



Effects of temperature and surfactant structure on the solubilisation of 4-chlorobenzoic acid by various surfactants



Nam-Min Lee, Byung-Hwan Lee*

Department of Applied Chemical Engineering, Korea University of Technology & Education, Cheonan, Chungnam 31253, Republic of Korea

ARTICLE INFO

Article history:

Received 8 April 2016

Received in revised form 3 May 2016

Accepted 4 May 2016

Available online 7 May 2016

Keywords:

Solubilisation

Thermodynamic parameters

Mixed surfactant system

Iso-structural temperature

ABSTRACT

The solubilisation constants (K_s) of 4-chlorobenzoic acid in aqueous solutions of various pure and mixed surfactants are determined by the UV–Vis spectrophotometric method. And the dependence of the K_s values on temperature has been measured and thermodynamic parameters are calculated to analyse the effects of head- and tail-groups on the solubilisation of 4-chlorobenzoic acid by various surfactants. The results show that the ΔG° values for all the surfactants are negative and decrease with the increase of temperature. On the other hand, the values of ΔH° and ΔS° are all positive within the measured temperature range and those values increase together with the increase of temperature. These thermodynamic parameters are depending severely on a chain length of alkyl-group as much as on a head-group of surfactant.

© 2016 Elsevier Ltd.

1. Introduction

Surfactants have hydrophilic head-groups and hydrophobic tail-groups in same molecules so that they make a micellar aggregation at a greater concentration than the critical micelle concentration (CMC). A micelle can be divided into an ionic surface and a hydrophobic core region [1–5]. Its surface is made with the head-groups of surfactants and an electric double layer is formed around the surface of the micelle. Its core part is constructed with the tail-groups of surfactants and can be divided into a palisade region and an inner core region. If the solubility of an insoluble substrate is plotted against the concentration of the surfactant, the solubility is very slight at concentrations below the CMC but rises abruptly once the CMC has been reached. Usually, the organic and inorganic substrates are solubilised into the polar palisade region or the hydrophobic core region of a micelle [6,7]. The solubilised sites of those substrates in a micelle are dependent on the properties of substrate and micelle, the interactions between them, and the strength of those interactions.

Nowadays various experimental methods and theories have been developed and used in order to study the solubilisation of various substrates by many surfactants [6–10]. In this work, we want to study the solubilisation phenomena of very polar and ionic substrate such as 4-chlorobenzoic acid by various pure and mixed surfactants, using the UV–Vis spectrophotometric method. An

atmosphere surrounding a solubilised substrate in a micelle is very different from that in pure water so that the absorbance values of solutions are varying with the concentration of surfactant and also on the degree of solubilisation of the substrate. Various surfactants such as cationic, non-ionic, and amphoteric surfactant were used for the solubilisation of 4-chlorobenzoic acid. Namely, cationic surfactants, having the same ammonium head-group but different alkyl-groups, such as DTAB (dodecyltrimethylammonium bromide), TTAB (tetradecyltrimethylammonium bromide), and CTAB (cetyltrimethylammonium bromide) were used. Non-ionic surfactants, having the same polyoxyethylene head-group but different alkyl-groups, such as Tween-20 (polyoxyethylene(20) sorbitan monolaurate), Tween-40 (polyoxyethylene(20) sorbitan monooleate), and Tween-80 (polyoxyethylene(20) sorbitan monooleate) were used. And LSB (lauryldimethyl(3-sulfopropyl) ammonium hydroxide) was used as an amphoteric surfactant to study the effects of mixed surfactants on the solubilisation of 4-chlorobenzoic acid. The mixed systems of LSB with cationic surfactants (DTAB, TTAB, and CTAB) and with non-ionic surfactants (Tween-20, Tween-40, and Tween-80) were used also to compare with the pure surfactant systems.

2. Experimental

2.1. Materials and making solutions

All the chemicals, used in this study, were obtained from Aldrich Corp. The provenances and purities of all the chemicals

* Corresponding author.

E-mail address: bhwanlee@kut.ac.kr (B.-H. Lee).

Table 1
Provenance and purity of reactants.

Chemical names	Source	Initial mass fraction purity	Purification method	Further treatments before use
4-Chlorobenzoic acid	Aldrich	0.99	None	Drying in a desiccator at $T = 298.15$ K for more than 24 h
DTAB	Aldrich	0.99	None	
TTAB	Aldrich	0.99	None	
CTAB	Aldrich	0.99	None	
Tween-20	Aldrich		None	
Tween-40	Aldrich		None	
Tween-80	Aldrich		None	
LSB	Aldrich	0.98	None	

used in this study are listed in Table 1 and were used directly without further purification except for drying in a desiccator for 24 h. Distilled and deionised water, made by using a Millipore system, was used to make the solutions. All the solutions were prepared by weighing methods as in the previous papers [6,7,11,12]. At first, the stock solutions of 4-chlorobenzoic acid (less than 10^{-5} mole/kg) was made and pure surfactant of solid or paste state was weighed and dissolved into this solution to make the concentrated solution of surfactant. This solution was diluted with the same stock solution of 4-chlorobenzoic acid continuously to make solutions, having the same concentration of 4-chlorobenzoic acid but different concentration of surfactant. For the mixed surfactant systems, the overall mole fraction (α_1) of LSB for the LSB/cationic and LSB/non-ionic mixed systems were fixed at 0.5, because at that mole fraction those mixed surfactants showed the greatest effects on the solubilisation of 4-chlorobenzoic acid.

