Chemometrics and Intelligent Laboratory Systems 118 (2012) 230–238

Contents lists available at SciVerse ScienceDirect

Chemometrics and Intelligent Laboratory Systems

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

Spectrophotometric thermodynamic study of orientational isomers formed by inclusion of methyl orange into β-cyclodextrin nanocavity

Mohsen Kompany-Zareh [a,b,*], Zeinab Mokhtari [a], Hamid Abdollahi [a]

[a] Institute for Advanced Studies in Basic Sciences (IASBS), Department of Chemistry, Zanjan 45137-66731, Iran
[b] Department of Food Science, Faculty of Life Sciences, University of Copenhagen, Rolighedsvej 30, 1958 Frederiksberg C, Denmark

ARTICLE INFO

Article history:
Received 23 November 2011
Received in revised form 18 April 2012
Accepted 8 June 2012
Available online 17 June 2012

Keywords:
Cyclodextrin
Nanocavity
Hard modeling
Newton–Raphson
Inclumer
Orientational isomers
Thermodynamic
Global analysis

ABSTRACT

Spectrophotometry has been used to investigate the interaction of methyl orange (MO), an azo dye as a guest, with β-cyclodextrin (CD) as the host. Inclusion of methyl orange into β-cyclodextrin nanocavity leads to two orientational isomers, so-called inclumers, because of the asymmetric structure of methyl orange. This study was performed in basic and acidic media to yield the microconstants and thermodynamic parameters for inclusion complex formation equilibria in each media.

The recorded data set at a constant temperature is rank deficient, because there is a linear dependency between concentration profiles of inclumers. This problem is overcome through the augmentation of multiwavelength data recorded at different temperatures. Titration of methyl orange solution with β-cyclodextrin solution was performed in five different temperatures, in order to calculate the formation microconstants for inclumers, pure spectra for absorbing components in each media and thermodynamic parameters such as change in enthalpy, entropy and Gibbs free energy for inclusion equilibria. Then globalization was performed to analyze the augmented data sets. The titration of acidic methyl orange with sodium hydroxide was also performed, to calculate the microconstants and thermodynamic parameters related to ionization.

The interaction of the basic form of methyl orange with β-cyclodextrin in basic medium led to two orientational isomers. In acidic medium methyl orange has two tautomeric forms, called ammonium and azonium. The inclusion of azonium in β-cyclodextrin has been neglected in the considered model for simplicity and the inclusion of ammonium is modeled, because it forms more stable complexes with β-cyclodextrin nanocavity.

Newton–Raphson algorithm was used to produce concentration profiles and Newton–Gauss–Levenberg/Marquardt algorithm was used to optimize the parameters of interest.

1. Introduction

1.1. Cyclodextrin host–guest interactions

Recently there has been a growing interest in the area of complex formations between cyclodextrins and different substances, so-called host–guest supramolecular chemistry. Cyclodextrins are cyclic oligosaccharides produced in enzymatic hydrolysis of starch [1]. They are molecules with the shape of a truncated cone, composed of D(+)glucopyranose subunits [2]. The specific arrangement of the functional groups of these subunits makes cyclodextrins soluble in water and helps them in complex formation with hydrophobic guests. In other words the hydrophilic exterior and hydrophobic interior of cyclodextrins make the solvation of hydrophobic organic, inorganic and biological molecules in water possible, through the formation of inclusion complexes of guest molecules with cyclodextrins [3]. Cyclodextrins are frequently used in drug delivery technologies [4–6], environmental science [7], textile industries [8], enantioseparation [1,9–11], food industries [2], cosmetic preparation [12], and many other industries.

The complexation of cyclodextrins with guest molecules does not include any covalent bond formation or dissociation [2,11]. The complex formed by the inclusion of a guest into the cyclodextrin nanocavity is somehow different in properties from the free guest molecule due to the different microenvironments of the CD nanocavity [13,14]. So, complex formation reaction can be monitored through the change in chemical and physical properties of the guest molecule. Many different possible strategies are applicable in this way. Some of them are as follows: absorption spectroscopy, fluorimetry, induced-circular dichroism spectroscopy, nuclear magnetic resonance spectroscopy, electron paramagnetic resonance spectroscopy, electrochemistry and so on [15–19]. In this study UV/VIS spectroscopy was used.

The structures of three kinds of cyclodextrins are shown in Scheme 1. They are different in the number of glucopyranose units. α-, β- and γ-cyclodextrins are composed of six, seven and eight units connected to each other through α-1,4-glycoside bonds. Consequently

* Corresponding author at: Institute for Advanced Studies in Basic Sciences (IASBS), Department of Chemistry, Zanjan 45137-66731, Iran. Tel.: +98 241 4153123; fax: +98 241 4153232.
E-mail address: kompanym@iasbs.ac.ir (M. Kompany-Zareh).

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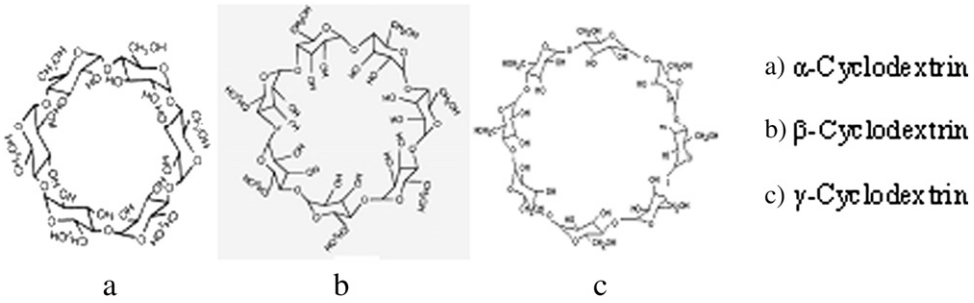
doi:10.1016/j.chemolab.2012.06.001



Scheme 1. The structure of α-, β- and γ-cyclodextrin.

these oligosaccharides have different cavity sizes. It has been reported that cyclodextrins have a nanocavity height of about 8 Å and an internal diameter of about 5, 6 and 8 Å for α-, β- and γ-cyclodextrin, respectively [2,20].

