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Complexation of inorganic anions by β-cyclodextrin studied by polarography and ^{1}H NMR

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Complexation of o-chloronitrobenzene with β-cyclodextrin has been studied in 0.1 M aqueous solutions containing PF_6^-, ClO_4^-, $C_2O_4^{2-}$, SCN^-, SO_4^{2-} and F^- anions by a polarographic method. Using an equation which takes account of the change in the cyclodextrin concentration due to the simultaneous complexation of the anion, both stability constants have been calculated. Interaction of the ClO_4^- anion with β-cyclodextrin has been confirmed by ^{1}H NMR techniques. It has been found that the ClO_4^- anion is trapped in the β-cyclodextrin cavity. The stability constant has been calculated. Results of polarographic and ^{1}H NMR studies have been compared.

INTRODUCTION

In the literature one observes a continuous interest in the study of the complexation of inorganic anions and cations by cyclodextrins (CDs). It has been found that the presence of inorganic salts can affect the complexation of other guest molecules by CDs as well as influence the solubility of CDs and their inclusion complexes.[1] These observations are often important in connection with the practical applications of CDs.

Among several methods so far available for the determination of the stability constants of various electrolytes with α and β-CDs the spectrophotometric, potentiometric, conductometric and calorimetric techniques have been the most popular. The literature data[2–13] on the stability constants are collected in Table 1.

It is generally accepted that the role of anions is predominant in the interactions with CDs, however the binding of cations has been also taken into account. β-CD binds anions roughly as well as does α-CD, and generally in the same order of stability. The most strongly complexed is the ClO_4^- anion. Increase in the ring size does not seem to affect the nature of the anionic complexation although the ring size does play a significant role in the binding of organic molecules. The numerical values of stability constants show however in many cases significant differences.

In our previous paper[14] we applied a polarographic method for the determination of the stability constants of inclusion complexes of electroactive guests with CDs based on the determination of the diffusion coefficients

Table 1 Stability constants of inorganic salts and anions with α and β-cyclodextrins at 25°C

	Stability constant (M^{-1})	
Salt	*α-CD*	*β-CD*
NaCl	3[2]0[4]	0[8]2.56[3]
NaBr	—	6.3[3]
NaJ	—	18[3]3.9[5]
KCl	5[2]	0[8]
KBr	3.5[4]	1.1[8]
KJ	12.4[4]13.2[5]13.5[9]	6.5[3]3.9[5]1.45[9]
HNO_3	11[2]	—
$NaNO_3$	4[2]	0.2[8]5.5[3]
KNO_3	1.4[4]	0.7[8]
$HClO_4$	60[2]39.8[6]	—
$LiClO_4$	22[2]	10.9[8]
$NaClO_4$	35[2]20.4[6]30.6[5]	9[8]26.7[3]24.5[5]
$KClO_4$	48[2]28.9[4]37[7]	—
$(CH_3)_4NClO_4$	8[2]	—
anilinium ClO_4	31.6[6]	—
CH_3COONa	0[4]	
Na_2SO_4	0[4]	<1[8]
KSCN	18.7[4]22.8[5]	5.7[8]9.9[4]4.5[5]
KIO_3	0.91[12]	0.98[12]
ClO_4^-	29.8[11]45.8[12]51 ± 8[12]	9.2[12]20[13]
Cl^-	≪1[10]	1.25[13]
Br^-	1[10]0.87[12]	0.36[12]1.66[13]
J^-	15[10]19[12]32 ± 12[12]	2.82[12]6.25[13]
SCN^-	34.6[12]41 ± 10[12]	3.88[12]11[13]
NO_3^-	2[10]1.96[12]	0.80[12]3.33[13]
SO_4^{-2}	1[10]	—

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of the free substrate, and in the presence of increasing concentrations of CD. We derived also an equation [15] which enabled us to calculate both stability constants – with the electroactive guest and with the second, non-electroactive guest e.g. solvent,[16] respectively.

