Journal of Molecular Liquids 191 (2014) 48–52

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Study on the inclusion and solubilization processes of inclusion complex of carboxymethyl-β-cyclodextrin with CDOTP

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ARTICLE INFO

Article history:
Received 22 August 2013
Received in revised form 12 November 2013
Accepted 28 November 2013
Available online 8 December 2013

Keywords:
Inclusion complex
β-Cyclodextrin
Bisquaternary ammonium salts
Solubilization
Spectroscopy
Association constant

ABSTRACT

The inclusion and solubilization processes of the inclusion complex between carboxymethyl-β-cyclodextrin and chloro1, 4-dibenzyl-1, 4-dinitrogen diheterocycly [2,2,2] octane tungstic peroxide were investigated using ultraviolet spectrophotometry characterization. Association constant $K_{CD,Q} = 1.07 \times 10^6$ L/mol and the inclusion ratio $n = 3$ were determined by means of competitive inclusion method with phenolphthalein. Moreover, based on solubilization experiment of inclusion complex, it can be found that the solubility is improved vastly compared with the guest without inclusion, especially in the condition of normal atmospheric temperature and weak alkaline solutions. Additionally, thermodynamic analysis of this inclusion process and relevant evaluation of thermodynamic parameters, such as ΔS, ΔH and ΔG have been investigated, which indicates that this process is unprompted, thermodynamically sustained and driven by both enthalpy and entropy, and especially depends on entropy. The possible prediction of inclusion structure has also been investigated.

1. Introduction

Chloro1, 4-dibenzyl-1, 4-dinitrogen diheterocycly[2,2,2] octane tungstic peroxide (CDOTP) is a kind of water–oil biphasic catalytic oxidizer that can be synthesized by divalent cationic bisquaternary ammonium salts and divalent anionic peroxide tungstate, which exhibits oxidation effects in water-organic catalytic oxidation reaction [1,2]. Moreover, the good surface activity that is exhibited by quaternary ammonium salt makes this substance present satisfying application prospect in oilfield [3,4]. However, in addition to the application in the organic phase, its poor water-solubility leads to restrictive applications to some oxidation processes such as aqueous catalytic oxidation. So how to enlarge the application range of this substance which especially improves its solubility in aqueous solution exhibits great significance.

Cyclodextrin (CD) is a general designation of a series of cyclic oligosaccharides produced by amylases interacting with cyclodextrin glycosyl transferase generated by bacillus [5,6]. It contains a hydrophobic cavity and hydrophilic surfaces, which are visually called "molecular capsule". The possible inclusion complex can be formed by hydrophobic interaction, hydrogen bonding force and van der Waals force between the host and guest, which has been widely used in chemical engineering, food and medicine industry. As we all know, inclusion technique is a useful method to improve the solubility of insoluble substance [7,8], so we intend to study the inclusion process between β-CD and CDOTP, and we also will investigate its solubilization in aqueous solution. However, because β-CD exhibits relative low solubility in aqueous solution, in order to improve the solubility of CDOTP to the maximum degree, we will modify the cyclodextrin to obtain carboxymethyl-β-cyclodextrin (CM-β-CD) to exhibit satisfying aqueous solubility [9].

In this paper, we have made an attempt to evaluate the inclusion process between CM-β-CD and CDOTP. Furthermore, we have conducted a series of experiments to analyze the guest solubilization property and established the investigation to the influence factors including temperature and pH value on solubilization process. Additionally, the thermodynamic analysis and prediction of possible inclusion molecular structure have also been investigated.

2. Experimental section

2.1. Materials

β-cyclodextrin (β-CD), methyl alcohol, sodium hydroxide, hydrochloric acid, triethylene diamine hexahydrate, absolute ethyl alcohol, 30% hydrogen peroxide, sodium carbonate, sodium bicarbonate, and oxalic acid were purchased from Kelong chemical regent factory (Chengdu, China). Hypochlorous acid was from Tianjin recovery fine

Abbreviations: CD, cyclodextrin; CM-β-CD, carboxymethyl-β-cyclodextrins; CDOTP, chloride-1, 4-dibenzyl-1, 4-dinitrogen double heterocycle[2,2,2] octane tungstic peroxide; UV spectroscopy, ultraviolet spectroscopy.

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http://dx.doi.org/10.1016/j.molliq.2013.11.031

chemical industry research institute. Benzyl chloride was from Shanghai Yongshen reagent factory. Sodium tungstate was purchased from the Tianjin regent chemicals corporation, LTD. Both of these materials were analytical reagent grade.

2.2. Apparatus

Absorption spectrum measurements were carried out with a UNICO UV-3802 spectrophotometer (UNICO, Shanghai, China) scanning the guest solutions during the range between 200 nm and 1000 nm with the consideration of different temperature and pH value.

2.3. Method

2.3.1. Synthesis of inclusion complex

CM-β-CD was prepared by a procedure detailed in a previous study [10]. The synthesis of the guest can be obtained with the method provided by Xianying Shi [1]. A certain amount of CM-β-CD was dispersed in distilled water, and then the turbid liquids of guests were added to the solution dropwise. Subsequently, the mixed liquids were put into the constant temperature vibrating incubator with vibrating at intermediate speed for 3 h, and the coordination complex was centrifugally separated after its complicate dissolution to obtain the inclusion complex with drying and grinding.

