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Effects of length and unsaturation of the alkyl chain on the hydrophobic binding of curcumin with Tween micelles

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ABSTRACT

This work studies the effects of length and unsaturation of alkyl chain on the hydrophobic binding of curcumin with Tween 20, 60 and 80 micelles. While Tween 20 and 60 possess 12 and 18 saturated carbons, respectively, in their alkyl chains, the alkyl chain of Tween 80, with one double bond, has the same length as Tween 60. Tween 60 micelles are superior to Tween 20 and 80 micelles for improving curcumin stability. The fluorescence measurement suggests that Tween 60 micelles provide curcumin with the most hydrophobic microenvironment, owing to the long and saturated alkyl chain of Tween 60. The pK_{a1} and binding constants of curcumin have the same order of Tween 60 > Tween 20 > Tween 80. These results show that the length increase, and unsaturation, of the alkyl chain of Tween surfactants have opposite effects on the hydrophobic binding of curcumin with Tween micelles.

1. Introduction

Increasing attention has been given to natural curcumin owing to its low intrinsic toxicity and wide range of biological and pharmacological activities, including antioxidant, antitumor and anticancer properties (Deters et al., 2008; Lantz, Chen, Solyom, Jolad, & Timmermann, 2005; Shi et al., 2006). Curcumin is a polyphenolic compound isolated from the rhizome of turmeric, which has been widely used as a food additive and traditional medicine for centuries. Chemically, curcumin is a diferuloyl methane molecule containing two ferulic acid residues linked by a methylene bridge. The hydroxyl groups of the benzene rings, double bonds in the alkene part and the central β-diketone moiety, may play crucial roles in the beneficial properties of curcumin. However, the major limitation in the application of curcumin, as a routine treatment agent, is the reduced bioavailability (Anand, Kunnumakkara, Newman, & Aggarwal, 2007). One reason for the low bioavailability of curcumin is that curcumin is poorly soluble in water at acidic pHs, which makes curcumin hard to absorb. Another reason for the low bioavailability of curcumin is its limited stability in aqueous environments. At basic pHs, curcumin is easily degraded to trans-6-(4′-hydroxy-3′-methoxyphenyl)-2,4-dioxo-5-hexanal, ferulic acid, feruloylmethane and vanillin (Tønnesen & Karlsen, 1985; Wang et al., 1997).

The problems of curcumin can be greatly resolved by surfactant micelles. Tønnesen reported that the addition of surfactant micelles can increase water solubility of curcumin by a factor of at least 10^5 (Tønnesen, 2002). Many people have demonstrated that the stability of curcumin under alkaline conditions was dramatically improved by binding with surfactant micelles (Iwunze, 2004; Leung, Colangelo, & Kee, 2008; Wang, Leung, Kee, & English, 2010), thereby markedly increasing curcumin bioavailabilities, such as anticarcinogenic and antioxidant activities (Sharma & Jani, 2013; Zhou, Yang, & Wang, 2014). The enhanced solubility, stability and bioactivity of curcumin are attributed to the binding of curcumin to the palisade layer of surfactant micelles, where the presence of free water is relatively limited. Our group and others have demonstrated that the interactions between surfactant micelles and curcumin are mainly driven by the interaction of the hydrophobic force of the alkyl chains of surfactant with the aryl group of curcumin, together with the interaction of the electrostatic force of the headgroup of surfactant with the β-diketone group of curcumin (Ke et al., 2011; Sharma & Jani, 2013). The importance of the surfactant headgroup in the interactions between surfactant micelles and curcumin has been well investigated (Boruah, Saikia, & Dutta, 2012; Wang et al., 2010). Curcumin has stronger binding affinity to neutral surfactant micelles than charged surfactant micelles, as shown by the higher solubility and stability of curcumin with neutral surfactant micelles, which can be attributed to more pronounced hydrophobic binding of curcumin with neutral surfactant micelles.

Compared to the surfactant with shorter akyl chains, the surfactant with longer akyl chains may form micelles with a more hydrophobic palisade layer, providing more favourable microenvironment to the bound molecules (Tašcioğlu, 1996). In two surfactant micelles of cetyl trimethylammonium bromide and dodecyl trimethylammonium

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bromide, Leung et al. found that the stability of curcumin is approximately 8 times higher than that in water (Leung et al., 2008). However, they did not observe significantly different stability behaviour of curcumin with these two surfactant micelles, which possibly resulted from the strong electrostatic attraction between cationic surfactants and anionic curcumin species. Mandal et al. determined the binding constants of curcumin with two neutral micelles of Tween 20 and Tween 80 as 6.2×10^5 and $4.6 \times 10^5\,M^{-1}$, respectively (Mandal, Banerjee, Ghosh, Kuchlyan, & Sarkar, 2013). They did not give an explanation, however, for the difference in the binding behaviour of curcumin with Tween micelles. Compared to the increase in the length of the alkyl chain, the unsaturation of the alkyl chain, due to the double bond, may be the reason for the reduction in the binding constant of curcumin with Tween 80 micelles. In fact, Began et al. found that soy phosphatidylcholine has lower binding affinity with curcumin than egg phosphatidylcholine, due to the different unsaturation degree in two kinds of phosphatidylcholines (Began, Sudharshan, Sankar, & Rao, 1999). Meanwhile, in mixed surfactant systems, Ćirin et al. (Poša, Vapa, & Ćirin, 2014; Ćirin, Poša, Krstonošić, & Milanović., 2012) and Akbar et al. (Akbar, Deubry, Marangoni, & Wettig, 2010) observed that the unsaturated alkyl chain may reduce the synergistic effect of mixed surfactants, which is even stronger than the enhanced effect induced by the increase in the length of the saturated alkyl chain of surfactant (Cirin, Poša, & Krstonošic, 2012). All these studies indicate that not only the length but also the unsaturation of the alkyl chain of surfactants may significantly influence the binding of curcumin with surfactant micelles.