As a result they interact differently with different sizes of guests. The better fit into the cyclodextrin cavity, the more stable is the complex formed. Obviously complex stability depends upon the polarity and chemical structure of the guest molecules, in addition to its dimension [15,21]. Another result of the difference in cyclodextrins' sizes can be seen in the stoichiometry of complexes. α-Cyclodextrin usually forms 1:1 and 1:2 complexes of guest–host, where β-cyclodextrin forms 1:1 and sometimes 1:2 and γ-cyclodextrin forms 2:1 in addition to 1:1 and 1:2 complexes. Sometimes guest molecules that are larger than the cyclodextrin nanocavity are also included in it through a mode, that just certain groups can penetrate the nanocavity [22].

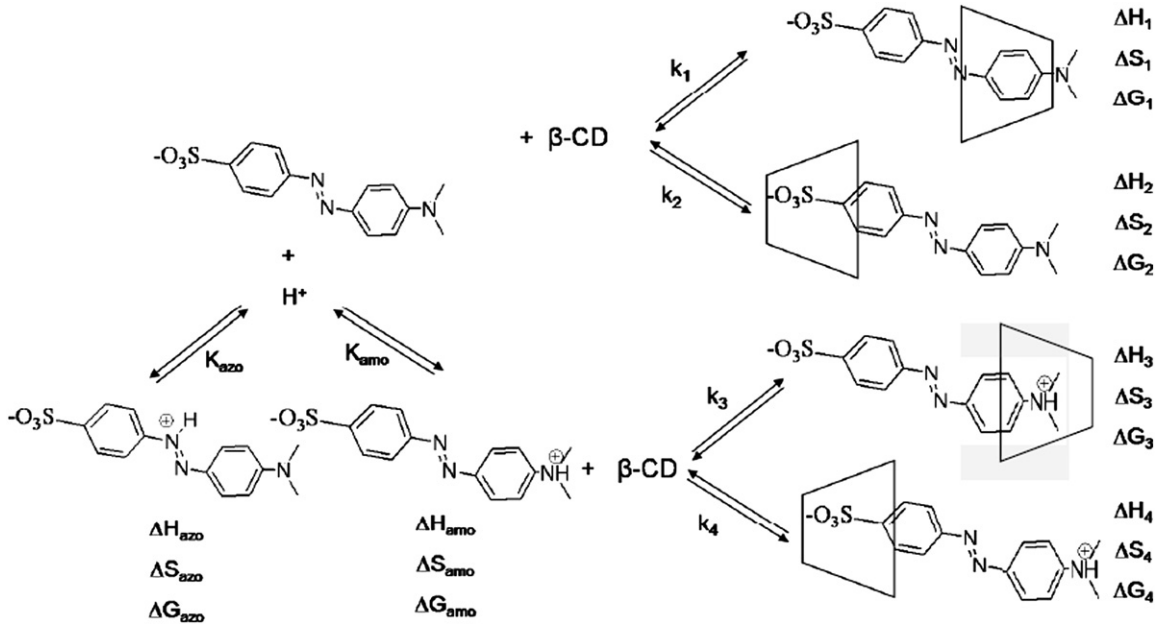
β-Cyclodextrin is the most useful cyclodextrin among the mentioned cyclodextrins, because it has an appropriate nanocavity size, good solubility in water, low price and easy accessibility [23]. The inclusion of an asymmetric guest molecule into the cyclodextrin nanocavity, through different ways, leads to orientational isomers [24,25]. These isomers, so-called inclumers, are shown schematically in Scheme 2. They are called as inclumers, because different ways of inclusion make these isomers.

The driving forces for the inclusion of guest molecules into the cyclodextrin nanocavity are as follows: the electrostatic forces; the hydrogen binding between the hydroxyl groups of CD and the guest; Van der Waals force interactions between host and guest molecules; hydrophobic interaction; the release of 'high-energy water' molecules from the cavities of CD to bulk water [12,26,27].

1.2. Methyl orange and its complexes with cyclodextrin nanocavity

Methyl orange is an azo dye, used as an acid–base indicator, with a pKa value of 3.5. It has a basic and two acidic forms, because of tautomerization [28]. These forms have been shown in Scheme 2. In basic medium the only form of methyl orange is its neutral form that is not protonated [29]. It makes inclusion complexes with cyclodextrin nanocavity. Acidic forms (azonium and ammonium) are the results of the protonation of the basic form in two positions. There exists an equilibrium between the two forms in acidic medium [28]. There is some evidence which shows that the ammonium form makes more stable complexes with cyclodextrin [30]. So the addition of the cyclodextrin solution to the solution of methyl orange will displace the equilibrium between two acidic forms [31]. It is noteworthy that MO.CD (formed by k_1) and MOH-Amo.CD (formed by k_3), and CD.MO (formed by k_2) and CD.MOH-Amo (formed by k_4), are structurally the same, respectively, and the only difference is the proton on the complexes formed in the acidic media.

The aim of this study is to investigate the complexation reaction of β-cyclodextrin and methyl orange with a fitting method. Various thermodynamic parameters such as the formation microconstant, change in enthalpy, entropy and free energy are calculated. The procedure of this study is the titration of a methyl orange solution with a cyclodextrin solution, in basic and acidic media, and following the absorption of the



Scheme 2. Inclusion of protonated and deprotonated methyl orange into cyclodextrin nanocavity.