Thermochimica Acta, 233 (1994) 205–210
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01469-J

Influence of inorganic ions on the enthalpies of solution of β-cyclodextrin in aqueous solutions

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(Received 9 May 1993; accepted 8 July 1993)

Abstract

The enthalpies of solution of anhydrous β-cyclodextrin in aqueous solutions containing Cl^-, NO_3^-, ClO_4^-, Na^+, K^+ ions of varying activity have been measured by a calorimetric method. The exothermicity of the solution process increases with increasing salt concentration in the order $KCl < NaClO_4 < KNO_3 \approx NaNO_3$: K^+ and Na^+ ions influence the ΔH_{sol} values in a similar way. The effects contributing to the ΔH_{sol} values are discussed.

INTRODUCTION

The increasing importance of cyclodextrins and their complexes in biochemistry and in the food and drug industries has stimulated intensive studies on this class of compounds. However, little experimental work has been done on the effect of inorganic ions on the thermodynamic characteristics of the solutions of cyclodextrins; moreover, the reported results are controversial [1]. This may be due to the indirect methods of measurements and arbitrary assumptions made for the calculations.

This work reports the effects of Na^+, K^+, NO_3^-, ClO_4^- and Cl^- ions on the enthalpy of solution of β-cyclodextrin (cyclomaltoheptaose) in water, measured by a direct calorimetric method and on the interaction of β-cyclodextrin with picric acid in aqueous solution (solubility method).

EXPERIMENTAL

Materials

β-Cyclodextrin (Chinoin, Budapest, Hungary) was recrystallized from water and dried in an oven at 370 K for 2 days. Picric acid (P.O.Ch. Gliwice, pure for analysis (p.a.)) was used without further purification. Water was distilled twice, just before use.

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TABLE 1

Enthalpies of solution in kJ mol^{-1} of β-cyclodextrin in aqueous solutions of inorganic salts at 298.2 K; final β-cyclodextrin concentration between 6×10^{-4} and 8×10^{-4} mol dm^{-3}; standard deviations do not exceed ±1

$NaClO_4$		$NaNO_3$		KNO_3	
c in mol dm^{-3}	$-\Delta H_{sol}$	c in mol dm^{-3}	$-\Delta H_{sol}$	c in mol dm^{-3}	$-\Delta H_{sol}$
0.0	72.5	0.0	72.5	0.0	72.5
0.09	74.7	0.20	79.5	0.21	79.5
0.20	80.2	0.23	83.7	0.27	82.5
0.75	82.0	0.38	86.2	0.41	87.5
1.02	87.7	0.62	88.1	0.52	90.2
1.57	86.8	0.78	90.3	0.90	91.0
		0.97	90.8	1.16	92.0
		2.11	92.3		

Measurements

The enthalpies of solution, $\Delta H^{\ominus}_{sol}$ of β-cyclodextrin were determined using a "constant-temperature environment" type of calorimeter (120 cm^3 glass vessel; 1 cm^3 Teflon ampoule with a thin glass bottom crushed to start the reaction). The temperature was measured with a 33 kΩ thermistor with a Wheatstone bridge (sensitivity 7×10^{-5} K). Electrical calibration was performed for each experiment. About 0.1 g of cyclodextrin was added to about 120 cm^3 of water or aqueous inorganic salt solution. All calorimetric measurements were repeated at least three times. The $\Delta H^{\ominus}_{sol}$ data listed in Table 1 are the average values. The uncertainty limits were calculated as standard deviations of the mean values. Solubility measurements were performed by the column method [2] at 298.2 K. The concentration of picric acid in the solutions was determined spectrophotometrically using a calibration curve. Electronic spectra were measured on a Perkin-Elmer UV–VIS 323 spectrophotometer in thermostatted (298.2 ± 0.1 K) cells.

RESULTS AND DISCUSSION

Effect of inorganic ions on the enthalpy of solution of β-cyclodextrin in water

The measured enthalpies of solution of β-cyclodextrin in aqueous $NaClO_4$, $NaNO_3$ and KNO_3 solutions are listed in Table 1. The results for

KCl solutions are not shown because their reproducibility was very low ($\pm 5\,\mathrm{kJ\,mol^{-1}}$) which was most probably due to the slow process of dis-solution of β-cyclodextrin in this medium. However even the highest values of $\Delta H^{\ominus}_{\mathrm{sol}}$ measured for KCl salt were much lower than those obtained for solutions of other salts at the same concentrations; they did not exceed $81\,\mathrm{kJ\,mol^{-1}}$, at concentrations of KCl as high as $2\,\mathrm{mol\,dm^{-3}}$. The enthalpies listed in Table 1 can be considered as those corresponding to infinite dilution because the final concentrations of β-cyclodextrin in the solutions were of the order of $10^{-4}\,\mathrm{mol\,dm^{-3}}$.

