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VOLUME AND HEAT CAPACITY STUDIES TO EVIDENCE INTERACTIONS BETWEEN CYCLODEXTRINS AND NICOTINIC ACID IN WATER

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Density and heat capacity of the water+cyclodextrin (CD), water+nicotinic acid (NA) and water+CD+NA mixtures were determined at 298.15 K. CDs with different cavity size and alkylation were selected. From the experimental data the apparent molar properties were calculated. Assuming the formation of inclusion complexes of 1:1 stoichiometry, these properties were modeled and provided the stability constants of CD/NA inclusion complexes and the corresponding property change. The binding of NA with the smallest sized α-cyclodextrin (α-CD) generates more stable complexes accompanied by the lower volume and the heat capacity changes. These results are in agreement with earlier proposed binding mode according to which deep insertion of NA into α-CD takes place and it is governed by the hydrophobic–hydrophilic forces. The volume and the heat capacity changes caused by the interactions of CDs with NA were interpreted in terms of cosphere overlap model and the release of water molecules from the CD cavity due to the NA incorporation.

Keywords: *apparent molar heat capacity, apparent molar volume, cyclodextrin, inclusion complex formation, nicotinic acid*

Introduction

The cyclodextrins (CDs) are cyclic oligosaccharides the most common made up of 6, 7 and 8 glucopyranose units, respectively, linked by α-1,4 glycosidic bonds. They are called α-cyclodextrin (α-CD), β-cyclodextrin (β-CD) and γ-cyclodextrin, respectively. These macromolecules have a cone shaped like structure with an external hydrophilic surface and a hydrophobic cavity therefore possessing the features of a micro-heterogeneous environment. Several native CDs have been modified to enhance their solubility in water and all of them present a different volume of the hydrophobic cavity compared to that of the native CDs. These modifications can improve the physico-chemical properties like the stability and/or the control of the chemical activity and the properties of the guest molecule. Theoretical studies [1] have shown that the alkylation or hydroxyalkylation of CD do not introduce a significant steric hindrance but rather the complexing abilities are improved.

A relevant scientific interest towards the CDs family is related to the unique capacity in forming inclusion complexes with different classes of compounds [2–8]. The complex formation of CDs with guest molecules takes place in accordance with the principles of geometric and energetic complementarity and it occurs via noncovalent interactions (hydrogen bonding, van der Waals, electrostatic and hydrophobic interactions, etc.) [2, 9–12]. The well known ability of CDs to form inclusion complexes determines the CDs numerous industrial applications as drug delivery systems and nontoxic encapsulating materials in food, cosmetic and pharmaceutical industries [2, 9–11, 13]. Moreover, in the last years, it has been showing the efficacy of CD in remediating contaminated aquifers and soils [14]. For instance, very recently [15] it was found a linear relationship between the logarithm of the equilibrium constant for the contaminant/CD inclusion complexes formation and the maximum amount of contaminant removed by CD solutions from a solid substrate.

Binding of CDs with biologically active molecules such as some B vitamins was of recent interest [16–19]. To give more light to this issue, an investigation of the complex formation between CDs and NA was planned through the determination of volumes and heat capacities. These thermodynamic functions are sensitive to molecular interactions and can provide information on the role of solute–solute and solute–solvent interactions exercised in the complexation process. It should be also mentioned that the number of papers concerning volumetric and heat capacity studies of binding of CDs with guest mole-

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cules is quite limited in the literature [20–27]. In the present study, the native and the hydroxypropylated α- and β-cyclodextrins were selected to evidence the influence of CD cavity size as well as the hydroxypropyl substituents. The guest chosen is nicotinic acid. The measured properties are volume and heat capacity.

