate the problem of using a large excess of the chelatable cations. Therefore, the extraction can be carried out in the presence of a comparable amount of the chelatable cations and organic anions, and a direct measurement of the extraction of the cations is possible. The present work was to use  $\text{TPB}^-$  as the organic anion to study the extraction of alkali metal cations by polyurethane foam and to determine the extraction mechanism under these conditions.

## EXPERIMENTAL

### Apparatus

UV absorbance measurements for the determination of  $\text{TPB}^-$  were made with a Hewlett-Packard Model 8452A diode-array spectrophotometer. A Fisher Accumet Model 520 pH-meter was used. The alkali metal concentrations were determined using a Waters Ion Chromatograph IIC-1 with a Waters WISP auto-sampler, a Waters 740 data module, a Waters 590 solvent pump, and a Waters 430 conductivity detector.

### Reagents

All chemicals were reagent grade, and water was purified by reverse osmosis and a Barnsted Nanopure II system before use. The polyether foam (#1338M) was obtained from G. N. Jackson Ltd. (Winnipeg, Manitoba). The polyester foam (DiSPo) was obtained from Canlab (Winnipeg, Manitoba).

### Procedure

Polyether foam plugs of approximately 0.4 g each were cut from a polyurethane sheet. The polyester material (DiSPo) was received from the manufacturer as foam plugs. These plugs were soaked in 1 *M* hydrochloric acid for 24 h with occasional squeezing to remove any possible inorganic contaminants and washed with water until acid free. They were then extracted with acetone in a Soxhlet apparatus for 6 h to remove any soluble organic contaminants and finally air dried in a 60°C oven. Powdered foam was prepared by freezing the cleaned foam plugs in liquid nitrogen and then grinding them in a stainless-steel container on a Waring blender. Sample solutions were prepared freshly by adding the necessary weight of

NaTPB solid and by pipetting the appropriate aliquots of the stock solutions.

For the extraction with foam plugs, the sample solution (100 mL) and the foam plug trimmed to  $0.300 \pm 0.005$  g were placed in a Pyrex extraction cell. The foam plug was squeezed by an automatic squeezing apparatus (19). For the extraction with powdered foam, the sample solution and powdered foam ( $0.300 \pm 0.005$  g for polyether foam and  $0.800 \pm 0.005$  g for polyester foam) were placed in gas-tight plastic vials and were manually shaken periodically.

The % extraction was calculated by using

$$\% \text{ Extraction} = (1 - C'/C_0) \times 100$$

where  $C_0$  = concentration in solution before extraction

$C'$  = concentration in solution after extraction

The distribution coefficient ( $D$ ) was calculated as follows:

$$D = \frac{\% \text{ extraction}}{(100 - \% \text{ extraction})} \times \frac{\text{volume of solution (L)}}{\text{weight of foam (kg)}}$$

## RESULTS AND DISCUSSION

To study the extractability of NaTPB,  $1.0 \times 10^{-3}$  M NaTPB solutions (100 mL) were extracted with polyether and polyester foams (0.300 g) using the automatic squeezing apparatus. The pH of the solution changed from 8.5 to 7.0 after 24 h of extraction. The distribution coefficients of  $\text{Na}^+$  and  $\text{TPB}^-$  ions for both types of foams are given in Table 1. It is evident that  $\text{TPB}^-$  can be used to extract  $\text{Na}^+$ . In contrast to the expected

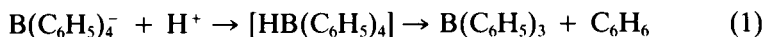
TABLE 1  
Extraction of NaTPB with Polyurethane Foam<sup>a</sup>

		$\text{Na}^+$	$\text{TPB}^-$
Polyester	% Extraction	$15.8 \pm 0.5$	$25.4 \pm 0.7$
	Amount extracted ( $\times 10^{-5}$ mol)	$1.58 \pm 0.05$	$2.54 \pm 0.07$
	Distribution coefficient (L/kg)	$62.4 \pm 2.5$	$113 \pm 4$
Polyether	% Extraction	$64.5 \pm 0.5$	$81.5 \pm 0.5$
	Amount extracted ( $\times 10^{-5}$ mol)	$6.45 \pm 0.05$	$8.15 \pm 0.05$
	Distribution coefficient (L/kg)	$602 \pm 11$	$1460 \pm 60$

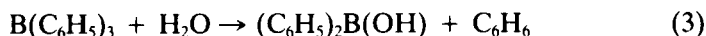
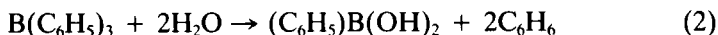
<sup>a</sup>Conditions:  $1.0 \times 10^{-3}$  M NaTPB, 0.300 g foam, 100 mL solution, 24 h extraction time, initial pH 8.5, final pH 7.0.

equal extraction of the cation ( $\text{Na}^+$ ) and the anion ( $\text{TPB}^-$ ),  $\text{TPB}^-$  is more extractable than  $\text{Na}^+$ . It should be noted that the species removed from solution was considered to be extracted by the foam. The decomposition of  $\text{TPB}^-$  with the production of decomposition products which can be extracted without accompanying  $\text{Na}^+$  by the foam could result in the apparent higher extraction of  $\text{TPB}^-$ .

