Thermodynamics of Complexation of Sodium Ion with 12-Crown-4 and 18-Crown-6 in Pyridine

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Dedicated to Prof. Hitoshi Ohtaki on the occasion of his 60th birthday

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The complexation of sodium ion with 1,4,7,10-tetraoxacyclododecane (12-crown-4) and 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) has been studied by titration calorimetry in pyridine (PY) containing 0.1 mol dm\(^{-3}\) (C\(_2\)H\(_5\))\(_4\)N\(\text{ClO}_4\) as a constant ionic medium at 25 °C. The calorimetric titration data were well explained in terms of the formation of the \([\text{Na}(12\text{-crown-4})]^+\), \([\text{Na}(12\text{-crown-4})_2]^+\), and \([\text{Na}(18\text{-crown-6})]^+\) complexes, and their formation constants, reaction enthalpies, and entropies were determined. The formation of \([\text{Na}(18\text{-crown-6})]^+\) is much pronounced in PY over N,N-dimethylformamide (DMF) and water, and the stability order is PY > DMF > water. The enthalpy values for the formation of \([\text{Na}(18\text{-crown-6})]^+\) are all negative in PY, DMF, and water, and increase in the order PY < DMF < water. The complexation is the least exothermic in water, though sodium ion is the most weakly solvated in water. This is because 18-crown-6 is much stabilized in water by forming hydrogen bonds with water molecules. Despite the stronger electron pair-donating ability of PY than DMF, the complexation is more exothermic in PY than in DMF. This is ascribed to the different solvation number of the sodium ion in PY and DMF, i.e., the sodium ion is coordinated with a smaller number of solvent molecules in the former solvent than in the latter.

1. Introduction

Complexation of crown ether with alkali metal ions has been widely investigated in aqueous and non-aqueous solutions [1]. In general, crown ether complexes are more stable in non-aqueous solvents than in water, regardless of the nature of the solvents [1]. We have investigated the complexation of 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) with alkali metal ions in aprotic N,N-dimethylformamide (DMF) with a stronger electron pair-donating ability than water [2]. The complexation is enthalpically more favorable but entropically not favorable in DMF over water. The different thermodynamic behavior of the 18-crown-6 complexation in DMF from that in water is mainly attributed to the different solvation of 18-crown-6 in the two solvents, i.e., 18-crown-6 is much more stabilized in water by forming hydrogen bonds between the oxygen atoms of the ligand and water molecules [2]. Also, it has been found that the thermodynamic data, especially reaction entropies, of the 18-crown-6 complexes with alkali metal ions are quite different even in aprotic solvents with similar donor and acceptor properties such as the nitrogen-donor acetonitrile (AN) and the oxygen-donor propylene carbonate (PC), which have a weaker electron pair-donating ability than water [1]. It is thus interesting to study the 18-crown-6 complexation in nitrogen-donor solvents having a stronger electron pair-donating ability than water. In this study, we have chosen pyridine (PY) as a solvent and investigated the complexation of sodium ion with 18-crown-6 by titration calorimetry. We also examined the complexation of sodium ion with 1,4,7,10-tetraoxacyclododecane (12-crown-4) in order to obtain the effect of ring size on the complexation.
2. Experimental

2.1. Reagents

All chemicals used were of reagent grade. 12-Crown-4 was distilled under reduced pressure and stored over molecular sieves 4 Å in a dark bottle. 18-Crown-6 was purified as described elsewhere [2]. Sodium perchlorate was used without further purification and dried at 100 °C in a vacuum oven. Tetraethylammonium perchlorate was recrystallized once from water and dried in a vacuum oven. Pyridine was dried for several weeks over molecular sieves 4 Å, then distilled under reduced pressure and stored over molecular sieves 4 Å in a dark bottle. All solutions were prepared and treated over P₂O₅ in a dry box under nitrogen.