Experimental

Materials

Nicotinic acid (NA), α-cyclodextrin (α-CD) and β-cyclodextrin (β-CD) were provided by Fluka. Hydroxypropyl-α-CD (HP-α-CD) and hydroxypropyl-β-CD (HP-β-CD) are from Aldrich. The chemicals were used without further purification. The modified CDs were randomly substituted and contained 0.6 hydroxypropyl substituents per glucose unit. α-CD, β-CD, HP-α-CD and HP-β-CD presented the water content of 9.5, 12.8, 8.5 and 18.2%, respectively, as determined by thermogravimetry. This quantity was considered in the computation of concentration.

All of the solutions were prepared by mass. For preparation of all solutions, water from reverse osmosis (Elga model Option) with a specific resistivity higher than 1 MΩ cm was used.

Equipment

The densities of solutions were determined by using a vibrating tube flow densimeter (Sodev Mod. 03D) sensitive to 3 ppm or better. The densimeter was calibrated according to a procedure reported elsewhere [24].

The specific heat capacities were determined with a Picker flow microcalorimeter (Setaram) by setting a temperature increment of approximately 0.5 K.

The temperature of both the densimeter and the calorimeter was maintained constant at 298.15 K with a stability of 0.001 K by using closed loop temperature controllers (Model CT-L, Sodev Inc.).

Calculation of the apparent molar properties

The apparent molar volumes of CDs ($V_{\Phi,CD}$; cm^3 mol^{-1}) were calculated from the density data using the relation [28–30]:

$$V_{\Phi,CD} = \frac{M_{CD}}{d} - \frac{10^3 (d - d_0)}{m_{CD} d d_0} \quad (1)$$

where M_{CD} is the molecular mass of CD (g mol^{-1}), m_{CD} is the CD molality (mol kg^{-1}), d and d_0 are the densities of the solvent and the solution, respectively, (g cm^{-3}). Water was the solvent in the binary system whereas the aqueous NA solution was the solvent in the ternary system. The apparent molar volumes of CDs were determined as functions of NA concentration at fixed CD composition (0.005 mol kg^{-1}). It is known [31, 32] that in the considered concentration range nicotinic acid exists as zwitterion in aqueous solution.

The apparent molar heat capacity ($C_{\Phi,NA}$; J mol^{-1} K^{-1}) of NA was calculated as [30, 33]

$$C_{\Phi,NA} = M_{NA} c_p + \frac{10^3 (c_p - c_{p_0})}{m_{NA}} \quad (2)$$

where M_{NA} is the molecular mass of NA, m_{NA} is the NA molality, c_p and c_{p_0} are the specific heat capacities of solution and solvent, respectively, (J g^{-1} K^{-1}). In this case, the solvent was the water+CD mixture. In these experiments, the concentration of NA was kept constant (0.01 mol kg^{-1}) and the CD composition was variable.

Results and discussion

The volumetric study

Figures 1–4 represent the dependences of the apparent molar volumes of CDs ($V_{\Phi,CD}$) on the NA concentration (m_{NA}). The shape of these curves

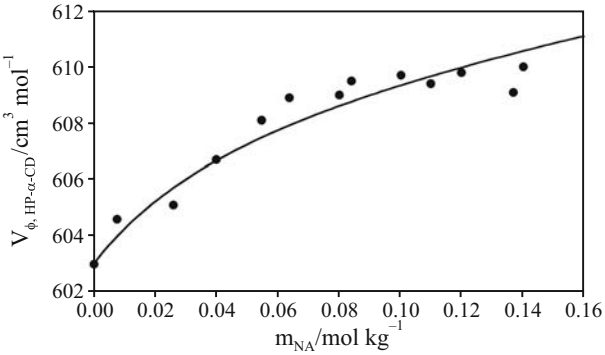

Fig. 1 Apparent molar volume of α-CD as a function of nicotinic acid concentration. Line is the best fit according to Eq. (7)

