

Donium Cations as Novel Sensing and Separation Reagents for Phthalates in Ion-Selective Electrode Method and in Ion-Pair Chromatography

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An ion selective electrode was prepared which exhibited selectivity for terephthalate over various interfering anions including phthalate under alkaline conditions; a donium cation, decamethylenebis(trioctylphosphonium) (abbreviated as $C_{10}BP$), was used as the sensing material. Ion selective electrodes based on conventional monoonium cations such as "Capriquat" did not exhibit such selectivity. The butyl analogs of C_nBP s were examined as ion-pair reagents in ion-pair chromatography for phthalates. Under alkaline elution conditions, the base-line separation of three phthalate isomers (phthalate, isophthalate and terephthalate) was achieved. When monoonium reagents such as tetrabutylammonium were used, the retentions of these isomers considerably decreased, compared to the case of donium reagents, and the separation could not be attained. The superiority of the donium cations in both the sensing and separation systems was discussed.

Keywords Donium cation, ion selective electrode, ion-pair chromatography, phthalate isomer dianions

In our previous paper¹, we have studied the solvent extraction of phthalate isomers (phthalate, isophthalate, and terephthalate) by the use of donium salts, polymethylenebis(trioctylphosphonium)dibromides (abbreviated as $C_nBP \cdot Br_2$; Fig. 1), as anion-exchange extractants. When the extraction of phthalates was carried out under highly alkaline conditions (pH 11), the extraction constants obtained were about one order of magnitude higher than those obtained in the systems using conventional monoonium extractants such as "Capriquat". Accordingly, the concept "multiple charge compatibility" could be verified, *i.e.*, the compatibility of charge number between extractant and extracted anion greatly affects the extractability.

The extraction ability of the donium extractants was also remarkably dependent on the length of "bridge-chain", which is defined as the bridging methylene chain connecting the two phosphonium cationic centers within the extractants. The donium extractants possessing long bridge-chains (long bridge-chain extractants) proved to be powerful extractants for terephthalate.

In the present study, based on such extraction behavior, an ion selective electrode (ISE) which would exhibit selectivity for terephthalate over phthalate was prepared. We have preliminarily reported an ISE selective for dianionic species, naphthalenedisulfonates, by the use of a donium salt as a sensing material.² Capriquat hydrogenphthalate ion-pair has been used as a sensing material of ISE, which exhibits high selec-

tivity for phthalate over isophthalate and terephthalate under the pH conditions of around 4.³⁻⁵ This is because the $pK_{a,s}$ of phthalic acid are 2.98 and 5.28, while those of isophthalic acid and terephthalic acid are 3.46 and 4.46, and 3.51 and 4.82, respectively. However, no report has been presented on the ISE selective for terephthalate and isophthalate.

By the use of butyl analogs of the donium extractants ($BuC_nBP \cdot Br_2$, Fig. 1) as ion-pair reagents for ion-pair chromatography (IPC), the complete separation among three phthalate isomers was attained under alkaline elution conditions. A donium cation (bolaform) was previously used as an ion-pair reagent for the IPC separation of metal-chelates.⁶

Experimental

Reagents

The syntheses of the donium salt, $C_{10}BP \cdot Br_2$, and monoonium salt, butyltrioctylphosphonium bromide ($BuMP \cdot Br$), were described in our previous papers.^{7,8} "Capriquat" was a commercial product (Dojindo Lab.). These onium salts (Fig. 1) were converted to terephthalate forms ($C_{10}BP^{2+} \cdot TPH^{2-}$, $(BuMP^+)_2 \cdot TPH^{2-}$ and $(Capriquat^+)_2 \cdot TPH^{2-}$) *via* the acetate forms by the use of silver acetate^{7,8}, and were used as sensing materials.

$BuC_nBP \cdot Br_2$ s and tetrabutylphosphonium bromide ($TBP \cdot Br$) were prepared in a similar manner to the $C_nBP \cdot Br_2$ synthesis⁸ by the use of tributylphosphine.