2.2. Calorimetric measurements

Calorimetric measurements were carried out at 25 °C by using a fully automatic on-line calorimetry system [3], consisting of a twin-type calorimeter (Tokyo Riko, Japan). All test solutions contained 0.1 mol dm⁻³ (C₅H₇N₅)₂CIO₄ as a constant ionic medium. A sodium perchlorate PY solution (40 cm³) was placed in a stainless-steel vessel, the inside wall of which was coated with Teflon. The vessel was inserted into an aluminum block thermostated at 25 ± 0.0001 °C in an air bath. The sodium perchlorate solution was titrated with either 0.1 mol dm⁻³ 12-crown-4 or 18-crown-6 PY solution by using an APB-118 autoburet (Kyoto Electronics, Japan) under dry nitrogen. A ligand replacement titration procedure, in which sodium perchlorate and 12-crown-4 in PY were titrated with a 0.1 mol dm⁻³ 18-crown-6 solution, was also performed. Heats of complexation ranging from 3.0 to 0.2 J at each titration point were measured with an error of ± 0.02 J and were corrected for heat of dilution of titrants, which had been determined in advance by separate experiments and was found to be very small.

2.3. Analysis of calorimetric data

Calorimetric titration data were analyzed by considering the formation of the following mononuclear [NaLₙ]⁺ complexes (L = 12-crown-4 or 18-crown-6):

\[ \text{Na}^+ + nL = [\text{NaL}_n]^+, \]

\[ \beta_n = [\text{NaL}_n^+]/[\text{Na}^+][L]^n. \]  

The total concentrations, \( C_{\text{Na},i} \) and \( C_{L,i} \), at an \( i \)th titration point are expressed with their respective free concentrations, [Na⁺] and [L], according to the mass-balance equations:

\[ C_{\text{Na},i} = [\text{Na}^+]_i + \Sigma \beta_n [\text{Na}^+][L]^n, \]  

\[ C_{L,i} = [L]_i + \Sigma \beta_n [\text{Na}^+][L]^n. \]  

The heat of complexation at the \( i \)th titration point, \( q_{i,\text{calc}} \), is calculated by using the overall formation constant \( \beta_n \) and enthalpy \( \Delta H^0_n \):

\[ q_i = -(V_1 \Sigma \beta_n (\Delta H^0_n)[\text{Na}^+][L]^n) - V_1 \Sigma \beta_n (\Delta H^0_n)[\text{Na}^+][L]^{n-1}_i, \]  

where \( V_i \) denotes the volume of the test solution. Formation constants and enthalpies were simultaneously obtained by minimizing the error-square sum \( \Sigma (q_{i,\text{obs}} - q_{i,\text{calc}})^2 \), using a non-linear least-squares program MOQCAL [4].

2.4. NMR measurements

Sodium-23 NMR spectra were measured at 105.84 MHz by using a Bruker AC-400 PS FT NMR spectrometer. Sample tubes of 5 mm diameter were used. The 23Na chemical shift of an aqueous NaClO₄ solution of 0.1 mol dm⁻³ was used as standard; \( \delta (\text{NaClO}_4) = 0 \) ppm. Sample solutions were prepared by dissolving sodium perchlorate and 18-crown-6 in PY, DMF, water, AN, PC, and nitromethane (NM). The composition of the sample solutions is given in Table I.

3. Results

3.1. Calorimetry

Calorimetric titration curves for the sodium 12-crown-4 system in PY are shown in Fig. 1. The \( -q/(\delta \nu C_{L,\text{obs}}) \) values are plotted against the ratio of the total concentrations of 12-crown-4 to sodium

