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Temperature effects on adsolubilization of aromatic solutes partitioning to different regions in cationic admicelles

Wasan Saphanuchart[a], Chintana Saiwan[a,*], John H. O'Haver[b]

[a] The Petroleum and Petrochemical College, Chulalongkorn University, Soi Chula#12, Phayathai Road,
Pathumwan, Bangkok 10330, Thailand
[b] Department of Chemical Engineering, The University of Mississippi, University 38677, USA

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Abstract

This study examines the effect of temperature on the adsolubilization partition coefficient of sparingly soluble polar solutes. The adsolubilization of polar solutes, i.e. diphenylmethane, diphenylether, 4-bromotoluene and *p*-tolunitrile into cetylpyridinium chloride admicelles adsorbed on precipitated silica at pH of 8 were examined. The investigated adsolubilization temperatures were 20, 35, 50 and 65 °C. It was found that the admicelle/aqueous partition coefficients for the solutes are governed by molecular packing density in the admicelles, solute–surfactant headgroup interaction and the aqueous solubility of the solute. As temperature increased, the loosening molecular packing and increasing solute–surfactant headgroup attraction enhances the ability of the solutes to partition into the admicellar phase, increasing the partition coefficient. On the other hand, increasing temperature increases the aqueous solubility of the solute, which would reduce the partition coefficient. For slightly polar solutes, e.g. diphenylmethane and 4-bromotoluene, the partition coefficient tended to decrease as temperature increased, implying that the impact of increasing aqueous solubility plays the dominant role. For the more polar diphenylether, the impact of increasing solubility appears to be offset by strong attractive force between solute and surfactant headgroups, resulting in nearly unchanged partition coefficient values even with increasing temperature. For the highly polar solute *p*-tolunitrile, the partition coefficient initially decreased with increasing temperatures in the examined range (thus the solubility effects dominated) and then increased at higher temperatures in the examined range, suggesting that looser molecular packing and the solute–surfactant attraction dominate here.

Keywords: Adsolubilization; Solubilization; Admicelle; Silica; Aromatics; Cationic surfactant; Temperature

1. Introduction

The formation of aggregates by surfactant adsorbed at the solid/liquid interfaces has been well studied for decades [1]. The nature of these aggregates is much like that of micelles, thus these aggregates have thus been termed admicelles (adsorbed micelles) [1,2]. As with micelles, admicelles can solubilize various kinds of sparingly soluble solutes in a phenomenon called adsolubilization. Numbers of its potential applications have been proposed and developed to date, including chemical separations [3,4], semiconductor fabrication [5,6], surface modification [7–11], drug delivery [12] and soil remediation [13].

Similar in nature to a micelle, the admicelle is characterized by three regions [14]. The outer region, consisting of the surfactant headgroups, is the most polar and forms the admicelle/water and admicelle/solid interfaces. The inner region is referred to as the core region. This region consists of the hydrocarbon chains and is non-polar in nature. The region between the headgroups and the core is the palisade region. This region is intermediate in polarity, consists of the carbons near the headgroups, and is also characterized by water molecules that have penetrated the admicelle. Various studies have indicated that organic solutes partition into the regions of the admicelle that possess similar polarity. Thus, alkanes or other non-polar solutes partition primarily to the core region, while polar components partition to the palisade region and the headgroup region. Admicelle/aqueous partition coefficients have been used to elucidate the locus of adsolubilization in admicelle. The following trends have been proposed concerning the locus of adsolubilization and the

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* Corresponding author. Tel.: +66 2 2184110/2184111; fax: +66 2 2154459.
E-mail addresses: wasansp@gmail.com (W. Saphanuchart), chintana.sa@chula.ac.th (C. Saiwan), johaver@olemiss.edu (J.H. O'Haver).

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partition coefficients [14–17]: (1) if the solute partitions primarily to the core, the partition coefficients will increase as the intra-admicellar mole fraction of the solute increases; (2) if the solute partitions primarily to the palisade region, the partition coefficients will decrease as the intra-admicellar mole fraction of the solute increases; and (3) if the solute partitions to both the core and the palisade, the partition coefficient will remain constant as the intra-admicellar mole fraction of the solute increases.