The aim of the present paper is to apply the polarographic method for study the influence of electrolytes, commonly used in electrochemistry, on the complexation of o-chloronitrobenzene (o-ClNB), and (using an equation derived by our group) to calculate both stability constants – that of the electroactive guest and that of the inorganic anion with β-CD.

Complexation of inorganic salts, which are used as supporting electrolytes in the electrochemical studies of CDs and their inclusion complexes, may significantly influence the results obtained. The above aspect was not taken into account in the majority of papers concerning this subject.

The second goal of this contribution is to prove that inorganic anions are included into the interior of β-CD. Therefore, measurements by ^{1}H NMR techniques were carried out.

RESULTS

Electroreduction of o-ClNB at the Hg electrode from aqueous solutions of $LiClO_4$, $NaClO_4$, NaF, KPF_6, KSCN, $K_2C_2O_4$ and Na_2SO_4 in the absence and in the presence of increasing concentrations of β-CD was studied polarographically. The diffusion coefficients, D_f, of o-ClNB and the observed diffusion coefficients, D_{obs}, in the presence of increasing concentrations of β-CD were determined from the polarographic limiting instantaneous diffusion currents using the Ilkovic equation corrected for spherical diffusion by the method of Koutecky.[17] The changes in D_{obs} vs. β-CD concentration for o-ClNB in 0.1 M solutions of the salts studied are shown in Fig. 1. Each curve represents the average data obtained from three independent measurements. The changes in D_{obs} in 0.1 M $LiClO_4$ and $KClO_4$ solutions were within the limit of experimental error the same as the changes observed in 0.1 M $NaClO_4$ solution.

The method by which the stability constants, K_s, were calculated has been described by Osa et al.[18] and by our group[14] previously. When there is one guest in solution, and a complex of 1:1 stoichiometry is formed, as it has been assumed for the complex of o-ClNB with β-CD on the basis of the data of Harata[19] for other disubstituted benzenes, the values of K_s and the diffusion coefficient of the complex of electroactive guest with CD, D_c, can be calculated by a linear regression analysis using equation (1)

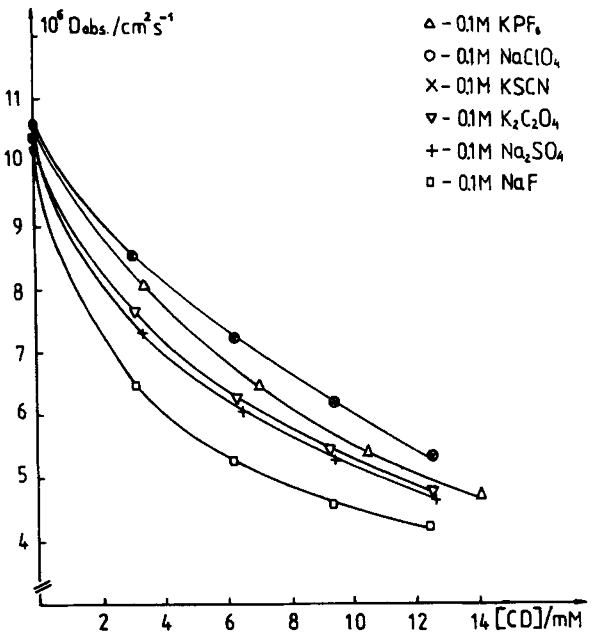

Figure 1 Changes in the observed diffusion coefficients D_{obs} of o-ClNB in 0.1 M solutions of KPF_6, $NaClO_4$, KSCN, $K_2C_2O_4$, Na_2SO_4, and NaF *vs.* β-CD concentration.

$$D_{obs} = \frac{D_f - D_{obs}}{K_s c_{CD}} + D_c \tag{1}$$

where C_{CD} is the concentration of free CD equal to its analytical concentration.

The values of K_s, D_c and D_f can also be calculated by non-linear regression analysis using equation (2)

$$D_i^{calc} = \frac{D_f^* + D_c^* K_s^* c_{CD}^*}{1 + K_s^* c_{CD}^*} \tag{2}$$

where K_s^*, D_c^* and D_f^* are the assumed values.