$\text{NaTPB}$  solution is known to be unstable and undergoes decomposition in acidic medium (20). The  $\text{TPB}^-$  ion is attacked by  $\text{H}^+$  to form benzene and triphenylboron:



Triphenylboron undergoes hydrolysis to phenylboric acid or diphenylboric acid:



Cooper (21) reported that  $\text{NaTPB}$  solution is stable for at least several weeks if the pH of the solution is about 8 or 9.

The decomposition products of  $\text{TPB}^-$  are highly hydrophobic and are likely to be extracted by foam. In addition,  $\text{HTPB}$  may also be extractable. To determine the effect of pH on the extraction, solutions (100 mL) containing  $1.0 \times 10^{-4} \text{ M}$   $\text{NaTPB}$  were extracted with 0.300 g foam at initial pH 3.8 and 5.2. Figure 1 shows the % extraction of the cation and the anion as a function of time. At pH 3.8 and after 1/2 h extraction, there is only 25%  $\text{Na}^+$  extracted but 96%  $\text{TPB}^-$  extracted, which may be a result of  $\text{NaTPB}$  decomposition and  $\text{HTPB}$  extraction. At pH 5.2 and after 1/2 h extraction, 35%  $\text{Na}^+$  and 84%  $\text{TPB}^-$  are extracted, suggesting a lower  $\text{NaTPB}$  decomposition and  $\text{HTPB}$  extraction.

To prevent the decomposition of  $\text{TPB}^-$ , it is necessary to keep the pH of the solution above 8. From the extraction of  $1.0 \times 10^{-3} \text{ M}$   $\text{NaTPB}$ , the pH lowers from 8.5 to 7.0 after 24 h due to  $\text{CO}_2$  absorption from air during the squeezing process. It was decided to raise the initial pH of the solution to higher pH by adding  $\text{NaOH}$ . Moreover, the extraction was carried out by bubbling  $\text{N}_2$  through the solution to prevent  $\text{CO}_2$  absorption. Solutions (100 mL) containing  $1.0 \times 10^{-4} \text{ M}$   $\text{NaTPB}$  and  $1.0 \times 10^{-4} \text{ M}$   $\text{NaOH}$  were extracted with 0.300 g polyether foam. There is a lowering of  $\text{TPB}^-$  extracted compared with the extraction at lower pH. However, after reaching a maximum, a decrease of  $\text{Na}^+$  extraction still occurs with increasing extraction time even though it is unlikely that  $\text{TPB}^-$  decomposes since the

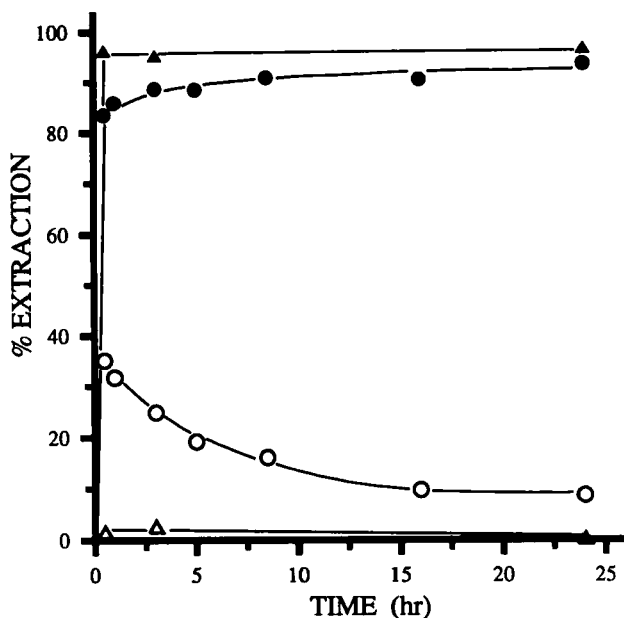
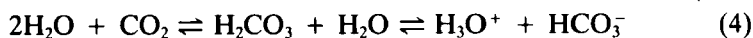


FIG. 1. Effect of pH on the extraction of  $\text{Na}^+$  and  $\text{TPB}^-$ . Conditions:  $1.0 \times 10^{-4} M$  NaTPB, 0.300 g polyether foam plug, 100 mL solution, (●)  $\text{TPB}^-$  extraction and (○)  $\text{Na}^+$  extraction at initial pH 5.2 and final pH 6.3, (▲)  $\text{TPB}^-$  extraction and (△)  $\text{Na}^+$  extraction at initial pH 3.8 and final pH 4.3.

final pH is 8.6. The pH change of the solution from 9.0 to 8.6 indicates that there may still be  $\text{CO}_2$  absorption from air. The up and down motion of the plunger could bring solution into contact with air, and the dissolved  $\text{CO}_2$  promotes the formation of  $\text{H}_3\text{O}^+$ :



It is possible that  $\text{H}_3\text{O}^+$  is more extractable than  $\text{Na}^+$  and can displace  $\text{Na}^+$  from the foam. This would result in the observed gradual decrease of  $\text{Na}^+$  extraction as  $\text{CO}_2$  absorption from air increased with time.