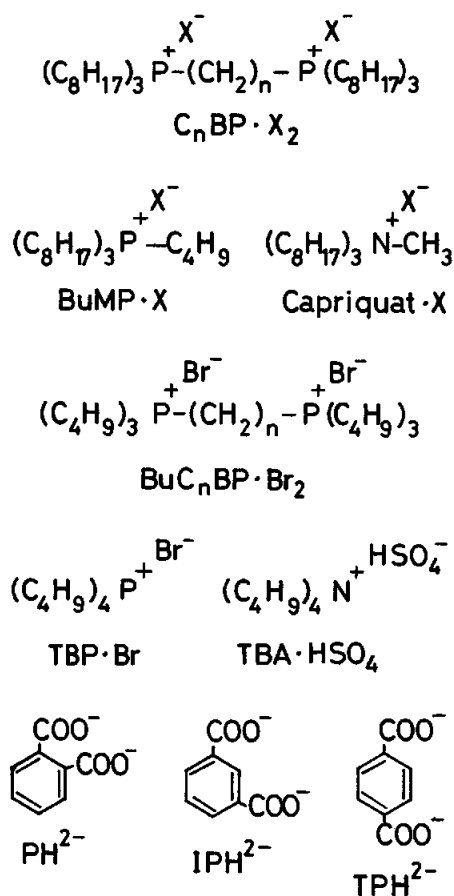


Fig. 1 Structures of di- and monoonium salts ($n=8, 10, 12$; X^- : Br^- , $1/2 \text{TPH}^{2-}$) and phthalate isomer dianions. Under the given pH condition (pH 11) in this study, the phthalate isomers (phthalate, isophthalate and terephthalate) act as dianions; thus hereafter these will be denoted as PH^{2-} , IPH^{2-} and TPH^{2-} , respectively.

Table 1 Elemental analysis and yield of $\text{BuC}_n\text{BP} \cdot \text{Br}_2$ s and $\text{TBP} \cdot \text{Br}$

Phosphonium compounds	C, %		H, %		Yield, %
	Found	Calcd	Found	Calcd	
$\text{BuC}_8\text{BP} \cdot \text{Br}_2$ ($\text{C}_{32}\text{H}_{70}\text{P}_2\text{Br}_2$)	56.69	56.80	10.43	10.43	85
$\text{BuC}_{12}\text{BP} \cdot \text{Br}_2$ ($\text{C}_{36}\text{H}_{78}\text{P}_2\text{Br}_2$)	58.88	59.01	10.92	10.73	88
$\text{TBP} \cdot \text{Br}$ ($\text{C}_{16}\text{H}_{36}\text{PBr}$)	56.81	56.63	10.86	10.69	84

The products were obtained as colorless amorphous solids. $^1\text{H-NMR}$ ($\text{BuC}_8\text{BP} \cdot \text{Br}_2$) (CDCl_3 , δ from TMS) $\delta=0.95$ (18H, t, CH_3), 1.2–1.9 (36H, br, $\text{C}(\text{CH}_2)_2\text{C}$, $\text{C}(\text{CH}_2)_6\text{C}$), 2.2–2.7 (16H, br, CCH_2P). Table 1 summarizes the yield and elemental analysis data of $\text{BuC}_n\text{BP} \cdot \text{Br}_2$ s ($n=8, 12$) and $\text{TBP} \cdot \text{Br}$. $^{31}\text{P-NMR}$ (CDCl_3) of these compounds exhibited only one singlet peak (δ^{P} (from H_3PO_4)=31.3–31.5). Tetrabutylam-

monium hydrogensulfate ($\text{TBA} \cdot \text{HSO}_4$) was a commercial product from Nacalai Tesque. Other chemicals were of reagent grade and were used without further purification.