In the case of independent complexation of two guests one of which is in much lower concentration than the second, both stability constants can be calculated using equation (3)

$$D_{obs} = \frac{K_s^{(1)}\{(D_f + D_c)[1 + K_s^{(2)}(c_2 - c_{CD})] + 2D_c K_s^{(1)} c_{CD} + (D_f - D_c) \times \sqrt{(1 + c_{CD}K_s^{(2)})^2 + c_2 K_s^{(2)}[2 + K_s^{(2)}(c_2 - 2c_{CD})]}\} - 2D_f K_s^{(2)}}{2[(c_{CD}K_s^{(1)} + 1)(K_s^{(1)} - K_s^{(2)}) + K_s^{(1)}K_s^{(2)}c_2]} \tag{3}$$

where C_2 and C_{CD} are the analytical concentrations of guest 2, and CD, respectively, D_f and D_c are the diffusion coefficients of free guest 1 and of the complex of guest 1 with CD, respectively, and $K_s^{(1)}$ and $K_s^{(2)}$ denote the stability constants of guest 1 and guest 2 with CD, respectively.

Stability constants of o-ClNB with β-CD calculated from data obtained in 0.1 M solutions of the electrolytes studied using equation (2) and equation (3) are reported in Table 2. The accuracy of the $K_s^{(1)}$ determination is 10%. The calculated value of D_c for o-ClNB with β-CD was $2.5 \pm 0.5 \times 10^{-6}\,cm^2\,s^{-1}$.

Table 2 Stability constants of o-ClNB with β-CD calculated using Equation (2)[a] and Equation (3)[b]

Electrolyte (0.1M)	$K_s^{(1)}(M^{-1})^a$	$K_s^{(1)}(M^{-1})^b$
KPF_6	115	230
$NaClO_4$	120	220
KSCN	170	220
$K_2C_2O_4$	190	230
Na_2SO_4	215	215
phosphate buffer	227[14]	240
NaF	240	320

Table 3 Stability constants of inorganic anions with β-CD

Anion	$K_s^{(2)}(M^{-1})$ a	b
PF_6^-	8.5	
ClO_4^-	9.0	11
SCN^-	9.0	
$C_2O_4^{2-}$	2.0	
phosphate buffer	2.0	
SO_4^{2-}	~1.0	~0
F^-	~0	

[a] Calculated from polarographic data obtained in 0.1 M sodium or potassium salt solutions using equation (3).

[b] Calculated from NMR data using adopted equation (2).

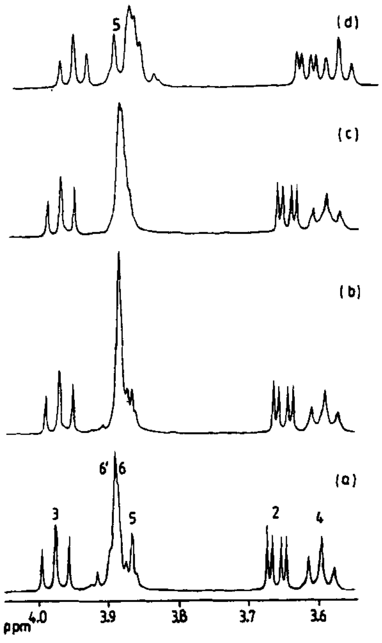

Figure 2 Partial ^1H NMR spectra (500 MHz, 35°C, D_2O) of 0.0078 M β-CD in the absence (a) and in the presence of 0.01 M $NaClO_4$ (b), 0.02 M $NaClO_4$ (c) and 0.1 M $NaClO_4$ (d).

