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Resonance Rayleigh scattering study of the inclusion complexation of chloramphenicol with β-cyclodextrin

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Abstract

The interaction of chloramphenicol and β-cyclodextrin (β-CD) in aqueous solution was studied using resonance Rayleigh scattering (RRS) technology. The molar ratio of the inclusion complex was 1:1 established by spectrophotometry. The RRS technology was first applied to the determination of the inclusion constant of chloramphenicol to β-CD. The RRS peak of chloramphenicol was at 331 nm. When β-CD interacted with chloramphenicol to form an inclusion complex, the RRS intensity was enhanced and increased with an increase in β-CD concentration. The inclusion constants at different temperatures were measured by the RRS technology. The determination results using the RRS technology corresponded with those of the UV-spectrophotometric method. Therefore, the RRS method can be used as a new technology for the determination of the inclusion constant. The thermodynamic parameters (ΔH, ΔS and ΔG) associated with the inclusion process were also determined. These values indicated that van der waals forces and hydrogen bonding could be considered as a main driving force for the encapsulation of chloramphenicol by β-CD.

Keywords: β-Cyclodextrin; Chloramphenicol; Inclusion constant; Resonance Rayleigh scattering

1. Introduction

Chloramphenicol is a lipophilic antibiotic which efficiently penetrates into tissues to attack parasites living within, and into organs where other antibiotics cannot go. It acts on the protein manufacturing system of bacteria yet does not affect mammalian, reptilian, or avian ribosomes. As a broad-spectrum antibiotic, chloramphenicol was discovered and found to be effective in inhibiting *Eberthella typhosa*, *Dysentery bacillus*, *Escherichia coli*, Infuenza virus and so on [1]. However, chloramphenicol has poor solubility and dissolution rate in aqueous solution, which affects its application in clinical therapy. Many researchers working in the field of molecular recognition processes have focused their studies on a number of therapeutic molecules, whose bioavailability is often affected by problems such as limited solubility or stability etc. Among the different methods proposed to improve the development of drug delivery systems, molecular complexation with cyclodextrins (CDs) has been generally accepted as one of the most efficient.

Cyclodextrins (CDs) are a well-known family of cyclic oligosacharides, which their structure is that of a truncated cone with the hydrophilic outer surface and a hydrophobic cavity [2]. Many hydroxy groups are situated on the outer part of the ring that makes the CDs both hydrophilic and soluble in water. Due to their special molecular cavity structure, CDs can include other 'guest' molecules as 'hosts' to form inclusion complexes. The formation of CD complexes improves physical, chemical and biological properties of the guest molecules. This leads to wide application of CD in pharmaceutical, cosmetic, food, chemical and several other industries, and analytical chemistry, etc. [3–5]. The inclusion constant, a quantitative description of the inclusion equilibrium between CD and guest molecule, reflects the strength of the binding force between them. Therefore, the inclu-

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sion constant is an important and basic parameter to the application of CD. Up to the present, the reported determination methods for the CD inclusion constant are: spectroscopic method [6,7], surface tension method [8], nuclear magnetic resonance method [9], phase-solubility technique [10], fluorometry [11,12], constant current coulometric titration method [13], high pressure liquid chromatography [14], electrochemistry [15], capillary electrophoresis [16] and resonance Rayleigh scattering (RRS) method [17].

Resonance Rayleigh scattering (RRS) is a special elastic scattering produced when the wavelength of Rayleigh scattering (RS) is located at or close to the molecular absorption band. In this case, the frequency of the electromagnetic wave absorbed by the electron is equal to its scattering frequency. Because of the intensive absorption of light energy of the electron, rescattering takes place. Thus, the scattering intensity is enhanced by several orders of magnitude, as compared with a single RS, and no longer obeys the Rayleigh law of $I \propto 1/\lambda^4$ [18]. RRS is not only related to forced vibration caused by the action of electromagnetic field of the incident light in a molecule, but is also affected by energy level transitions of electrons. It, therefore, shows the characteristics of the scattering spectrum as well as that of the electronic absorption spectrum and not only has high signal levels, but also can provide new information concerning molecular structure, size, form, charge distribution, state of combination and so on. It has been applied successfully to the study of aggregation of chromophores on biological macromolecules [19,20] and applied to the determination of biological macromolecules such as nucleic acid, proteins and heparin [21–23]. Moreover this method has been used to the study and determination of trace amounts of inorganic ions [24–26], the cationic surfactant [27] and the critical micelle concentration of surfactant [28].