ISE procedure

The membrane of an ISE selective for TPH^{2-} was prepared according to the common method.⁹ A mixture of poly(vinyl chloride) (PVC) (0.4 g), dioctyl phthalate (1.0 g), and the sensing material ($\text{C}_{10}\text{BP} \cdot \text{TPH}$, 0.2 g) was dissolved in 10 ml of tetrahydrofuran (THF). The THF solution was poured onto a flat Petri dish (i.d. 6 cm), and THF was allowed to evaporate slowly at room temperature. A piece of the PVC membrane was fixed to a PVC tube with THF. A portion of aqueous solution containing 10 mM ($1 \text{M}=1 \text{mol}/\text{dm}^3$) TPH^{2-} , 10 mM potassium chloride, and 20 mM $\text{Na}_2\text{HPO}_4\text{-NaOH}$ buffer (pH 11) was added as an internal reference solution.

The potentiometric measurements with the $\text{C}_{10}\text{BP-ISE}$ (ISE based on $\text{C}_{10}\text{BP} \cdot \text{TPH}$) were carried out at 25°C with an ion meter (IOC-10, Denki Kagaku Keiki (DKK)) and a double junction Ag/AgCl reference electrode (DKK 4083) under agitation of the sample solution with a magnetic stirrer (200 rpm). The pH of the sample solution of TPH^{2-} was adjusted at 11 (20 mM $\text{Na}_2\text{HPO}_4\text{-NaOH}$ buffer). Activity coefficients were calculated from the Debye-Hückel equation. No leakage of phthalate from the membrane *via* the hydrolysis of the plasticizer was observed on soaking the membrane in an alkaline solution (pH 11) for several days. The electrochemical cell was Ag-AgCl/reference solution/PVC membrane/sample solution/1 M $\text{CH}_3\text{COOLi}/3 \text{M KCl}/\text{Ag-AgCl}$. BuMP-ISE and Capriquat-ISE were similarly prepared by the use of (BuMP)₂·TPH and (Capriquat)₂·TPH, respectively.

The potentiometric selectivity coefficients ($K_{\text{TPH,A}}^{\text{pot}}$) were determined by a mixed solution method.⁹ The constant background concentrations of diverse ions were 10 mM, except for phthalate ion: 1 mM.

IPC procedure

The chromatograph was a Shimadzu LC-6AD liquid chromatograph pump equipped with a Rheodyne injector, an UV spectrometer SPD-6A (240 nm), and an integrator C-R6A. A column packed with octadecylsilyl (ODS) silica (250 mm×4 mm, Wakosil 5C18-200, Wako Pure Chemical) was used. The typical eluent was a mixed solution (water/methanol 7:3) containing 5 mM $\text{BuC}_8\text{BP} \cdot \text{Br}_2$ and 50 mM $\text{Na}_2\text{HPO}_4\text{-NaOH}$ buffer (pH 11). The flow rate was 0.5 ml/min, and the column temperature was 25°C. The void volume of the column was determined by injecting water. The performance of the column did not become inferior after 50 h use under such elution conditions.

Results and Discussion

Ion selective electrode based on dionium salt

Figure 2 shows the potential responses of $C_{10}BP$ -ISE, BuMP-ISE and Capriquat-ISE to TPH^{2-} . The $C_{10}BP$ -ISE exhibited a Nernstian response (27 mV/decade) in the range of $5 \times 10^{-5} - 1 \times 10^{-2}$ M TPH^{2-} . When the potentials were plotted against the activities, a similar slope was obtained. Such a theoretical Nernstian response indicates the formation of a 1:1 ion-pair association complex between $C_{10}BP^{2+}$ and TPH^{2-} .

