CHAPTER I

INTRODUCTION

1.1 Background

Environmental contamination due to wastewater discharges containing a trace amount of aromatic compounds can cause severe problems because of their toxicity either known or suspected carcinogens or mutagens (Bai *et al.*, 2001). Benzene, toluene, and ethylbenzene are common pollutants of great environmental concern originating from industrial effluents. A novel class of separation processes utilizing an environmentally friendly surface active agent is known as surfactant-based separations (Bai *et al.*, 2001; Scamehorn and Harwell, 1989). These techniques involve technologies such as surfactant enhanced oil recovery, foam fractionation, and froth flotation. These are increasingly used in process engineering (Scamehorn and Harwell, 2000). Cloud point extraction (CPE) is one of the surfactant-based separation technologies, which is effective in removal of organic compounds from polluted water (Bai *et al.*, 2001; Quina and Hinze, 1999; Huddleston *et al.*, 1999; Kimchuwanit *et al.*, 2000; Sakulwongyai *et al.*, 2000; Trakultamupatam *et al.*, 2002; Frankewish and Hinze, 1994; Hinze and Pramauro, 1993). This technique is economical and benign comparing to classical extraction methods, which are energy intensive and consume toxic organic solvents. Quina and Hinze (1999) provided a comprehensive review about CPE as an alternative separation approach. They reported that more than 94 % of polychlorinated biphenyls (PCBs), 88 % of polychlorinated dibenzofurans (PCDF), and 81 % of polycyclic aromatic hydrocarbons (PAHs) were extracted from wastewater by CPE in which Triton X-100, Brij-56, and Triton X-114 were utilized as nonionic surfactants, respectively.

An aqueous solution of nonionic surfactant undergoes a phase separation when it is at a temperature above its cloud point, attained either by heating or lowering the cloud point of the surfactant below the operating temperature (Bai *et al.*, 2001; Scamehorn and Harwell, 1989; Scamehorn and Harwell, 2000; Quina and Hinze, 1999; Huddleston *et al.*, 1999; Kimchuwanit *et al.*, 2000; Sakulwongyai *et al.*, 2000; Trakultamupatam *et al.*, 2002; Frankewish and Hinze, 1994; Hinze and Pramauro, 1993; Rosen, 1989). Two isotropic micellar phases are formed. One phase is generally less in volume and contains most of surfactant micelles and is known as a micellar-rich phase or coacervate phase. The other phase is an aqueous solution lean in surfactant micelles, known as a micellar-dilute phase. When nonionic surfactant is added to polluted water above the cloud point, the organic solutes contained in the solution will solubilize into surfactant micelles. After phase separation, the surfactant and pollutants are concentrated in the coacervate phase. The dilute phase, which contains a low concentration of organic pollutants, can be discharged to the environment as the effluent water. If a single stage results in insufficient purification, multiple stages can be used as with other traditional liquid-liquid extraction units.

Although many researchers have showed that the cloud point extraction is a promising technique to remove the organic contaminants from the wastewater, few works have dealt with the volatile organic compounds (VOCs) (Huddleston *et al.*, 1999). It is probably due to the experimental difficulty of making accurate measurements on these systems since leakage of these species is difficult to overcome. However, it is economically worthwhile to study the removal of these pollutants from water since the surfactant recovery is conceivable. These solutes have high volatility enough to be released from the coacervate phase by vacuum stripping, leaving the solute-free coacervate phase for reuse. In the other circumstances, when the organic solutes are non-volatile organic compounds, the coacervate phase, which contains a high solute concentration in small volume, can be disposed or incinerated.

For economic prospective, it is necessary to study the CPE in continuous operation on multistage extractor for large scale application. The principles of CPE and traditional liquid-liquid extractions are similar, except that two contacted phases in CPE can be completely miscible. The phase separation of CPE occurs because of the cloud point phenomenon of the nonionic surfactant solution at temperature beyond the cloud point. But the phase separations in the common liquid-liquid extraction systems occur by the immiscibility of two contacted liquids.