The inclusion constant of procaine hydrochloride–β-CD complex has been studied by using the RRS method in our research group [17]. In our previous work, the RRS method was first applied to study on the interaction of β-CD with procaine hydrochloride. A new method for the determination of the β-CD inclusion constant by RRS technology was developed. The results obtained by this method are satisfactory. Under the experimental conditions, the RRS intensity of free β-CD was too weak to make any significant contribution to the total RRS intensity. Therefore, it was negligible in our previous study. Although the neglect of the RRS intensity of free β-CD almost did not affect the results of the determination, the treatment method in our previous report was a simplified one. In order to illustrate the principles involved, however, a precise treatment method dealing with the weak RRS intensity of free β-CD was considered here.

In the present work, the host–guest complexation of chloramphenicol with β-CD was investigated by using the RRS technology. The developed calculation methods are based on the statement that the light scattering is not only due to that of chloramphenicol in its free and bound forms but also due to that of free β-CD. Based on the changes in the RRS intensity, an improved method for the determination of the inclusion constant of β-CD–chloramphenicol complex at different temperatures was obtained. The results showed that the inclusion constant gotten from the RRS method was the same as those from spectrophotometric methods. The method was highly sensitive, concise and easily operated, and was not affected by the system whether it has fluorescence or not. Using the RRS technology, the thermodynamic parameters such as ΔH, ΔS and ΔG associated with the inclusion process were also determined.

2. Experimental

2.1. Reagents

Chloramphenicol was from Huamei Biological Engineering Company. β-CD was from Aldrich. Doubly distilled water was used throughout.

2.2. Apparatus

A Hitachi F-2500 spectrofluorophotometer (Tokyo, Japan) was used for recording the RRS spectra and measuring the RRS intensity at a given wavelength using a 1 cm path length. The slit (EX/EM) was 5.0/5.0 nm; the PMT voltage, 400 V. A UV–vis 8500 spectrophotometer (Tianmei Co., China) was used for recording the absorption spectra. A super-thermostat with ±0.5 °C precision (Thermostat Factory of Shanghai) was used for controlling temperature of the system.

2.3. General procedure

To 1 ml of 6.0×10^{-4} mol l^{-1} chloramphenicol solution in a 10 ml volumetric flask, different amounts of β-CD solution was added and the solution was diluted to the mark with water and mixed thoroughly. After the temperature of the solution was kept constant with a thermostated water bath for a time, the RRS spectra of the system were immediately recorded with synchronous scanning at $\lambda_{ex} = \lambda_{em}$ (i.e. $\Delta\lambda = 0$ nm), and the RRS intensity, I, for the system with different concentration of β-CD at the maximum RRS wavelength was measured.

3. Results and discussion

3.1. Formation of the inclusion complex of chloramphenicol–β-CD and its molar ratio

Chloramphenicol is a medicine of antibiotics and its structure is shown in Fig. 1. The diameter of the cavity of β-CD is estimated at 6.8 Å, while the diameter of benzene ring in chloramphenicol is about 6.7–6.8 Å, which matches the diameter of the cavity of β-CD. Therefore, chloramphenicol

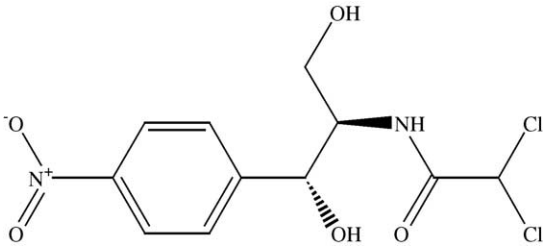

Fig. 1. Structural formula of chloramphenicol.

can enter the cavity of β-CD and interact with β-CD to form a steady inclusion complex.

