

# Solvent Extraction of Phthalate Isomer Dianions by the Use of Dicationic Anion-Exchange Extractants

Akira OHKI\*, Masanobu YAMURA\*, Yuko SUMIYOSHI\*, Makoto TAKAGI\*\* and Shigeru MAEDA\*

\*Department of Applied Chemistry, Faculty of Engineering, Kagoshima University, Kagoshima 890, Japan

\*\*Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Fukuoka 812, Japan

The extraction of phthalate isomer dianions (phthalate, isophthalate and terephthalate) was studied by the use of dicationic anion-exchange extractants, polymethylenebis(triethylphosphonium)s (abbreviated as  $C_nBP$ ). Extraction equilibrium studies confirmed that the extraction reaction of phthalate isomers under high pH condition ( $pH > 11$ ) occurs *via* the formation of a 1:1 ion-pair complex between  $C_nBP$  and the phthalate isomer. The extraction ability of dicationic extractants was greatly superior to that of conventional monocationic extractants. Further, the extraction ability of dicationic extractants was dependent on the length of the bridging methylene-chain between two phosphonium cationic centers within the extractants. In the extractions of phthalate, isophthalate and terephthalate, the most favorable extractants were  $C_4BP$ ,  $C_6BP$  and  $C_8BP$ , respectively. Thus, since the distance between the two anionic centers of phthalate isomer is longer, the bridge-chain length of the most preferable extractant is longer.

**Keywords** Anion-exchange extraction, lipophilic diphosphonium ion, dicationic extractant, phthalate isomer dianion

In previous studies<sup>1-3</sup> we have prepared a series of lipophilic diphosphonium ions, polymethylenebis(triethylphosphonium)s (abbreviated as  $C_nBP$ s) as dicationic anion-exchange extractants, and studied the extraction of anionic metal complexes with the extractants. The dicationic extractants ( $C_nBP$ s) proved to be much more effective for the extraction of doubly charged anionic metal complexes ( $MX_4^{2-}$  etc.;  $M^{2+}$ :  $Zn^{2+}$ ,  $Cd^{2+}$ ;  $X^-$ :  $Cl^-$ ,  $Br^-$ ,  $CN^-$ ) compared to conventional monocationic extractants, such as "Capriquat" (methyltriethylammonium). Further, in the previous paper<sup>3</sup> we reported that the extraction ability of dicationic extractants was greatly dependent on the "bridge-chain length" which is defined as the length of the bridging methylene chain connecting the two phosphonium cationic centers within the extractants. We have also studied the extraction of lipophilic organic dianions such as naphthalenedisulfonates.<sup>4,5</sup>

In the present study, the extraction of dicarboxylate species, phthalate isomers (phthalate, isophthalate and terephthalate) was investigated in detail by the use of the dicationic extractants ( $C_nBP$ s). The dicarboxylates are considerably hydrophilic under the state of dianionic species and, hence, have extremely low extractabilities. Therefore, the extraction of such hydrophilic dianions has been scarcely dealt with solvent extraction studies. To our knowledge, the ion-pair extraction (anion-exchange extraction) of phthalate isomers has not yet been studied in detail under alkaline conditions.

## Experimental

### Reagents

The synthesis of dicationic extractants (diphosphonium dibromides,  $C_nBP$ ) as well as monocationic extractant, butyltriethylphosphonium bromide (BuMP) was described in our previous papers.<sup>1,3</sup> "Capriquat" was a commercial product (Dojindo Lab.), and the

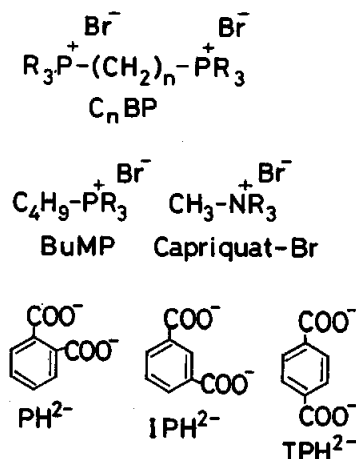


Fig. 1 Structures of anion-exchange extractants ( $n=2-12$ ;  $R=octyl$ ) and phthalate isomer dianions.

chloride form was converted to bromide (abbreviated as Capriquat-Br) *via* the acetate form by the use of silver acetate. Other chemicals were of reagent grade and used without further purification. The structures of the extractants are indicated in Fig. 1.