As shown in Table 1, all the enthalpies of solution are negative, including that for pure water solution. The last value can be compared with the $\Delta H^{\ominus}_{\mathrm{sol}}$ value determined by Danil de Namor et al. [3] ($-75.52\,\mathrm{kJ\,mol^{-1}}$ for anhydrous β-cyclodextrin) and with the value derived from the temperature dependence of the solubility of β-cyclodextrin in water which was reported as equal to $34.7\,\mathrm{kJ\,mol^{-1}}$ or $31\,\mathrm{kJ\,mol^{-1}}$ (recalculated) at 298.2 K [1, 4]. The difference between the last two values and that determined in the present work lies in the fact that our value refers to the process of dissolution of anhydrous β-cyclodextrin, the final solution being an infinitely dilute one, while the results obtained by the solubility method represent the enthalpy of solution of the solid phase in equilibrium with the saturated solution, this phase being $C_{42}H_{70}O_{35}$ (12 ± 0.5) H_2O [5]. From these two sets of data the enthalpy of hydration of β-cyclodextrin

$$C_{42}H_{70}O_{35} + 12H_2O \xrightleftharpoons{\Delta H_{\mathrm{hydr}}} C_{42}H_{70}O_{35} \cdot 12H_2O \qquad \Delta H_{\mathrm{hydr}} = -106\,\mathrm{kJ\,mol^{-1}}$$

can roughly be estimated if we neglect the enthalpy of dilution of the saturated solution to infinite dilution (the appropriate calorimetric measurements of the heat of dilution are unreliable because the process of dissolution near the saturation point is very slow).

Addition of inorganic ions to water increases the exothermicity of the dissolution process (Table 1). There are several hypothetical steps which can constitute the overall process of dissolution: cavity formation, restructuring the solvent and solute–solvent interactions. All of them can be influenced by the presence of inorganic ions. The cavity formation (endoergic process) should be disfavoured by increasing salt concentration because of increasing surface tension, as shown for cyclodextrins by Orstan and Ross [6], making the $\Delta H^{\ominus}_{\mathrm{sol}}$ values less exothermic in electrolyte containing solutions. Thus this step of the dissolution process cannot be the determining one in spite of the bulkiness of the solute, which should make the cavity term important. The effect of the inorganic ions on the two remaining processes, i.e. the solute–solvent interactions and solvent reorganization can be best discussed in terms of the enthalpies of transfer of the solute (β-cyclodextrin) from pure water to the salt-containing aqueous

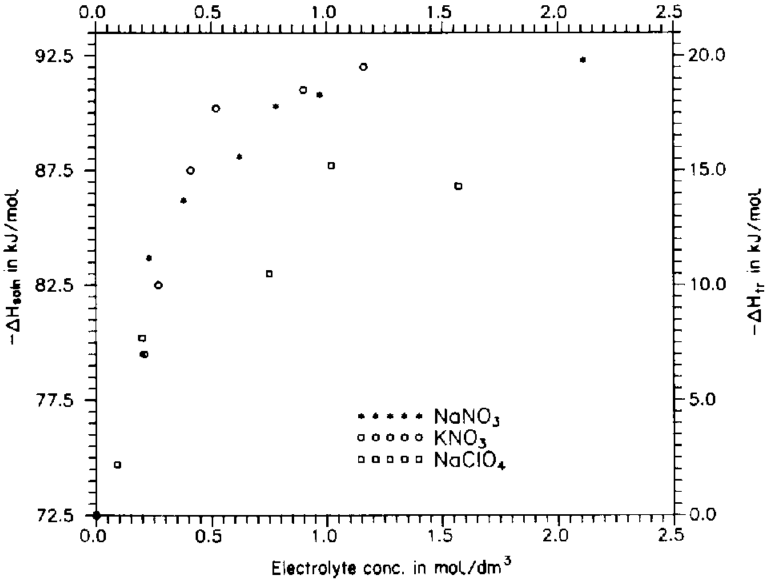

Fig. 1. Dependence of the enthalpy of solution (left) and the enthalpy of transfer from pure water (right) of β-cyclodextrin on electrolyte concentration in aqueous solution.

solutions, ΔH_{tr}, calculated from the measured $\Delta H^{\ominus}_{sol}$ values. Unfortunately they refer to the overall process and cannot be simply divided into the two constituent parts. As can be seen from Fig. 1, ΔH_{tr} decreases (is more negative) in the order $NaNO_3 \approx KNO_3 > NaClO_4 > KCl$. Approximately equal ΔH_{tr} values for KNO_3 and $NaNO_3$ solutions suggest that both the Na^+ and K^+ ions influence the hydration of β-cyclodextrin in a similar way. Thus the observed differences in the overall effect of the salt on the dissolution process should be due to anions.