1.2 Objectives

The objectives of this research were to study the CPE of volatile aromatic solutes: benzene, toluene, and ethylbenzene from wastewater as batch experiments in a laboratory scale. The factors affecting the extraction were studied as follows: operating temperature, total surfactant concentration, added electrolyte concentration, and degree of alkylation of aromatic solutes. For large scale application, CPE requires a continuous, steady-state operation as with other liquid-liquid extraction units. Hence, the CPE was subsequently scaled up to continuous operation in a multistage, differential extractor. A standard size of rotating disc contactor was fabricated as a pilot scale apparatus. The effects of rotation speed of rotor disc, wastewater/surfactant flowrate ratio, operating temperature, added electrolyte concentration, and degree of alkylation of aromatic solutes on the extraction were studied. In addition, the number of transfer unit, the height of transfer unit, and the overall volumetric mass transfer coefficient were determined. Moreover, a comparison between results obtained from batch and continuous operation was present.

Prior to this work, a preliminary study on the CPE was studied in the systems containing di-, tri-, and tetrachloroethane as the organic solutes in laboratory scale at equilibrium condition in order to understand the extraction process in principles as outlined in the following section. This work was presented as a part of published paper in Langmuir as shown in the appendix.

1.3 Preliminary Study on the CPE of Chlorinated Hydrocarbon

1.3.1 Introduction

As the temperature of an aqueous solution of nonionic surfactant is increased, a temperature may be reached where the solution turns cloudy; this temperature is referred to as the cloud point. Above the cloud point, the solution may separate into a micellar concentrated or coacervate phase, and a dilute phase (Scamehorn and Harwell, 1989; Frankewish and Hinze, 1994; Hinze and Pramauro, 1993; Rosen, 1989). The concentration of surfactant in the dilute phase can be very low but is generally above the critical micelle concentration. When an organic solute is originally present in an aqueous solution and nonionic surfactant is added to the water, at temperatures above the cloud point, the organic solute will tend to partition into the coacervate phase as shown in Fig. 1. The vast majority of surfactant is present in the coacervate phase in some kind of aggregated form of the concentrated micellar solution. For example, Yoesting and Scamehorn (1986) showed that the nonideality of mixed aggregate formation between anionic and nonionic surfactants is very similar in coacervate and in micelles. This liquid/coacervate extraction (sometimes referred to as cloud point extraction) is a specific example of aqueous biphasic extractions (Roger and Eiteman, 1995). This technique shows great potential for removing toxic solutes from polluted water. The present study focuses on chlorinated hydrocarbons, a major class of pollutants, and quantifies the effect of the degree of chlorination of the solute.

1.3.2 Experimental

Octylphenoxypoly (ethyleneoxy) ethanol with an average of 7 moles of ethylene oxide per mole of octylphenol [$OP(EO)_7$] from Rhodia was the nonionic surfactant used as received in this study. Reagent grade 1,2-dichloroethane and 1,1,1,2-tetrachloroethane from Fluka Chemika-Biochemika, and 1,1,1-trichloroethane, from J.T. Baker Inc. were used as received. The water was deionized and distilled. In order to measure the distribution of solutes between dilute and coacervate phases, several identical 100-mL separatory funnels containing aqueous solutions with 50 mM $OP(EO)_7$ and an 1.0 mM of organic solute were placed in an isothermal water bath until equilibrium was reached, generally after about 2 days. After phase separation had occurred, the fractional volume of each phase was measured. The $OP(EO)_7$ and organic solute concentrations were measured by using CE 2000 series UV spectrometer at 224 nm. and gas chromatography with a flame ionization detector, respectively, in both the coacervate and dilute phases.

The cloud points were visually determined as the temperature at which a 50 mM surfactant solution became turbid at a heating rate of 1°C/minute.

1.3.3 Results and Discussion

1.3.3.1 Effect of temperature on coacervate extraction

The cloud point of the 50 mM $OP(EO)_7$ system is shown in Table 1 at several solute concentrations. The cloud point is only mildly dependent on the presence of the solute at the low solute concentrations used. The cloud point depression is greater as the degree of chlorination of the solute increases.

Table 2 shows the concentrations in coacervate and dilute phases, fractional distributions of components in phases, and partition ratio of solute and surfactant. Up to 99 % of $OP(EO)_7$, 79 % of 1,2-dichloroethane, 84 % of 1,1,1-trichloroethane, and 87 % of 1,1,1,2-tetrachloroethane are removed in the coacervate phase. As the temperature increases, the separation improves; the fractional volume of the coacervate decreases, partition ratio* increases, and fraction of solute in coacervate increases. The reason is when the temperature of the system increases, the system is further from the lower consolute solution temperature (which is approximately the cloud point), resulting in increasing dissimilarity between the coacervate phase and dilute phase, causing a decrease in the coacervate phase volume. The concentration of the surfactant and the chloroethanes in the coacervate phase increases with increasing temperature while these concentrations in the dilute phase are not much affected.