In the cases of BuMP-ISE and Capriquat-ISE, which were based on monoonium salts, the Nernstian response range was remarkably reduced (ca. $1 \times 10^{-3} - 1 \times 10^{-2}$ M TPH^{2-}). Accordingly, the high performance of the $C_{10}BP$ -ISE is ascribed to the fact that $C_{10}BP$ possesses two cationic centers within a molecule, so that it is capable of forming the 1:1 ion-pair with TPH^{2-} . The concept "multiple charge compatibility" can be found

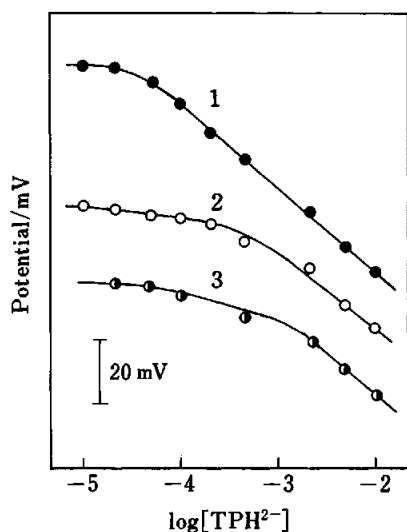


Fig. 2 Potential responses of $C_{10}BP$ -ISE (1), Capriquat-ISE (2) and BuMP-ISE (3) for TPH^{2-} .

Table 2 Selectivity coefficients for TPH^{2-} selective electrodes against some interfering anions

Interfering anion (A^-)	$\log K_{TPH,A}^{pot}$		
	$C_{10}BP$ -ISE	Capriquat-ISE	BuMP-ISE
CH_3COO^-	<0	1.0	0.81
F^-	<0	0.90	0.93
Cl^-	0.72	1.4	1.3
Phosphate ^a	-2.7	-1.7	-1.5
PH^{2-}	-0.90	0.17	0.10

a. External interfering anion was not added, and thus the buffer (phosphate) only served as an interfering anion. The calculation was performed by assuming that all the phosphate species are taken as HPO_4^{2-} .

as well in the sensing with ISE.

Table 2 summarizes the selectivity coefficients for TPH^{2-} against various interfering anions in the cases of $C_{10}BP$ -ISE, BuMP-ISE and Capriquat-ISE. The $C_{10}BP$ -ISE exhibited an excellent selectivity for TPH^{2-} over various interfering anions, including not only monovalent anions but also divalent anions such as PH^{2-} , compared to the BuMP-ISE and Capriquat-ISE.

The extractabilities of TPH^{2-} and PH^{2-} are very similar to each other when monoonium extractants such as BuMP·Br and Capriquat are used, whereas the long bridge-chain extractants much prefer TPH^{2-} to PH^{2-} ; the extraction constants ($\log K_{ex}$) in the extraction reaction of TPH^{2-} and PH^{2-} by $C_8BP \cdot Br_2$ (1,2-dichloroethane/water system) were -1.9 and -2.8, respectively.¹ Consequently, the high separation ability of the long bridge-chain extractants could be successfully applied to the ISE system.

Ion-pair chromatography using dionium reagents

The butyl analogs of dionium extractants ($BuC_nBP \cdot Br_2$ s) were used as ion-pair reagents for reversed phase IPC. Figure 3 shows the representative chromatograms obtained under three elution conditions. When a monoonium reagent ($TBA \cdot HSO_4$) was used as an ion-pair reagent, the base-line separation of phthalate isomers could not be attained, and the elution order was $TPH^{2-} \rightarrow PH^{2-} \rightarrow IPH^{2-}$ (Fig. 3(a)). When the counter anion of the monoonium reagent was switched from hydrogensulfate to bromide, IPH^{2-} turned out to be more retained to some extent, whereas the separation between PH^{2-} and TPH^{2-} was not improved at all.

When a dionium reagent $BuC_8BP \cdot Br_2$ was used as an ion-pair reagent, quite a different result was obtained; the retentions of the species (PH^{2-} , IPH^{2-} and TPH^{2-}) were remarkably increased, and the complete base-line separation could be attained among these phthalate isomers (Fig. 3(c)). Further, the elution order turned

