Effect of Eluent Countercation on Anion-chromatographic Retention of Aromatic Dianions

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Abstract
Anion-chromatographic retention behavior of several positional isomers of dianionic anthraquinonedisulfonates (ADS\(^{2-}\)) on using various alkali and tetraalkylammonium bromides as eluents was investigated, and the electrostatic effect of eluent countercation to chromatographic retention of anions was evaluated. In use of bulky countercations such as cesium and tetraalkylammonium, several ADS\(^{2-}\) anions do not acted as simple dianionic species but as monoanionic species in part. Furthermore, this tendency was affected by the distance between the two sulfonate groups in the ADS\(^{2-}\) anions.

Key words: anion chromatography, eluent countercation, electrostatic effect, anthraquinonedisulfonates

1 Introduction
Anion chromatography is a powerful analytical method for separation and determination of anionic species in aqueous samples. This method is based on anion-exchange equilibria between sample and eluent anions, and its separation performance is essentially governed by selectivity coefficients between the anions. Therefore, the use of additional chemical equilibria together with the anion-exchange is necessary to deviate the separation selectivity significantly. From this viewpoint, we studied previously the effect of Brønsted acid-base equilibria \[1,2\] and Lewis acid-base equilibria \[3,4\] on the anion-chromatographic retention.

Cationic species in eluent, namely eluent countercation, can interact electrostatically with the sample anions, resulting in possible change on chromatographic retention of the anions. The nature has been applied to ion-pair chromatography using reversed-phase columns. Furthermore, Okada \[5\] reported previously that anion-chromatographic retention of several aromatic dianions is affected by polyammonium polycations co-existing in eluent. However, in these previous studies, the electrostatic interaction resulted in formation of neutral or cationic species. In other words, the effect of forming anionic species having lower charge has not been investigated systematically. In this study, we investigated the electrostatic effect of monocationic eluent counterions to anion-chromatographic retention behavior of polyanions with using several anthraquinonedisulfonate dianions (ADS\(^{2-}\)) as model samples.

2 Experimental
2.1 Reagents
As sample anions, four positional ADS\(^{2-}\) isomers were used. Fig. 1 shows their chemical structures and
Values in parentheses are the S-S distances calculated with a CAChe system.

As eluents, aqueous solutions of lithium bromide (LiBr), sodium bromide (NaBr), potassium bromide (KBr), ammonium bromide (NH4Br) and cesium bromide (CsBr) and mixed aqueous solutions of NaBr and tetraalkylammonium bromides (R4NBr), such as tetraethylammonium bromide (R = C2H5), tetrabutylammonium bromide (R = C4H9) and tetrapentylammonium bromide (R = C5H11), were used. These solutions were prepared by dissolving respective salts into distilled deionized water. In all cases, eluent anion was fixed as bromide (Br⁻) since many kinds of tetraalkylammonium salts are supplied commercially as bromides in general.

2.2 Apparatus and chromatographic condition

A Shimadzu model LC-10ATvp computer-controlled pump, a CTO-6AS column oven, an SPD-10Avp ultraviolet detector (254 nm) and a Rheodyne 7161 sample injector (100 mm³) were used as ion chromatographic system. A Tosoh model TSKgel IC-Anion-PWXL column (35 mm × 4.6 mm i.d., polymethacrylate gel, particle size 6 μm, anion-exchange capacity 30±3 meq dm⁻³) was used for anion separation. The flow rate of eluent was maintained at 0.7 cm³ min⁻¹. The column was placed in an oven regulated at 40 °C. The chromatogram was recorded by a Shimadzu model Chromatopack C-R8A recorder.

