

Headspace Solid-Phase Microextraction for Determination of Micellar Solubilization of methyl *tert*-butyl ether (MTBE)

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Abstract—Headspace analysis using solid-phase microextraction (SPME) was tested as a rapid method to evaluate micellar solubilization of methyl *tert*-butyl ether (MTBE) with sodium dodecyl sulfate (SDS) and cetylpyridinium chloride (CPC). At equilibrium between aqueous phase and vapor phase, free MTBE in vapor phase (i.e., not solubilized MTBE by SDS or CPC) was analyzed by GC-FID (Hewlett Packard 5890 series II) equipped with a capillary HP1 column (30 m×0.25 mm). This method showed a good analytical performance such as linearity of calibration curve and precision (RSD less than 5%). Extent of MTBE solubilization was expressed as a function of molar ratio of SDS to MTBE and CPC to MTBE, and was saturated at about 57% and 37% with over the value of ratio 13 for SDS and CPC, respectively. This technique can be applied to analyze micellar solubilization potential of various surfactants on volatile and semi-volatile compounds.

Key words: MTBE, Solid-Phase Microextraction, Micelle, Solubilization, Sodium Dodecyl Sulfate

INTRODUCTION

Methyl *tert*-butyl ether (MTBE) has been widely used as an oxygenate and octane enhancer in gasoline. It is also used in reformulated gasoline in order to reduce tail-pipe emission of volatile organic compounds and carbon monoxide. However, because of vehicular emissions and underground petroleum storage leaking, MTBE has become a known contaminant of surface water and groundwater due to its high solubility in water, and raised serious concerns regarding toxicity hazard.

Solid-phase microextraction (SPME) has been successfully used to rapidly concentrate a wide variety of polar and nonpolar compounds in aqueous matrixes. Recently, SPME techniques were used for analysis of MTBE instead of purge-and-trap or direct aqueous injection. Several researchers have reported an SPME-GC/FID or MS method for the determination of MTBE in surface water [Achten and Puttmann, 2000; Piazza et al., 2001; Llompарт et al., 1998; Casada et al., 2000]. Surfactants have been used for remediation of soils and groundwater contaminated with petroleum [Yang et al., 1996; Park et al., 1997; Cho and Chang, 1998; Cho and Kim, 2002]. Solubilization potential, the ability of surfactant micelles to increase the total hydrocarbon concentration in solution beyond the aqueous solubility component, is quantified by the micelle-water partitioning. To determine the solubility potentials for aqueous hydrocarbon concentrations below the solubility limit, semi-equilibrium dialysis (SED) cells have been used [Rouse et al., 1995; Park et al., 1997]. SED cells are time-consuming and may require at least 24 hours to reach the equilibrium. Thus, there is a need for a rapid and conve-

nient analytical method to determine solubility potentials of surfactants for separation of MTBE from groundwater.

In groundwater, MTBE can co-exist with organic compounds including surfactants, non-aqueous phase liquid, and polycyclic aromatic hydrocarbon. These organic compounds cause interference problems during extraction due to direct contact between samples and SPME probes. The SPME fibre can be suspended in the headspace above the aqueous sample to eliminate the interference problems due to other organic compounds [Piazza et al., 2001; Cho et al., 2003]. This work reports a new rapid and effective analytical method for micellar solubilization of MTBE using SPME combined with GC/FID.

MATERIALS AND METHODS

1. Chemicals

MTBE, sodium dodecyl sulfate (SDS), cetylpyridinium chloride (CPC) and other chemicals were supplied by Sigma-Aldrich (St. Louis, USA). SPME holder and polydimethylsiloxane (PDMS) coating fibre (100 µm film thickness) were purchased from Supelco (Bellefonte, USA). MTBE analysis was performed with a Hewlett Packard (Sunnyvale, USA) GC 6890 coupled with an FID.

2. SPME Extraction

The extraction was performed in an open-top screw vial (20 ml) equipped with a teflon-coated septum. A sample of 10 ml containing surfactant and MTBE was stirred at 20 °C for 120 min in order to achieve phase equilibrium. After the headspace extraction during 10 min, the SPME fibre was removed from the vial and immediately inserted into the GC injector. Desorption of MTBE from SPME fibre was executed during 3 min at 250 °C (GC injector temperature).

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3. GC-FID Analysis

The chromatographic capillary column was an HP5 (Hewlett Packard, 30 m×0.25 mm). The injector program was as follows: injector temperature, 250 °C, from 40 °C to 110 °C at a rate of 10 °C/min for column and the detector temperature, 250 °C. Helium was used as the carrier gas and the column flow rate was 1 ml/min with the split ratio 20 : 1.