Izatt and coworkers (22) reported the preparation of a complex,  $[\text{H}_3\text{O}, \text{C}_{20}\text{H}_{36}\text{O}_6]^+[\text{ClO}_4]^-$ , formed by  $\text{H}_3\text{O}^+$  with a cyclic polyether. Behr et al. (23) determined the structure of the complex between tetracarboxylic 18-crown-6 and  $\text{H}_3\text{O}^+$  by x-ray crystallography. The  $\text{H}_3\text{O}^+$  cation is positioned in the center of the cavity by three  $\text{OH} \cdots \text{O}$  hydrogen bonds with a pyramidal geometry.

Heo and Bartsch (24) were also able to prepare the complex between 18-crown-6 and  $\text{H}_3\text{O}^+$ . They attempted to prepare solid  $\text{H}_3\text{O}^+$  complexes with tetraglyme, an acyclic polyether, and with 15-crown-5. It was found that  $\text{H}_3\text{O}^+$  only complexes with tetraglyme. They suggested that the greater flexibility of acyclic polyether allows the oxygens to provide a better arrangement for the formation of hydrogen bonds with the pyramidal  $\text{H}_3\text{O}^+$ , and hence increases complexation.

Kolthoff et al. (25) determined the complexation constants of  $\text{H}_3\text{O}^+$  and  $\text{K}^+$  with 18-crown-6 (L) and with dibenzo-18-crown-6 (L') in acetonitrile. The dibenzo groups are electron withdrawing, which lowers the electron density of the oxygen binding sites. Therefore the complexation constants for  $(\text{L}'\text{H}_3\text{O}^+)$  and  $(\text{L}'\text{K}^+)$  are lower than those for  $(\text{LH}_3\text{O}^+)$  and  $(\text{LK}^+)$ . The dibenzo effect can be calculated as  $[K(\text{LH}_3\text{O}^+) - K(\text{L}'\text{H}_3\text{O}^+)]$  and  $[K(\text{LK}^+) - K(\text{L}'\text{K}^+)]$  for  $\text{H}_3\text{O}^+$  and  $\text{K}^+$ , respectively ( $K$  is the association constant). This effect on  $(\text{LH}_3\text{O}^+)$  is two orders of magnitude greater than that on  $(\text{LK}^+)$ . It was concluded that  $\text{H}_3\text{O}^+$  is strongly bound to the ether oxygens by hydrogen bonding and, in addition, by ion-dipole interaction, whereas  $\text{K}^+$  is bound only by the latter.

It is evident that  $\text{H}_3\text{O}^+$  can complex with crown ethers and acyclic polyethers by hydrogen bonding and ion-dipole interaction. It appears that a similar interaction of  $\text{H}_3\text{O}^+$  with foam can take place because polyether and polyester foams can be considered to act as acyclic polymers with flexible chains.

Pinvonkova and Kyrs (26) reported that the extraction of NaTPB from water into nitrobenzene is pH independent above 9. There is a significant competitive extraction of HTPB below pH 8.5. For this study, some extraction of HTPB may take place because the final pH of the solution was 8.6.

Since  $\text{CO}_2$  absorption from air may cause the displacement of cations and lower the pH of the solution, further extractions were carried out in gas-tight plastic vials to minimize  $\text{CO}_2$  absorption. Powdered foam was used to provide a better contact between the foam and the solution, and the vials were periodically shaken manually.

The results with  $1.0 \times 10^{-3} M$  NaTPB demonstrate that 0.300 g polyether foam extracts  $6.5 \times 10^{-5} \text{ mol Na}^+$  and  $8.2 \times 10^{-5} \text{ mol TPB}^-$ . Due to the low solubility of TPB salts with  $\text{K}^+$  and other alkali metal ions, a maximum of  $1.0 \times 10^{-4} M$  NaTPB was used for further experiments. The total amount of  $\text{TPB}^-$  present in 100 mL solution is  $1.0 \times 10^{-5} \text{ mol}$ . Thus 0.300 g polyether foam is enough to extract a 100-mL solution containing  $1.0 \times 10^{-4} M \text{ TPB}^-$ .