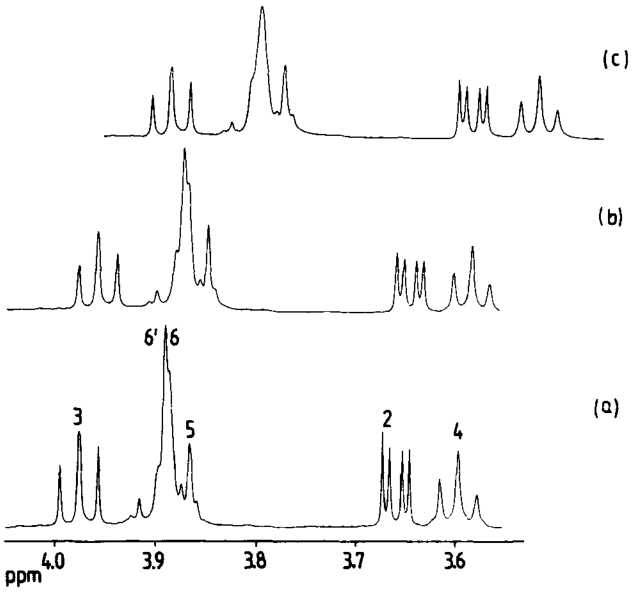

Figure 3 Partial ^1H NMR spectra (500 MHz, 35°C, D_2O) of 0.0078 M β-CD in the absence (a) and in the presence of 0.1 M Na_2SO_4 (b) and 0.5 M Na_2SO_4 (c).

Stability constants of inorganic anions with β-CD calculated using equation (3) from data measured in 0.1 M solutions are collected in Table 3. The accuracy of the $K_s^{(2)}$ determination is 20% for the higher values with relative decreases for lower values.

The 500 MHz ^1H NMR spectra of β-CD and mixture of 0.0078M β-CD with increasing concentrations of $NaClO_4$ in D_2O at pD 7 are shown in Fig. 2. The corresponding spectra for β-CD solution containing various concentrations of Na_2SO_4 are shown in Fig. 3.

DISCUSSION

The results presented show that the most strongly complexed anions by β-CD are PF_6^-, ClO_4^-, and SCN^-. Complexation of $C_2O_4^{2-}$, SO_4^{2-}, phosphate buffer and F^- anion is much weaker. The numerical values of K_s for the PF_6^-, ClO_4^- and SCN^- anions are similar. The K_s value for the ClO_4^- anion is in good agreement with the value reported by Buvari and Barcza,[8] and the K_s value for the SCN^- anion with that reported by Wojcik and Rohrbach.[4] In view of the rather small, but not negligible, value of K_s for the $C_2O_4^{2-}$ anion obtained in our experiments the very high value reported for that anion in the literature[20] seems to be unreliable.

The role of the alkali counter cations seems to be not important in the complexation process because in spite of different cations being used the magnitudes of K_s for ClO_4^- anion complexation were similar. This result is in good agreement with the generally accepted view that the role of anions is predominant in the interactions with CDs.

Comparing the values of stability constants for various anions, one finds that the order of stability is connected with the structure breaking properties of anions, and is related to their position in the lyotropic or Hofmeister series: $PO_4^{3-} > SO_4^{2-} > F^- > Cl^- > Br^- > J^- > SCN^- > ClO_4^- > PF_6^-$. On the left-hand side there are strongly hydrated multivalent anions with a high charge density on the ion surface responsible for the strong ion-dipole interactions. On the right-hand side one finds large weakly hydrated monovalent anions with lower charge density. Low charge density on large monovalent anions may lead to an additional binding force (London dispersion interactions). The fact that the order of stability parallels the structure breaking properties of anions was underlined by Rohrbach et al.[3,4]

On the basis of existing data one cannot unambiguously decide whether the inorganic anions form real inclusion complexes or are attached to the CD from the outside by hydrogen bonds. Especially, in the case of ClO_4^- anions the formation of a straddle-type complex has been suggested.[3]

More direct insight into the anion complexation may be obtained from the ^1H NMR spectra. From the data presented in Figs. 2 and 3 one may read out directly the chemical shifts (δ) and coupling constants (J) of signals ascribed to protons from H(2) to H(4). Because of the severely overlapped spectra at 3.9 ppm the chemical shifts and coupling constants of the signals of protons H(5), H(6) and H(6′) were obtained by simulation. In this manner we obtained δ values sufficiently accurate for further discussion of the host-guest complexation. The values of δ and J for pure β-CD and in the presence of the highest concentrations of the salts studied are presented in Table 4. Similar simulations have been also carried out for other salt concentrations studied.