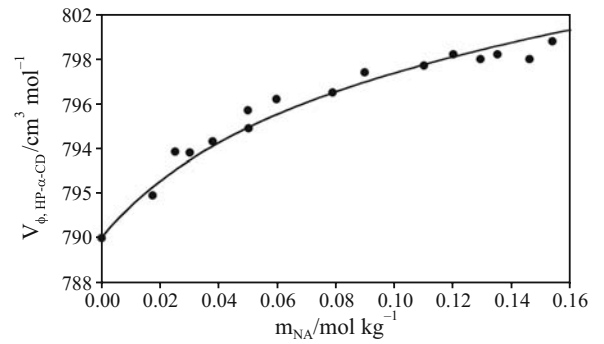

Fig. 2 Apparent molar volume of HP-α-CD as a function of nicotinic acid concentration. Line is the best fit according to Eq. (7)

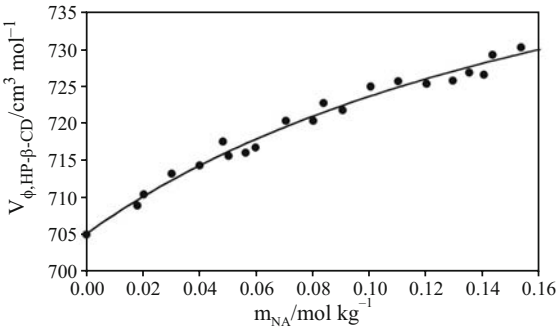

Fig. 3 Apparent molar volume of β-CD as a function of nicotinic acid concentration. Line is the best fit according to Eq. (7)

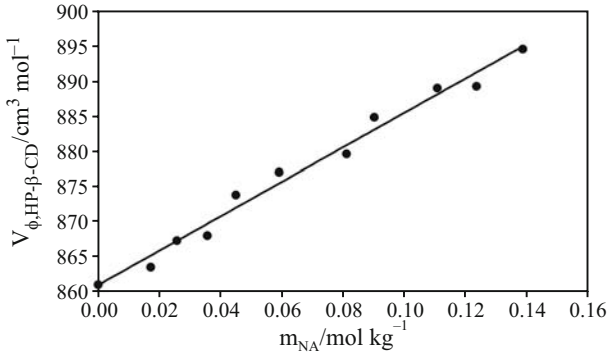

Fig. 4 Apparent molar volume of HP-β-CD as a function of nicotinic acid concentration. Line is drawn for guide of eyes

shows that α-CD, β-CD and HP-α-CD undergo the binding with NA whereas HP-β-CD exhibits a small affinity to NA. Several experimental methods [16, 17] proved that α-CD and HP-α-CD in aqueous solution form with NA inclusion complexes of 1:1 stoichiometry. Consequently, the process of complexation of CDs with NA can be described by the following equilibrium:

$$CD+NA \overset{K}{\longleftrightarrow} CD{\cdot}NA \qquad (3)$$

where K is the equilibrium constant. According to the Young's rule [34] for the 1:1 binding model, $V_{\Phi,CD}$ can be expressed in terms of volumes of all of the species present in the system:

$$V_{\Phi,CD} = (1-\alpha_{cpx})V_{\Phi,free} + \alpha_{cpx}V_{\Phi,cpx} \qquad (4)$$

where $V_{\Phi,free}$ and $V_{\Phi,cpx}$ are the volumes of the free and the complexed CD, respectively; α_{cpx} is the fraction of the complexed CD which can be expressed as:

$$\alpha_{cpx} = \frac{Km_{CD,f}\, m_{NA,f}}{m_{CD}} \qquad (5)$$

$$m_{CD} = m_{CD,f}\,(1+Km_{NA,f}) \qquad (6)$$

where m_{CD} is the stoichiometric CD concentration whereas $m_{CD,f}$ and $m_{NA,f}$ are the concentrations of the CD and the NA in the free state, respectively.

