Dependence of Chlorine Isotope Separation in Ion Exchange Chromatography on the Nature and Concentration of the Eluent

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In a heterogeneous electrolyte system of a strongly basic anion exchanger and solutions of NaBF₄ or NaClO₄, we established the influence of the nature and concentration of the eluent in chromatographic experiments on chlorine isotope separation. Results show that when the electrolyte concentration is increased the degree of isotope separation decreases. With NaBF₄ the separation factor is greater than with NaClO₄ under conditions which otherwise are the same. For electrolyte solutions containing ClO₄⁻, NO₃⁻ and BF₄⁻ there is a linear relation between the separation factor of the chlorine isotopes and the logarithm of the ratio of anion hydration of the elution electrolyte.

Previous experiments with labeled compounds have mainly used radioactive isotopes, but at present there is an increasing tendency to work with stable isotopes. For this reason, both the development of systems for the chemical enrichment of stable isotopes and the knowledge of isotope effects are of great interest. Whereas previous experiments on isotope enrichment in ion exchange chromatography were almost entirely carried out on cations, we have recently begun to study anionic systems using chlorine isotopes for this purpose. In these investigations a NaN₃ solution has been used as eluent. The isotope exchange reaction examined between ³⁵Cl⁻ and ³⁷Cl⁻ can be described by equation (1):

\[ \text{³⁵Cl}^-_{\text{resin}} + \text{³⁷Cl}^-_{\text{sol}} \rightleftarrows \text{³⁷Cl}^-_{\text{sol}} + \text{³⁵Cl}^-_{\text{resin}} \] (1)

The equilibrium constant \( K_e \) of this isotope exchange reaction is equal to the separation factor \( a \). Thus:

\[ K_e = a = 1 + \varepsilon \] (2)

where \( \varepsilon \) is the deviation from 1.

In the experiments with NaNO₃ as eluent, the influence of concentration [1], temperature [2] and degree of cross linkage of the ion exchanger [3] on the separation factor of chlorine isotopes was established. The purpose of this paper is to investigate the dependence of chlorine isotope enrichment on the anion of the eluent and to determine whether the concentration of the electrolyte has any influence as in the case of NaNO₃. Furthermore, we aimed at establishing a connection between chlorine isotope separation and the heat of anion hydration of the elution electrolyte. This was justified by the fact that Lee [4] had established a relationship between the isotope separation factor of lithium and the heat of cation hydration of the elution electrolyte.

Experimental

Glass columns of 1.5 cm diameter thermostatically controlled at a temperature of 20 °C were used. The columns were filled up to a height of 85 cm with the strongly basic anion exchange resin AG1-X 10 (200–400 mesh, Bio-Rad) which had been loaded with the anion of the elution electrolyte. For each elution 200 mg chloride of natural isotopic abundance was used. The chloride was added to the column as a weighed quantity of exchanger in the Cl⁻ form. After each experiment an appropriate amount of exchanger was taken out of the column so that the quantity of exchanger remained constant throughout the experiments. 0.05 M, 0.1 M and 0.5 M solutions of the electrolytes NaClO₄ (p.a., Merck) and NaBF₄ (pure, Riedel-de-Haen AG) were used. Because tetrafluoroborate solutions are partly hydrolyzed [5], these solutions were used in hydrolysis equilibrium. The flow rate was set at 0.38 ± 0.06 ml/min using a peristaltic pump. The eluate was collected in fractions of 2 ml. The chloride concentration distribution in the eluate was measured using a chloride selective electrode (Orion Research, Type 96–17). Chloride was isolated as AgCl in some fractions of the eluate and purified by means of precipitation. For mass spectrometric ³⁵Cl/³⁷Cl isotope ratio measurement, part of the AgCl was converted into soluble [Ag(NH₃)₂]Cl with 1–2 drops of a 15% NH₃-solution. A sample of 30 µg chloride was deposited on one filament of a double filament thermal ion source of a mass spectrometer (Varian MAT, Type CH5–TH). The ionization method used in the mass spectrometer...
entailed producing negative ions of chlorine on a hot metal surface (Re-filament). This mass spectrometric technique has been described in detail [6]. The $^{35}\text{Cl}/^{37}\text{Cl}$ isotope ratio was measured 10 times in succession in cycle (1 series of measurements). 5 Series of measurements were taken for each sample. The standard deviation for the mean of these 5 series was about 0.1%.