Table I. Composition of sample solutions containing sodium perchlorate and 18-crown-6 (L) for 23Na NMR measurements.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>( C_{\text{Na}} ) [mol dm⁻³]</th>
<th>( C_L ) [mol dm⁻³]</th>
<th>( C_L/C_{\text{Na}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>NM</td>
<td>0.02042</td>
<td>0.02300</td>
<td>1.126</td>
</tr>
<tr>
<td>AN</td>
<td>0.1008</td>
<td>0.1120</td>
<td>1.111</td>
</tr>
<tr>
<td>PC</td>
<td>0.1011</td>
<td>0.1126</td>
<td>1.144</td>
</tr>
<tr>
<td>DMF</td>
<td>0.1032</td>
<td>0.1066</td>
<td>1.033</td>
</tr>
<tr>
<td>PY</td>
<td>0.1011</td>
<td>0.1122</td>
<td>1.110</td>
</tr>
<tr>
<td>Water</td>
<td>0.1017</td>
<td>0.05225</td>
<td>0.5138</td>
</tr>
<tr>
<td>Water</td>
<td>0.09989</td>
<td>0.09992</td>
<td>1.000</td>
</tr>
<tr>
<td>Water</td>
<td>0.1014</td>
<td>0.2971</td>
<td>2.930</td>
</tr>
<tr>
<td>Water</td>
<td>0.1022</td>
<td>0.5003</td>
<td>4.895</td>
</tr>
<tr>
<td>Water</td>
<td>0.1043</td>
<td>0.7043</td>
<td>6.753</td>
</tr>
<tr>
<td>Water</td>
<td>0.1018</td>
<td>1.014</td>
<td>9.961</td>
</tr>
</tbody>
</table>
Cl/CM

Fig. 1. Calorimetric titration curves for sodium ion and 12-crown-4 pyridine solutions containing 0.1 mol dm\(^{-3}\) \((\text{C}_2\text{H}_5\text{N})_4\text{NCIO}_4\) at 25 °C. Concentrations of sodium ions in initial test solutions: 10.24 (○), 15.53 (■), 20.09 (■■), 25.55 (△). Solid lines were calculated by using the constants under “Ternary” in Table II.

ion, \(C_{\text{L}}/C_{\text{Na}}\), where \(q\), \(\delta v\), and \(C_{\text{L,\text{tit}}}\) are the heat of complexation measured, the volume of the titrant added, and the concentration of the ligand in the titrant solution, respectively. The calorimetric titration data were analyzed by considering the formation of a set of complexes, and the Hamilton \(R\) factor and the standard deviation of the observed heats \(\sigma\) for various sets were compared. As seen in Fig. 1, the \(-q/(\delta vC_{\text{L,\text{tit}}} )\) values first decrease with increasing \(C_{\text{L}}/C_{\text{Na}}\) and then increase after passing through a minimum around \(C_{\text{L}}/C_{\text{Na}} \approx 0.4-1.0\), suggesting the formation of at least two complex species. In fact, the calorimetric curves were hardly explainable in terms of the formation of either \([\text{Na}(12\text{-crown-4})]^+\) \((R = 0.36, \sigma = 0.55\ \text{J})\) or \([\text{Na}(12\text{-crown-4})_2]^+\) \((R = 0.023, \sigma = 0.035\ \text{J})\). We successfully reproduced the titration curves by considering the formation of both \([\text{Na}(12\text{-crown-4})]^+\) and \([\text{Na}(12\text{-crown-4})_2]^+\), the result being given in Table II under “Binary”.

Calorimetric curves obtained by titrating sodium ion in PY with 18-crown-6 solution are shown in Fig. 2a. The \(-q/(\delta vC_{\text{L,\text{tit}}} )\) values are practically constant in the range \(0 < C_{\text{L}}/C_{\text{Na}} < 1\), indicating the formation of \([\text{Na}(18\text{-crown-6})]^+\). The \(-q/(\delta vC_{\text{L,\text{tit}}} )\) values drastically change at \(C_{\text{L}}/C_{\text{Na}} = 1\), and no exothermicity is found in the range \(C_{\text{L}}/C_{\text{Na}} > 1\). Thus, the calorimetric titration curves were well explained in terms of the formation of \([\text{Na}(18\text{-crown-6})]^+\). The result is shown under “Binary” in Table II. The formation of \([\text{Na}(18\text{-crown-6})_2]^+\) was also considered but rejected because no significant improvement of the \(R\) and \(\sigma\) values resulted.