The present work is intended to elucidate the effects of alkyl chain structure on the hydrophobic binding of curcumin with surfactant micelles. The surfactants selected were Tween surfactants (Tween 20, 60 and 80), which are neutral polyoxyethylene surfactants and widely used in the food industry. The three Tween surfactants have the same headgroups with variations in their hydrophobic tails. While Tween 20 and 60 possess 12 and 18 saturated carbons in the alkyl chain, respectively, Tween 80 has 18 carbons in its alkyl chain, with one double bond. Surface tension experiments were carried out to determine the critical micelle concentrations of Tween surfactants with and without curcumin. The absorption and fluorescence spectroscopic properties of curcumin were used to study the stability, acid-base equilibrium and thermodynamics of curcumin with three Tween micelles.

2. Materials and methods

2.1. Materials

Curcumin, Tween 20 (polyoxyethylene (20) sorbitan monolaurate), Tween 60 (polyoxyethylene (20) sorbitan monostearate) and Tween 80 (polyoxyethylene (20) sorbitan monooleate) were purchased from Sigma–Aldrich Chemical Co. All other chemical reagents used were of analytical grade, and water was double distilled.

2.2. Methods

2.2.1. Sample preparation

As curcumin is poorly soluble in water, curcumin was dissolved in ethanol to produce a stock solution containing 4 mM curcumin. A small quantity of this stock solution was added to 5 ml solutions of Tween surfactants to achieve the desired curcumin concentrations. The obtained curcumin samples were clear solutions without any precipitate even after centrifugation at 12000 rpm. Tween 20, 60, and 80 micelles with and without curcumin were prepared at a constant surfactant concentration of 1 mM, which is far above their critical micelle concentrations of Tween surfactants.

2.2.2. Surface tension measurement

Surface tension measurement was used to determine the critical micelle concentrations of Tween surfactants with and without 10 μM curcumin. At 25 °C, surface tension measurements were carried out on a Sartorius DCAT11 tensiometer using the Wilhelmy plate method. For the comparability of equilibrium surface tension, the measurements were stopped when the standard deviation of surface tension values was less than 0.01 mN/m.

2.2.3. UV–vis absorption measurement

The absorption spectra of curcumin in water and Tween 20, 60, 80 micelles were measured using a Shimadzu UV-1800 spectrophotometer. In the test of the stability of curcumin at 25 °C, curcumin samples were protected from light and the maximum absorption of 10 μM curcumin in water, Tween 20, 60 and 80 micelles were recorded at different time intervals within 180 min.

In the pH titration for the determination of the lowest pK_a (pK_{a1}) of curcumin in water, Tween 20, 60 and 80 micelles, the pH of curcumin samples was adjusted with concentrated sodium hydroxide or hydrochloric acid. The pKa_1 of curcumin was determined as the half point of sigmoidal transition curves of the absorption spectral mean ($\bar{\lambda}$) of curcumin, as a function of pH. The value of $\bar{\lambda}$ was calculated as (Wang et al., 2010):

$$\bar{\lambda} = \frac{\sum_{\lambda=300nm}^{\lambda=600nm} OD(\lambda) \times \lambda}{\sum_{\lambda=300nm}^{\lambda=600nm} OD(\lambda)} \quad (1)$$

where OD is the optical density at a given wavelength λ.

The binding constants (K_b) of curcumin with Tween 20, 60 and 80 micelles at 25 °C, 30 °C and 35 °C were determined using the change of maximum absorption of curcumin according to Benesi-Hildebrand equation (Stephanos, 1996).

$$\frac{1}{A-A_0} = \frac{1}{a} + \frac{1}{a \cdot K_b} \times \frac{1}{[\text{curcumin}]} \quad (2)$$

where A_0 corresponds to the maximum absorption of free curcumin, A is the maximum absorption of curcumin at different curcumin concentrations with Tween 20, 60 and 80 micelles, [curcumin] is curcumin concentration ranging from 2 to 12.5 μM, and a is a constant. The double reciprocal plot of $1/(A - A_0)$ vs. 1/[curcumin] is linear and the binding constant K_b can be estimated from the ratio of the intercept to the slope.

2.2.4. Steady-state fluorescence measurement

Steady-state fluorescence measurement was performed with a Shimadzu RF-5301 spectrofluorophotometer at 25 °C. The steady-state fluorescence spectra of curcumin in water, Tween 20, 60 and 80 micelles were taken from 450 to 600 nm with the excitation wavelength at 420 nm.

2.2.5. Statistical analysis

Data are presented as mean and standard deviations. For all measurements, a minimum of three replicates was taken for data analysis.

3. Results and discussion

3.1. Micellization of Tween surfactants in the absence and presence of curcumin

The micellizations of three Tween surfactants with and without 10 μM curcumin were studied using surface tension measurements at 25 °C. As shown in Fig. 1, with increasing surfactant concentration, the surface tension has a markedly higher decreasing rate below the critical micelle concentration (CMC) than above the CMC. The CMC values of Tween surfactants are taken as the concentration corresponding to the intercepts of two furnished straight lines in the curves of surface tension against surfactant concentration (Cirin, Poša, & Krstonošic, 2012). The CMC values of Tween 20, 60 and 80 without curcumin were 0.045,

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