To determine the time required to reach equilibrium, the extraction of solutions (100 mL) containing  $1.0 \times 10^{-4} M \text{ NaTPB} + 1.0 \times 10^{-4} M$

NaOH +  $2.0 \times 10^{-5} M$  KCl with 0.3 g foam was studied as a function of time. The results are given in Fig. 2.  $\text{TPB}^-$  extraction increases rapidly after 1 h and then slowly up to 24 h.  $\text{Na}^+$  and  $\text{K}^+$  extractions reach a maximum after 1 h and decrease with increasing extraction time. No decomposition of  $\text{TPB}^-$  should take place since the pH of the solution is 9.0. Although the extraction was carried out in closed containers,  $\text{CO}_2$  may still diffuse into the container and the decrease of  $\text{Na}^+$  and  $\text{K}^+$  extracted may be due to a slow continuous  $\text{CO}_2$  absorption from air. The ratio of total cations extracted/anion extracted, i.e.,  $(\text{Na}^+ + \text{K}^+ \text{ extracted})/\text{TPB}^- \text{ extracted}$  is very close to 1 for the first hour of extraction. It is reasonable to assume that no decomposition or displacement of cations takes place if the ratio of cation extracted/anion extracted is 1. Although a time for the cation extraction reaching equilibrium could not be obtained, the extractability of different cations can still be evaluated by comparing the values of cation extraction when the cation/anion is about 1. Results similar to these, as shown in Fig. 2, were also obtained for extraction in the presence of rubidium or cesium salt.

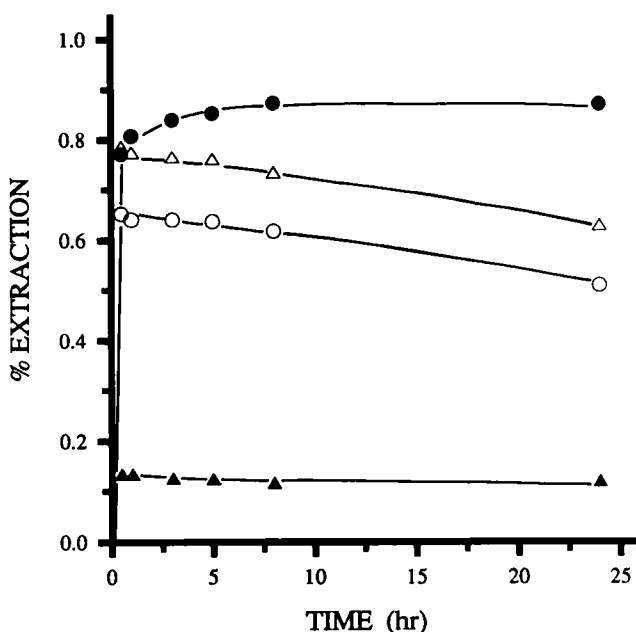


FIG. 2. Extraction of NaTPB and KCl with polyether foam as a function of time. Conditions:  $1.0 \times 10^{-4} M$  NaTPB +  $1.0 \times 10^{-4} M$  NaOH +  $2.0 \times 10^{-5} M$  KCl, 0.300 g powdered polyether foam, 100 mL solution, pH 9.0, (●)  $\text{TPB}^-$ , (○)  $\text{Na}^+$ , (▲)  $\text{K}^+$ , and (△) total cations ( $\text{Na}^+ + \text{K}^+$ ).

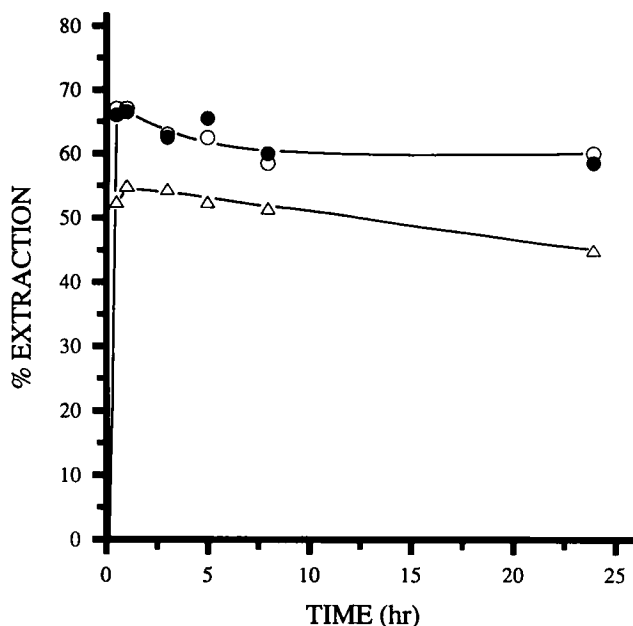


FIG. 3. Plot of % cation extraction as a function of time for the extraction of NaTPB and alkali metal chlorides with polyether foam. Conditions:  $1.0 \times 10^{-4} M$  NaTPB +  $1.0 \times 10^{-4} M$  NaOH +  $2.0 \times 10^{-5} M$  alkali metal chloride, 0.300 g powdered polyether foam, 100 mL solution, pH 9.0, (○) K<sup>+</sup>, (●) Rb<sup>+</sup>, and (△) Cs<sup>+</sup>.