Table II. Least-squares refinements of formation constants, log \(\beta_1(\text{mol}^{-n} \text{dm}^3)^n\), and enthalpies, \(\Delta H_{f1}/\text{kJ mol}^{-1}\), of \([\text{Na}(12\text{-crown-4})]^+\) and \([\text{Na}(18\text{-crown-6})]^+\) in pyridine containing 0.1 mol dm\(^{-3}\) \((\text{C}_2\text{H}_5\text{N})_4\text{NCIO}_4\) as a constant ionic medium at 25 °C.

<table>
<thead>
<tr>
<th></th>
<th>12-Crown-4</th>
<th>18-Crown-6</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Binary</td>
<td>Ternary</td>
</tr>
<tr>
<td>log (\beta_1)</td>
<td>2.00 (0.12)</td>
<td>1.99 (0.10)</td>
</tr>
<tr>
<td>log (\beta_2)</td>
<td>5.26 (0.03)</td>
<td>5.27 (0.02)</td>
</tr>
<tr>
<td>(\Delta H_{f1})</td>
<td>-21.0 (1.4)</td>
<td>-19.3 (1.1)</td>
</tr>
<tr>
<td>(\Delta H_{f2})</td>
<td>-49.2 (0.3)</td>
<td>-49.2 (0.2)</td>
</tr>
<tr>
<td>(R)</td>
<td>0.013</td>
<td>0.013</td>
</tr>
<tr>
<td>(\sigma/\bar{I})</td>
<td>0.020</td>
<td>0.020</td>
</tr>
<tr>
<td>(N)</td>
<td>102</td>
<td>235</td>
</tr>
</tbody>
</table>

a Values in parentheses refer to three standard deviations; \(b\) Hamilton \(R\) factor; \(c\) standard deviation of the observed heats; \(d\) the number of calorimetric data points.

Fig. 2. Calorimetric curves obtained by titrating (a) sodium perchlorate solutions and (b) various sodium ion and 12-crown-4 solutions with 18-crown-6 in pyridine. Concentrations of (a) sodium ions and (b) sodium ions and 12-crown-4 in initial test solutions: (a) 5.154 (○), 10.19 (■), 15.04 (■■), 20.04 (△), 32.28 (©); (b) 22.28, 40.55 (○), 32.31, 60.31 (■), 21.17, 21.32 (△). Solid lines were calculated by using the constants under “Ternary” in Table II.
The formation constants for the 12-crown-4 and 18-crown-6 complexes are quite large. In order to ascertain the parameter values, calorimetric data for titrating various sodium ion and 12-crown-4 solutions with 18-crown-6 solution as depicted in Fig. 2 were measured, and the whole data including the binary systems were simultaneously analyzed. The results are summarized under “Ternary” in Table II. The formation constants and enthalpies are in good agreement with those in “Binary”.

The solid lines, calculated by using the parameter values thus obtained, reproduce well the experimental points over the whole range of $C_L/C_{Na}$ examined, as seen in Fig. 1 and 2.

3.2. NMR data

According to the stability constants of 18-crown-6 complexes [1], almost all the sodium ions form the [Na(18-crown-6)]$^+$ complex in NM, AN, PC, DMF, and PY. The $^{23}$Na chemical shifts of aqueous solutions depend on the 18-crown-6 concentrations, owing to the small value ($log K_1 = 0.57$) of the formation constant of [Na(18-crown-6)]$^+$ in water [5]. In Fig. 3 the $^{23}$Na chemical shifts of aqueous solutions are plotted against the $C_L/C_{Na}$ ratios. The values are not constant in any range of $C_L/C_{Na}$ examined. The $^{23}$Na chemical shift for [Na(18-crown-6)]$^+$ in water was evaluated on the basis of the stability constant [5] and found to be $-12.0$ to $-13.3$ ppm. In Table III the $^{23}$Na chemical shifts of [Na(18-crown-6)]$^+$, and those of the solvated sodium ion in NM, AN, PC, water, DMF, and PY [6], along with Gutmann’s donor number [7], are compared.

