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I am submitting herewith a dissertation written by ZHOU SHI entitled "Surfactant-Enhanced Dissolution and Photolysis of Chlorinated Aromatic Compounds (CACs)". I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy with a major in Civil Engineering.

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We have read this dissertation
and recommend its acceptance:

Accepted for the Council:

Associate Vice Chancellor
and Dean of The Graduate School

SURFACTANT-ENHANCED DISSOLUTION AND PHOTOLYSIS OF CHLORINATED AROMATIC COMPOUNDS (CACS)

A Dissertation

Presented for the

Doctor of Philosophy

Degree

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Zhou Shi

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DEDICATION

This dissertation is dedicated to

谨以本文献给

my parents, Professors Kai Shi and Yunzhong Zhou

我的父母 施凯和周云中教授

who have provided me invaluable educational opportunities
and dedicated love support

以报答他们的养育和爱护；

and

my wife, Jun Wang and my daughter, Phebe

我的妻子 王俊和女儿菲碧

who have brought me constant inspiration and joy

以感谢她们带来的灵感和欢乐；

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ABSTRACT

The dissolution and photochemical behavior of 2-chlorophenol (2CP) and polychlorinated biphenyls (PCBs) in micellar surfactant solutions were evaluated.

The solubility of all PCBs examined were enhanced in surfactant solutions, even at surfactant dosages below the critical micelle concentration (CMC). However, at supra-CMC dosages of surfactants, the extent of solubility enhancement was much greater, the solubility being linearly related to surfactant concentration up to a dosage of 4 g/L. Nonionic surfactants were more effective than their anionic counterparts in dissolving PCBs. For three nonionic surfactants, polyoxyethylene (POE) lauryl ethers, the apparent solubility of 2,2',4,4'CB was inversely related to the hydrophile-lipophile balance (HLB) or the POE chain length in this case. Further, a linear relationship between K_m and K_{ow} was observed for several PCBs in polyoxyethylene (10) lauryl ether (POL (10)) solution. The UV spectra of 2,2',4,4'CB dissolved in micellar POL(10), hexane, and DME were similar indicating that the PCB molecules were possibly located at the micellar core or its vicinity. In 3 days of washing, POL(10) could extract 47-74% Soxhlet-extractable PCBs from two aged, PCB-contaminated soils. Linear Solvation Energy Relationship (LSER) was used to compare the degree of association of 2CP, a relatively soluble chlorophenol, with micelles in nonionic and anionic surfactant solutions. While only 15% of the 2CP molecules was associated with anionic sodium dodecyl sulfate (SDS) micelles, 38% was associated with the micelles of Brij35, a nonionic POE surfactant.

Photolysis of chlorinated aromatic hydrocarbons (CACs) was enhanced when dissolved in surfactant solutions. Acting as H-atom donors, surfactants promoted photodegradation rate and quantum yield of CACs, even at sub-CMC dosages. At supra-CMC dosages, formation of surfactant micelles further increased the reaction ability between CACs and surfactant molecules through micellar "cage" effects. The non-aqueous, solvent-like micellar "cage" allowed the reactants and intermediates to remain longer at higher local concentrations inside the micelles. Dechlorination followed by H abstraction from surfactant molecules appeared to be the principal mechansim of photodegradation PCBs in surfactant solutions. In stepwise photodechlorination of PCBs, *ortho* chlorine atoms were found to be more labile than the *para* chlorine atoms. For the photolysis of 2CP (pK_a=8.5), two pathways were identified. At pH > 8.5, the excited anionic species is dechlorinated to form a singlet carbene that can either be transformed to cyclopentadienecarboxylic acid through a ring contraction via the Wolff rearrangement, or be converted to phenol via a triplet carbene mechanism involving abstraction of two H atoms from an H donor, a surfactant for example. UV-irradiation of undissociated form of 2CP leads to the formation of catechol via a nucleophilic displacement of chloride in the presence of water, while in non nucleophilic media, the 2CP undissociated form was phototransformed to phenol, presumably by homolytic scission of the C-Cl followed by hydrogen abstraction. Phenol was observed to sensitize 2CP photodegradation involving a charge transfer dechlorination reaction.

Photolysis of PCBs in surfactant soil-washing solutions is effective, even in the presence of moderately high turbidity. The highly chlorinated congeners that are usually recalcitrant to biodegradation are likely to become biodegradable following photodegradation. Therefore, surfactant washing and photolysis, used in tandem, could be a viable technology for remediation of PCB contaminated soils.