Figures 3 and 4 show the extraction of the cation and anion as a function of time for potassium, rubidium, and cesium TPBs. Table 2 gives the % extraction and distribution coefficient ( $D$ ) of the cations when the ratio of total cations extracted/anion extracted, i.e., ( $\text{Na}^+ + \text{alkali metal ions extracted}$ )/TPB<sup>-</sup> extracted, is about 1. Although TPB<sup>-</sup> extraction in the presence of potassium, rubidium, or cesium chloride is about the same, the extraction of these cations is not. It is because the initial concentration of TPB<sup>-</sup> ( $1.0 \times 10^{-4} M$ ) is higher than that of potassium, rubidium, or cesium cations ( $2.0 \times 10^{-5} M$ ), and a large portion of TPB<sup>-</sup> is extracted in combination with Na<sup>+</sup>.

From Figs. 3 and 4 and Table 2 the extractability follows the order of  $\text{K}^+ \approx \text{Rb}^+ > \text{Cs}^+$ . Assuming that alkali metal ions form ion-pairs with TPB<sup>-</sup>, Cs<sup>+</sup> and Rb<sup>+</sup> are expected to form ion-pairs with TPB<sup>-</sup> more readily than K<sup>+</sup> because the Cs<sup>+</sup> and Rb<sup>+</sup> salts are less soluble than the K<sup>+</sup> salt. The solubilities (27) in water are  $1.8 \times 10^{-4} M$ ,  $0.23 \times 10^{-4} M$ , and  $0.28 \times 10^{-4} M$  for KTPB, RbTPB, and CsTPB, respectively. The extract-

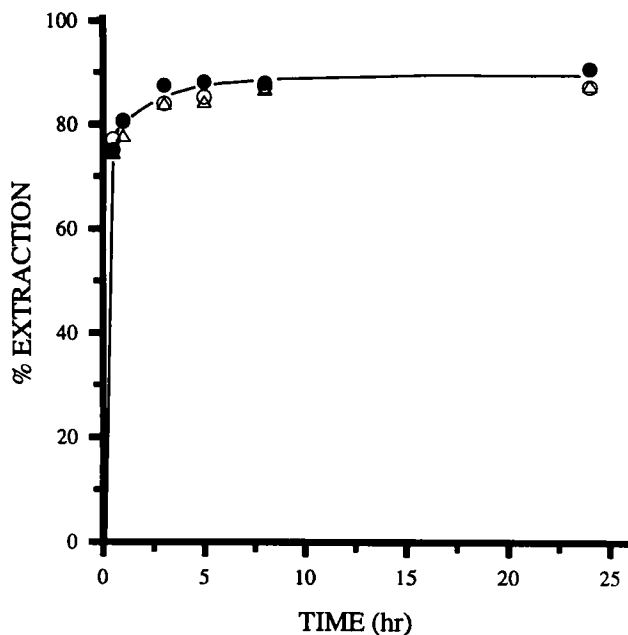


FIG. 4. Plot of %  $\text{TPB}^-$  extraction as a function of time for the extraction of NaTPB and alkali metal chlorides with polyether foam. Conditions:  $1.0 \times 10^{-4} M$  NaTPB +  $1.0 \times 10^{-4} M$  NaOH +  $2.0 \times 10^{-5} M$  alkali metal chloride, 0.300 g powdered polyether foam, 100 mL solution, pH 9.0, (○)  $\text{TPB}^-$  extraction for solution with KCl, (●)  $\text{TPB}^-$  extraction for solution with RbCl, and (△)  $\text{TPB}^-$  extraction for solution with CsCl.

TABLE 2  
Distribution Coefficient and % Extraction of Alkali Metal Ions When Total Cations Extracted/ $\text{TPB}^-$  Extracted  $\approx 1$  for the Extraction of NaTPB and Alkali Metal Chlorides with Polyether Foam<sup>a</sup>

Cation	% Extraction	Distribution coefficient (L/kg)
$\text{K}^+$	67.0	669
$\text{Rb}^+$	66.5	660
$\text{Cs}^+$	55.0	404

<sup>a</sup>Conditions:  $1.0 \times 10^{-4} M$  NaTPB +  $1.0 \times 10^{-4} M$  NaOH +  $2.0 \times 10^{-5} M$  alkali metal chloride, 0.300 g powdered polyether foam, 100 mL solution, pH 9.0.

ability of  $K^+$  is higher than  $Cs^+$  due to some stronger interaction between  $K^+$  and the foam. This process can be explained by the cation chelation mechanism because  $K^+$  fits more closely into the cavity in the foam, and hence has a stronger interaction.