4. Analysis of Overall Solubilization

Overall extent of solubilization of MTBE in the micelle may be expressed as,

$$S = \left[1 - \frac{C_{MTBE-f}}{C_{MTBE-i}} \right] \times 100$$

where C_{MTBE-i} and C_{MTBE-f} are initial total concentration of MTBE and concentration of free MTBE in the vapor phase and in the aqueous phase, respectively.

RESULTS AND DISCUSSION

1. SPME Method Optimization

It has been shown that addition of salts to a sample greatly improves the extraction efficiency for volatile organic carbons. In the case of MTBE, addition of 25% (w/v) sodium chloride increased by 10-fold the mean recovery of MTBE by the fibre [Piazza et al., 2001]. However, addition of sodium chloride affects the formation of micelle in surfactants system [Huang et al., 2001]. In this study, salts were not added into the system to eliminate the salt effects on solubilization. Extraction time (i.e., the adsorption equilibrium time between sample and fibre) was also investigated for optimization of the method. The optimized extraction time is reached when a significant increase in peak area is not observed. A series of experi-

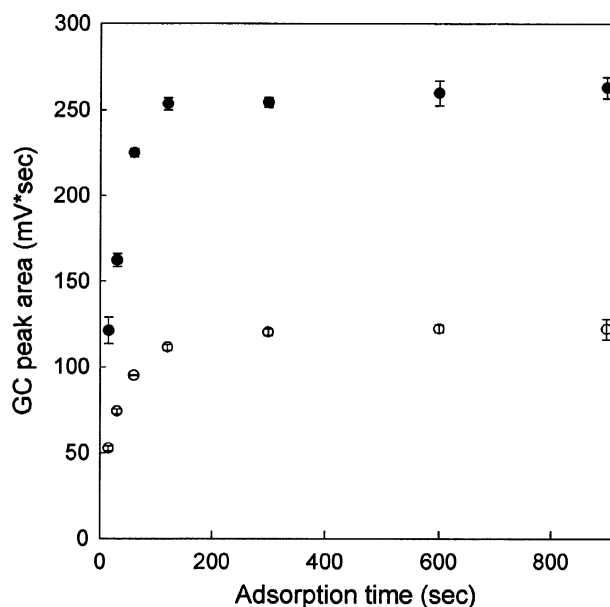


Fig. 1. Adsorption kinetics of MTBE on SPME fibre coated with 100 µm polydimethylsiloxane. Blank circle was result of headspace analysis with pure 100 mg/l MTBE solution, and black one was that of headspace analysis with 100 mg/l MTBE in 5 wt% SDS solution. Each sample volume of solution and headspace was 10 ml.

ments were conducted using a solution spiked with 100 ppm MTBE, varying extraction time between 1 and 15 min. The SPME fibre reached equilibrium within 2 min, after which no substantial changes in peak area were observed as shown in Fig. 1. Adsorption kinetics of 100 mg/l MTBE in 5 wt% SDS was also investigated. In both cases, the system reached equilibrium within 2 min, then, adsorption with SPME fibre was executed during 10 min throughout the entire experiments in this study.

2. Analytical Performance

2-1. Linearity

In order to evaluate the linearity of the headspace SPME method, a calibration curve over the concentration range of interest (10-1,000 ppm) was determined. All the experiments were carried out in triplicate at each concentration point. This gave a linear regression with a correlation coefficient (R^2) of 0.992 (data was not shown).

2-2. Precision

Precision was evaluated by calculating the relative standard deviation (RSD) of the triplicate runs used to peak area at each point. RSD ranged between 0.1% and 5%, which indicates a good reproducibility of the SPME method compared to the RSD (i.e., 2-8%) reported by Piazza et al. [2001].

3. Solubilization

3-1. Solubilization Potential of Various Surfactants

To maximize solubilization of MTBE, various surfactants were investigated at concentration of 2.5 wt%. Table 1 shows the potential of solubilization by various surfactants. Ionic surfactants with low molecular weight (i.e. SDS, CPC, BHAC) have higher potential than polymeric nonionic surfactants (i.e. PVA, PEG, Pluronic). SDS showed the maximum solubilization potential of MTBE among surfactants tested in this study.

3-2. Effects of Surfactant Concentration

To evaluate the effects of SDS and CPC concentration on micellar solubilization, headspace analysis was executed at several concentrations of SDS and CPC. Fig. 2 shows relative peak area of MTBE as a function of surfactant concentration. As shown in Fig. 2, solubilization of MTBE by SDS increased as the concentration of SDS increased. At SDS concentration of 5.0 wt%, solubilization of MTBE reached saturation at which the value was 57%. The tendency of solubilization by CPC was similar to that by SDS. However, the amount of MTBE solubilized was less than that of SDS at the same surfactant concentration. At the saturation point, solubilization of MTBE by CPC reached to 37%.