4. Discussion

The thermodynamic quantities for the stepwise formation of the sodium complexes in PY are summarized in Table IV.
The formation of \([\text{Na}(12\text{-crown-4})]^+\) in PY is less favorable than \([\text{Na}(12\text{-crown-4})]^+\), while the enthalpy and entropy values change normally, \(\Delta H_i^\circ > \Delta H_2^\circ\), and \(\Delta S_i^\circ > \Delta S_2^\circ\). The formation of \([\text{Na}(12\text{-crown-4})]^+\) is enthalpically much more favorable but entropically less favorable than that of \([\text{Na}(12\text{-crown-4})]^+\), which causes the unusual sequence, \(\Delta G_i^\circ > \Delta G_2^\circ\). It is expected that the sodium-PY interaction is much weakened in \([\text{Na}(12\text{-crown-4})]^+\). The more negative enthalpy for the stepwise formation of \([\text{Na}(12\text{-crown-4})]^+\) is caused by the much easier replacement of solvating PY molecules within \([\text{Na}(12\text{-crown-4})]^+\) than within the solvated sodium ion.

The cavity size of 12-crown-4 (57 pm in radius) [8a] is smaller than the size of sodium ion (102 pm in radius) [9], thus the sodium ion is located outside the ether ring. In crystals of \([\text{Na}(12\text{-crown-4})_2\text{(ClO}_4\text{)}_2\text{]}\) [10] and \([\text{Na}(12\text{-crown-4})_2\text{(OH)}_2\text{H}_2\text{O}]\) [11], the sodium ion is 150 pm apart from the mean plane of 12-crown-4. On the other hand, the cavity size of 18-crown-6 (130-160 pm in radius) [8b] is large enough to fully accommodate the sodium ion as found in the crystal of \([\text{Na}(18\text{-crown-6})(\text{H}_2\text{O})\text{SCN}]\) [12]. The Na-O bond lengths are 247-254 pm (average 249 pm) for the 12-crown-4 complex [10] and 245-262 pm (average 255 pm) for the 18-crown-6 one [12], which are not significantly different. Assuming that the Na-O bond lengths for \([\text{Na}(12\text{-crown-4})]^+\) and \([\text{Na}(18\text{-crown-6})]^+\) in PY are not much different from those in the crystal, the metal-ligand interaction per bond is almost the same in the two complexes. Also, assuming that a pyridine molecule coordinates to the sodium ion within the \([\text{Na}(18\text{-crown-6})]^+\) complex in PY similar to aqueous solution [13], which will be discussed below, there are eight Na-O bonds within \([\text{Na}(12\text{-crown-4})]^+\) and seven bonds of six Na-O and one Na-N within \([\text{Na}(18\text{-crown-6})(\text{PY})]^+\). The smaller coordination number of \([\text{Na}(18\text{-crown-6})(\text{PY})]^+\) than \([\text{Na}(12\text{-crown-4})]^+\) leads to the less negative enthalpy (\(\Delta H_i^\circ = -42.3 \text{ kJ mol}^{-1}\)) for the former complex than that (\(\Delta H_2^\circ = -49.2 \text{ kJ mol}^{-1}\)) for the latter. However, the more negative entropy of \([\text{Na}(12\text{-crown-4})]^+\) than of \([\text{Na}(18\text{-crown-6})]^+\) compensates the more favorable enthalpy change of \([\text{Na}(12\text{-crown-4})]^+\), leading to a similar stability of the two complexes. For the complexes fully coordinated with ligands, an unmatched cavity size of crown ether to sodium ion does not play an important role for the stability of the crown ether complexes in solution.

