

A Spectrophotometric Study on the Host - Guest Complexation of β -Cyclodextrin with 3-Indolyl Acetate in Dilute Aqueous Solution by Determining Solubility of Guest Substance

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Abstract: 3-Indolyl acetate can be solubilized in dilute aqueous solution of beta cyclodextrin, due to the formation of host-guest complex through hydrophobic interaction between the indolyl group and the inside cave of the cyclodextrin molecule. The thermodynamic parameters of the complexing process can be estimated utilizing the spectrophotometric data.

Keywords: β -Cyclodextrin; 3 - indolyl acetate; host - guest complex.

Interest in cyclodextrins has increased steadily, because their inclusion compounds have proved more and more useful in both research and industry¹. Furthermore, they are of great importance for supramolecular chemistry, since they are members of a homologous series of water-soluble and chiral host molecules which can be used as models for studying weak interactions¹⁻⁶. On the other hand, indolyl group exists in some important biogenic substances such as tryptophan. So investigation on the interactions between indolyl derivatives and such biologic model substances as cyclodextrins may be of significance. In the present work, we have determined the solubilities of 3-indolyl acetate (3IA) in dilute beta cyclodextrin (β -CD) solution at 298.2, 303.2, 308.2, 313.2, and 318.2 K respectively. The experimental results show that β -cyclodextrin and 3-indolyl acetate form host-guest complex in 1:1 stoichiometry through an enthalpy driven process.

Experimental Procedure

A set of β -CD dilute solutions (the concentration range was 0 - 5.00×10^{-3} M) were prepared by volumetric method, and sealed in bottles with excessive 3IA sample added and were shaken in a thermostatic water bath at a certain temperature (T) until equilibrium. After that, excessive 3IA was removed by centrifugation. Then, the absorbance of the equilibrium aqueous solutions was determined on UV-2401 PC Spectrophotometer (Shimadzu, Japan) at the equilibrium temperature (T) and at the wavelength 384nm. The extinction coefficient of the host-guest complex formed with β -

CD and 3IA, ϵ_{GH} was approximately determined as below: 3.50 mg 3IA sample was accurately weighed with a balance whose accuracy was 0.01 mg. Then, it was dissolved in $100.00 \text{ cm}^3 \times 5 \times 10^{-3} \text{ M}$ β -CD aqueous solution at 303.2 K. The concentration of the complex was approximately regarded as the same as the total concentration of 3IA ($2.00 \times 10^{-4} \text{ M}$). The value of ϵ_{GH} was calculated to be $918 \text{ M}^{-1} \text{ cm}^{-1}$. Additional experiments showed that the influence of temperature on ϵ_{GH} could be neglected. The extinction coefficient of un-complexed 3IA was easily gotten in the following way: Solid β -CD was excessively added into the 3IA saturated aqueous solution, so that the concentration of β -CD reached $5.00 \times 10^{-3} \text{ M}$ (at 303.2K) and most of the 3IA molecules were in complexed state. Then, the absorbances of both the original 3IA saturated solution and the same solution with excessive β -CD added were determined at 384 nm and the ratio, $\epsilon_G / \epsilon_{HG}$ was calculated which is 0.926 and was also regarded as a parameter independent from temperature and any other solute. So we obtained: $\epsilon_G = 850 \text{ M}^{-1} \text{ cm}^{-1}$.

The experimental correlation of the absorbance (Abs) with the original concentration of β -CD was linear at every determining temperature (with our own simulation program, the correlative coefficients were all better than 0.997, please see **Table 1**). As the concentration of β -CD increasing from 0 to $5.00 \times 10^{-3} \text{ M}$, the absorbance increased 2 to 5 times. The facts show that β -CD can enhance the solubility of 3IA in water. According to the viewpoint of literature¹, β -CD and 3IA can form host-guest adduct (or inclusion complex) in aqueous solution, since β -CD molecule has hydrophobic inside cave and 3IA molecule has hydrophobic indolyl double cycle. So the complexing process of 3IA with β -CD in water medium should be an energy releasing one. This point can be supported by the combination of thermodynamic reasoning with the experimental results.

Suppose that the host (β -CD) can form complex with the guest (3IA) and with 1:1 stoichiometry, there are two equilibrium process in the ternary system:



Or an overall process



Table 1. The experienced linear equation of the absorbance (Abs) of the solubilized guest substance (3IA) versus the original concentration of the host substance β -CD (C_H), $\text{Abs} = A \cdot C_H + b$, along with the corresponding correlative coefficient (R).