The UV-spectra experimental results indicated that β-CD had no absorption band in the UV-region, but chloramphenicol had a maximum absorption peak at 278 nm. The absorbance at the ultra violet absorption peak increased along with an increase in concentration of β-CD, illustrating an obvious interaction between chloramphenicol and β-CD. The molar ratio of the inclusion complex was performed using Job's method of continuous variation. The result showed that the maximum ratio of [β-CD]/([G] + [β-CD]) was 0.5, which indicated that the inclusion complex of β-CD with chloramphenicol had a 1:1 stoichiometry.

3.2. RRS Spectra

The RRS spectra of β-CD and the chloramphenicol–β-CD system in different β-CD concentrations at 25 °C were recorded with synchronous scanning at $\lambda_{ex} = \lambda_{em}$ and are shown in Fig. 2. The shapes of the RRS spectra obtained at other temperatures were similar to those at 25 °C. The RRS spectrum of the chloramphenicol aqueous solution in the absence of β-CD had an obvious peak at 331 nm. When chloramphenicol was included by β-CD in the presence of β-CD, the RRS intensity at 331 nm was enhanced with an increase in concentration of β-CD. However, when the quantity of β-CD was greatly excessive the RRS intensity at the peak wavelength tends to level off. From Fig. 2 it can be seen that the RRS intensity of β-CD solution alone was weak and the RRS peak appeared at 282 nm. The RRS intensity of β-CD almost did not change with an increase in β-CD concentration.

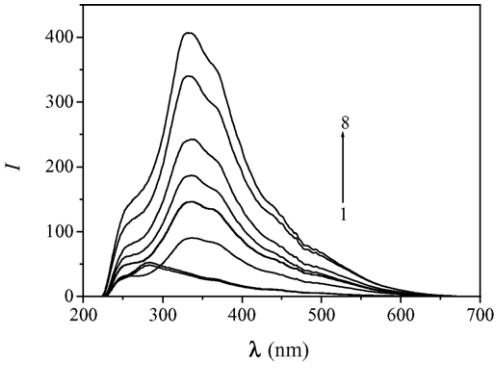

Fig. 2. RRS spectra of chloramphenicol–β-CD system. (1) β-CD (6.0×10^{-5} mol l^{-1}). (2) β-CD (2.0×10^{-4} mol l^{-1}). (3 – 8) chloramphenicol (6.0×10^{-5} mol l^{-1})–β-CD system, concentrations of β-CD (from 2 to 7) 0 mol l^{-1}, 4.0×10^{-5} mol l^{-1}, 6.0×10^{-5} mol l^{-1}, 1.0×10^{-4} mol l^{-1}, 2.0×10^{-4} mol l^{-1}, 3.0×10^{-4} mol l^{-1}.

3.3. Theory for the determination of the inclusion constant between β-CD and chloramphenicol by RRS

For RRS is an absorption rescattering process produced when resonance takes place between the Rayleigh scattering and the light absorption with equal frequency, it is certain that RRS spectral characteristics are closely related to the absorption spectra. The RRS spectrum band of the complex is located in its absorption band. The RRS intensity can be obtained by using the equation [29,30]

$$I = KcbE_{ex}(\lambda_{ex})E_{em}(\lambda_{em})$$

where E_{ex} is the excitation function at the fixed wavelength of excitation, E_{em} is the emission function at the fixed wavelength of emission, K is the characteristic constant comprising the instrumental geometry factor and related parameters, c is the analyte concentration, and b is the thickness of the sample cell. Therefore, when the conditions of the instrument are fixed, we can obtain the following:

$$I \propto c$$

Namely, linear relationship between the RRS intensity and the analyte concentration can be obtained.