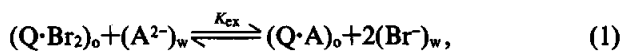
#### Extraction procedure

An aqueous solution (10 ml) containing 1 mM (1 M = 1 mol/dm<sup>3</sup>) of a phthalic acid isomer (phthalic acid or terephthalic acid), 0–4 mM sodium bromide, and 10 mM Na<sub>2</sub>HPO<sub>4</sub>–NaOH buffer (pH 11) was shaken with an organic solution (10 ml) containing a 5 mM anion-exchange extractant in a stoppered centrifuge tube at 25°C for 30 min. After phase separation, the concentration of the phthalate isomer in the aqueous phase was determined by high performance liquid chromatography with a Shimadzu LC-6AD instrument (4×250 mm ODS column; UV detector: 240 nm; eluent: water–methanol–acetic acid (50:50:1)). The amount of the organic dianion extracted into the organic phase was taken as the difference between the amount initially added and that remaining in the aqueous phase after equilibrium. In some runs, the material balance on the organic dianion distribution between the aqueous and organic phases was confirmed by back-extraction experiments.<sup>1</sup>

## Results and Discussion

#### Extraction equilibrium

One can assume that the extraction reaction of phthalate or terephthalate (A<sup>2-</sup>) occurs *via* the formation of a 1:1 ion-pair association complex between the extractant and the dianion as follows:



where Q·Br<sub>2</sub> represents the dicationic extractant (C<sub>n</sub>BP), and subscripts w and o denote the aqueous and organic phase, respectively.

The extraction constant, K<sub>ex</sub>, of the reaction Eq. (1) is given as

$$K_{ex} = [Q \cdot A]_o [Br^-]_w^2 / [Q \cdot Br_2]_o [A^{2-}]_w. \quad (2)$$

This equation can be rewritten as

$$\log [Q \cdot A]_o / [A^{2-}]_w [Q \cdot Br_2]_o = \log K_{ex} - 2 \log [Br^-]_w. \quad (3)$$

The dicationic extractant, Q·Br<sub>2</sub> and complex, Q·A, are highly lipophilic and do not appreciably dissolve in the aqueous phase. Further, phthalate and terephthalate act as dianion under relevant pH conditions (pH 11); in the later, these are abbreviated as PH<sup>2-</sup> and TPH<sup>2-</sup>, respectively. PH<sup>2-</sup> and TPH<sup>2-</sup> alone were not extracted into the organic phase. Thus, the values of log [Q·A]<sub>o</sub> / [A<sup>2-</sup>]<sub>w</sub> [Q·Br<sub>2</sub>]<sub>o</sub> and log [Br<sup>-</sup>]<sub>w</sub> can easily be obtained experimentally.

With the monocationic extractant (BuMP) calculations were performed in such a way that [Q·Br<sub>2</sub>]<sub>o</sub> and [Q·A]<sub>o</sub> in Eq. (3) were taken as 2×[BuMP<sup>+</sup>·Br<sup>-</sup>]<sub>o</sub> and [(BuMP<sup>+</sup>)<sub>2</sub>·A<sup>2-</sup>]<sub>o</sub>, respectively.

#### Extraction of PH<sup>2-</sup> and TPH<sup>2-</sup>

Figure 2 shows the plot of log [Q·A]<sub>o</sub> / [A<sup>2-</sup>]<sub>w</sub> [Q·Br<sub>2</sub>]<sub>o</sub>

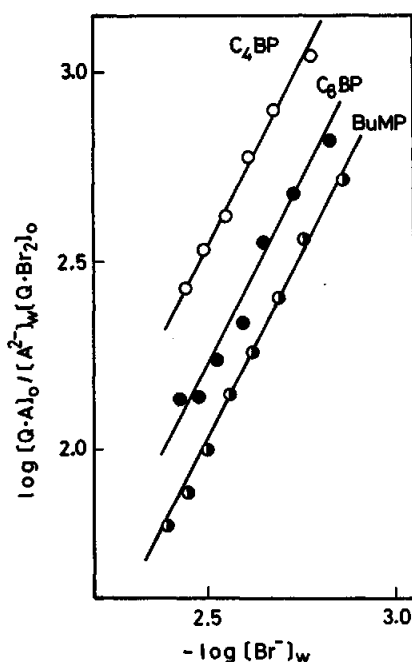


Fig. 2 Extraction of PH<sup>2-</sup> (DCE solvent).

