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Solubilization Isotherms of Chlorobenzene in Ionic Surfactant Solutions

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Abstract

Solubilization isotherms of 1-chlorobenzene (MCB) and 1,2-dichlorobenzene (DCB) were investigated in ionic surfactant solutions such as sodium dodecyl sulfate (SDS), cetylpyridinium chloride (CPC), and dedecyltrimethylammonium chloride (DMAC). The solubilization extent of DCB was much higher than that of MCB because of the main driving force of solubilization is hydrophobic interactions between chlorobenzenes and hydrophobic interior of ionic micelles and DCB is more hydrophobic than MCB. CPC showed highest solubilization capacity because of longest hydrophobic tails. Simultaneous solubilization of MCB and DCB decreased slightly the extent solubilization of both MCB and DCB because the solubilization locus in the micelles is same.

key word : 1-chlorobenzne, 1,2-dichlorobenzne, sodium dodecyl sulfate, cetylpyridnium chloride, dodecyltrimethylammonium chloride, solubilizaiton

1. Introduction

Groundwater contamination by organic pollutants such as non-aqueous phase liquids (NAPLs) has threatened human health. NAPLs have high hydrophobicity, moderate to low water solubility, and toxicity to human beings. Remediation or removal of NAPLs is very difficult due to physico-chemical properties. Chlorinated benzenes are dense NAPL detected in groundwater.

Application of surfactant-enhanced aquifer remediation (SEAR) for remediation of chlorobenzenes has been reported as preliminary studies such as solubilization by cyclodextrins (1), solubilization (2-3), micellar-enhanced ultrafiltration (4). Application of SEAR is based on the hydrophobic interaction due to hydrophobicity of chlorobenzene. Even though some researcher reported the micellar solubilization of chlorobenzenes (2-3), there is no enough information on micellar solubilization for design of micellar-enhanced ultrafiltration. For application of micellar-enhanced ultrafiltration for removal of chlorobenzenes, solubilization isotherms of chlorobenzene should be studied in detail.

In this study, detail solubilizationisotherms of 1-chlorobenzene and 1,2-dichlorobenzene in ionic surfactant solutions were investigated as terms of molar fraction of chlorobenzenes in

the micelle-chlorobenzene complexes, equilibrium solubilization constants, and solubilization efficiency.

2.Materials and Methods

1-chlorobenzene (MCB), 1,2-dichlorobenzene (DCB), sodium dodecyl sulfate (SDS), decyltrimethylammonium chloride (DMAC), and cetylpyridinium chloride (CPC) were purchased from Sigma-Aldrich (St. Loouis, USA). MCB and DCB analysis were performed with a GC (Hewlett Packard 6890, USA) coupled with a FID. The chromatographic capillary column was a HP5 (Hewlett Packard, 30 m x 0.25 mm). The GC condition was as follows: injector temperature, 250°C; 40°C during 2 min, after then from 40°C to 190°C at a rate of 20°C/min for column; the detector temperature, 250°C. Helium was used as the carrier gas and the column flow rate was 1 ml/min without split. The head space analysis was performed in an open-top screw vial (20ml) equipped with a teflon-coated septum. A sample of 10 ml containing surfactant and MCB/DCB was shaken at the desired temperature for overnight in order to achieve phase equilibrium. Head space of 100 ul was sampled with gas tight syringe, and immediately inserted into the GC injector.

3.Results and Disccusions

Fig. 1. shows the mole fraction of MCB in SDS, DMAC, and CPC solutions. Generally, the mole fraction increased with the free concentration of organics in aqueous phase. The mole fraction of MCB followed the general trend of mole fraction. In CPC and SDS solutions, the mole fraction of MCB increased as the surfactant concentration increased from 20 mM to 50 mM, however, the mole fraction decreased as the surfactant concentration increased from 50 mM to 100 mM. This result was different to the solubilization of benzene in CPC and SDS solutions (5). Gadelle et al. (5) reported that the solubilization isotherms of aromatic solutes are independent of the surfactant concentration. However, this results shows that there are maximum mole fraction in the solubilization of MCB (one of aromatic solute). The solubilization of MCB by DMAC and SDS was investigated to compare effects of polar head group on solubilization isotherms of MCB. DMAC has 12 carbon in hydrophobic tail, which length of carbon chain is the exactly sameof SDS. However, DMAC has trimethyl ammonium in polar head group, but SDS has sulfate in polar head groups. Generally, solubilization capacity of surfactant micelles shows the following order : anionic surfactant < cationic surfactant < non ionic surfactant. Both a looser packing of the surfactant molecules in the cationic micelles and specific attractive interactions between the positive charge of the head groups and -electrons of the aromatic solutes enhanced solubilization of aromatic hydrocarbons in cationic surfactant compared to anionic surfactant (5). This is the reason why the solubilization extent of MCB in cationic surfactants, CPC, was higher than that in anionic surfactant, SDS. However, solubilization by CMAC was similar to that by SDS because extend of solubilization was also affected by other factors such as micellar volume.