T/K	298.2	303.2	308.2	313.2	318.2
$a/10^2$	1.71	1.54	1.39	1.25	1.13
b/M^{-1}	0.149	0.196	0.269	0.350	0.456
R	0.999	0.999	0.998	0.997	0.998

Here G and H represent 3IA and β -CD, the subscript, s and aq show solid and aqueous solution phase states respectively, and GH stands for the complex. Because the concentration of G, H, and GH are all quite low, the activity coefficient of every solute is actually equal to one. Therefore, the standard equilibrium constants of the overall process (3) can be written as:

$$K^{\circ}_3 = [GH] / [H] \quad (4)$$

Where [H] and [G] are the uncomplexed concentrations of the host substance (β -CD) and the guest substance (3IA) respectively. The absorbance of the aqueous solution can be deduced from equation (1) - (4):

$$\text{Abs} = \epsilon_G [G] + \epsilon_{GH} C_H K^{\circ}_3 / (1 + K^{\circ}_3) \quad (5)$$

Where $\epsilon_G [G]$ is the absorbance of un-complexed 3IA, and $\epsilon_{GH} C_H K^{\circ}_3 / (1 + K^{\circ}_3)$ is that of the 3IA complexed with β -CD, because $[GH] = C_H K^{\circ}_3 / (1 + K^{\circ}_3)$ can be easily deduced from Equation (3) and $C_H = [H] + [GH]$. Equation (5) shows that the absorbance of the equilibrium aqueous phase is indeed a linear function of the original concentration of β -CD (C_H). So it is most possible that β -CD form 1:1 adduct with 3IA. Now the equilibrium constant of the overall process (3), K°_3 can be gotten from the slope of the experienced equation (5):

$$a = \epsilon_{GH} K^{\circ}_3 / (1 + K^{\circ}_3) \quad (6)$$

Then, equilibrium constants (K°) of the complexing process (1) and (2) can be easily calculated.

Since the experimental temperature range was quite narrow, it would be reasonable to deal with the enthalpy changes of processes (1) - (3) as constants respectively. Now, the thermodynamic parameters can be calculated according to the fundamental thermodynamic equations (Table 2).

Table 2 Thermodynamic parameters of the dissolving process (1), complexing process (2), and overall process (3).

	T/K				
	298.2	303.2	308.2	313.2	318.2
$K^{\circ}_1/10^{-4}$	1.79	2.27	3.15	4.10	5.39
$K^{\circ}_2/10^3$	1.28	0.890	0.565	0.385	0.261
K°_3	0.229	0.202	0.178	0.158	0.141
$\Delta G^{\circ}_1/\text{KJ.Mol}^{-1}$	21.4	21.2	20.7	20.3	19.9
$-\Delta G^{\circ}_2/\text{KJ.Mol}^{-1}$	17.7	17.1	16.2	15.5	14.7
$\Delta G^{\circ}_3/\text{KJ.Mol}^{-1}$	3.65	4.30	4.42	4.80	5.18
$T\Delta S^{\circ}_1/\text{KJ.Mol}^{-1}$	22.7	22.9	23.4	23.8	24.2
$-T\Delta S^{\circ}_2/\text{KJ.Mol}^{-1}$	45.5	46.1	47.0	47.7	48.5
$-T\Delta S^{\circ}_3/\text{KJ.Mol}^{-1}$	22.7	23.1	23.5	23.9	24.3
$\Delta H^{\circ}_1/\text{KJ.Mol}^{-1}$	44.1				
$\Delta H^{\circ}_2/\text{KJ.Mol}^{-1}$	-63.2				
$\Delta H^{\circ}_3/\text{KJ.Mol}^{-1}$	-19.1				

The data in Table 2 shows that the interaction between the β -CD and 3IA is quite strong (the standard enthalpy change of the complexing process is about $-63.2 \text{ KJ}\cdot\text{mol}^{-1}$). The phenomenon is evidently caused by the indolyl group getting into the molecular cave of β -CD. A 5 nm of red shift of the 3IA absorbance peak at 379.5 nm was observed before the concentration of β -CD reaching $2.0 \times 10^{-3} \text{ mol/L}$ (Table 3), which indicates that the multiple C-H bonds inside the CD molecule put some influence on the aromatic double indolyl ring. Earlier report⁵ also proves that indolyl group (of L-tryptophan) can be enveloped in the cave of the CD. The data in Table 2 indicate that the complexing process (2) is exothermic, while the overall process (3) is enthalpy-entropy compensating, which reflects the characteristic of host - guest complexing process⁶.

Table 3 The peak wavelength at the spectra of 3IA saturated aqueous solutions in the presence of different concentrations of β -CD (298.2K).

$C_{\beta\text{-CD}}/10^{-3}\text{mol}\cdot\text{L}^{-1}$	0.0	0.46	1.20	1.69	2.83	4.45
Peak Wavelength/nm	379.5	382.0	383.5	384.5	384.5	384.5

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