The combination of Eqs (4)–(6) yields:

$$V_{\Phi,CD} = \frac{V_{\Phi,free} + KV_{\Phi,cpx}\, m_{NA,f}}{1+Km_{NA,f}} \qquad (7)$$

By applying Eq. (7) to the data in Figs 1–4 using a nonlinear least-squares fitting method, the $V_{\Phi,free}$, $V_{\Phi,cpx}$ and K parameters were provided; their values are collected in Table 1. A good agreement between $V_{\Phi,free}$ obtained herein and the literature values was observed. Note that from the minimizing procedure no equilibrium constant for the inclusion complexes between HP-β-CD and NA was obtained. Since the $V_{\Phi,CD}$ variation with m_{CD} reveals the presence of interactions between NA and CD, such a result indicates that K is very low to be detectable with this approach.

A careful inspection of data in Table 1 shows that complexes of CDs with NA are characterized by low stability constants, the values of which are close to those obtained from calorimetry [16, 17] and capillary electrophoresis [18]. The stability constants decrease with increasing the CD cavity dimension. Consequently, the size of α-CD cavity is more appropriate for the binding with NA. The partial substitution of hydroxyl groups surrounding the macrocyclic rim with the hydroxypropyl ones does not produce detectable changes in the affinity of the macromolecule to NA suggesting that the interactions between CD and NA basically involve the CD cavity.

The process for the inclusion complex formation generates positive volume ($\Delta V_{\Phi,cpx}=V_{\Phi,cpx}-V_{\Phi,free}$). For the studied CDs, $\Delta V_{\Phi,cpx}$ follows the order:

$$\beta\text{-CD} > \text{HP-}\alpha\text{-CD} \approx \alpha\text{-CD} \qquad (8)$$

Table 1 Thermodynamic properties for the complex formation of cyclodextrins with nicotinic acid at 298.15 K

CDs	$V_{\Phi,free}$/ cm^3 mol^{-1}	$V_{\Phi,cpx}$/ cm^3 mol^{-1}	$\Delta V_{\Phi,cpx}$/ cm^3 mol^{-1}	K/kg mol^{-1}		
				densitometry	calorimetry	CE[a]
α-CD	603, 604[b]	613±1	10	17±5	33±5[c]	32±2[d]
HP-α-CD	790, 791[e]	802±1	12	14±2	23±4[c]	17±1[d]
β-CD	705, 706.4[f]	760±9	55	5±1	nd[g]	nc[h]
HP-β-CD	861, 861[e]	–	–	nc[h]	nc[h]	nc[h]

[a]Capillary electrophoresis, [b]from [22], [c]from [16], [d]from [18], [e]from [26], [f]from [21], [g]not detectable, [h]no complex formation

That is opposite to the order of the equilibrium constant K

$$\alpha\text{-CD} \approx \text{HP-}\alpha\text{-CD} > \beta\text{-CD} \quad (9)$$

The stronger is the inclusion complex stability the smaller is the volume change associated to the inclusion complex formation. The positive $\Delta V_{\Phi,cpx}$ values for α-CD and HP-α-CD are unusual compared to the negative values [16] of the enthalpies of the complex formation. However, these experimental findings can be interpreted by considering that to a given thermodynamic property (volume or enthalpy) contribute several terms in a different way. The $\Delta V_{\Phi,cpx}$ basically contains the following contributions. One deals with the expulsion of water molecules from the CD cavity. Wilson and Verrall [20, 21] as well as Spildo and Høiland [22] pointed out that in the case of the inclusion complex formation the partial or the complete replacement of water molecules located inside the cavity upon penetration of the guest molecule takes place generating a positive volume change. Similarly, the desolvation process of NA molecules upon the inclusion process should be also taken into account. Another contribution is caused by the overlap of hydration cospheres of the solutes during the binding. Based on the model developed by Friedman and Krishnan [35], the overlap of cospheres of polar groups of interacting species induces a volume increase; on the contrary, the overlap of hydrophobic-hydrophobic or hydrophilic-hydrophobic groups produces a volume decrease. Finally, the hydrogen bonds formation causes a negative volume change [36]. Consequently, the sign of $\Delta V_{\Phi,cpx}$ depends on the predominance of a contribution over another.