Fig. 2 shows the mole fraction of MCB in the ionic surfactant micelles such as CPC, SDS, and DMAC. When the hydrophobic interaction is the main driving force for solubilization of MCB, the similar phenomenon occurs in the solubilization of DCB because DCB is more hydrophobic than MCB based on the Kow. As shown in the figure, the mole fraction of DCB was higher than that of MCB. In the case of cationic surfactants, CPC and DMAC, the molar fractions were independent of the surfactant concentration. An increase in the surfactant concentration can increase the free counterion concentration (chloride ion for the CPC and DMAC; sodium ion for SDS), thereby decreasing the energy of repulsion between charged head groups (pyridinium for CPC; trimethylammonium for DMAC; sulfate for SDS). This decrease in the repulsion between the head groups results in a decrease in the CMC andan increase in the aggregation number of the micelles. However, the decrease in the repulsion between head groups is also responsible for a crowded palisade layer, reducing solubilization of polar molecules (5). Independence of DCB mole fraction in the surfactant micelles proves that the main mechanism of solubilization for DCB is hydrophobic interaction

3.Conclusions

The solubilization characteristics of MCB and DCB were investigated in the ionic surfactants solutions, SDS, CPC, and DMAC. Most of MCB and DCB were solubilized at the hydrophobic interior of micelles due to hydrophobic interactions, and some of those were solubilized at the interface of water-micelles due to attractive interactions of between positive charges of cationic micelles and pi-electrons of MCB and DCB. CPC showed highest solubilization capacity for MCB and DCB because CPC has the larger hydrophobic interior volume due to longer hydrophobic tail groups. At the same concentration of surfactants, extent of DCB solubilization was higher than that for MCB because DCB is more hydrophobic than MCB. In the co-existence of MCB and DCB, the solubilization of MCB was inhibited by the presence of DCB because the two compounds were solubilized at the same locus in the micelles, and MCB decreased slightly the extent of DCB solubilization.

4. Acknowledgement

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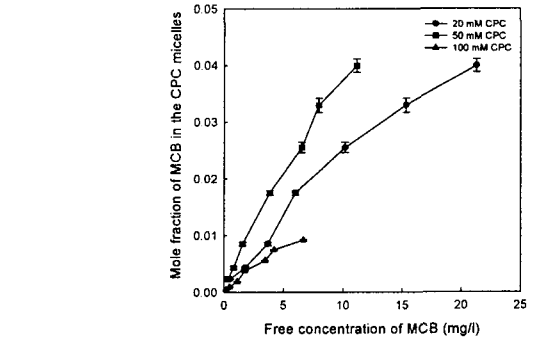
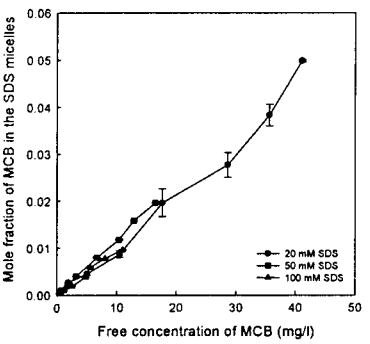




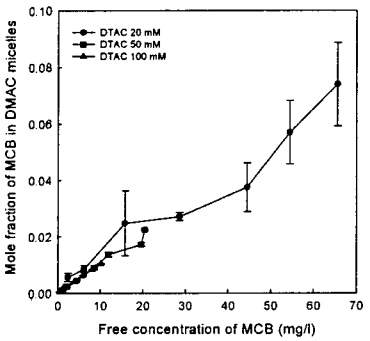
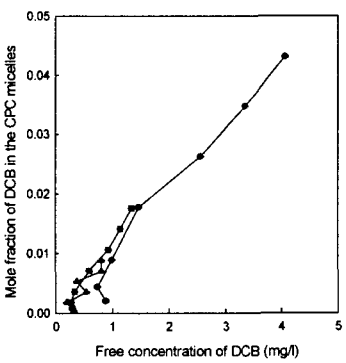
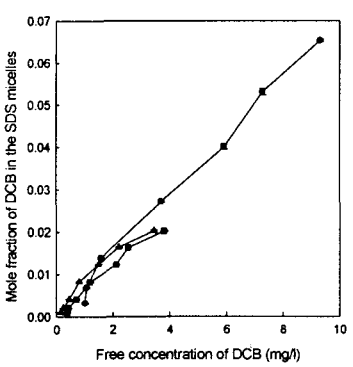


Figure 1





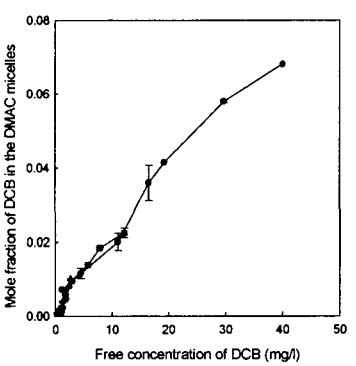


Figure 2