2.3.2. Measurement of standard curves

A series of neutral inclusion complex solutions were prepared with 30% ethanol water at 298.15 K. 2 mL separating medium was taken out to make 10 mL sample inclusion complex solution with 30% ethanol water in volumetric flasks. The standard curves for guest concentration determination were evaluated by ultraviolet (UV) spectroscopy between the range of 200 nm–1000 nm, and the adsorption curves were built at 215.5 nm to obtain the standard curves between guest concentrations and host concentrations.

2.3.3. Solubilization experiment

In this process, the inclusion ratio n and association constant K have been evaluated and the influence factors on solubilization have also been considered. A series of host solutions whose concentrations were ranging from 15 g/L, 30 g/L, 45 g/L, 60 g/L to 70 g/L were respectively prepared. 25 mL solutions was taken out from each sample host solution into conical flasks and 0.08 g guests were added to each flask to obtain the mixed solutions, which were placed on the swing table with 40 rpm for 2 h at 298.15 K, 303.15 K, 308.15 K, 313.15 K and 323.15 K. The solutions were stewed for overnight stratification after the reaction, and 2 mL centrifugal supernatant liquids were respectively taken out and diluted with ethanol to 10 mL. The absorbance values of each sample solutions were determined at 215.5 nm, and relevant soluble guest concentrations could be obtained corresponding to standard curves measured before. Analogously, on the basis of abovementioned solubilization experiments, a series of experiments only with the change of pH value were conducted, which aimed to investigate the impacts of pH on solubilization process.

2.3.4. Thermodynamic and inclusion structure analysis

The thermodynamic analysis of solubilization process depending on Van't Hoff expressions has been provided and possible prediction of inclusion molecular structure could be obtained combining the analysis of molecular recognition with inclusion ratio, non-covalent interactions and thermodynamic results. Moreover, detailed reasons for this structure analysis have also been provided.

3. Theory

The association constant K value can be determined with competitive inclusion method [11]. When the host has finished the inclusion process with the guest, the addition of another guest (phenolphthalein) can lead to the competitive inclusion process between these two guests, and corresponding changes can be reflected on the ultraviolet spectrum if the host exhibits higher recognition to the latter. In this way, the concentration of the replaced guest will reflect regular changes with the changes of the concentration of competitive guest, which can be applied in the calculation of association constant K by Eq. (1).

$$K_{CD\cdot Q} = \frac{\frac{[CD]_0 - [CD]}{n}}{[CD]^n \bullet \left([Q]_0 - \frac{[CD]_0 - [CD]}{n}\right)} \tag{1}$$

where n is the inclusion ratio of inclusion complex, $[CD\cdot Q]$is the inclusion complex concentration when the host, guest and competitive guest reach the equilibrium states, $[CD]_0$ is the initial concentration of cyclodextrins, $[Q]_0$ is the initial concentration of guest, and $[CD]$ is the equilibrium concentration of host.

Moreover, under the condition of known $[CD]_0$, $[Q]_0$ and inclusion ratio n, the key point for solving the association constant K is to evaluate the equilibrium concentration of host $[CD]$. Additionally, in the competitive inclusion process of phenolphthalein and guest, the inclusion complex whose ratio is 1:1 has been formed between the host and phenolphthalein [12], and the three substances have also reach the equilibrium states in the aqueous solution, so $[CD]$ can be determined by the following expression.

$$[CD] = \frac{1}{K_{CD\cdot PP}} \bullet \frac{[CD\cdot PP]}{[PP]} = \frac{1}{K_{CD\cdot PP}} \bullet \frac{A_{PP_0} - A}{A - A_{inc}} \tag{2}$$

where A_{PP0} is the initial absorbance value of phenolphthalein, A_{inc} is the absorbance value of phenolphthalein after the inclusion process, A is the absorbance value of phenolphthalein after the competitive inclusion process with guest, $[CD\cdot PP]$ is the concentration of inclusion complex when the host, guest and phenolphthalein reach equilibrium state after competitive inclusion process, $[PP]$ is the concentration of phenolphthalein when the host, guest and phenolphthalein reach equilibrium state after competitive inclusion process, and $K_{CD\cdot PP}$ is the association constant of phenolphthalein.

The evaluation of $K_{CD\cdot PP}$ can be obtained by Hildebrand–Benesi expression (Eq. (3)) [13], which has been illustrated as follows:

$$\frac{1}{\Delta A} = \frac{1}{\varepsilon K_{CD\cdot Q}[CD]_0[Q]_0} + \frac{1}{\varepsilon[Q]_0} \tag{3}$$

where ΔA is the change of absorbance value of the guest after the addition of the host, which can be expressed as $\Delta A = A_{inc} - A_Q$. ε is the molar absorption coefficient of inclusion complex.

The thermomechanical analysis of solubilization process depends on Van't Hoff expression (Eqs. (4)–(6)) [14]:

$$\frac{d \ln K_{CD\bullet Q}}{dT} = -\frac{\Delta H}{RT} \tag{4}$$

$$\ln K_{CD\bullet Q} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{5}$$

$$\Delta G = \Delta H - T\Delta S. \tag{6}$$

According to the plotting lines between $lnK_{CD\cdot Q}$ and T^{-1}, ΔS and ΔH can be obtained so as to get ΔG further.

4. Results and discussion

4.1. Standard curves for guest concentration determination

A series of guest solutions with the mixture of 30% ethanol water were prepared, the concentrations of which were 10×10^{-3} g/L,