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LIST OF ABBREVIATIONS AND SYMBOLS

$A_{ISs:}$ Peak area of internal standard in sample;

A_{ISstd}: Peak area of internal standard in standard solution;

$A_{Xs:}$ Peak area of peak X in sample solution;

A_{Xstd}: Peak area of peak X in standard solution;

A/V: Exposed area: volume of sample, m^{-1};

a: System dependent coefficients corresponding to $\Sigma\alpha_2$ or Proportionality constant of C_{EO};

b: System dependent coefficients corresponding to $\Sigma\beta_2$ or Proportionality constant of C_R;

c: constant for linear solvation energy relationship (LSER);

C_∞: Surfactant concentration at which S is evaluated, [g/L] or [M];

C_0: Concentration at time zero, [mg/L] or [M];

C_{mc}: Concentration fraction of surfactant as micelles, [dimensionless];

C_{mn}: Concentration fraction of surfactant as monomers, [dimensionless];

C_t: Concentration at time t, [mg/L] or [M];

C_∞: Cl^- concentration from photodechlorination of 2CP at infinite time. It is equal to the initial concentration of 2CP, [mg/L] or [M];

C_{EO}: Concentration of surfactant oxyethylene group, [equivelent/L];

C_R: Concentration of surfactant alkyl chain moiety, [equivelent/L];

CACs: Chlorinated aromatic compounds;

CB: Chlorobiphenyl;

CEB: Center for Environmental Biotechnology;

CMC: Critical micelle concentration, [mg/L] or [M];

CP: Chlorophenol;

DME: 1,2-dimethoxyethane;

DI: Deionized;

ECD: Electron-capture detector;

FID: Flame-ionized detector;

GC: Gas chromatography;

GEM: Genetically engineered microorganism;

HB: Hydroxybiphenyl;

HCB: Hexachlorobenzene;

HLB: Hydrophile-lipophile balance;

I_i: Extrapolated flux of incident light at weavlength λ_i, photons cm^{-2} sec^{-1};

$I_{o\lambda}$: Incident light intensity at weavlength λ, einsteins m^{-2} sec^{-1};

$[IS]_s$: Concentration of internal standard in sample;

$[IS]_{std}$: Concentration of internal standard in standard;

isc: Intersystem crossing;

j: Unit convert constant, in this study, $j = 6.023 \times 10^{20}$ when I_i and ε_i are in the unit of photons cm^{-2} sec^{-1} and M^{-1} cm^{-1}, respectively;

K_m: Micelle/water partitioning coefficient, [dimesionless];

K^e_m: Micelle/water partitioning coefficient, defined in eq (2.3), [dimesionless];

K^j_m: Micelle/water partitioning coefficient, defined in eq (2.4), [M^{-1}];

K^k_m: Micelle/water partitioning coefficient; defined in eq (2.1), [dimesionless];

K_{mc}: Partition constant between water and micelles, [dimesionless];

K_{mn}: Partition constant between water and monomers, [dimesionless];

K_{ow}: Octanol/water partition coefficient, [dimesionless];

k_0: Zero order rate constant, M min^{-1};

k_1: First order rate constant, min^{-1};

k_p: Rate constant;

LC: Liquid chromatography;

LSER: Linear solvation energy relationship;

MS: Mass spectrometer;

MSR: Molar solubilization ratio, [dimesionless];

MW: Molecular weight;

m/z: Ratio of mass to charge of an ion;

N_{aggr}: Micellar aggregation number;

N_{occ}: Micellar occupancy number;

NTU: Nephelometric turbidity unit;

n: $n = C_{EO}/C_R$;

OD: Optical Density;

P_L: Laplace presure acting across the curved micelle-water interface;

PAS: Phosphate buffered mineral salt medium;

PCBs: Polychlorinated biphenyls;

PhCl: Chlorinated biphenyl;

POE: Polyoxyethylenes

POL(6): Polyoxyethylene 6 lauryl ether;

POL(10): Polyoxyethylene 10 lauryl ether;

PSSS-VN: Poly(sodium styresulfonate-co-2-vinylnaphthalene);

p: System dependent coefficients corresponding to π_2;

R: Gas constant, $JK^{-1}mol^{-1}$;