2.3 Evaluation of the electrostatic effect

In anion chromatography, logarithmic adjusted retention time (log tR') of sample anion and logarithmic concentration of eluent anion shows linear relationship, the slope of which is the ratio of the charge of the sample anion to that of the eluent anion. Namely, in the case of ADS₂⁻ as sample anion and Br⁻ as eluent anion, the relationship can be expressed as follows:

\[
\log t_{R'} = -2 \log [Br^-] + \text{const.}
\]

On the contrary, if ADS₂⁻ forms stable ion-pair with eluent countercation (C⁺), the sample anion is converted to monoanionic [C(ADS)]⁻ species and, therefore, the relationship can be expressed as follows:

\[
\log t_{R'} = -\log [Br^-] + \text{const.}
\]

Therefore, when ADS₂⁻ interacts electrostatically with C⁺ partly on retention, the slope of the log tR' vs. log [Br⁻] plot can range between -2 and -1. Although the obtained slope is not equal to average charge but to apparent charge and this relationship is not quantitative, the slope value can be used as a qualitative indicator for evaluation of the interaction. In this study, the slope value was calculated with using the data on Fig. 2 Relationship between tR' of 2,6-ADS₂⁻ and eluent concentration in LiBr, NaBr and CsBr systems.
Table 1 Obtained slope values of log $t_R'$ vs. log $[\text{Br}^-]$ plot.$^a$

<table>
<thead>
<tr>
<th>Sample anion</th>
<th>Eluent counterion ($C^+$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Li⁺</td>
</tr>
<tr>
<td>1,8-ADS²⁻</td>
<td>−2.05</td>
</tr>
<tr>
<td>1,5-ADS²⁻</td>
<td>−1.96</td>
</tr>
<tr>
<td>2,7-ADS²⁻</td>
<td>−2.02</td>
</tr>
<tr>
<td>2,6-ADS²⁻</td>
<td>−1.99</td>
</tr>
</tbody>
</table>

$^a$ $[C^+] = [\text{Br}^-] = 35, 40, 50 \text{ mmol dm}^{-3}$.

$[\text{Br}^-] = 35, 40$ and $50 \text{ mmol dm}^{-3}$.

### 3 Results and Discussion

#### 3.1 Comparison between alkali metal and ammonium countercations

Figure 2 shows relationship between log $t_R'$ for 2,6-ADS²⁻ and log $[\text{Br}^-]$ in use of LiBr, NaBr or CsBr as eluent. Use of LiBr and NaBr resulted in similar retention behavior of 2,6-ADS²⁻ and both log $t_R'$ vs. log $[\text{Br}^-]$ plots showed slope close to −2. This suggested that 2,6-ADS²⁻ acted as dianion and that neither Li⁺ nor Na⁺ interact with 2,6-ADS²⁻ electrostatically. On the contrary, use of CsBr resulted in the enhancement of the retention of 2,6-ADS²⁻ with the increase in eluent concentration compared with the use of LiBr or NaBr. Furthermore, the slope of log $t_R'$ vs. log $[\text{Br}^-]$ plot shifted a little from −2. This result suggested that Cs⁺ interacts partly with 2,6-ADS²⁻ and that 2,6-ADS²⁻ acts as monoanion in part.

The obtained slope values of log $t_R'$ vs. log $[\text{Br}^-]$ plot for the ADS₂⁻ anions in use of LiBr, NaBr, KBr, NH₄Br and CsBr as eluent are listed in Table 1. Although Li⁺, Na⁺ and K⁺ showed no electrostatic effect to all of the sample anions, NH₄⁺ and Cs⁺ affected to some of them electrostatically. Crystal radii of these cations are 0.060 nm, 0.095 nm, 0.133 nm, 0.148 nm and 0.169 nm for Li⁺, Na⁺, K⁺, NH₄⁺ and Cs⁺, respectively [6], and relatively bulky (hydrophobic) cations showed the electrostatic effect. In addition, 1,8-ADS²⁻ having the closest S–S distance showed no electrostatic effect even if using the largest Cs⁺ countercation.

#### 3.2 Comparison between tetraalkylammonium countercations

To evaluate the electrostatic effect in detail, tetraalkylammonium cations were used as countercations. Since the R₄NBr salts have relatively low solubility to water and the R₄N⁺ cations are surface-active to some extent, R₄NBr–NaBr mixed eluent systems with a fixed R₄NBr concentration were used. As mentioned above, the electrostatic effect by Na⁺ is negligible.