The chemical shifts of protons of β-CD as a function of salt concentrations are shown in Figs. 4 and 5 for

Table 4 ^1H NMR chemical shift, δ(ppm), and coupling constants, J_{HH}(Hz), of β-CD before and after mixing with salt[a]

	β-CD 0.078 M	*β-CD 0.0078 M + NaClO₄ 0.1 M*	*β-CD 0.0075 M + Na₂SO₄ 0.5 M*
δ H(1)	5.080_9	5.054_8	5.001_7
δ H(2)	3.659_4	3.628_8	3.581_6
δ H(3)	3.975_8	3.801_6	3.883_3
δ H(4)	3.596_0	3.582_8	3.515_2
δ H(5)	3.877_5	3.896_7	3.780_8
δ H(6)	3.883_5	3.860_7	3.786_8
δ H(6′)	3.901_5	3.890_7	3.804_8
$^3J_{12}$	3.8	3.7	3.8
$^3J_{23}$	10.0	9.9	10.0
$^3J_{34}$	9.5	9.4	9.5
$^3J_{45}$	9.1	9.3	9.1
$^3J_{56}$	2.5	2.5	2.5
$^3J_{56'}$	3.8	3.8	3.8
$^2J_{66'}$	−12.0	−12.0	−12.0

[a] In D_2O at pD 7 and T = 35°C, external TSP.

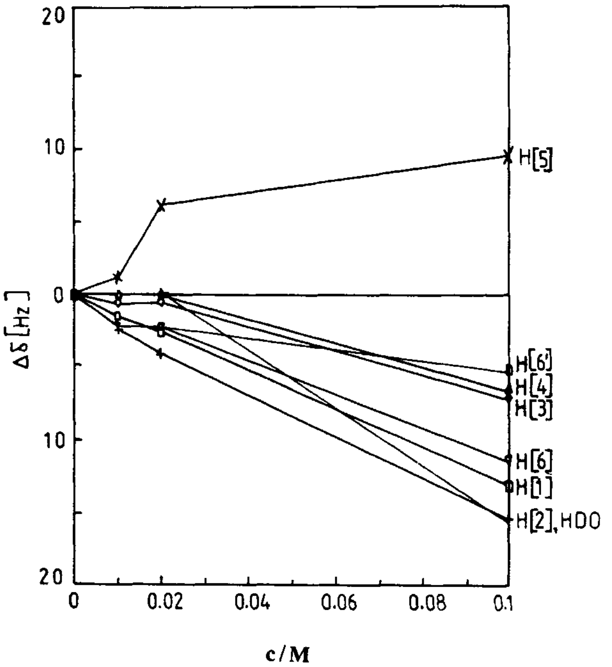

Figure 4 Changes of chemical shifts of protons of β-CD as a function of $NaClO_4$ concentration (external TSP as a standard).