R_2: Parameter accounting for solute excess molar refraction;

RH: Alkane;

ROH: Alchol;

r: System dependent coefficients corresponding to R_2

S: Apparent solubility of solute in surfactant solution; [mg/L] or [M];

S_w: Intrinsic solubility of solute in deionized water, [mg/L] or [M];

S_{cmc}: Apparent solubility of solute at surfactant concentration of CMC, [mg/L] or [M];

SDBS: Sodium dodecyl benzene-sulfonate;

SDS: Sodium dodecyl sulfate;

SdiS: Sodium dioctyl sulfsuccinate;

SIM: Selected ion monitoring;

$[\text{total PCB}]_{std}$: Total concentration of commercial PCB (Aroclor) standard, [mg/L];

T: Thermodynamic temperature, °K;

TX100: Triton X-100;

t: Photolysis time, [min];

$t_{1/2}$: Half-life, [min];

UV: Ultra vilet;

VIS: Visible;

V_o^*: Molar volume of octanol saturated with water, [L/mole];

V_s: Molar volume of surfactant, [L/mole];

V_w: Molar volume of water, [L/mole];

V_w^*: Molar volume of water saturated with octanol, [L/mole];

V_x Parameters accounting for solute molar volume, ($cm^3\ mol^{-1}$);

v: System dependent coefficients corresponding to V_x;

v_A: Molar volume of solute, [L/mole];

v_o: Volume fraction of solute in octanol phase, [dimensionless];

v_s: Volume fraction of solute in micelle in dilute condition, [dimensionless];

v_w: Volume fraction of solute in distilled water;

v^*_w: Volume fraction of solute in octanol-saturated water phase, [dimensionless];

wt%: Weight percent of peak X in the commercial PCB;

X_a: Molar fraction of the solute in the aqueous pseudophase, [dimensionless];

X_m:	Molar fraction of the solute in the micellar pseudophase, [dimensionless];
$[X]_s$:	Concentration of peak X in sample, [mg/L] or [M];
$[X]_{std}$:	Concentration of peak X in standard, [mg/L] or [M];
Y_n:	Distribution of the solute between the mantle and the core of a nonionic surfactant micelle;
Φ:	Quantum yield;
Σ:	Sum;
$\Sigma\alpha_2$:	Parameters accounting for solute hydrogen bond acidity;
$\Sigma\beta_2$	Parameters accounting for solute hydrogen bond basicity;
ε:	Molar extinction coefficient, [M^{-1} cm^{-1}];
κ:	κ band
λ:	Wavelength, [nm];
π_2	Parameters accounting for solute dipolarity;
τ_a:	Solute activity coefficient in aqueous pseudophase;
τ_m:	Solute activity coefficient in micellar pseudophase
τ_o^*:	Solute activity coefficient in octanol;

CHAPTER 1

INTRODUCTION

Many chlorinated aromatic compounds (CACs), such as 2-chlorophenol (2CP) and polychlorinated biphenyls (PCBs), are EPA priority pollutants due to their toxicity and widespread distribution in the environment (DHEW Subcommittee, 1978; Callahan *et al.*, 1979; Safe, 1990; Silberhorn *et al.,* 1990; Ahlborg *et al.*, 1994; Beck *et al.*, 1995). 2CP has been widely used in pulp and paper, herbicide, and pesticide industries and has been identified in industrial effluents, soils, and finished drinking waters (Suntio *et al.*, 1988; Shiu *et al.*, 1994). PCBs saw extensive industrial use as dielectric fluids, transformer oils, and as fire retardants, among others (Hutzinger *et al.*, 1974; Sawhney, 1986). Because of their recalcitrance, CACs are biodegraded very slowly in the environment (Ettinger and Ruchhoft, 1950; Iwata *et al.*, 1973; Pal *et al.*, 1980; Rochkind *et al.*, 1986; Brown Jr. *et al.*, 1987; Bedard *et al.,* 1987, 1996; Qurnsen III *et al.*, 1988; Abramowicz, 1990; Van Port *et al.*, 1991; Harkness *et al.*, 1993; Jarnberg *et al.*, 1993; Alcock *et al.*,1993; Tiedje *et al.*, 1993; Rhee *et al.*, 1993; Sokol *et al.*, 1994; Ofjord *et al.*, 1994; Pagano 1995; O'Connor and Young, 1996; Chitra and Chandrakasan, 1996). The toxicity and carcinogenic potential of PCBs are of great concern (DHEW Subcommittee, 1978; Callahan *et al.*, 1979; Silberhorn *et al.*, 1990; Luthe *et al.*, 1994).