Table 1. Solubilization potential of various surfactants

Surfactants	Solubilization (%)	Surfactants	Solubilization (%)
Lecithin	6.1	SDS	56.1
PEG	0.4	CPC	37.2
Pluronic F-127	4.9	BHAC*	19.8
Aerosol OT	8.2	Brij 30	14.3
PVA	0.6	Triton X-100	12.1

Whole experiments were executed at surfactant concentration of 2.5 wt% with 500 mg/l MTBE. Each test was repeated three times and shown as mean values.

*Benzyl dimethyl hexadecyl ammonium chloride.

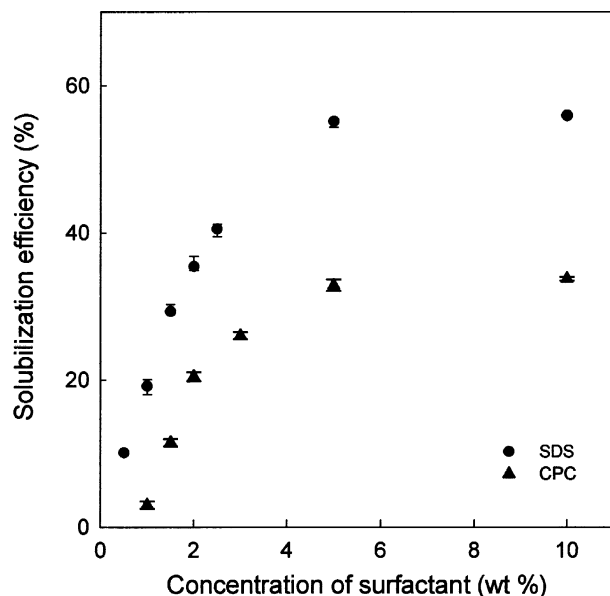


Fig. 2. Effects of SDS and CPC concentration on micellar solubilization of MTBE. MTBE concentration used in these tests was 1,000 mg/l.

3-3. Effects of Initial Concentration of MTBE

Effects of initial concentration on solubilization of MTBE were investigated. Range of MTBE concentration tested in this study was 10 mg/l to 1,000 mg/l. The solubilization was constant, and 57% of MTBE was solubilized by SDS micelles and 37% of MTBE by CPC in 5.0 wt% surfactant solution (data was not shown).

Variations of the extent of MTBE solubilization with SDS to MTBE molar ratio and CPC to MTBE molar ratio are shown in Fig. 3. The figure reveals a very interesting trend, that is, the extent of solubilization of MTBE increases rapidly and then gradually (even-

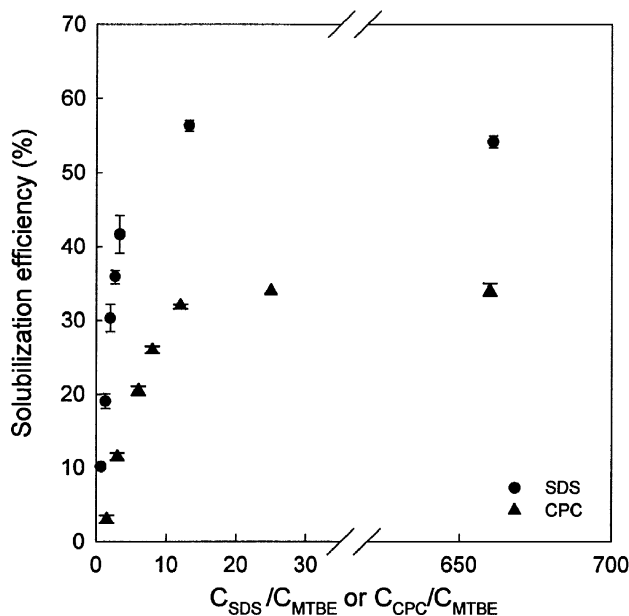


Fig. 3. Effects on micellar solubilization according to molar ratio of surfactant to MTBE.

tually reaching a plateau) with increase in the molar ratio in the aqueous solution. This result is similar to phenol solubilization by CPC reported by Syamal et al. [1997]. In this study, the maximum solubilization of MTBE by SDS and CPC was 57% and 37%, respectively, with the SDS to MTBE molar ratio greater than 13, without regard to surfactant and MTBE concentration.

CONCLUSIONS

Headspace analysis by SPME coated with PDMS (100 μ m film thickness) and GC-FID was a rapid means to determine extent of micellar solubilization of MTBE by SDS. Adsorption equilibrium in headspace between SPME fibre and vapor phase reached within 2 min without regard to presence of surfactant. Thermal desorption in GC injector was completed within 3 min. Solubilization potential of MTBE by SDS and CPC was expressed as a function of molar ratio SDS to MTBE and CPC to MTBE, and there are saturation values, 57% and 37% for SDS and CPC, respectively, over the value of ratio 13. The SPME headspace analysis in water/volatile and semi-volatile organic/surfactant system can be an effective method to determine micellar solubilization by surfactant.

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