

Synergistic solubilization of low-brominated diphenyl ether mixtures in nonionic surfactant micelles



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ABSTRACT

The present study investigated the co-solubilization of three representative low-brominated diphenyl ethers (low-BDEs) in nonionic surfactant micelles. Co-solubilization effects were quantified in terms of molar solubilization ratio (MSR), micelle–water partition coefficient ($\log K_m$), extent of synergism/inhibition ($R_{\Delta MSR}$), first stepwise association constant (K_1), the average number of solute molecules per micelle (S^M), excess Gibbs energy (ΔG_0 excess), and interaction parameter (ω/RT). The solubilities of low-BDEs during co-solubilization were increased (i.e., synergism) in all of the surfactants tested, relative to their respective solubilities during solubilization. In each surfactant system, synergism was weaker for BDE-15/BDE-28 than that for BDE-15/BDE-47 because BDE-15 and BDE-28 may be partitioned more uniformly in the micelle core than BDE-47, which increased the possibility of their competition. Unexpectedly, BDE-28 and BDE-47 with similar $\log K_{ow}$ values demonstrated enhanced co-solubility. This phenomenon was attributed to the positive electrostatic potentials of bromines (computed by Gaussian program) on BDE-28 and BDE-47 which may provide additional attractions to oxygen atoms of the hydrophilic chains. The synergism observed for BDE-15/BDE-28 and BDE-15/BDE-47 was stronger in the Brij35 system than that in Brij58 and Brij78 systems, suggesting that a surfactant with lower aggregation number and/or longer hydrophilic chain length can avoid the competition between solutes for the micelle core. This study may improve the understanding of multi-solutes interactions in surfactant micelles.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are one class of brominated flame retardants (BFRs) which are used as nonreactive additives in plastics, textiles, building materials, and electronic appliances [1,2]. As PBDEs are physically bonded to the products, they can be released into the environment during disposal activities [3], leading to serious environmental pollution. Among the PBDE congeners, low-brominated diphenyl ethers (low-BDEs) are generally of highest concern because (i) they are more toxic than high-BDEs [4], and (ii) they are accumulating in the environment via biotic [5] and abiotic debromination [6] of high-BDEs. Due to the hydrophobic properties of BDEs, they exhibit high partitioning to soil organic matter [7] increasing the difficulty of their soil remediation.

Surfactant-aided soil washing is a promising remediation technology for soils contaminated with hydrophobic organic contaminants [8]. During soil washing, several processes determine the remediation efficiency and/or overall cost: (i) the decrease in the soil–water interfacial tension induced by the surfactant [9]; (ii) the sorption of surfactant onto soil [10]; (iii) the incorporation of contaminants into surfactant micelles (i.e., solubilization) [11,12]; and (iv) the partition of contaminants to the soil-sorbed surfactant [13]. At contaminated sites, the co-occurrence of mixed-contaminants further complicates remediation because contaminants co-solubilization, rather than solubilization, in surfactant micelles occurs during soil washing [14], a process whose importance is not well understood.

Some researchers investigated the co-solubilization of polycyclic aromatic hydrocarbons (PAHs) in surfactant micelles [15–17]. Synergism may occur between PAH congeners with large difference in hydrophobicities due to (i) their different loci (i.e., solubilization sites) within micelles and (ii) the palisade layer solubilization of PAHs that leads to increased micelle core volume. In contrast, inhibition may occur for PAHs with similar hydrophobicities because of their competition for the same loci within micelles. However, it was reported that a low-

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BDE congener (4,4'-dibromodiphenyl ether, BDE-15) may interact with surfactant hydrophilic chains (i.e., halogen bonds) and thus affect co-solubilization [18]; that is, BDE-15 and pyrene with similar $\log K_{ow}$ values (5.55 and 5.18, respectively), showed enhanced co-solubility. As the $\log K_{ow}$ values of other low-BDEs (i.e., tri-, tetra-, and penta-BDEs) are all larger than BDE-15 [19], the micelle core solubilization of these BDEs will be the dominant process, and thus solubilization inhibition should occur between BDE congeners because of their competition for the micelle core. However, assuming that other low-BDEs also interact with the surfactant hydrophilic chains, the net impact of hydrophobicity and halogen bonds would make their co-solubilization effects difficult to predict. Therefore, additional work is needed to further investigate the effects of co-solubilization when halogen bonds are anticipated. However, the validation of the halogen bonding hypothesis through infrared spectroscopy [20], or Raman spectroscopy [21] appears to be impossible because the concentrations of other low-BDEs are too low to observe even a weak frequency change of C—Br bond. Therefore, we employed computational methods to test this hypothesis.

The main objectives of this study were to investigate the co-solubilization of BDE-15, 2,4,4'-tribromodiphenyl ether (BDE-28), and 2,2',4,4'-tetrabromodiphenyl ether (BDE-47) binary mixtures in non-ionic surfactant micelles. BDE-15, BDE-28, and BDE-47 were selected as the representatives of low-BDEs because of their large contribution to the total low-BDEs load at contaminated sites [22].

