Thermochimica Acta, 85 (1985) 443–446
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

INTERACTION OF α-CYCLODEXTRIN WITH NON ELECTROLYTES IN WATER AT 298.15 K

G. BARONE, G. CASTRONUOVO, V. ELIA and M. MUSCETTA

Department of Chemistry, University of Naples, via Mezzocannone 4, 80134 Naples (Italy)

ABSTRACT

A calorimetric study is reported on the interaction between hexacycloamylose (α-cyclodextrin) and simple non electrolytes in water. The results show that compounds bearing normal or moderately branched alkyl chains undergo an inclusion process. The mixtures of hexacycloamylose with hydrophilic or highly branched hydrophobic cosolutes can be treated on the basis of McMillan Mayer theory of solutions.

INTRODUCTION

The complexes between cyclodextrins and "guest" molecules constitute a family of inclusion compouns widely studied. However, the hypotheses concerning the nature of the binding forces involved in these interactions are to be partially verified. For these reasons, we are carring on a calorimetric study on the interactions between α-cyclodextrin (hexacycloamylose, α-CD) and simple non electrolytes of different nature (alchols, urea and urea derivatives, sugars etc....). Calorimetric studies in principle can offer the possibility of determining both the enthalpy of "binding" and the equilibrium constant of the inclusion complex, given that the interaction is sufficiently strong and/or a plausible model of the binding is available. Generally the enthalpy data determined by calorimetry are much more reliable than those determined by temperature derivatives of the free energies and activities or of the equilibrium constants measured spectroscopically or by other methods. If, as usually occurs for the cyclodextrines, the stoichiometry of the inclusion compound is very simple, a reliable binding constant can be also determined. Gibbs free energies and entropies then are derived by very simple thermodynamic relations. However, if the interaction is very weak, the information given by calorimetry allow only to describe the solutions in terms of excess enthalpy. In this case the Kauzmann (ref.1) and Friedman (ref.2) extension of the McMillan Mayer theory of solution (ref.3) is more appropriate to get an insight into the weak, non bonding molecular interactions that probably occur in these mixtures.

INCLUSION COMPOUND FORMATION

The binding enthalpy, per mole of α-cyclodextrin $\Delta H(\text{bin})$, can be obtained from the experimental heats of mixing and dilution of binary aqueous solutions of α-CD and the ligand L. The values of $\Delta H(\text{bin})$ are proportional to the amounts of formed complex. Keeping constant the initial cycloamylose conentration [αCD] and assuming a 1:1 stoichiometry the following linear relationships can be deduced (ref.4):

$$1/\Delta H(\text{bin}) = 1/\Delta H(\text{max}) + 1/\Delta H(\text{max})\ K_A\ [L] \qquad (1)$$

and

$$[L] = [L_0] - [\alpha CD]\Delta H(\text{bin})/\Delta H(\text{max}) \qquad (2)$$

where K_A is the association equilibrium constant, $\Delta H(\text{max})$ the saturation value for $\Delta H(\text{bin})$ and $[L_0]$ and $[L]$ the initial and residual concentrations of the ligand. By iterative least square treatment of Eqs. (1) and (2) a convergence value of K_A can be evaluated and then the molar free energy, ΔG_A, enthalpy, ΔH_A, and entropy, ΔS_A. (This procedure is not thermodynamically rigorous, as the activity coefficients are neglected). In table I the values of the parameters found for the interactions between αCD and a series of alkanols at 298.15 K are given. The binding constant increases at increasing alkyl chain length and decreases with the degree of branching. For tert-BuOH the preceding approach cannot be applied and this fact suggests that the cavity of αCD is too small for accommodating this bulky alkyl group. It is also interesting that ΔH_A increases about linearly with the number of aliphatic carbon atoms. The entropic driving force seems to decrease at increasing length and branching of alkyl chains.

WEAK NON BONDING INTERACTIONS

For mixtures of simple non electrolytes in water (or other solvents) the excess enthalpies can be represented by a power expansion series of molalities according to the Friedman notation (ref.2):

$$H^E = h_{xx}m_x^2 + 2h_{xy}m_xm_y + h_{yy}m_y^2 + h_{xxx}m_x^3 + 3h_{xxy}m_x^2m_y + \ldots\ldots \qquad (3)$$

The h coefficients have a statistical mechanical significance, as they are the

TABLE 1
Values of the thermodynamic parameters for the association of some alkanols with hexacycloamilose in water at 298.15 K.

System	K_A 1 mol^{-1}	$-\Delta G_A$ kJ mol^{-1}	$-\Delta H_A$ kJ mol^{-1}	$T\Delta S_A$ kJ mol^{-1}
αCD - EtOH	6.7	4.7	2.5	2.2
αCD - nPrOH	27.0	8.1	6.1	2.0
αCD - nBuOH	99.9	11.4	9.9	1.5
αCD - secBuOH	28.7	8.3	9.0	-0.7
αCD - isoBuOH	21.9	7.6	9.4	-1.8

TABLE 2
Values of the virial enthalpy coefficients and their 95% confidence limits for aqueous solutions of hexacycloamylose and non bonding cosolutes at 298.15 K.

x	y	h_{xx}	h_{yy} J mol^{-2} kg	h_{xy}
αCD	- tertBuOH	-3917(64)	656(33)	2167(104)
αCD	- urea	"	-350(3)	-6872(196)
αCD	- methylurea	"	- 85(2)	-1545(30)
αCD	- D-xylose	"	332(9)	- 246(13)
αCD	- L-xylose	"	336(5)	- 250(10)

enthalpic part of the free energy virial coefficients that are a measure of the interaction between pairs, triplets and higher numbers of solute particles. However they include also the changes in the solute-solvent and solvent-solvent interactions respect to the infinitely dilute standard state (refs.5-9). Often these changes can be more remarkable than the solute-solute interactions.

In Table 2 the coefficients characterizing the aqueous solutions of αCD and tert-BuOH, urea, methylurea and some sugars, respectively, are given. For tert-BuOH the cross coefficient h_{xy} show an unfavorable contribution to the interaction with the αCD. For the polar compounds the favourable contribution is very low and/or attributable to processes different from inclusion and concerning the relative stability of hydration shell of αCD, urea and other solutes.

AKNOWLEGMENTS

This work has been financially supported by the Italian Ministry of Public Instruction and by the National Research Council.

REFERENCES

1 J.J.Kozak, W.S.Knight and W.Kauzmann, J.Chem.Phys., 48 (1968) 675-690
2 H.L.Friedman and C.V. Krishnan, J.Solution Chem., 2 (1973) 119-138
3 W.G.McMillan,jr and J.E.Mayer, J.Chem.Phys., 13 (1945) 276-305
4 M.Eftink and R.Biltonen in A.E.Beezer (Ed.), Biological Microcalorimetry, Academic Press, London, New York (1980) pp. 343-412
5 F.Franks, M.Pedley and D.S.Reid, J.Chem. Soc., Faraday Trans.1, 74 (1976) 359-367
6 G.Barone,P.Cacace,G.Castronuovo and V.Elia, Carbohydr. Res., 91 (1981) 101-11
7 G.Barone,G.Castronuovo, D. Doucas, V. Elia and C.A. Mattia, J. Phys. Chem., 87 (1983) 1931-1937
8 V.Abate,G. Barone, G. Castronuovo, V. Elia and V. Savino, J.Chem.Soc., Faraday Trans.1, 80 (1984) 759-768
9 G. Barone, G. Castronuovo, V. Elia and V. Savino, J. Solution Chem., 13 (1984) 209-219