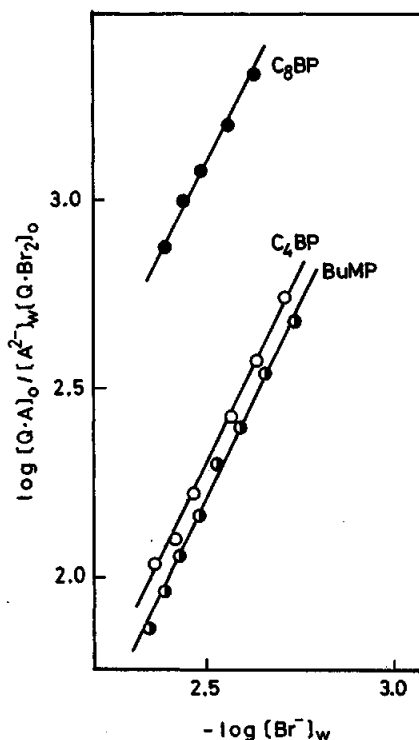


Fig. 3 Extraction of TPH<sup>2-</sup> (DCE solvent).

Table 1 Extraction constant ( $\log K_{ex}$ )

Solvent	PH <sup>2-</sup>			TPH <sup>2-</sup>		
	C <sub>4</sub> BP	C <sub>8</sub> BP	BuMP	C <sub>4</sub> BP	C <sub>8</sub> BP	BuMP
DCE	-2.5	-2.8	-3.0	-2.7	-1.9	-2.8
OCT	-2.0	-2.6	-3.2	-2.3	-1.8	-2.8

DCE, 1,2-dichloroethane.

OCT, 1-octanol/1,2-dichloroethane (8:2).

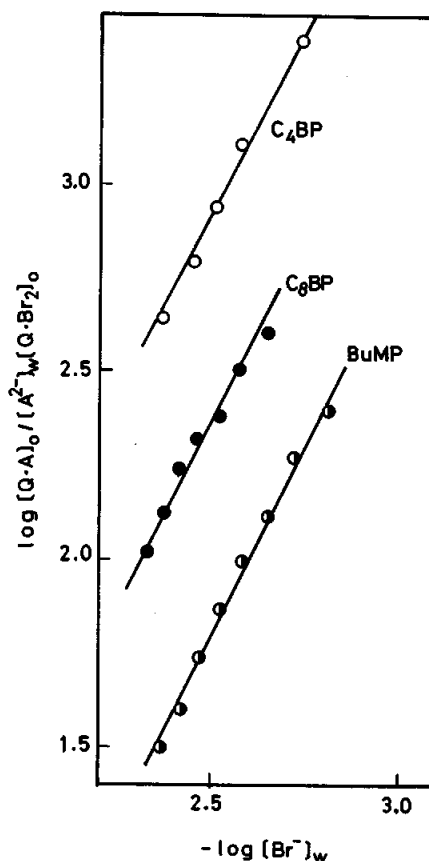
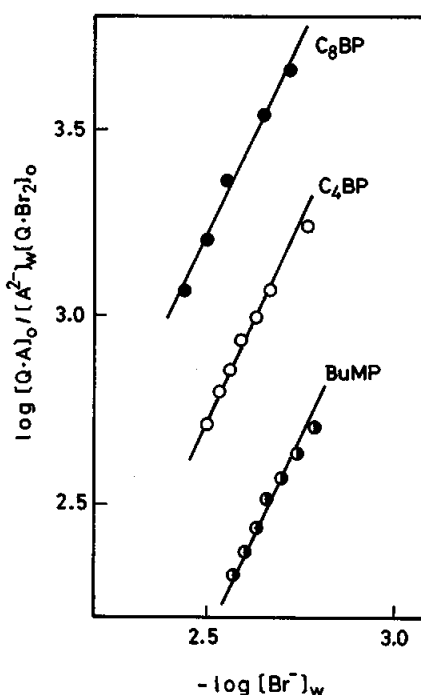
against  $-\log[\text{Br}^-]_w$  in the extraction of PH<sup>2-</sup> by the use of C<sub>8</sub>BP, C<sub>4</sub>BP and BuMP in 1,2-dichloroethane (DCE). Similar plots for the extraction of TPH<sup>2-</sup> are indicated in Fig. 3. All of the plots in Figs. 2 and 3 gave straight lines with a slope of 2, suggesting that the reaction depicted in Eq. (1) takes place, *i.e.*, the extraction reaction occurs *via* the formation of a 1:1 ion-pair complex between C<sub>n</sub>BP and PH<sup>2-</sup> (or TPH<sup>2-</sup>), while in the case of monocationic extractant BuMP, a 2:1 ion-pair forms between BuMP and PH<sup>2-</sup> (or TPH<sup>2-</sup>).