If a guest molecule G forms a 1:1 inclusion complex with CD, the complex formation can be described by the following equation:

$$\mathrm{CD} + \mathrm{G} \leftrightarrows \mathrm{CD\text{–}G} \quad (1)$$

The inclusion constant is defined as:

$$K_f = \frac{[\mathrm{CD\text{–}G}]}{[\mathrm{CD}][\mathrm{G}]} \quad (2)$$

If the complex and the guest molecule form RRS at a measured wavelength, the intensity of RRS for the guest solution after adding CD is given by the following equation:

$$I = K_1[\mathrm{G}] + K_2[\mathrm{CD\text{–}G}] + K_3[\mathrm{CD}] \quad (3)$$

where K_1, K_2 and K_3 are the ratio coefficients between the RRS intensity and concentrations of the guest molecule, the complex formed and the free CD.

In our experiment, the RRS intensity of β-CD solution was weak and the RRS peak appeared at 282 nm. When the β-CD concentration was increased, the RRS intensity of β-CD almost did not change (Fig. 2). Therefore, the change of the free β-CD concentration did not affect I described in Eq. (3) and the Eq. (3) can be rewritten as follows:

$$\Delta I = I - K_3[\mathrm{CD}] = K_1[\mathrm{G}] + K_2[\mathrm{CD\text{–}G}] \quad (4)$$

3.3.1. Method I

The total concentration of the guest molecule, C_G, is given by the material balance:

$$C_G = [G] + [CD–G] \quad (5)$$

When [CD] = 0, (i.e. CD is not added),

$$K_1 = \frac{I_0}{C_G} \quad (6)$$

However, when the guest molecule interacted completely with CD to form the complex, CD–G, there is a following equation:

$$K_2 = \frac{I_\infty}{C_G} \quad (7)$$

where I_0 and I_∞ are the RRS intensity of the guest molecule without addition of CD and of the complex formed completely. Using Eqs. (6) and (7), Eq. (4) can be transformed into

$$\Delta I = \frac{I_0[G]}{C_G} + \frac{I_\infty[CD–G]}{C_G} \quad (8)$$

Eq. (8) can be further transformed into

$$\frac{\Delta I - I_0}{I_\infty - \Delta I} = K_f[CD] \quad (9)$$

From the expression of Eq. (9), it indicates that $(\Delta I - I_0)/(I_\infty - \Delta I)$ is directly proportional to [CD]. Plotting $(\Delta I - I_0)/(I_\infty - \Delta I)$ as a function of [CD], a straight line with a slope can be obtained, and the slope is K_f.

Under experimental conditions, because the quantity of CD was greatly excessive, [CD] can be replaced approximately with the concentration of CD, C_{CD}. According to Eq. (9), the I_0, I_∞ and ΔI were measured in the experiment. Therefore, the value of K_f can be obtained from the slope of the straight line which is obtained by plotting $(\Delta I - I_0)/(I_\infty - \Delta I)$ against C_{CD}.

3.3.2. Method II

According to the material balance, one obtains:

$$C_G = [G] + [CD–G] \quad (5)$$

$$C_{CD} = [CD] + [CD–G] \quad (10)$$

where C_G and C_{CD} are the total concentrations of the guest molecule and CD, respectively.