2. Materials and methods

2.1. Materials

Brij-series nonionic surfactants (Brij78, Brij58, and Brij35) were obtained from Sigma Aldrich Chemical Company. BDE-15 (purity $\geq 99.8\%$) was obtained from Alfa Aesar Company. BDE-28 and BDE-47 (purity $\geq 98.0\%$) were synthesized and provided by Shandong Analysis and Test Center, China. The structures and selected properties of the surfactants and low-BDEs are shown in Fig. 1.

2.2. Methods

2.2.1. Solubilization/co-solubilization experiment

Experiments were conducted in triplicate to determine the solubility of BDE-15, BDE-28, and BDE-47 in micellar solutions. Samples (25 mL) of each surfactant at various concentrations (2.56–8 mM) were placed in 30 mL borosilicate tubes covered with Teflon-lined screw caps, and then low-BDEs (single solute or binary mixtures) were added to excess. The samples were then equilibrated on a reciprocating shaker for 60 h at 150 rpm and $25 \pm 1^\circ\text{C}$, and centrifuged (4000 rpm, 30 min). Supernatant was withdrawn and analyzed by an Agilent 1260 HPLC fitted with a diode array detector (DAD) and Luna-PFP2 column (250 mm \times 4.6 mm, 5 μm) with acetonitrile–water (*v/v*, 85:15) as the mobile phase (1 mL/

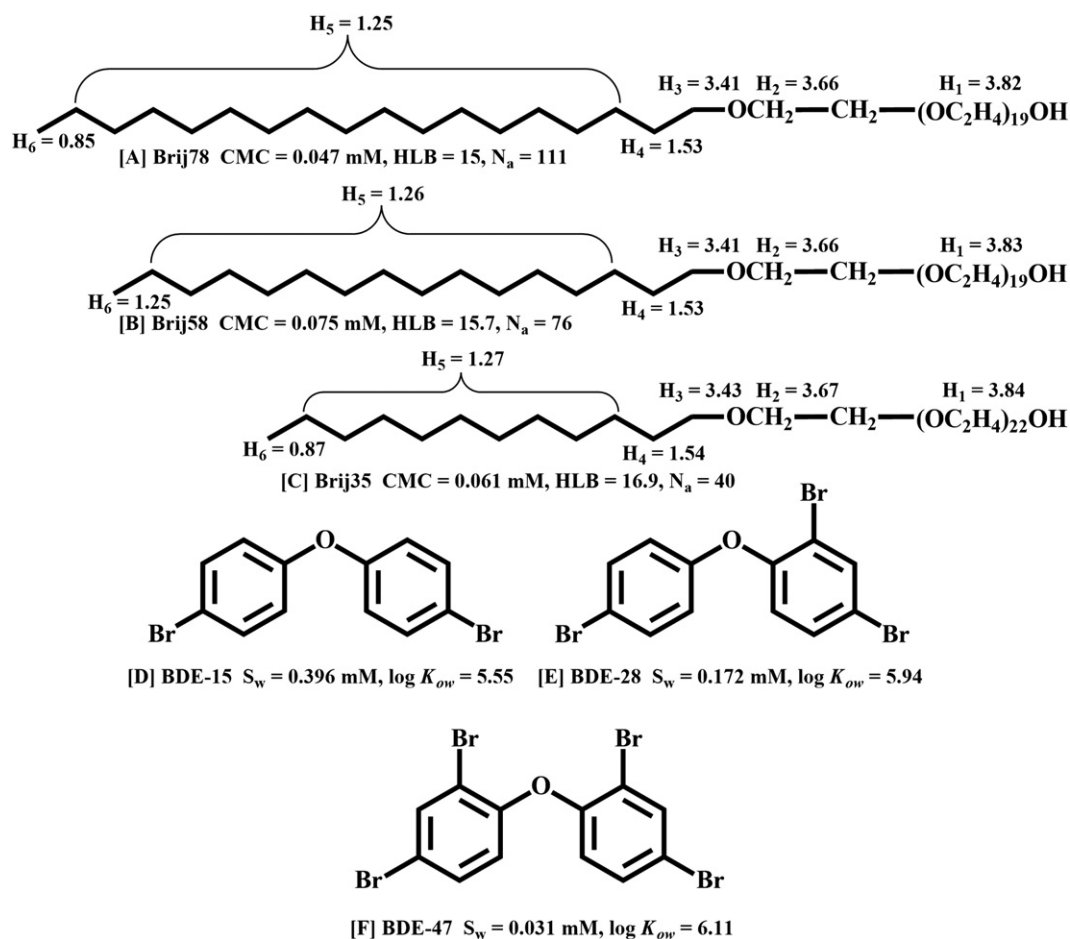


Fig. 1. Structures and properties of selected surfactants and low-BDE congeners. CMC and HLB are acronyms for the critical micelle concentration and hydrophile–lipophile balance, respectively. N_a is the aggregation number of a surfactant. S_w is the water solubility of a particular BDE congener, and H_1 – H_6 represent the nuclear magnetic resonance (NMR) chemical shifts of different protons in the surfactants.

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