It is known that while the complexation of the Na^+ cation with cyclodextrin is negligible [1], the anions interact with β-cyclodextrin with the stability constants of 1:1 adducts decreasing in the order $ClO_4^- > NO_3^- > Cl^-$ [9]. This is not the order found for $\Delta H^{\ominus}_{sol}$ in this work because ΔH_{tr} for ClO_4^- is less exothermic than that for NO_3^-. This behaviour may reflect the contribution of the water-restructuring effect, which can be pronounced in the case of a strong structure breaker, the ClO_4^- ion. It was found [7] that the ΔH value for ClO_4^- complexation with α-cyclodextrin (the value for β-cyclodextrin complex was unobtainable because of the errors involved in the indirect method of measurements) was negative and so was the ΔS value. The same can be expected for β-cyclodextrin complex. The release of the ClO_4^- ion from the bulk water in the process of complexation with cyclodextrin should result in increased water structure and rebuilding water–water hydrogen bondings, thus increasing the negative enthalpic effect. This effect should be much stronger for the ClO_4^-

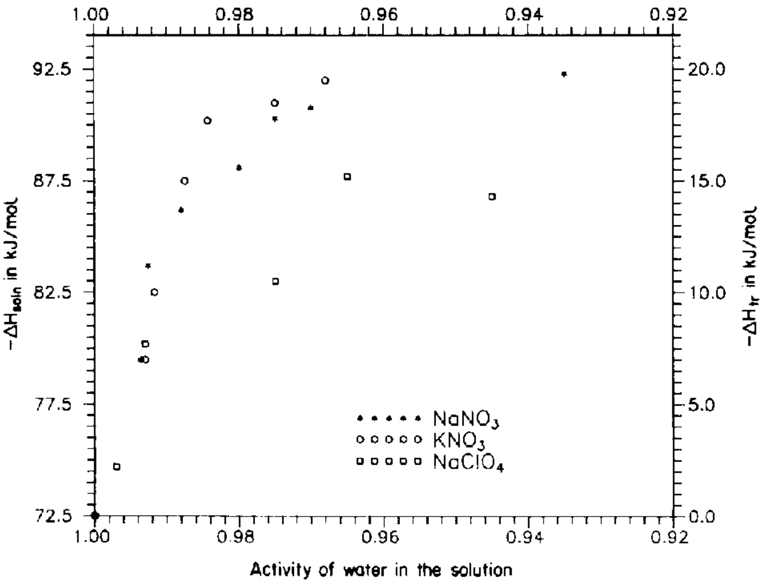

Fig. 2. Dependence of the enthalpy of solution (left) and the enthalpy of transfer from pure water (right) of β-cyclodextrin on water activity in solutions containing inorganic ions.

ion than for NO_3^- and Cl^-. The process of rebuilidng of the water structure is not accounted for in the thermodynamic characteristics of the cyclodextrin–ion interactions. This can be the reason why $\Delta H^{\ominus}_{sol}$ and ΔH_{tr} for ClO_4^- do not follow the order of the stability constants.

We also tried to account for the effect of the structure and activity of water. However the plots of $\Delta H^{\ominus}_{sol}$ values versus water activity a_{H_2O}, in solutions of $NaNO_3$, KNO_3 and $NaClO_4$ salts, calculated from ref. 8, show that activity of water alone does not account for the sequence in the $-\Delta H^{\ominus}_{sol}$ values (Fig. 2), the overall pattern of the $\Delta H^{\ominus}_{sol}$ variation with the type and concentration of the salt being unaltered. Thus the $\Delta H^{\ominus}_{sol}$ values of β-cyclodextrin must be a much more complicated function of water properties in the inorganic ion-containing solutions.

Solubility of picric acid in aqueous solutions containing β-cyclodextrin and $NaClO_4$ or $NaCl$ salts

The data listed in Table 2 show that β-cyclodextrin increases the solubility of picric acid in water. This can be the result of the decrease of the activity coefficient of the picric acid in solution due to its complexation with β-cyclodextrin. Addition of NaCl salt does not appreciably change the solubility, while $NaClO_4$ seems to increase the activity coefficient of the picric acid in the mixed water–cyclodextrin solvent; the competitive ClO_4^-–cyclodextrin interactions can be operative here.

TABLE 2

Solubility s of picric acid in aqueous solutions containing β-cyclodextrin and $NaClO_4$ or NaCl salts at 296.2 K

Picric acid s in mol dm^{-3} [a]	β-Cyclodextrin	c in mol dm^{-3}	
		$NaClO_4$	NaCl
0.053	–	–	–
0.062	Nearly sat. soln.	–	–
0.042	Nearly sat. soln.	0.2	–
0.058	Nearly sat. soln.	–	0.14

[a] Standard deviation ±0.001 M.

ACKNOWLEDGEMENT

This work was carried out with the financial support of the Polish Ministry of National Education, grant number 919087.

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