Abstract

From extraction experiments and γ-activity measurements, the exchange extraction constants corresponding to the general equilibrium $M^+(aq) + NaL^+(nb) \Leftrightarrow ML^+(nb) + Na^+(aq)$ taking place in the two-phase water-nitrobenzene system ($M^+ = Li^+, NH_4^+, Ag^+, K^+, Rb^+, Tl^+, Cs^+$; $L = \text{tetra-}\text{-}\text{ tert-butyl p-}\text{-}\text{ tert-butylcalix}[4]\text{arene tetraacetate}; aq = \text{aqueous phase, nb = nitrobenzene phase}$) were evaluated. Further, the stability constants of the $ML^+$ complexes in water saturated nitrobenzene were calculated; they were found to increase in the series $Cs^+ < Rb^+ < Tl^+ < K^+ < NH_4^+ < Ag^+ < Li^+$.

Keywords: Univalent cations, calix[4]arene, water-nitrobenzene system, extraction and stability constants

1. Introduction

Calixarene-based molecules have received intense attention in the last years. One of the most important features of these compounds is their diversity. Calixarenes find applications as selective binders and carriers, as analytical sensors, as catalysts and model structures for biomimetic studies.\(^1,2\)

Recently, solvent extraction of Ba\(^{2+}\), Pb\(^{2+}\) and Cd\(^{2+}\) into nitrobenzene by using strontium dicarbollylcobaltate and tetraethyl $p$-tert-butylcalix[4]arene tetraacetate has been investigated.\(^3\) The aim of the present communication was to determine the stability constants of the complex species $ML^+$, where $M^+ = Li^+, NH_4^+, Ag^+, K^+, Rb^+, Tl^+, Cs^+$ and $L$ is tetra-tert-butyl $p$-tert-butylcalix[4]arene tetraacetate (see Scheme 1), in nitrobenzene saturated with water.

2. Experimental

Tetra-tert-butyl $p$-tert-butylcalix[4]arene tetraacetate was synthesized as published in Reference 4. Cesium dicarbollylcobaltate, CsDCC, was supplied by Katchem, Rež, Czech Republic. A nitrobenzene solution of hydrogen dicarbollylcobaltate (HDCC)\(^5\) was prepared from CsDCC by the method described in Reference 6. The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity. The equilibration of the nitrobenzene solution of hydrogen dicarbollylcobaltate, HDCC, with stoichiometric NaOH, which was dissolved in an aqueous solution of NaCl (0.2 mol L\(^{-1}\)), yielded the corresponding solution in nitrobenzene. The radionuclide $^{22}\text{Na}^+$ (DuPont, Belgium) was of standard radiochemical purity.

The extraction experiments were carried out in 10 mL glass test-tubes covered with polyethylene stoppers: 2 mL of an aqueous solution of $MNO_3$ ($M^+ = Li^+, NH_4^+, Ag^+, K^+, Rb^+, Tl^+, Cs^+$) of the concentration in the range from $1 \times 10^{-3}$ to $1 \times 10^{-2}$ mol L\(^{-1}\) and microamounts of $^{22}\text{Na}^+$ were added to 2 mL of a nitrobenzene solution of tetra-tert-butyl $p$-tert-butylcalix[4]arene tetraacetate and NaDCC, whose initial concentrations varied also from $1 \times 10^{-3}$ to $1 \times 10^{-2}$ mol L\(^{-1}\) (in all experiments, the initial concentration of tetra-tert-butyl $p$-tert-butylcalix[4]arene tetraacetate in nitrobenzene, $C_{L^{\text{in}},\text{nb}}$, was always equal to the...
initial concentration of NaDCC in this medium, \( C_{\text{NaDCC}} \). The test-tubes filled with the solutions were shaken for 12 hours at 25 ± 1°C, using a laboratory shaker. Then the phases were separated by centrifugation. Afterwards, 1 mL samples were taken from each phase and their \( \gamma \)-activities were measured using a well-type NaI(T1) scintillation detector connected to a \( \gamma \)-analyzer NK/350 (Gamma, Budapest, Hungary).

The equilibrium distribution ratio of sodium, \( D_{\text{Na}} \), was determined as the ratio of the measured radioactivities of \(^{22}\text{Na}^+\) in the nitrobenzene and aqueous samples.