According to previous findings [16], the inclusion complex formation between NA and α-CD takes place through the inclusion of the charged carboxylic group of NA into macrocyclic cavity; a process which should generate a negative contribution to the volume [35]. The location of the –COOH group inside the CD cavity was also detected for the binding of CDs to benzoic acid and its derivatives [37–39].

Taking into account for the above mentioned contributions, the higher $\Delta V_{\Phi,cpx}$ value obtained for the NA/β-CD system compared to that of NA/α-CD mixture can be explained by invoking the expulsion of larger amount of water molecules from the β-CD cavity. Calorimetric data showed that the interactions between β-CD and NA generate positive enthalpic effects caused by the prevalence of the contribution from the dehydration processes [17]. The endothermicity of binding follows the same order as $\Delta V_{\Phi,cpx}$. The NA/β-CD inclusion complexes are weak and it is likely due to the fact that the β-CD cavity is so large that cannot tightly fit the NA molecule. These arguments are consistent with the previous ^{1}H NMR findings [16, 19].

The heat capacity study

Based on the earlier results, we decided to study the α-CD/NA and HP-α-CD/NA systems which evidenced the stronger interactions for the inclusion complex formation. The difference between $C_{\Phi,NA}$ in water+CD mixture and in water ($\Delta C_{\Phi,NA}$) as a function of the cyclodextrin concentration (m_{CD}) is illustrated in Fig. 5. $\Delta C_{\Phi,NA}$ exhibits positive values in the presence of both CDs and increases with m_{CD}. To a first sight, such a dependence appears peculiar because usually [26, 27] the heat capacity for the complex formation assumes values which are opposite to those of the volume. However, one has to be reminded that the heat capacity is the second derivative of Gibbs energy and consequently compared to the properties first derivatives of Gibbs free energy (volume or enthalpy) it contains the relaxation term for the temperature change. In other words, by assuming that the inclusion complexes of 1:1 stoichiometry are formed, the following equation may be written

$$\Delta C_{\Phi,NA} = \chi_{cpx} \Delta C_{p_{cpx}} + (\delta \chi_{cpx} / \delta T) \Delta H_{cpx} \quad (10)$$

where χ_{cpx} is the fraction of NA in the complexed state; $\Delta C_{p_{cpx}}$ and ΔH_{cpx} are the heat capacity and the enthalpy for the complex formation, respectively. The second term at the right hand side of Eq. (10) is the relaxation contribution of the inclusion complex formation equilibrium induced by the temperature change. Equation (10) was used to simulate the experimental $\Delta C_{\Phi,NA}$ in both α-CD and HP-α-CD by using K obtained from the volume data and the ΔH_{cpx} literature values [16]; to this purpose, some arbitrary $\Delta C_{p_{cpx}}$ values were introduced (Fig. 6). From these calculations one may state that: 1) the $\Delta C_{\Phi,NA}$ positive

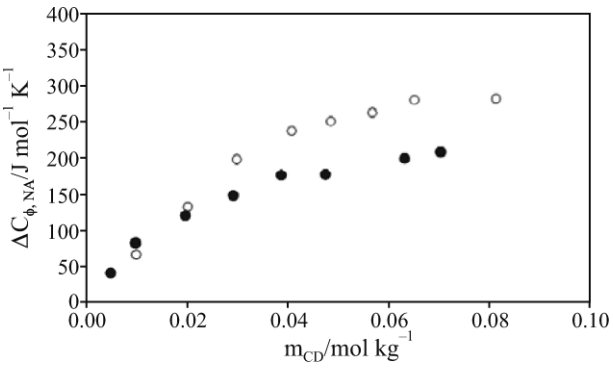

Fig. 5 Dependence on the CD concentration of the excess of the apparent molar heat capacity of nicotinic acid in the ● – water+α-CD and ○ – water+HP-α-CD mixtures with respect to that in water