2.2. Apparatus and methods

Absorbance values of all the solutions were measured at the same wave length of 250 nm and plotted against the concentrations of surfactant. Until the concentration of surfactant was increased to the CMC value, there was no change at an absorbance value. But after the CMC value, the absorbance value of solution is decreased abruptly by increasing the concentration of surfactant because of the solubilisation of 4-chlorobenzoic acid into a micelle. From the absorbance changes of the solutions with the concentration of surfactant, a straight line was obtained and the K_s values could be obtained from the slope of that straight line. The concentration of surfactant was changed from the CMC value continuously up to about 5 times of the CMC to determine the K_s values [6,11,12]. The pH values of all the solutions were almost 4.2 and not changed severely at every solution because the concentration of 4-chlorobenzoic acid and surfactant were not great. The UV-Vis spectrophotometer of Scinco Corp. (model S-4100) was used for the measurement of absorbance. The temperature was changed from 284 K to 312 K at every 7 K interval for the thermodynamic study. To control the temperature accurately (± 0.01 K), each solution was kept in a Fisher Scientific thermostat (model 9101) for 20 min before the measurement of absorbance. The experimental pressure was $0.101(\pm 0.005)$ MPa and was not changed during all the experiments.

3. Results and discussion

3.1. Determination of solubilisation constants

Solubilisation may be defined as the spontaneous dissolving of a substrate by reversible interaction with the micelles. Hirose et al. had developed the UV-Vis spectrophotometric method and theory to determine the degree of interactions of a substrate with a micelle (namely a solubilisation constant) [13]. They describe the solubilisation equilibrium as Eq. (1), where S_a and S_m denote the

substrates dissolved in aqueous phase and in a micellar phase respectively and D_m is total surfactants in a micellar form. They show that there is a relationship between absorbance values (A) of solutions and the solubilisation constant (K_s) as Eq. (2). At this equation, $[D_t]$ means total concentration of surfactant and A_a and A_m mean, respectively, the absorbance values in pure water and in a solubilised state into a micelle. When the left hand-side of Eq. (2) is plotted against A values for the solutions whose surfactants' concentrations are greater than the CMC value, a linear line is obtained that its slope is $-K_s$ and its intercept is $A_m \cdot K_s$.

$$S_a + D_m \rightleftharpoons S_m \quad (1)$$

$$(A - A_a)/[D_t] = K_s \cdot A_m - K_s \cdot A \quad (2)$$

By applying the same method and theory, we can determine the solubilisation constants (K_s) of 4-chlorobenzoic acid in various surfactant solutions. The K_s values in pure and mixed surfactant solutions have been measured at various temperatures for the thermodynamic study and the results were plotted against temperature for several surfactants in Fig. 1. Every plot in Fig. 1 is a little curved and increases with increasing temperature so that we can apply a second order equation of temperature to the $\ln K_s$ values of every plot as in Eq. (3). The K_s values for pure surfactants, which have the same hydrophobic alkyl-group but with different hydrophilic head-groups, are in the order of amphoteric < non-ionic < cationic. This means that the cationic surfactant is the most effective for the solubilisation of 4-chlorobenzoic acid and also that an electric interaction is occurred between substrate and micelle as well as a hydrophobic interaction between them. From Fig. 1, we

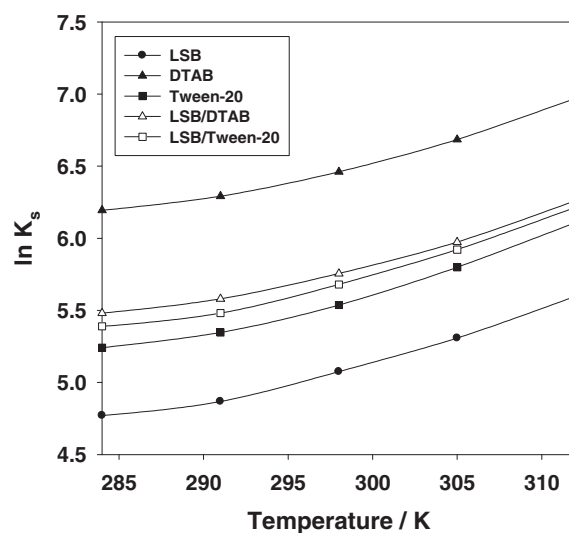


Fig. 1. Plots of $\ln K_s$ values against temperature for the solubilisation of 4-chlorobenzoic acid in aqueous solutions of various surfactants: (●) LSB; (▲) DTAB; (■) Tween-20; (△) LSB/DTAB; (□) LSB/Tween-20.

Download English Version:

<https://daneshyari.com/en/article/214922>

Download Persian Version:

<https://daneshyari.com/article/214922>

[Daneshyari.com](https://daneshyari.com)