CACs are sensitive to UV irradiation. Phototransformation has been reported as one of the major pathways of CACs degradation in the aqueous environment (Safe *et al.*, 1976, Sawhney, 1986). Direct irradiation of 2CP in the aquatic environment forms dechlorinated products such as cyclopentadienecarboxylic acid and catechol (Guyon *et. al.*, 1982; Boule *et al.*, 1982, 1984, 1987). The major photochemical reaction observed in PCBs is reductive dechlorination (Hutzinger *et al.*, 1974; Safe *et al.*, 1976; Sawhney 1986). PCBs with high chlorine substitutions undergo photolysis faster than those with lower chlorine substitutions (Hutzinger *et al.*, 1974). Chlorine atoms at the *ortho* positions (2, 2', 6, and 6') are most photolabile (Ruzo *et al.*, 1974a, b; Safe *et al.*, 1976); removal of *ortho*-chlorines relieves the steric compression much more than that of the *meta*- or *para*- chlorines at the excited state. Thus, multiply chlorinated biphenyls will lose *o*-chlorine relatively efficiently and fast. That the most bio-recalcitrant *o*-chlorines are most photoreactive, makes photolysis an attractive method for PCB remediation. However, byproducts such as polychlorinated dibenzo-*p*-dioxins (PCDDs) (Vollmuth *et al.*, 1994) and polychlorinated dibenzofurans (PCDFs) (Crosby *et al.*, 1973), reportedly more toxic than the parent PCBs themselves (Safe, 1990), should be eliminated to take advantage of PCB-photoremediation.

Soil-bound CACs, such as PCBs, can both be mobilized and solubilized using surfactants (Kile and Chiou, 1989; McDermott *et al.*, 1989; Jafvert *et al.*, 1995; Abdul *et al.*, 1991; 1992, Shi, 1995). Fortuitously, surfactants may serve as H atom source to enhance photodechlorination of CACs and minimize of hydroxyl substitution in dechlorinated CACs (Romsted, 1984; Bunton, 1984; Ionescu *et al.*, 1984; Pelizzetti *et al.*,

1984; Ramamurthy, 1986; Kalyanasundaram, 1987; Epling *et al.*,1988; Chu and Jafvert, 1994; Shi *et al.*, 1997). Further, the cage and localization effects imposed by surfactant micelles can speed up the dechlorination reaction. PCDFs and PCDDs are reportedly less stable than PCBs under UV irradiation, especially when a H source is present (Crosby *et al.*, 1973; Safe *et al.*, 1976; Wong and Crosby, 1978; Wipf *et al.*, 1978; *Waste Age,* 1980; Choudhry *et al.*, 1987; Dung *et al.* 1994; Friesen *et al.*, 1996). Thus, they are not likely to form if photolysis of PCBs occurs in micellar surfactant solutions.

Effects of surfactant on the photolysis of CACs have not been studied in depth. Such information is crucial for incorporating photolysis into existing CAC remediation schemes. The purpose of this research is to evaluate the photochemical behavior of CACs in surfactant solutions. The specific objectives are:

1. To evaluate distribution of CACs between micellar and aqueous pseudophases in commercial nonionic and anionic surfactant solutions and to study mobilization of soil-bound PCBs;

2. To investigate mechanism(s) and kinetics of photodegradation of micelle-incorporated CACs.

CHAPTER 2

SOLUBILIZATION OF CHLORINATED AROMATIC COMPOUNDS (CACS) IN MICELLAR SURFACTANT SOLUTIONS

2.1 BACKGROUND

Due to their hydrophobic and inert nature, many chlorinated aromatic compounds (CACs) such as polychlorinated biphenyls (PCBs) and chlorophenols, strongly sorb to soil (especially the soil with high organic contents) and resist degradation (Sawhney, 1986; Chou and Griffin, 1986). Remediation of PCB contaminated soils is a challenging environmental problem.

