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

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In our previous paper, we have studied the solvent extraction of phthalate isomers (phthalate, isophthalate, and terephthalate) by the use of dionium salts, polymethylenebis(triethylphosphonium)dibromides (abbreviated as CnBP•Br2; 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 dionium 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 dionium 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 dionium salt as a sensing material.2 Capriquat hydrogenphthalate ion-pair has been used as a sensing material of ISE, which exhibits high selectivity for phthalate over isophthalate and terephthalate under the pH conditions of around 4. This is because the pKa'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 dionium extractants (BuCnBP•Br2, 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 dionium cation (bolaform) was previously used as an ion-pair reagent for the IPC separation of metal-chelates.

**Experimental**

Reagents

The syntheses of the dionium salt, C10BP•Br2, and monoonium salt, butyltrimethylphosphonium bromide (BuMP•Br), were described in our previous papers. "Capriquat” was a commercial product (Dojindo Lab.). These onium salts (Fig. 1) were converted to terephthalate forms (C10BP2+•TPH2−, (BuMP+)2•TPH2− and (Capriquat+)2•TPH2−) via the acetate forms by the use of silver acetate, and were used as sensing materials.

BuCnBP•Br2 and tetrabutylphosphonium bromide (TBP•Br) were prepared in a similar manner to the CnBP•Br2 synthesis by the use of tributylphosphine.
Fig. 1 Structures of di- and monoonium salts \( (n=8, 10, 12; \ X = \text{Br}, \frac{1}{2} \text{TPH}_2^-) \) 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 BuC\(_n\)BP•Br\(_2\)s and TBP•Br.

<table>
<thead>
<tr>
<th>Phosphonium compounds</th>
<th>C, %</th>
<th>H, %</th>
<th>Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>BuC(_n)BP•Br(_2)</td>
<td>56.69</td>
<td>10.43</td>
<td>85</td>
</tr>
<tr>
<td>(C(<em>{12})H(</em>{25})P•Br)</td>
<td>55.88</td>
<td>10.92</td>
<td>88</td>
</tr>
<tr>
<td>BuC(_{12})BP•Br(_2)</td>
<td>58.88</td>
<td>10.73</td>
<td>88</td>
</tr>
<tr>
<td>(C(<em>{16})H(</em>{33})P•Br)</td>
<td>56.81</td>
<td>10.86</td>
<td>84</td>
</tr>
<tr>
<td>TBP•Br</td>
<td>56.81</td>
<td>10.86</td>
<td>84</td>
</tr>
<tr>
<td>(C(<em>{16})H(</em>{33})Br)</td>
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</table>

The products were obtained as colorless amorphous solids. \(^1\text{H}-\text{NMR} (\text{BuC}_n\text{BP}•\text{Br}_2) \) (CDCl\(_3\), \( \delta \) from TMS \( \delta =0.95 \) (18H, t, CH\(_3\)), 1.2–1.9 \( (36 \text{H}, \text{br, C(CH}_2)_2C\), C(CH\(_3\)_)C), 2.2–2.7 \( (16 \text{H, br, CCH}_2P)\). Table 1 summarizes the yield and elemental analysis data of BuC\(_n\)BP•Br\(_2\) \( (n = 8, 12) \) and TBP•Br. \(^{31}\text{P}-\text{NMR} \) (CDCl\(_3\)) of these compounds exhibited only one singlet peak \( (\delta^p \text{ from H}_3\text{PO}_4)=31.3–31.5 \). Tetrabutylammonium hydrogensulfate (TBA•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 (C\(_{10}\)BP•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 \( (1 \text{M}=1 \text{mol/dm}^3) \) TPH\(_2^-\), 10 mM potassium chloride, and 20 mM Na\(_2\)HPO\(_4\)-NaOH buffer (pH 11) was added as an internal reference solution.

The potentiometric measurements with the C\(_{10}\)BP-ISE (ISE based on C\(_{10}\)BP-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 \( (20 \text{mM Na}_2\text{HPO}_4-\text{NaOH buffer}) \). 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 CH\(_3\)COOLi/3 M KCl/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 \( (K_{TPH^A}) \) 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 BuC\(_2\)BP•Br\(_2\) and 50 mM Na\(_2\)HPO\(_4\)-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 $5\times10^{-5}$ to $1\times10^{-2}$ 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. $1\times10^{-3}$ to $1\times10^{-2}$ 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 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_{8}BP•Br_{2} (1,2-dichloroethane/water system) were −1.9 and −2.8, respectively. 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_{n}BP•Br_{2}) 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•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-} → PH^{2-} → 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_{8}BP•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

![Figure 2](image1.png)

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

![Figure 3](image2.png)

**Fig. 3** Representative chromatograms of the three IPC systems. a) TBA-IPC; b) TBP-IPC; c) BuC_{8}BP-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

<table>
<thead>
<tr>
<th>Run</th>
<th>Ion-pair reagent (mM)</th>
<th>Water/methanol ratio</th>
<th>Retention ratio ($k'$)</th>
<th>PH$^2^-$</th>
<th>IPH$^2^-$</th>
<th>TPH$^2^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BuC$_8$BP•Br$_2$ (5)</td>
<td>70/30</td>
<td>1.31</td>
<td>2.67</td>
<td>1.75</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>BuC$_8$BP•Br$_2$ (2)</td>
<td>70/30</td>
<td>1.21</td>
<td>2.55</td>
<td>1.53</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>BuC$_8$BP•Br$_2$ (5)</td>
<td>70/30</td>
<td>1.93</td>
<td>5.13</td>
<td>3.12</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>TBP•Br (10)</td>
<td>70/30</td>
<td>0.56</td>
<td>0.82</td>
<td>0.55</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>TBA•HSO$_4$ (5)</td>
<td>70/30</td>
<td>0.48</td>
<td>0.55</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>BuC$_8$BP•Br$_2$ (5)</td>
<td>60/40</td>
<td>0.78</td>
<td>1.48</td>
<td>1.10</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>TBP•Br (10)</td>
<td>60/40</td>
<td>0.26</td>
<td>0.33</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>BuC$_8$BP•Br$_2$ (5)</td>
<td>80/20</td>
<td>2.64</td>
<td>6.57</td>
<td>3.33</td>
<td></td>
</tr>
</tbody>
</table>

a. The pH (in water component) was adjusted at 11 by using Na$_2$HPO$_4$-NaOH buffer (50 mM).

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 BuC$_8$BP•Br$_2$ and BuC$_8$BP•Br$_2$ is capable of the base-line separation of three phthalate isomers, whereas such a separation could not be achieved when the mononium reagents were used. When the dionium reagent having longer bridge-chain (BuC$_8$BP•Br$_2$) 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, BuC$_8$BP•Br$_2$ and BuC$_8$BP•Br$_2$ proved to possess an excellent separation ability compared to those of conventional mononium reagents such as TBA•HSO$_4$ 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 $\alpha$=ca. 1.2). The $\alpha$ 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.

References


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