The thermodynamic data for the formation of \([\text{Na}(18\text{-crown-6})]^+\) in PY, DMF, and water [2, 5] are compared in Table V.

The formation of \([\text{Na}(18\text{-crown-6})]^+\) is much more enhanced in PY than in water. The electron pair-donating ability of PY (donor number \(D_N = 33.1\)) is stronger than that of water (\(D_N = 18.0\)) [7], and the enthalpy of transfer of the sodium ion from water to PY is negative [14]. Thus, the sodium ion is more strongly solvated in PY than in water. The complexation is expected to be more endothermic in PY than in water, because more energy is needed for the desolvation process of the metal ion in PY upon complexation. However, the complexation is more exothermic in PY than in water. Three typical conformations, \(C_3\), \(C_1\), and \(D_{3d}\), have been found in the crystals of neat 18-crown-6 [15, 16], \([\text{Na}(18\text{-crown-6})(\text{H}_2\text{O})\text{SCN}]\) [12], and other 18-crown-6 complexes with univalent cations [17-21], respectively. The Monte Carlo simulation of aqueous 18-crown-6 solutions has revealed that the \(D_{3d}\) and \(C_1\) conformations are strongly stabilized in water by forming hydrogen bonds between oxygen atoms of 18-crown-6 and water molecules [22]. Regardless of which conformation, \(D_{3d}\) or \(C_1\), free 18-crown-6 takes in water, much energy is needed for the dehydration process upon complexation. On the other hand, 18-crown-6 is weakly solvated in PY because PY molecules cannot form any hydrogen bonds with oxygen atoms of 18-crown-6. In fact, the heat of solution of neat 18-crown-6 in water is exothermic (-22.1 kJ mol\(^{-1}\)), but that in PY is endothermic (31.5 kJ mol\(^{-1}\)) [23]. Much less energy is needed

### Table V. Thermodynamic quantities, \(\log K_i / \text{mol}^{-1} \text{ dm}^3\), \(\Delta G_i^\circ / \text{kJ mol}^{-1}\), \(\Delta H_i^\circ / \text{kJ mol}^{-1}\), \(\Delta S_i^\circ / \text{J K}^{-1} \text{ mol}^{-1}\), for the formation of \([\text{Na}(18\text{-crown-6})]^+\) in pyridine, \(N,N\)-dimethylformamide and water at 25 °C\(^a\).

<table>
<thead>
<tr>
<th></th>
<th>PY</th>
<th>DMF(^b)</th>
<th>Water(^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\log K_i)</td>
<td>5.54 (0.05)</td>
<td>2.43 (0.01)</td>
<td>0.57 (0.08)</td>
</tr>
<tr>
<td>(\Delta G_i^\circ)</td>
<td>-31.1 (0.3)</td>
<td>-13.8 (0.1)</td>
<td>-3.3 (0.4)</td>
</tr>
<tr>
<td>(\Delta H_i^\circ)</td>
<td>-42.3 (0.1)</td>
<td>-22.2 (0.2)</td>
<td>-13.8 (1.8)</td>
</tr>
<tr>
<td>(\Delta S_i^\circ)</td>
<td>-37.6 (1.1)</td>
<td>-28.2 (0.7)</td>
<td>-35 (7)</td>
</tr>
</tbody>
</table>

\(^a\) Values in parentheses refer to three standard deviations; \(^b\) ref. [2]; \(^c\) ref. [5].
for the desolvation of 18-crown-6 in PY compared with water. Thus, the 18-crown-6 complexation is more exothermic in PY than in water.