Using Eq. (5), one would write Eq. (4) as:

$$\Delta I = K_1 C_G + (K_2 - K_1)[CD–G] \quad (11)$$

According to the expression of the inclusion constant and substituting Eq. (6) into Eq. (11), yields:

$$\Delta I' = \Delta I - I_0 = \frac{(K_2 - K_1)K_f[CD]C_G}{1 + K_f[CD]} \quad (12)$$

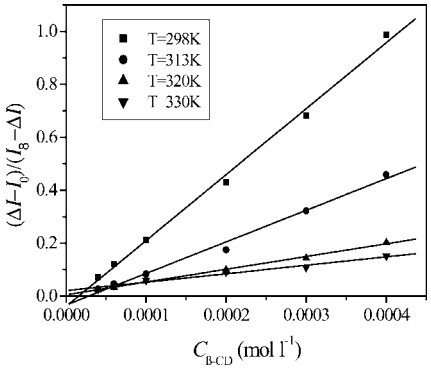

Fig. 3. Plots of $(\Delta I - I_0)/(I_\infty - \Delta I)$ vs. $C_{\beta\text{-CD}}$ for the inclusion of β-CD at different temperatures.

Therefore, one obtains:

$$\frac{1}{\Delta I'} = \frac{1}{(K_2 - K_1)C_G} + \frac{1}{(K_2 - K_1)K_f C_G[CD]} \quad (13)$$

where C_G represents the concentration of the guest molecule, and [CD] is the equilibrium concentration of CD. $K_2 - K_1$ is the coefficient, and $\Delta I'$ is the change in the RRS intensity of the guest molecule caused by the addition of CD. The curve of $1/\Delta I'$ versus 1/[CD] at the optimum RRS wavelength will give a good linearity and K_f can be obtained when the composition ratio of the inclusion complex is 1:1.

3.4. Determination of the inclusion constant of β-CD with chloramphenicol by RRS

According to the basic principle of the method, Eqs. (9) and (13) are the quantitative basis for the following determinations. The RRS intensity, ΔI, of the inclusion complex of β-CD with chloramphenicol was measured by the RRS technology. The RRS intensity without addition of any β-CD was I_0. When the amount of β-CD was greatly excessive in the experiment, the RRS intensity of the inclusion complex could be regarded as I_∞.

The data of I, I_0 and I_∞ at the RRS peak of 331 nm were measured, respectively. The RRS intensity of β-CD solution

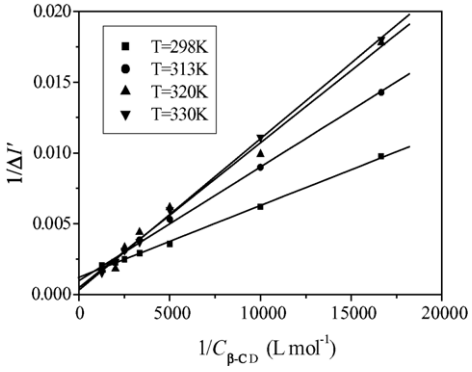

Fig. 4. Plots of $1/\Delta I'$ vs. $1/C_{\beta\text{-CD}}$ for the inclusion of β-CD at different temperatures.

Table 1
Inclusion constants of chloramphenicol–β-CD complex with different determination methods

Temperature (*K*)	K_f (L mol^{-1})		
	Method I[a]	Method II[a]	UV spectroscopy
298	2489.3	2410.9	[b]
313	1192.1	1222.2	1201.6
320	481.3	489.8	475.0
330	319.5	305.6	295.7

[a] The number of determination (*n*) is 3.
[b] 1922.8 (T = 303 K).

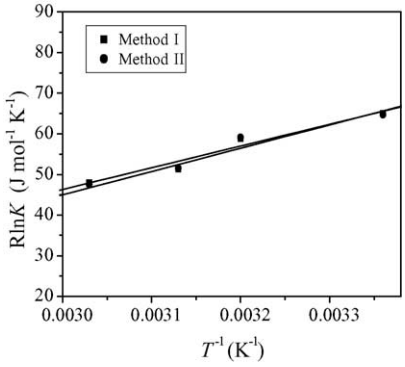

Fig. 5. Van't Hoff plots for the inclusion complexation of β-CD and chloramphenicol with methods I and II.

was also measured at 331 nm, which almost did not change with β-CD concentration increase. According to method I, the curve of $(\Delta I - I_0)/(I_\infty - \Delta I)$ versus the concentrations of β-CD ($C_{\beta\text{-CD}}$) at different temperatures were plotted and gave a good linearity, and the slopes were the inclusion constant, K_f (as shown in Fig. 3).