A majority of the work done to date has examined the effects of various system parameters on the maximum amount of adsolubilized solutes. These have included studies of the effects of solute polarity, surfactant type, solution pH, solution ionic strength and solid substrate on adsolubilization [1,18]. The results have indicated that the maximum amount of a solute adsolubilized can be altered by controlling the amount of surfactant present at the solid/liquid interface as well as the structure of the adsorbed layers and the chemical conditions of the solution. To-date, most of these studies has been conducted at ambient temperature. However, to undergoes corresponding reactions, some of the applications such as admicellar polymerization have to be performed at higher temperatures [2,7–11,16,19] which will change equilibrium of both surfactant adsorption and adsolubilization. Because it is still lack of information about temperature effect on adsolubilization, this study therefore aims to investigate the impact of temperature on the ability of the admicelle to adsolubilize various sparingly soluble solutes possessing different polarities. The studied solutes were neutral and organic. This study will provide insight into changes in adsolubilization as a function of changing system temperature.

2. Materials and methods

2.1. Materials

Precipitated silica, Hi-Sil® 233, with a specific surface area of 150 m^2/g was supplied by PPG Industries Inc. (Pittsburgh, PA) and used as the solid substrate. The cationic surfactant cetylpyridinium chloride (CPC) was obtained from Sigma (St. Louis, MO). The studied solutes include diphenylmethane (99+ wt%) from Aldrich (St. Louis, MO), diphenylether (99+ wt%) from Aldrich (St. Louis, MO), 4-bromotoluene (99+ wt%) from Fluka (St. Lois, MO) and *p*-tolunitrile (98+ wt%) from Fluka (St. Louis, MO) as shown in Table 1 with their physicochemical properties [20]. The solvent was de-ionized water with a resistivity of 18.2 MΩ cm purified by a Barnstead E-pure water system. All chemicals were used as received.

2.2. Experimental procedures

2.2.1. Surfactant adsorption/admicelle formation

Surfactant stock solutions were made and adjusted to pH 8 with a dilute sodium hydroxide solution. These solutions were diluted with pH 8 de-ionized water to form a series of 20 mL solutions with varying surfactant concentrations. These were added to vials containing 0.4 g of silica and then sealed. The mixtures were shaken daily and allowed to equilibrate for 2 days at temperatures of 20, 35, 50 or 65 °C. They were then allowed to settle at those constant temperatures for 1 day. After that the supernatants were removed and centrifuged by a Fisher Scientific model MARATHON 300 at 3000 rpm for 15 min. The supernatants were removed and analyzed for the bulk surfactant concentrations through UV spectroscopy at $\lambda = 258$ nm [21] by using a SHIMADZU UV spectrophotometer model UV-1201S. Through a simple mass-balance, the amount of surfactant adsorbed per gram of silica was calculated.

2.2.2. Adsolubilization

The adsolubilization isotherms have also been examined at 20, 35, 50 and 65 °C. The appropriate initial surfactant concentrations for the adsolubilization studies were determined from the adsorption isotherms. An “appropriate concentration” is one that equilibrates just below (∼90%) of the critical micelle concentration (CMC), 0.91 mM [22], ensuring that (1) no micelles is present in the bulk solution and (2) near maximum surface coverage is achieved. The initial surfactant concentration was chosen for each temperature. Solute was then added into a pH 8 surfactant solution to make a stock solution with a concentration equal to the aqueous solubility of the solute. The solute stock solutions were then diluted to varying solute concentrations by adding pH 8 surfactant solution of the same surfactant concentration. Twenty milliliters was added to a vial with 0.4 g of silica and then sealed. The vials were shaken daily and allowed to equilibrate for 3 days at constant temperature. The samples were allowed to settle for 1 day before the supernatant was removed from the vials and then quickly centrifuged at room temperature. The supernatant was removed for analysis of the equilibrium solute bulk concentration using a dual-wavelength UV spectroscopic technique [14]. The wavelengths used for analyzing diphenylmethane, diphenylether, 4-bromotoluene and *p*-tolunitrile were 262, 269, 248 and 272 nm, respectively [23]. Calibration curves were developed, and the measured absorbance used to calculate the solute concentrations in the supernatant. Through a simple mass-balance, the amount of adsolubilized solute in the admicelles per gram of silica was calculated. This data was converted

Table 1
Physicochemical properties of the studied solutes [20]

Solutes	Chemical formula	Aqueous solubility at 25 °C (mole/L)	Melting point (°C)	Boiling point (°C)
Diphenylmethane	$C_{13}H_{12}$	8.381×10^{-5}	25.2	264
Diphenylether	$C_{12}H_{10}O$	1.06×10^{-4}	26.8	259
4-Bromotoluene	C_7H_7Br	6.43×10^{-4}	28.5	184
p-Tolunitrile	C_8H_7N	7.86×10^{-3}	29.5	217