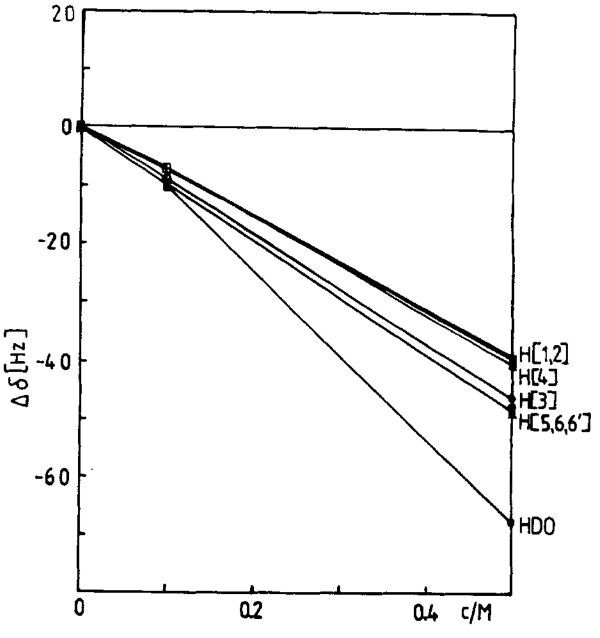

Figure 5 Changes of chemical shifts of protons of β-CD as a function of Na_2SO_4 concentration (external TSP as a standard).

$NaClO_4$ and Na_2SO_4, respectively. One can observe that the increasing concentration of Na_2SO_4 causes an upfield shift of the signals of all protons (ca. 35 to 45 Hz). The relative differences of the chemical shifts of the signals remain below 10 Hz. Particularly, the highly coupled region [H(5), H(6), H(6')] at 3.9 ppm remains unaffected even at the highest concentration of Na_2SO_4. However, the picture observed at increasing concentrations of $NaClO_4$ is different. The region of the spectra around 3.9 ppm now exhibits significant changes with increasing salt concentration. One observes a downfield shift (ca. 10 Hz) arising from proton H(5), whereas the chemical shifts of the other protons drift upfield similarly as in Na_2SO_4.

The above-presented chemical shifts were measured relative to an external TSP. In order to substract the effect caused by changes in bulk susceptibility of solution an internal reference system is needed. One can consider analyzing changes in chemical shifts with respect to changes the in chemical shift of the water (HDO) signal. However, in the latter case the chemical shift is also due to the changes in hydrogen bonding. Therefore, we estimated the changes in chemical shift of each proton relative to the shift of the H(1) proton in pure β-CD, assuming that the complexation has a minimal influence on the shielding of outer surface hydrogens. Such a procedure has been used in the literature.[21]

In Figs. 6 and 7 the Δδ values are plotted for protons of β-CD as a function of molar concentration of $NaClO_4$ and Na_2SO_4, respectively. It is seen that in the presence of Na_2SO_4 (Fig. 7) the values of Δδ for all protons change no more than 0.015 ppm over the entire range of concentrations studied. This means that in this case the chemical shifts presented in Fig. 5 are mainly due to the changes in the bulk susceptibility of the solution. In the presence of $NaClO_4$ (Fig 6) the Δδ values for all protons except H(5) also do not exceed 0.015 ppm. However, the Δδ for H(5) amounts to 0.045 ppm.

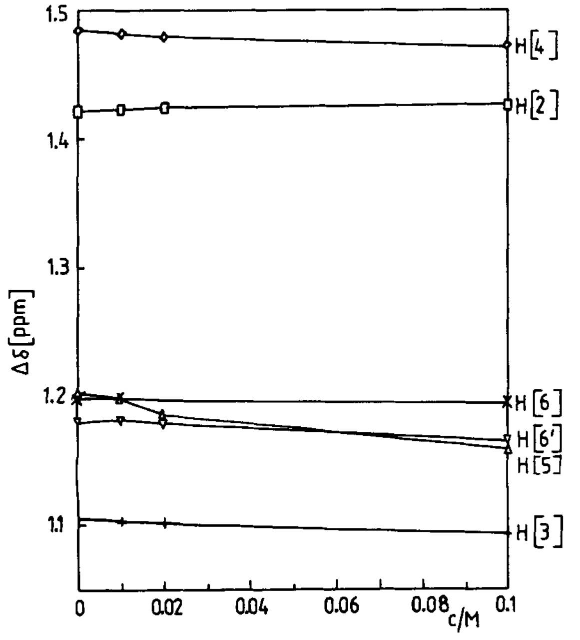

Figure 6 Changes in relative chemical shifts of protons of β-CD as a function of $NaClO_4$ concentration (δ of H(1) as a standard).