The extraction constants derived from Eq. (3) are summarized in Table 1. The extractability of PH<sup>2-</sup> was decreased in the order C<sub>4</sub>BP > C<sub>8</sub>BP > BuMP, while that of TPH<sup>2-</sup> was decreased in the order C<sub>8</sub>BP > C<sub>4</sub>BP > BuMP. The extraction ability of the dicationic extractants, C<sub>4</sub>BP and C<sub>8</sub>BP, was greatly superior to that of the monocationic extractant, BuMP. Such a situation is very similar to that observed in the extraction of doubly charged anionic metal complexes (MX<sub>4</sub><sup>2-</sup>, *etc.*).<sup>1-3</sup> The concept "multiple charge compatibility" can be found in the extraction of PH<sup>2-</sup> and TPH<sup>2-</sup>, which has been proposed for the extraction of anionic metal complexes by the authors.<sup>2,3</sup>

PH<sup>2-</sup> extraction by the use of C<sub>4</sub>BP surpassed that by C<sub>8</sub>BP, whereas in the case of TPH<sup>2-</sup> extraction, quite the opposite result was obtained: the extraction ability of C<sub>8</sub>BP was superior to that of C<sub>4</sub>BP. This can be explained as follows. The distance between anionic centers of TPH<sup>2-</sup> is longer than that of PH<sup>2-</sup>, so that TPH<sup>2-</sup> prefers the dicationic extractant possessing long bridge-chain length (long bridge-chain extractant), whereas PH<sup>2-</sup> prefers a shorter bridge-chain extractant. The concept "geometrical charge distribution compatibility" can be presented.

In extractions using the monocationic extractant, BuMP, the extractability of TPH<sup>2-</sup> was slightly higher than that of PH<sup>2-</sup>. When Capriquat-Br was used as the extractant, similar extraction constants to those with BuMP were obtained; the value was -2.9 for the PH<sup>2-</sup> extraction and -2.8 for the TPH<sup>2-</sup> extraction.

Figure 4 and 5 show the extraction of PH<sup>2-</sup> and TPH<sup>2-</sup>, respectively, by use of 1-octanol/1,2-dichloroethane (8:2) (abbreviated as OCT) instead of DCE. C<sub>n</sub>BPs were not liable to dissolve in pure 1-octanol. The extraction constants are also summarized in Table 1. The extraction behavior was essentially similar to that observed in the DCE solvent system: PH<sup>2-</sup> and TPH<sup>2-</sup> preferred C<sub>4</sub>BP and C<sub>8</sub>BP, respectively. However, the

Fig. 4 Extraction of PH<sup>2-</sup> (OCT solvent).Fig. 5 Extraction of TPH<sup>2-</sup> (OCT solvent).

OCT system exhibited somewhat higher extraction ability than the DCE system. 1-Octanol possesses a

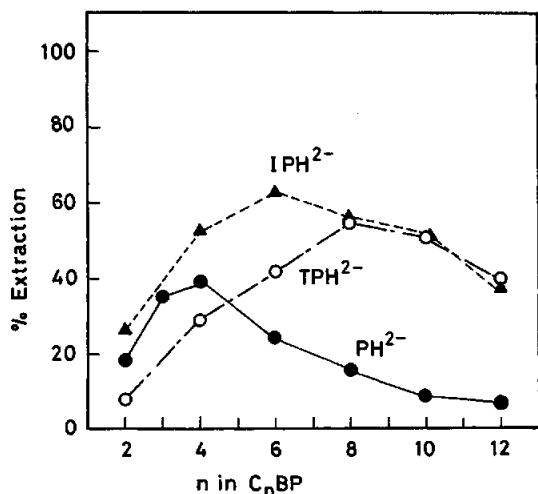


Fig. 6 Dependence of extractability of phthalate isomers on  $n$  in  $C_nBP$  (●,  $PH^{2-}$ ; ▼,  $IPH^{2-}$ ; ○,  $TPH^{2-}$ ). Aqueous phase initially contained 1 mM phthalic acid isomer, 20 mM sodium hydroxide ( $pH > 11$ ), while organic phase (OCT) contained 1.5 mM  $C_nBP$ .