### 3. Results and Discussion

Regarding the results of previous papers,\(^7\)-\(^9\) the two-phase water–MNO\(_3\) (\( M^+ = \text{Li}^+, \text{NH}_4^+, \text{Ag}^+, \text{K}^+, \text{Rb}^+, \text{Tl}^+, \text{Cs}^+\))-nitrobenzene-NaDCC extraction system can be described by the following general equilibrium

\[
M^+(\text{aq}) + \text{Na}^+(\text{nb}) \Leftrightarrow M^+(\text{nb}) + \text{Na}^+(\text{aq});
\]

with the corresponding exchange extraction constant \( K_{\text{ex}}(M^+, \text{Na}^+) \)

\[
\log K_{\text{ex}}(M^+, \text{Na}^+) = \log K_{\text{ex}}^M - \log K_{\text{ex}}^\text{Na}^+;
\]

where \( K_{\text{ex}}^M \) and \( K_{\text{ex}}^\text{Na}^+ \) are the individual extraction constants for \( M^+ \) and \( \text{Na}^+ \), respectively, in the water–nitrobenzene system.\(^7\) Knowing the values \( \log K_{\text{ex}}^M \) (\( M^+ = \text{Li}^+, \text{Na}^+, \text{NH}_4^+, \text{Ag}^+, \text{K}^+, \text{Rb}^+, \text{Tl}^+, \text{Cs}^+\))\(^7\) the single exchange extraction constants \( K_{\text{ex}}(M^+, \text{Na}^+) \) were simply calculated on the basis of Eq. (2). The corresponding data are given in Table 1.

In terms of previous papers,\(^7\)-\(^11\) the two-phase water-MNO\(_3\) (\( M^+ = \text{Li}^+, \text{NH}_4^+, \text{Ag}^+, \text{K}^+, \text{Rb}^+, \text{Tl}^+, \text{Cs}^+\))-nitrobenzene–L (\( L = \text{tetra-tert-butyl \text{p-tert-butylcalix}[4]arene tetraacetate}\))-NaDCC extraction system (see Experimental), chosen for determination of stability of the complexes \( ML^+ \) in nitrobenzene saturated with water, can be characterized by the main chemical equilibrium

\[
M^+(\text{aq}) + \text{NaL}^+(\text{nb}) \Leftrightarrow ML^+(\text{nb}) + \text{Na}^+(\text{aq});
\]

with the general equilibrium extraction constant \( K_{\text{ex}}(M^+, \text{NaL}^+) \):

\[
K_{\text{ex}}(M^+, \text{NaL}^+) = \frac{[ML^+]_{\text{nb}}[\text{Na}^+]_{\text{aq}}}{[M^+]_{\text{aq}}[\text{NaL}^+]_{\text{nb}}}
\]

It is necessary to emphasize that the tetra-tert-butyl \text{p-tert-butylcalix[4]arene tetraacetate} ligand forms – with the mentioned univalent cations – the very stable complexes \( ML^+ \) and \( \text{NaL}^+ \) in the nitrobenzene phase. Taking into account the conditions of electroneutrality in the organic and aqueous phases of the system under study, the mass balances of the considered univalent cations at equal volumes of the nitrobenzene and aqueous phases, as well as the measured equilibrium distribution ratio of sodium, \( D_{\text{Na}} = [\text{Na}^+]_{\text{nb}}/[\text{Na}^+]_{\text{aq}} \), combined with Eq. (4), we gain the final expression for \( K_{\text{ex}}(M^+, \text{NaL}^+) \) in the form

\[
K_{\text{ex}}(M^+, \text{NaL}^+) = \frac{1}{D_{\text{Na}}} \frac{C_{\text{in, nb}}^{\text{MNO}_3}}{C_{\text{in, aq}}^{\text{MNO}_3}} \frac{(1 + D_{\text{Na}})}{C_{\text{in, aq}}^{\text{NaDCC}}}.
\]

where \( C_{\text{in, nb}}^{\text{MNO}_3} \) is the initial concentration of MNO\(_3\) in the aqueous phase of the system under consideration.

In this study, from the extraction experiments and \( \gamma \)-activity measurements by means of Eq. (5), the logarithms of the constants \( K_{\text{ex}}(M^+, \text{NaL}^+) \) (\( M^+ = \text{Li}^+, \text{Na}^+, \text{NH}_4^+, \text{Ag}^+, \text{K}^+, \text{Rb}^+, \text{Tl}^+, \text{Cs}^+\)) were determined and given in Table 1.