Despite the stronger electron pair-donating ability of PY than DMF ($D_N = 26.6$) [7], the formation of $[\text{Na}(18\text{-crown-6})]^+$ is more exothermic in PY than in DMF. The heats of solution of neat 18-crown-6 in PY and DMF are 31.5 and 34.7 kJ mol$^{-1}$, respectively [23], showing that the ligand-solvent interactions are virtually the same in the two solvents. The more negative enthalpy and entropy values for the formation of $[\text{Na}(18\text{-crown-6})]^+$ in PY than in DMF indicate that less desolvation occurs upon complexation and then more solvent molecules coordinate to the sodium ion within $[\text{Na}(18\text{-crown-6})]^+$ in PY as follows:

$$[\text{Na(DMF)}]^+ + 18\text{-crown-6} = [\text{Na}(18\text{-crown-6})]^+ + p\text{DMF},$$

$$[\text{Na(PY)}]^+ + 18\text{-crown-6} = [\text{Na}(18\text{-crown-6})(\text{PY})]^+ + (p - 1)\text{PY}.  \quad (6)$$

It is well-known that the $^{23}\text{Na}$ chemical shift of the fully solvated sodium ion increases with increasing electron pair-donating ability of the solvent except for water [6]. On the other hand, as seen in Table III, the $^{23}\text{Na}$ chemical shifts of $[\text{Na}(18\text{-crown-6})]^+$ solutions fall in a narrow range ($-12$ to $-15$ ppm) compared with the solvated ion, suggesting that the sodium ion is accommodated in the cavity of 18-crown-6. In NM with its very poor electron pair-donating ability it is reasonably expected that no solvent molecule coordinates to the sodium ion within $[\text{Na}(18\text{-crown-6})]^+$. The $^{23}\text{Na}$ NMR resonance appears at $-15$ ppm in NM. The $[\text{Na}(18\text{-crown-6})]^+$ complex in PC is not solvated because the $^{23}\text{Na}$ chemical shift is practically the same as that in NM. The $^{23}\text{Na}$ NMR signal shifts downfield in PY, DMF, water, and AN. In water the sodium ion is coordinated with an additional water molecule and the 18-crown-6 complex is described as $[\text{Na}(18\text{-crown-6})(\text{H}_2\text{O})]^+$. The downfield shift relative to NM and PC is thus ascribed to the increased coordination number of the sodium ion within $[\text{Na}(18\text{-crown-6})]^+$ in PY, DMF, water, and AN, i.e., the sodium ion is coordinated with an additional solvent molecule. The different thermodynamic behavior in PY and DMF is not explainable according to the reactions (6) and (7).

The enthalpies of transfer of the sodium ion from water to PY and DMF are $-30.3$ and $-32.4$ kJ mol$^{-1}$, respectively [14, 24]. The sodium ion is not stabilized in the transfer process from DMF to PY, despite the stronger electron pair-donating ability of PY as compared to DMF. This strongly suggests that the sodium ion has a different solvation number in PY and DMF, i.e., the sodium ion has a smaller solvation number in PY than in DMF. The $[\text{Na}(18\text{-crown-6})]^+$ complex is coordinated with an additional solvent molecule in both PY and DMF, and the reduced number of solvent molecules is then removed from the first coordination sphere of the sodium ion in PY upon complexation. Thus, the more negative enthalpy and entropy values for the formation of $[\text{Na}(18\text{-crown-6})]^+$ in PY than in DMF is explainable according to the following reactions:

$$[\text{Na(DMF)}]^+ + 18\text{-crown-6} = [\text{Na}(18\text{-crown-6})(\text{DMF})]^+ + (p - 1)\text{DMF},$$

$$[\text{Na(PY)}]^+ + 18\text{-crown-6} = [\text{Na}(18\text{-crown-6})(\text{PY})]^+ + (q - 1)\text{PY},$$

where $p > q$. The decreased coordination number of the sodium ion contributes to the more enhanced formation of $[\text{Na}(18\text{-crown-6})]^+$ in PY than in DMF.

   b) A. I. Popov, Pure Appl. Chem. 41, 275 (1975).