The extraction of alkali metal TPBs by polyester foam was also studied for comparison. From the preceding experiments it was determined that 0.300 g polyester foam can extract  $2.5 \times 10^{-5}$  mol  $TPB^-$  and  $1.6 \times 10^{-5}$  mol  $Na^+$  from 100 mL of  $1.0 \times 10^{-3}$  M NaTPB (Table 1). The total amount of  $TPB^-$  present in 100 mL of  $1.0 \times 10^{-4}$  M NaTPB solution is  $1.0 \times 10^{-5}$  mol. The capacity of the foam is not exceeded in using 0.300 g polyester foam to extract 100 mL of  $1.0 \times 10^{-4}$  M NaTPB. However, the extraction of  $TPB^-$  was found to be rather low, about 50%. The cation extraction would also be low if  $TPB^-$  extraction is low, and therefore it would be difficult to compare the extractability of the cations if the extractions were low and very close to one another. For this reason, it was decided to

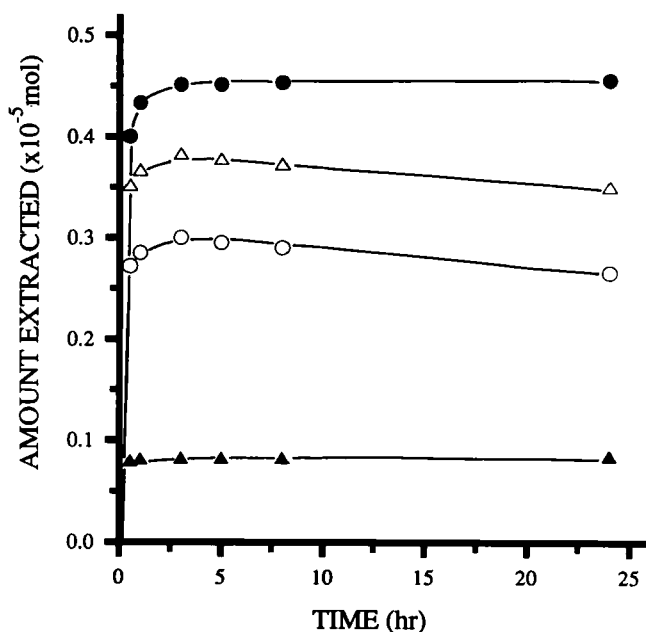


FIG. 5. Extraction of NaTPB and KCl with polyester foam as a function of time. Conditions:  $1.0 \times 10^{-4}$  M NaTPB +  $1.0 \times 10^{-4}$  M NaOH +  $2.0 \times 10^{-5}$  M KCl, 0.800 g powdered polyester foam, 50 mL solution, initial pH 9.0, final pH 8.4, (●)  $TPB^-$ , (○)  $Na^+$ , (▲)  $K^+$ , and (△) total cations ( $Na^+ + K^+$ ).

increase the weight of foam to 0.800 g and to reduce the volume of solution extracted to 50 mL so that the extraction of  $\text{TPB}^-$  increased to about 90%.

Solutions (50 mL) of  $1.0 \times 10^{-4} \text{ M NaTPB} + 1.0 \times 10^{-4} \text{ M NaOH} + 0.2 \times 10^{-4} \text{ M}$  alkali metal chloride were extracted with 0.800 g foam. Figure 5 shows the extraction of  $1.0 \times 10^{-4} \text{ M NaTPB} + 1.0 \times 10^{-4} \text{ M NaOH} + 0.2 \times 10^{-4} \text{ M KCl}$  as a function of time. The same phenomenon of a decrease of  $\text{Na}^+$  extraction after reaching a maximum was observed. The maximum of the ratio of total cations extracted/ $\text{TPB}^-$  extracted is only about 0.9 as opposed to about 1.0 for the extraction with polyether foam. The pH of the solution decreased to 8.4 from 9.0, which may be due to a residual amount of  $\text{H}_3\text{O}^+$  present in the foam rather than  $\text{CO}_2$  absorption from air because the final pH of the solution was 9.0 for the extraction with polyether foam. Since 50 mL solution was extracted with 0.8 g polyester foam as opposed to 100 mL solution with 0.3 g polyether foam, the effect of the residual  $\text{H}_3\text{O}^+$  is expected to be more significant for the extraction with polyester foam. It is likely that the competitive