Results and Discussion

In all the experiments an enrichment of the heavier $^{37}\text{Cl}^-$ is found in the first fractions of the elution, whereas in the last fractions an enrichment of $^{35}\text{Cl}^-$ takes place ($K_c > 1$). This tendency agrees with the experiments where NaN0$_3$ is used and the curves obtained plotting the isotope ratio $^{35}\text{Cl}/^{37}\text{Cl}$ as a function of the eluted amount of chloride are comparable to those in the NaN0$_3$ experiments [3]. The different degree of selectivity of the anion exchanger to the chlorine isotopes can be explained by the different hydrated ionic radii of $^{35}\text{Cl}^-$ and $^{37}\text{Cl}^-$. This interpretation is supported by calculations made by Knyazev [7] who established a difference in the Pauling ionic radii of the two chlorine isotopes.

Using the technique described by Glueckauf [8], the $\epsilon$-value of the chlorine isotopes can be established from the chromatographic results. We recently discussed in detail the application of Glueckauf’s technique to chlorine isotope separation [3]. The evaluations of experiments with NaBF$_4$ and NaClO$_4$

<table>
<thead>
<tr>
<th>Electrolyte solution</th>
<th>Concentration $[\text{mol} \times 1^{-1}]$</th>
<th>$\epsilon$-Value $\times 10^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaClO$_4$</td>
<td>0.05</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.1</td>
</tr>
<tr>
<td>NaBF$_4$</td>
<td>0.05</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1.5</td>
</tr>
<tr>
<td>NaNO$_3^*$</td>
<td>0.1</td>
<td>3.0</td>
</tr>
</tbody>
</table>

* From ref. [1].

are summarized in Table I. For comparison, one $\epsilon$-value is included in this Table which was previously determined using 0.1 M NaNO$_3$ solution as an eluent [1].

In the case of both NaClO$_4$ and NaBF$_4$, $\epsilon$ definitely depends on the concentration of the eluent, and isotope separation decreases as the concentration increases. This result is in accordance with those obtained for the same system, but using NaNO$_3$ as an eluent [1]. Isotope experiments carried out by Lee and Drury using lithium [9] and those by Heumann et al. using calcium [10] showed that $\epsilon$ decreases in a comparable cation system when the electrolyte concentration increases. This effect can be explained by increased dehydration of the isotopic ions when electrolyte concentrations are increased. It is quite probable that this partial dehydration reduces the differences between the effective ionic radii of the isotopes and this leads to smaller $\epsilon$-values.

Table I shows that between 0.05 to 0.5 M electrolyte solutions $\epsilon$ is also greatly dependent on the anion of the eluent. Using the same electrolyte concentration chlorine isotope separation increases in the following order: $\epsilon$ (ClO$_4^-$) $< \epsilon$ (NO$_3^-$) $< \epsilon$ (BF$_4^-$). Experiments for lithium isotope enrichments showed that $\epsilon$ depends on the cation of the eluent [4]. Thus we can say that the effects which were first proved for anionic isotope exchange equilibria in this work are comparable with those of cation systems. In connection with the assumption that isotope dehydration is responsible for different $\epsilon$-values, it is remarkable that chlorine isotope separation increases in magnitude, the greater the heat of anion hydration $\Delta H_{\text{hydr}}$ of the eluent. Lee has already referred to this relationship in his experiments with lithium isotopes [4]. He found that there was an almost linear relation between the logarithm of $\Delta H_{\text{hydr}}$ and $\epsilon$, which confirms the results of our experiments with the anions ClO$_4^-$, NO$_3^-$ and BF$_4^-$ of a 0.1 M

![Fig. 1. $\epsilon$-Value as a function of the logarithm of the heat of anion hydration of the elution electrolyte.](image-url)
eluent solution (see Fig. 1; \( \Delta H_{\text{hydr}} \)-values from [11, 12]).

In summary, it can be seen that the results show a strong dependence of isotope separation of the chloride ion on the nature and concentration of the eluent. The electrolyte behaviour of the chlorine isotopes is comparable with that of isotope pairs of cations in analogous systems. Furthermore, the present results are an important prerequisite for further investigations on the chemical enrichment of stable isotopes.

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