However, the inclusion constant of β-CD with chloramphenicol, K_f, can also be obtained using experimental data of ΔI and I_0 at 331 nm by Method II. A curve of $1/\Delta I'$ against $1/C_{\beta\text{-CD}}$ (if [β-CD]≫[G], [β-CD] can be replaced with $C_{\beta\text{-CD}}$) at different temperatures were plotted, and then a straight line with slope equal to $1/[(K_2 - K_1)K_f C_G]$ was obtained (as shown in Fig. 4). K_f was the ratio of the intercept to the slope.

In order to confirm the experimental and theoretical methodology described above, the determination results of the inclusion constant of β-CD with chloramphenicol by using UV–vis spectroscopic method reported was used to compare with those of the two methods. The inclusion constant values of β-CD with chloramphenicol, K_f, obtained with different spectroscopy method are listed in Table 1. The results present clearly that the determination values with the RRS method correspond with those of the UV-spectroscopy method reported [31], illustrating that the novel method, the RRS spectroscopy method, is feasible and the determination results are reliable.

It can be observed in Table 1 that as long as the temperature increases, the inclusion constant decreases. The thermodynamic parameters for the formation of inclusion complexes were also determined from temperature dependence of inclusion constant by using Van't Hoff equation. Fig. 5 shows the Van't Hoff plots with the RRS data. If $\Delta C_p = 0$, the experimental R ln K_f values fit the well-known linear equation [32]

$$\mathrm{R}\ \ln K_f = -\frac{\Delta H}{T} + \Delta S \tag{14}$$

and ΔH and ΔS, which are temperature independent, can be estimated from the slope and intercept of the fit, respectively. The results of the thermodynamic parameters with methods I and II are shown in Table 2. The thermodynamics of the complexation process is usually complicated [33,34]. It has been generally accepted that the main driving forces for complexation are hydrophobic interactions, van der waals interactions, release of high energy water molecules from CD cavity and hydrogen bonding. Hydrophobic interaction essentially involves a favorable positive ΔS together with a slightly positive ΔH, while the other forces involve negative ΔH and ΔS. The higher negative ΔH value obtained with β-CD could be related to stronger hydrogen bonding with the hydroxyl groups [35]. The negative ΔH and ΔS obtained (as listed in Table 2) suggest that a combination of van der waals forces and hydrogen bonding can be considered as a main driving force for the inclusion complexation of chloramphenicol with β-CD. The report [36] also illustrated that hydrogen bonding occurred in the inclusion of neurotransmitters in β-CD. And the values of the thermodynamic parameters obtained in our experiment also illustrated that the inclusion process of chloramphenicol by β-CD is exothermic and enthalpy driven ($|\Delta H| > T|\Delta S|$), as found [32,37] for associations between small guest molecules and an apolar cavity in water.

Table 2
Thermodynamic parameters for inclusion complexation of chloramphenicol with β-CD

Temperature (*K*)	Method I[a]			Method II[a]		
	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})
298	−19.4	−53.9	−115.9	−19.3	−54.1	−116.2
313	−18.4			−18.5		
320	−16.4			−16.5		
330	−15.7			−15.7		

[a] The number of determination (*n*) is 3.

4. Conclusions

The RRS method was applied to the determination of the inclusion constant of chloramphenicol with β-CD with simplicity, rapidness and sensitivity. The main driving forces for the encapsulation of chloramphenicol by β-CD is van der waals interactions and hydrogen bonding. The RRS technology as a new method for the determination of the inclusion constant has been proposed. Particularly for the inclusion complexes formed by some guest molecules that has weak absorption band in the UV-region, the present method has much advantage.

Acknowledgements

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