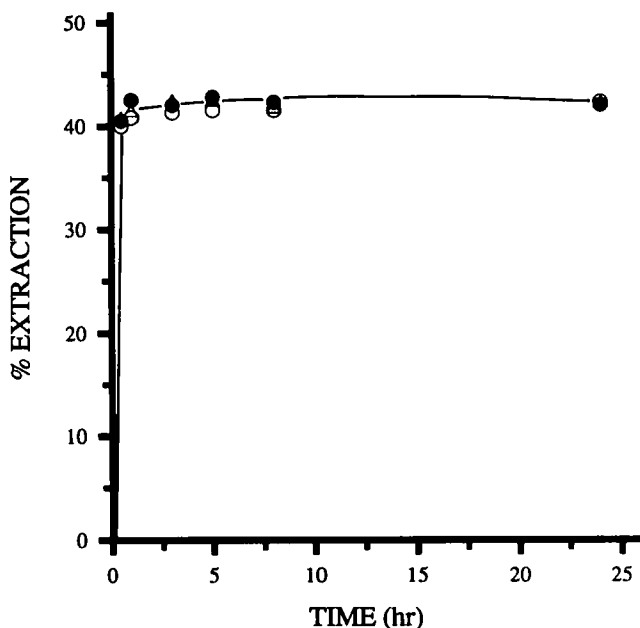


FIG. 6. Plot of % cation extraction as a function of time for the extraction of NaTPB and alkali metal chlorides with polyester foam. Conditions:  $1.0 \times 10^{-4} \text{ M NaTPB} + 1.0 \times 10^{-4} \text{ M NaOH} + 2.0 \times 10^{-5} \text{ M}$  alkali metal chloride, 0.800 g powdered polyester foam, 50 mL solution, initial pH 9.0, final pH 8.4, (○)  $\text{K}^+$ , (●)  $\text{Rb}^+$ , and (△)  $\text{Cs}^+$ .

extraction of HTPB may take place at pH 8.4 and cause the lower extraction of the cations. It should be noted that only  $\text{Na}^+$  is displaced but not  $\text{K}^+$ . It is possible that the interaction of  $\text{Na}^+$  with polyester foam is relatively weaker than that of  $\text{K}^+$ . Similar extraction behavior of only  $\text{Na}^+$  displacement was obtained for the extraction with rubidium or cesium chloride present.

Figures 6 and 7 show the extraction of the cation and the anion as a function of time for the extraction of potassium, rubidium, and cesium TPBs. Table 3 gives the maximum extraction and distribution coefficient for each of the cations. Since there is no displacement of  $\text{K}^+$ ,  $\text{Rb}^+$ , or  $\text{Cs}^+$  with increasing extraction time, the extractability of the cations is compared after 24 h extraction time. The extractability sequence of the cations is  $\text{K}^+ \approx \text{Rb}^+ \approx \text{Cs}^+$ . This order is different from that obtained with polyether foam of  $\text{K}^+ \approx \text{Rb}^+ > \text{Cs}^+$ . As polyester foam does not readily adopt a helical structure, a hole-size/cation-diameter relationship may not exist. The relative strength of the interaction between  $\text{K}^+$  and polyester foam

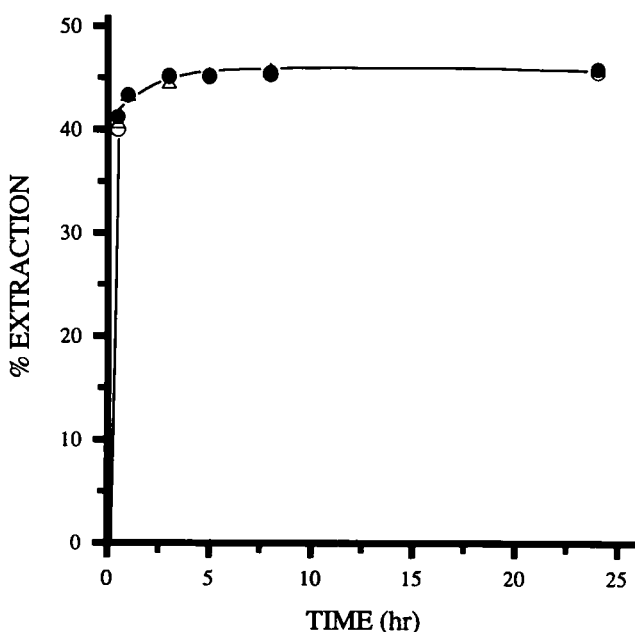


FIG. 7. Plot of %  $\text{TPB}^-$  extraction as a function of time for the extraction of NaTPB and alkali metal chlorides with polyester foam. Conditions:  $1.0 \times 10^{-4} M$  NaTPB +  $1.0 \times 10^{-4} M$  NaOH +  $2.0 \times 10^{-5} M$  alkali metal chloride, 0.800 g powdered polyester foam, 50 mL solution, initial pH 9.0, final pH 8.4, (○)  $\text{TPB}^-$  extraction for solution with KCl, (●)  $\text{TPB}^-$  extraction for solution with RbCl, and (△)  $\text{TPB}^-$  extraction for solution with CsCl.

TABLE 3  
Maximum % Extraction and Distribution Coefficient of the  
Cations for the Extraction of NaTPB and Alkali Metal  
Chlorides with Polyester Foam<sup>a</sup>

Cation	% Extracted	Distribution coefficient (L/kg)
K <sup>+</sup>	42.3	335
Rb <sup>+</sup>	42.0	322
Cs <sup>+</sup>	42.3	339

<sup>a</sup>Conditions:  $1.0 \times 10^{-4}$  M NaTPB +  $1.0 \times 10^{-4}$  M NaOH  
+  $2.0 \times 10^{-5}$  M alkali metal chloride, 0.800 g powdered  
polyester foam, 50 mL solution, initial pH 9.0, final pH 8.4,  
24 h extraction time.

compared with Rb<sup>+</sup> and Cs<sup>+</sup> is not as high as in the case for polyether foam. Thus, the extractability of K<sup>+</sup>, Rb<sup>+</sup>, and Cs<sup>+</sup> is about the same for polyester foam.