Table 2 shows the obtained slope values of log $t_R'$ vs. log $[\text{Br}^-]$ plot for the ADS²⁻ anions in use of

Table 2 Obtained slope values of log $t_R'$ vs. log $[\text{Br}^-]$ plot in R₄NBr–NaBr mixed eluent system.$^b$

<table>
<thead>
<tr>
<th>Sample anion</th>
<th>Control$^b$</th>
<th>R = C₂H₅</th>
<th>R = C₄H₉</th>
<th>R = C₂H₁₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,8-ADS²⁻</td>
<td>−2.13</td>
<td>−2.15</td>
<td>−1.99</td>
<td>−1.80</td>
</tr>
<tr>
<td>1,5-ADS²⁻</td>
<td>−2.01</td>
<td>−2.00</td>
<td>−1.75</td>
<td>−1.51</td>
</tr>
<tr>
<td>2,7-ADS²⁻</td>
<td>−1.97</td>
<td>−2.02</td>
<td>−1.66</td>
<td>−1.26</td>
</tr>
<tr>
<td>2,6-ADS²⁻</td>
<td>−1.99</td>
<td>−1.94</td>
<td>−1.71</td>
<td>−1.28</td>
</tr>
</tbody>
</table>

$^a$ $[R_N^+] = 30 \text{ mmol dm}^{-3}$, $([R_N^+] + [Na^+]) = [\text{Br}^-] = 35, 40, 50 \text{ mmol dm}^{-3}$.

$^b$ NaBr alone.
R₄NB₉-–NaBr mixed eluents. Here, [R₄N⁺] was fixed at 30 mmol dm⁻³. The values of van der Waals radii for (C₂H₅)₄N⁺, (C₄H₉)₄N⁺ and (C₅H₁₁)₄N⁺ are 0.337 nm, 0.413 nm and 0.443 nm, respectively [6] and, also in this case, relatively bulky counterion showed high electrostatic effect.

Figure 3 shows relationship between the slope values for the ADS²⁻ anions and eluent (C₅H₁₁)₄N⁺ concentration in use of (C₅H₁₁)₄NBr–NaBr mixed eluent systems. With the increase in [(C₅H₁₁)₄N⁺], shift of the slope value was enhanced.

The order of magnitude of the slope shift was generally 1,8-ADS²⁻ < 1,5-ADS²⁻ < 2,6-ADS²⁻. This order is similar to that of the S-S distance (1,8-ADS²⁻ < 1,5-ADS²⁻ < 2,7-ADS²⁻ < 2,6-ADS²⁻). In addition, this tendency was the opposite to that in use of polyammonium cations (1,8-ADS²⁻ > 1,5-ADS²⁻).[5]

These results suggested that the monoanionic [C(ADS)⁻] species are formed on (or near) the anion-exchanger rather than in the (bulk) mobile phase. In ADS²⁻ anions, the negative charge distributes mainly onto the two sulfonate groups. Namely, on retention of the anions as monoanionic [C(ADS)⁻], C⁺ is situated near one sulfonate group and an anion-exchange group is situated near another sulfonate group. Therefore, in the case that the two sulfonate groups are close, such as 1,8-ADS²⁻, the monoanionic retention seems to be prevented by the electrostatic repulsion between the C⁺ and the anion-exchange group or the competitive electrostatic interaction by other anion-exchange group which is situated near the C⁺. On the contrary, in the case that the groups have relatively long distance, such as 2,7-ADS²⁻ and 2,6-ADS²⁻, the monoanionic retention seems to be promoted by using hydrophobic C⁺.

As mentioned above, the anion-chromatographic retention of ADS²⁻ anions was affected by hydrophobic monocationic eluent counterion. Since the effect was governed by the distance between the two sulfonate groups, it was considered that this concept can be applied to improve the anion-chromatographic separation between various positional isomers of polyanions.

References