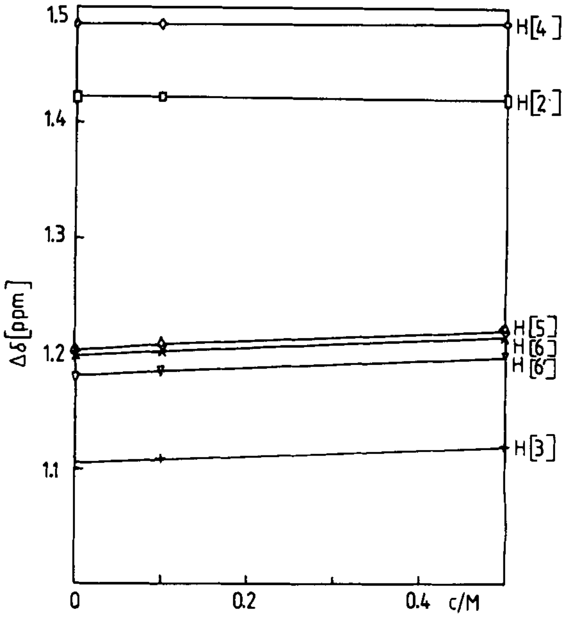

Figure 7 Changes in relative chemical shifts of protons of β-CD as a function of Na_2SO_4 concentration (δ of H(1) as a standard).

Since proton H(5) is located on the inner surface of β-CD its chemical shift is most likely to be influenced by the guest trapped in the cavity as it has been discussed for the case of complexation of various organic molecules by CDs.[21-23]

The magnitude of the observed effect is much smaller than that observed for aromatic molecules but it suggests that the nature of the interactions between the ClO_4^- anion and the β-CD molecule is similar to that found for typical host-guest systems and that an inclusion complex might be formed in the case under study. We realize that our analysis is qualitative but to our knowledge it is the first direct observation of interaction of inorganic anion with the interior of CD utilizing ^1H NMR spectra.

Simulations of the spectra allowed assignment of the particular shifts to protons H(6) and H(6'). We ascribed the upfield signal to H(6), and downfield one to H(6'), respectively (Table 4). In addition, the coupling constants used in that simulation allowed the calculation of the population of particular rotamers on the C(5)–C(6) bond (Fig 8, Table 5). We found that the mostly populated is rotamer gg, which

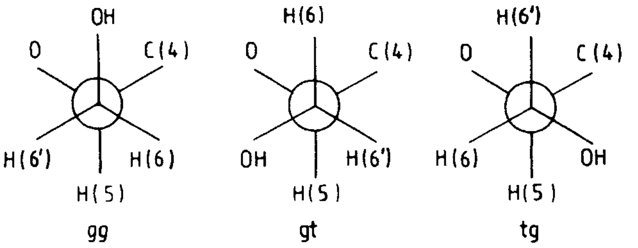

Figure 8 Possible rotamers on the C(5)–C(6) bond of β-CD.

Table 5 Relative populations of rotamers on C(5)–C(6) bond of β-CD in complex with the ClO_4^- anion

observed coupling constant	*rotamer*	*calculated population*[a]
$^3J_{H(5)H(6)}$ 2.5 Hz	gg	0.77
	gt	0.12
$^3J_{H(5)H(6')}$ 3.8 Hz	tg	0.11

[a] Calculated using following equations[24–25]:
$0.90\ P_{gg} + 10.68\ P_{tg} + 5.01\ P_{gt} = J_{56}$
$2.84\ P_{gg} + 3.07\ P_{tg} + 10.68\ P_{gt} = J_{56'}$
$P_{gg} + P_{tg} + P_{gt} = 1$

is in agreement with literature results.[22] In the calculation of populations we have used values obtained using Altona program.[24,25]

On the basis of the $\Delta\delta$ values for H(5) in the presence of $NaClO_4$ the value of the K_s for the complexation of the ClO_4^- anion with β-CD has been estimated using an equation similar to equation (2) in which D_f was replaced with the chemical shift of H(5) of β-CD without salt added, calculated D_i was compared with the actual chemical shift of that proton, c_{CD} was replaced with the salt concentration, and the chemical shift of H(5) in the anion-β-CD complex was fitted instead of D_c. The calculations yielded $K_s = 11$ (Table 3) which is in excellent agreement with the value obtained from polarographic data.