similar polarity (dielectric constant  $\epsilon = 10.3$ ) to that of 1,2-dichloroethane ( $\epsilon = 10.1$ ). However, the former solvent has a much higher hydrogen-bonding power than the latter. It is assumed that these facts reflect the extraction nature (solvent effect) mentioned above.

#### Dependence of the extraction of phthalate isomers on the bridge-chain length of the extractant

Figure 6 shows the dependence of extractabilities of  $PH^{2-}$ , isophthalate ( $IPH^{2-}$ ), and  $TPH^{2-}$  (OCT solvent system) on the bridge-chain length ( $n$ ) of dicationic extractants. The extraction conditions were somewhat different from those described in the experimental section (see figure caption). In the extraction of  $PH^{2-}$ ,  $IPH^{2-}$  and  $TPH^{2-}$ , the most preferable extractants among  $C_nBP$ s ( $n = 2 - 12$ ) were  $C_4BP$ ,  $C_6BP$  and  $C_8BP$ , respectively. Accordingly, since the anionic center distance of phthalate isomer dianions was longer ( $PH^{2-} \rightarrow IPH^{2-} \rightarrow TPH^{2-}$ ), the bridge-chain length of the most efficient  $C_nBP$  was longer. These results strongly support the concept "geometrical charge distribution compatibility". This concept was preliminarily verified in our previous study; in the extraction of 1,5- and 2,6-naphthalenedisulfonates, the most favorable extractants were  $C_6BP$  and  $C_{10BP}$ , respectively.<sup>4</sup>

As a result, such long bridge-chain extractants as  $C_8BP$ ,  $C_{10BP}$  and  $C_{12BP}$  were found to have excellent extraction ability for  $IPH^{2-}$  and  $TPH^{2-}$ , compared to

Table 2 Extraction separation (%) of phthalate isomers

Extractant	TPH <sup>2-</sup> /PH <sup>2-</sup> extraction		IPH <sup>2-</sup> /PH <sup>2-</sup> extraction	
	TPH <sup>2-</sup>	PH <sup>2-</sup>	IPH <sup>2-</sup>	PH <sup>2-</sup>
$C_8BP$	60.7	14.2	58.5	9.1
$C_{10BP}$	57.7	7.7	43.8	5.4
$C_{12BP}$	43.7	5.0	34.9	4.4

Aqueous phase initially contained 0.5 mM phthalic acid isomers and 20 mM sodium hydroxide ( $pH > 11$ ), while organic phase (OCT) contained 1.5 mM  $C_nBP$ .

that for  $PH^{2-}$ . Table 2 shows the competitive extraction of  $TPH^{2-}$  and  $PH^{2-}$  as well as that of  $IPH^{2-}$  and  $PH^{2-}$  from an aqueous solution containing their mixture. By the use of long bridge-chain extractants, the extractabilities (distribution ratios) of  $TPH^{2-}$  and  $IPH^{2-}$  were 10–15 times higher than that of  $PH^{2-}$ . Consequently, these extractants proved to be powerful extractants in regard to the separation between such phthalate isomers.

In conclusion, the dicationic extractants are superior to the conventional monocationic extractants with respect to the extraction of organic dianions such as phthalate isomers. The extraction ability of dicationic extractants was remarkably dependent on the bridge-chain length of the extractants. The long bridge-chain extractants ( $C_8BP$ ,  $C_{10BP}$  and  $C_{12BP}$ ) proved to be powerful extractants in regard to the separations between  $TPH^{2-}$  and  $PH^{2-}$  as well as between  $IPH^{2-}$  and  $PH^{2-}$ . These phenomena can be extended to analytical systems related to ion-pair extraction including sensing by ion-selective electrode and ion-pair chromatography, which will be reported in a following paper.

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