The extractability of the cations by polyether foam is  $K^+ \approx Rb^+ > Cs^+$ , whereas the solubility of the TPB salts in water is  $Rb^+ \approx Cs^+ < K^+$ . This result suggests that the interaction between K<sup>+</sup> and polyether foam is stronger than between Rb<sup>+</sup> and Cs<sup>+</sup>. The extractability order for polyester foam is  $K^+ \approx Rb^+ \approx Cs^+$ . This indicates that the interaction between K<sup>+</sup> and polyester foam is still stronger than between Rb<sup>+</sup> and Cs<sup>+</sup>, but to a lesser extent in comparison to that with polyether foam. The cation chelation mechanism may be used to explain the stronger interaction of K<sup>+</sup> with polyether foam relative to polyester foam; however, this cannot account for the stronger interaction of K<sup>+</sup> compared to Rb<sup>+</sup> and Cs<sup>+</sup> with polyester foam. Although polyester foam does not readily assume a helical structure, K<sup>+</sup> still has the highest interaction with polyester foam. Therefore, more work is still necessary to determine whether a helical structure is required for the selectivity for alkali metals and other cations. Further work is in progress to clarify this.

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### REFERENCES

1. G. J. Moody and J. D. R. Thomas, *Analyst*, **104**, 1 (1979).
2. T. Braun, *Z. Anal. Chem.*, **314**, 652 (1983).
3. H. D. Gesser, E. Bock, W. G. Baldwin, A. Chow, D. W. McBride, and W. Lipinsky, *Sep. Sci.*, **11**, 315 (1976).

4. J. J. Oren, K. M. Gough, and H. D. Gesser, *Can. J. Chem.*, **57**, 2032 (1979).
5. H. D. Gesser, G. A. Horsfall, K. M. Gough, and B. Krawchuk, *Nature*, **268**, 323 (1977).
6. R. F. Hamon, A. S. Khan, and A. Chow, *Talanta*, **29**, 313 (1982).
7. S. Al-Bazi and A. Chow, *Ibid.*, **29**, 507 (1982).
8. S. Al-Bazi and A. Chow, *Ibid.*, **30**, 487 (1983).
9. S. Al-Bazi and A. Chow, *Ibid.*, **31**, 189 (1984).
10. S. Al-Bazi and A. Chow, *Anal. Chim. Acta*, **157**, 83 (1984).
11. R. Caletka, R. Hausbeck, and V. Krivan, *Talanta*, **33**, 315 (1986).
12. A. S. Khan and A. Chow, *Ibid.*, **30**, 173 (1983).
13. L. Schumack and A. Chow, *Ibid.*, **34**, 957 (1987).
14. P. Fong and A. Chow, *Ibid.*, **39**, 497 (1992).
15. R. C. Fix, Thesis, Massachusetts Institute of Technology, 1956.
16. T. H. Handley and C. L. Burros, *Anal. Chem.*, **31**, 332 (1959).
17. T. Sekine and D. Dyrssen, *Anal. Chim. Acta*, **45**, 433 (1969).
18. M. Koeva and J. Hala, *J. Radioanal. Chem.*, **51**, 711 (1979).
19. R. F. Hamon, Ph.D. Thesis, University of Manitoba, 1981.
20. H. Flaschka and A. J. Barnard Jr., "Tetraphenylboron (TPB) as an Analytical Reagent," in *Advances in Analytical Chemistry and Instrumentation*, Vol. 1 (C. N. Reilley, ed.), Interscience, New York, 1960.
21. S. S. Cooper, *Anal. Chem.*, **29**, 446 (1957).
22. R. M. Izatt, B. L. Haymore, and J. J. Christensen, *J. Chem. Soc., Chem. Commun.*, p. 1308 (1972).
23. J. P. Behr, P. Dumas, and D. Moras, *J. Am. Chem. Soc.*, **104**, 4540 (1982).
24. G. S. Heo and R. A. Bartsch, *J. Org. Chem.*, **47**, 3557 (1982).
25. I. M. Kolthoff, W. J. Wang, and M. K. Chantooni Jr., *Anal. Chem.*, **55**, 1202 (1983).
26. M. Pivonkova and M. Kyrs, *J. Inorg. Nucl. Chem.*, **31**, 175 (1969).
27. H. Stephen and T. Stephen, *Solubilities of Inorganic and Organic Compounds*, Vol. 1, Part 1, Pergamon, New York, 1963.

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