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[*] Partition ratio of substance is defined as the ratio of coacervate substance concentration to dilute phase substance concentration.

1.3.3.2 Effect of organic solute structure on coacervate extraction

The 1,1,1-trichloroethane and 1,1,1,2-tetrachloroethane both partition more effectively into the coacervate phase than 1,2-dichloroethane as seen in Table 2. The large increase in the partition ratio with an increase in solute hydrophobicity is probably mainly due to the decrease in the water solubility of the hydrocarbon compounds with increasing degree of chlorination (Nawakowska *et al.*, 1989). However, the degree of chlorination of the solute affects the partition ratio of the surfactant also as seen in Table 2, complicating the interpretation of data. For example, in a cloud point (or coacervate) extraction of a series of chlorinated phenols, Frankewich and Hinze observed an increase in the fraction of solute in the coacervate from mono- to di- to tri- chlorination, a decrease for the tetra-, and a large increase for the penta- (Frankewish and Hinze, 1994).

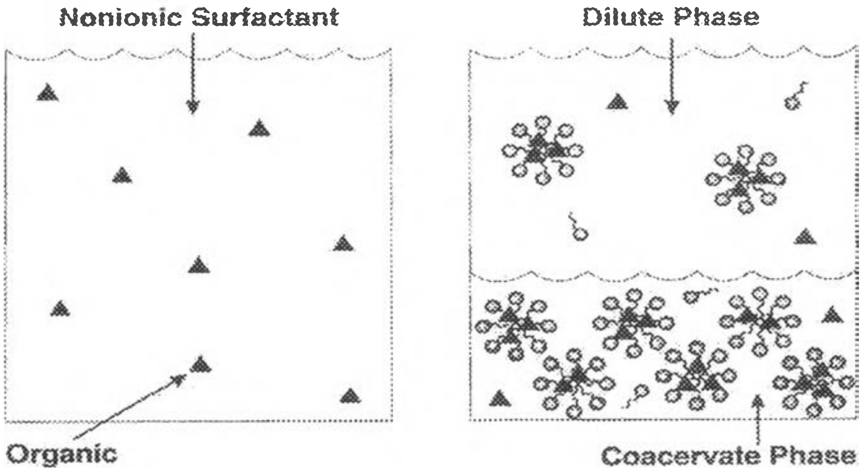

Figure 1 Schematic of liquid-coacervate extraction.

Table 1 Cloud points of 50 mM $OP(EO)_7$ system.

Solute Concentration (mM)	0	1.0
1,2-dichloroethane	22 °C	19 °C
1,1,1-trichloroethane	22 °C	16 °C
1,1,1,2-tetrachloroethane	22 °C	15 °C

Table 2 Liquid-coacervate extraction data : initial [$OP(EO)_7$] = 50 mM, initial [solute] = 1.0 mM.

System	Temperature (°C)	Fractional coacervate volume	[$OP(EO)_7$] (mM)		[Solute] (mM)		Fraction in Coacervate		Partition Ratio = [in coacervate]/ [in dilute phase]	
			Dilute	Coacervate	Dilute	Coacervate	$OP(EO)_7$	Solute	$OP(EO)_7$	Solute
$OP(EO)_7$/ dichloroethane	30	0.12	1.13	393	0.28	4.05	0.98	0.66	348	14.5
	40	0.08	1.05	560	0.29	7.47	0.98	0.69	533	25.8
	50	0.06	0.74	777	0.25	12.46	0.99	0.79	1050	49.8
$OP(EO)_7$/ trichloroethane	30	0.12	0.98	409	0.23	7.06	0.98	0.81	417	30.7
	40	0.08	0.72	603	0.18	8.81	0.99	0.81	838	48.9
	50	0.06	0.59	816	0.11	9.00	0.99	0.84	1383	81.8
$OP(EO)_7$/ tetra chloroethane	30	0.13	0.76	422	0.22	7.14	0.99	0.83	555	32.5
	40	0.08	0.52	633	0.17	9.26	0.99	0.83	1217	54.5
	50	0.07	0.49	846	0.15	12.90	0.99	0.87	1727	86.0