Moreover, with respect to References 10 and 11, for the extraction constants \( K_{\text{ex}}(M^+, \text{Na}^+) \) and \( K_{\text{ex}}(M^+, \text{NaL}^+) \) defined above, as well as for the stability constants of the

<table>
<thead>
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<th>Quantity</th>
<th>Li(^+)</th>
<th>Na(^+)</th>
<th>NH(_4^+)</th>
<th>Ag(^+)</th>
<th>K(^+)</th>
<th>Rb(^+)</th>
<th>Tl(^+)</th>
<th>Cs(^+)</th>
</tr>
</thead>
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<tr>
<td>( \log K_{\text{ex}}^M )</td>
<td>-6.7</td>
<td>-6.0</td>
<td>-4.7</td>
<td>-4.5</td>
<td>-4.1</td>
<td>-3.4</td>
<td>-3.4</td>
<td>-2.7</td>
</tr>
<tr>
<td>( \log K_{\text{ex}}(M^+, \text{Na}^+) )</td>
<td>-0.7</td>
<td>-1.3</td>
<td>1.5</td>
<td>1.9</td>
<td>2.6</td>
<td>2.6</td>
<td>3.3</td>
<td>4.2</td>
</tr>
<tr>
<td>( \log K_{\text{ex}}(M^+, \text{NaL}^+) )</td>
<td>-1.1</td>
<td>-0.6</td>
<td>-0.1</td>
<td>-0.4</td>
<td>-0.5</td>
<td>-0.4</td>
<td>-0.4</td>
<td>-0.4</td>
</tr>
<tr>
<td>( \log \beta_{\text{ex}}(ML^+) )</td>
<td>10.8</td>
<td>11.2</td>
<td>9.3</td>
<td>9.6</td>
<td>8.9</td>
<td>8.1</td>
<td>8.2</td>
<td>7.6</td>
</tr>
</tbody>
</table>

\(^{a}\) Ref. 7.  
\(^{b}\) Ref. 9.  
\(^{c}\) Calculated from Eq. (2) using data from Refs 7 and 9.  
\(^{d}\) Calculated from Eq. (5).  
\(^{e}\) Calculated from Eq. (6) using data from Refs 7, 9 and 12.  
\(^{f}\) Ref. 12.
complexes ML+ and NaL+ in nitrobenzene saturated with water, denoted by $\beta_{nb}(ML^+)$ and $\beta_{nb}(NaL^+)$, respectively, one gets

$$\log \beta_{nb}(ML^+) = \log \beta_{nb}(NaL^+) + \log K_{ex}(M^+, NaL^+) - \log K_{ex}(M^+, Na^+)$$

Using the constants of $K_{ex}(M^+, Na^+)$ and $K_{ex}(M^+, NaL^+)$ given in Table 1, the value $\log \beta_{nb}(NaL^+) = 11.2$ (L = tetra-tert-butyl p-tert-butylcalix[4]arene tetraacetate), determined from the distribution of sodium p-nitrophenolate in the water–nitrobenzene system containing tetra-tert-butyl p-tert-butylcalix[4]arene tetraacetate, and applying Eq. (6), we obtain the stability constants of the complexes ML+ (M+ = Li+, NH4+, Ag+, K+, Rb+, Tl+, Cs+) in water saturated nitrobenzene. These data are also summarized in Table 1. Thus, the $\log \beta_{nb}(ML^+)$ values from this table indicate that the stability of the complex cation ML+ in nitrobenzene saturated with water increases in the Cs+ < Rb+ < Tl+ < K+ < NH4+ < Ag+ < Li+ < Na+ order. Besides, as depicted in Fig. 1, the dependence of $\log \beta_{nb}(ML^+)$ on the crystallographic radius of the alkali metal cation displays a maximum for M+ = Na+. In organic solvents, the occurrence of such maxima seems to be a general feature also in the case of the alkali metal complex formation with calix[4]arenes similarly as in the case of cyclic or acyclic polyethers.

4. Acknowledgement

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5. References

12. E. Makrlík, P. Vanůra, unpublished results.
Povzetek
Iz podatkov, dobljenih pri eksperimentih ekstrakcije ter meritvah γ-aktivnosti, smo določili konstante ekstraktijskih ravnotež, ki jih za dvo fazni sistem voda-nitrobenzen lahko zapišemo splošno kot $M^+(aq) + NaL^-(nb) \Leftrightarrow ML^+(nb) + Na^+(aq)$; ($M^+ = Li^+, NH_4^+, Ag^+, K^+, Rb^+, Tl^+, Cs^+$; $L = \text{tetra-tert-butil p-tert-butilcalix[4]aren tetraacetate}$; $aq = vodna faza$, $nb = faza nitrobenzena$). Izračunali smo konstante stabilnosti kompleksov tipa $ML^+$ v vodi, nasičeni z nitrobenzenom. Izkaže se, da konstante stabilnosti naraščajo v smeri $Cs^+ < Rb^+ < Tl^+ < K^+ < NH_4^+ < Ag^+ < Li^+$. 

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