The influence of salts on the complexation of various aromatic guests has been discussed in the literature.[3,8,11,13,14] Most of the authors claimed that the values of K_s for aromatic guests with CDs decreased with the addition of anions undergoing complexation (particularly the ClO_4^- anion). This was mainly ascribed to the competition of those anions with the aromatic guest for the cyclodextrin binding site. On the other hand, in the presence of non-complexed anions (especially the SO_4^{-2} anion) the values of K_s for aromatic guests increased which was mainly attributed to the increase in hydrophobic interactions connected with the change in water activity. Only Rohrbach et al.[3] found that the K_s value for 4-nitrophenyloazo-2'-hydroxy-6'-sulfononaphtalene with β-CD measured in the presence of added electrolyte (0.1 M Na_2SO_4) and in its absence was the same within experimental error.

Our calculations using equation (2) presented in Table 2 showed a decrease in the K_s value for o-ClNB in the presence of strongly complexed anions and a lack of the influence of weakly complexed anions. However, calculations using equation (3) which was derived taking into account independent complexation of two guests by CD showed that the kind of anion has no influence on the K_s value of o-ClNB (Table 2).

On the basis of these results we can conclude that the decrease of the K_s of o-ClNB complex with β-CD in the presence of complexed anions was due to the fact that the change in the concentration of free CD connected with complexation of these anions was not taken into account. A similar effect has been observed by our group[16] in the case of complexation of ClNB with β-CD in the presence of organic solvents which are also complexed by β-CD. Therefore, we think that our results have general significance.

METHODS AND MATERIALS

The reduction of o-ClNB at the Hg electrode from aqueous solutions of commonly used inorganic salts in the absence and in the presence of increasing concentrations of β-CD was studied by a polarographic method. All experiments were carried out in a three-electrode system at 25 ± 0.5°C. The counter electrode was a Pt cylinder. A 1 M NaCl aqueous calomel electrode (NCE) was used as the reference electrode. It was connected to the electrode cell via an intermediate vessel filled with the solution under investigation. Solutions were deaerated by flushing with pure and dried argon presaturated with the solution under investigation. Since ClNB is very volatile, the time of deaeration was strongly controlled and two wash bottles with the solution under investigation were placed upstream of the measuring cell itself.

The polarographic curves were recorded using a measuring system constructed from an EP-20A potentiostat, an EG-20 function generator (both produced by ELPAN, Poland) and an XY/t- 102 recorder (ZDEMP, Poland).

The 500 MHz ^1H NMR spectra of β-CD in D_2O solutions in the absence and in the presence of added guest (salt) were recorded on a Bruker AM 500 spectrometer at 35°C. The temperature was controlled within 0.1°C using a BVT-1000 temperature control unit. Spectra were acquired using 90° flip angle pulses and 32K data points to achieve a digital resolution of 0.3 Hz (or 0.0006 ppm) per point. No internal ^1H NMR reference was added since the possibility of reference binding to β-CD could not be excluded. An external TSP (in D_2O) sample was used instead.

β-CD (Chinoin, Hungary) was used as received. Thermogravimetric analysis showed that it contained 11 wt.% H_2O. The concentration of o-ClNB in all polarographic experiments was 1.25×10^{-4} M. The concentration of CD was always in great excess to that of the electroactive substrate, in order that the complexation reaction remained at equilibrium everywhere in the diffusion layer, and the adsorption of CD had no effect on the recorded currents. The o-ClNB as well as all salts used in the experiments were p.a. grade reagents (POCh, Poland). TSP was p.a. grade reagent (Merck). Triply distilled H_2O was used for preparation of the solutions.

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