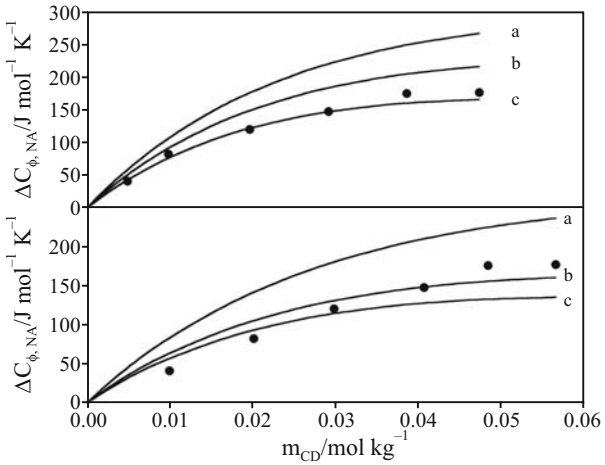

Fig. 6 Excess of the apparent molar heat capacity of nicotinic acid in the water+CD mixture with respect to that in water as a function of CD concentration. Lines are calculated by using Eq. (10): top, α-CD: a – $\Delta C_{p_{cpx}}$=120 J K^{-1} mol^{-1}; b – $\Delta C_{p_{cpx}}$=0 J K^{-1} mol^{-1}; c – $\Delta C_{p_{cpx}}$ = –120 J K^{-1} mol^{-1}; bottom, HP-α-CD: a – $\Delta C_{p_{cpx}}$=120 J K^{-1} mol^{-1}; b – $\Delta C_{p_{cpx}}$ = –60 J K^{-1} mol^{-1}; c – $\Delta C_{p_{cpx}}$ = –120 J K^{-1} mol^{-1}

values are controlled by the relaxation term being negative ΔH_{cpx} and 2) the inclusion complex formation produces the negative $\Delta C_{p_{cpx}}$ value. Moreover, as Fig. 6 shows, the calculated $\Delta C_{\Phi,NA}$ points match reasonably well the experimental data at the $\Delta C_{p_{cpx}}$ values of –120 and –60 J K^{-1} mol^{-1} for α-CD and HP-α-CD, respectively. The sign of this property is consistent with the NA inclusion into the CD cavity. Accordingly, the transferring of a molecule from a polar solvent (like water) to an apolar environment generates a decrease in the heat capacity. Going further, the structural changes occurring in solution during the binding can be explained by applying the cosphere overlap model to the heat capacity data [40–42]. Namely, the $\Delta C_{p_{cpx}}$ values may reflect the positive contribution due to the hydrophilic–hydrophilic interactions and the negative contribution generated by the hydrophobic–hydrophilic and hydrophobic–hydrophobic forces. In the case of the CDs under study, the contributions for the desolvation processes are expected to be comparable. The balance of these forces therefore determines the $\Delta C_{p_{cpx}}$ value.

Conclusions

Thermodynamic properties of the water+CD+NA mixtures were determined at 298.15 K. The effect of the cyclodextrin cavity size and the hydrophobic modifications was analyzed. For all the mixtures investigated, the apparent molar volume of CD monotonically increases with m_{NA}. Unusually, the excess of the apparent molar heat capacity of NA in water+CD with respect to that in water as a function of m_{CD} is an increasing monotonic curve. Assuming the formation of inclusion complexes of 1:1 stoichiometry, these thermodynamic functions were modeled giving the equilibrium constant for the CD/NA inclusion complexes formation and the corresponding property change. As concerns the heat capacity data, they reflected not only the contribution for the 1:1 inclusion complex formation which produces negative heat capacity but also the relaxation term produced by the temperature change which contributes positively to the heat capacity.

The obtained findings showed that α-CD forms complexes more stable than β-CD does. This process is accompanied by positive volume and negative heat capacity variations. These results were interpreted in terms of the model based on the overlap of cospheres of the interacting solutes and the release of water molecules from the CD inner cavity.

The alkylation of the CD, the size of which is kept constant, does not produce relevant changes in the inclusion complex formation and in the case of HP-β-CD no complexes formation is detected. These findings are consistent with the NA penetration into the CD cavity.

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