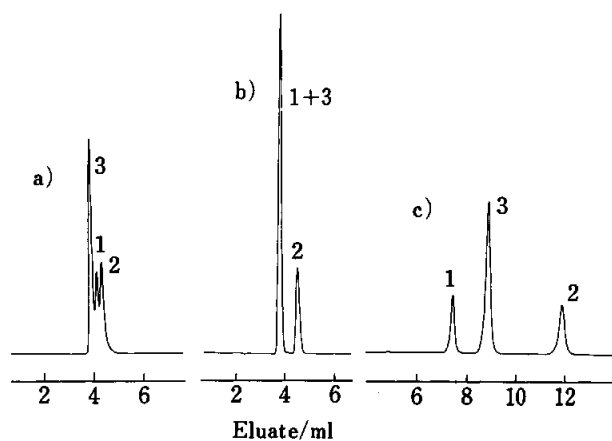


Fig. 3 Representative chromatograms of the three IPC systems. a) TBA-IPC; b) TBP-IPC; c) BuC_8BP -IPC. 1, PH^{2-} ; 2, IPH^{2-} ; 3, TPH^{2-} . The elution conditions were the same as those in Table 3 (runs 5, 4 and 1, respectively).

Table 3 Retention ratios of phthalate isomer dianions under various elution conditions

Run	Eluent ^a		Retention ratio (<i>k'</i>)		
	Ion-pair reagent (mM)	Water/methanol ratio	PH ²⁻	IPH ²⁻	TPH ²⁻
1	BuC ₈ BP·Br ₂ (5)	70/30	1.31	2.67	1.75
2	BuC ₈ BP·Br ₂ (2)	70/30	1.21	2.55	1.53
3	BuC ₁₂ BP·Br ₂ (5)	70/30	1.93	5.13	3.12
4	TBP·Br (10)	70/30	0.56	0.82	0.55
5	TBA·HSO ₄ (5)	70/30	0.48	0.55	0.37
6	BuC ₈ BP·Br ₂ (5)	60/40	0.78	1.48	1.10
7	TBP·Br (10)	60/40	0.26	0.33	0.25
8	BuC ₈ BP·Br ₂ (5)	80/20	2.64	6.57	3.33

a. The pH (in water component) was adjusted at 11 by using Na₂HPO₄-NaOH buffer (50 mM).

into PH²⁻ → TPH²⁻ → IPH²⁻. The dionium reagent (BuC₈BP²⁺) presumably interacts with the dianionic species more strongly than the monoonium reagents do, leading to the remarkable increase in the retentions. Further, the dionium reagent can recognize the distance between two ionic centers of phthalates as a result of the double ion-pair formation within a complex, and thus the base-line separation of phthalates is realized. The retention order was inconsistent with the order of the extractability obtained in the batchwise extraction experiments; the extractability was decreased in the order (TPH²⁻ > IPH²⁻ > PH²⁻) by the use of the dionium extractant C₈BP·Br₂.¹

Table 3 summarizes the retention ratio (*k'*) of phthalate isomers under various elution conditions. These results suggest that the IPC using the dionium reagent such as BuC₈BP·Br₂ and BuC₁₂BP·Br₂ is capable of the base-line separation of three phthalate isomers, whereas such a separation could not be achieved when the monoonium reagents were used. When the dionium reagent having longer bridge-chain (BuC₁₂BP·Br₂) was used (run 3), increases in the retentions of all phthalates resulted.

Consequently, in regard to the separation among

dianionic phthalate isomers under alkaline elution conditions, BuC₈BP·Br₂ and BuC₁₂BP·Br₂ proved to possess an excellent separation ability compared to those of conventional monoonium reagents such as TBA·HSO₄ and TBP·Br. The phthalate isomers (or phthalic acid isomers) were separated *via* the simple reversed phase chromatography (ODS column) under weakly acidic elution conditions. However, the resolution between isophthalate and terephthalate was relatively low (separation factor $\alpha \approx ca. 1.2$). The α value 1.5–1.6 was obtained in the present IPC system.

In conclusion, the high extraction ability of the dionium extractants toward dianionic species could be effectively applied to the sensing with ISE as well as to IPC separation. The use of dionium reagents should offer new possibilities in the analysis and separation of various polyanionic species.

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