Desorption of soil-bound CACs is a primary step in many remediation practices. Most often desorption of PCBs from soils and sediments must be facilitated using organic solvents such as alcohols (Li and Andren, 1994) or other aqueous lixiviants such as humic and fulvic acids (Chiou *et al.*, 1986, 1987). However, either the potential toxicity of the solvents or inefficiency of the lixiviants limits its application to soil remediation. On the other hand, with their amphipathic structure, surfactants have the ability to increase solubility of CACs and enhance mobility of CACs in soils (Vigon and Rubin,

1989; Abdul *et al.*, 1990, 1991, 1992). In addition, degradation of CACs by photolysis, discussed in chapters 3 and 4, can be enhanced when CACs are dissolved in micellar solutions of surfactants. Increasingly, surfactants are being studied for environmental applications. The enhancement of solubilization and mobilization of CACs by surfactants, in particular, their distribution and localization within the surfactant micelles, are reviewed in this section.

2.1.1 Mechanism of Solubilization by Surfactants

All surfactants possess an amphiphilic structure consisting of at least one hydrophobic moiety and one hydrophilic moiety. The hydrophobic moiety has little affinity for polar solvents such as water, while the hydrophilic moiety has a strong affinity for polar solvents. High surface activities of surfactants arise from this unique structure.

Presence of surfactants in aqueous solution causes a distortion of the ambient water structure, mainly due to the incompatibility of the hydrophobic moiety with water. As a result, the free energy of the system is increased. To minimize the free energy increase in the system, surfactant molecules tend to concentrate at the interface of the two phases with the hydrophilic moiety remaining in the aqueous phase and the hydrophobic moiety moving away from it. Therefore the surface tension (surface excess free energy

per unit interface area) is decreased. When all interfaces are saturated, to reduce the overall free energy of the system, the surfactant molecules aggregate to form a cluster called "micelle". The hydrophobic groups of the surfactant form the micell's core while the hydrophilic groups form its outer layer shielding the core from surrounding water. The surfactant concentration at which micelles begin to form is called the critical micellar concentration (CMC).

One of the most important consequences of micelle formation is the enhancement of solubilization of hydrophobic organic compounds (HOCs) of limited intrinsic aqueous solubilities. HOCs are incompatible with water due to H-bonding between water molecules; thus they are expelled from aqueous solutions. The core of micelles provides a hydrophobic environment for HOCs to reside, resulting in a small increase of free energy of the system. Such a process is defined as 'micellar solubilization'.

By definition, micellar solubilization is the preparation of a thermodynamically stable, isotropic solution of a substance (the "additive") normally insoluble or only slightly soluble in a given solvent by addition of one or more amphiphilic compounds at or above their CMC (Attwood and Florence, 1983; Myers, 1991). It is different from 'emulsification', defined as a dispersion of one liquid in another in the form of droplets (Becher, 1965). In micellar solubilization, the dissolved material (solute) and the solvent are in the same phase while in emulsification the emulsified material (droplets) is a separate phase from the surround liquid. Solubilization is a thermodynamically favored

process while emulsification is not. Thus, HOCs dissolved in surfactant micelles form stable solutions; emulsions are inherently unstable.

2.1.2 Solubilization of CACs in Aqueous Surfactants

Solubilization of CACs in aqueous surfactants is a process in which the solute (CAC) partitions between the aqueous and micellar pseudophases (Valsaraj and Thibodeaux, 1989). Two different methods for evaluating CAC partitioning are discussed here, one for equilibrium (saturated) solutions of solutes and the other for unsaturated solutions. The former usually occurs in the dissolution of extremely hydrophobic compounds such as PCBs and the latter in the dissolution of less hydrophobic CACs like chlorophenols.

PCB Partitioning Between Micellar and Aqueous Pseudophases: PCBs represent a group of extremely hydrophobic compounds. The intrinsic solubility of all of the possible 209 PCB congeners and biphenyl ranges from $(1.2 \pm 0.5) \times 10^{-6}$ mg/L to 7.0 ± 0.5 mg/L at 25°C (Shiu and Mackay, 1986). It has been demonstrated that the aqueous solubility of PCBs is enhanced in surfactant solutions (Zitko, 1970; Hutzinger *et al.*, 1974; Sawhney, 1986; Chou and Griffin, 1986; Kile and Chiou, 1989; Dulfer *et al.*, 1995; Jafvert *et al.*, 1995; Shi *et al.*, 1995). Since the solubility enhancement results from a partitioning-like interaction between the solute and the non-polar group of the surfactant molecules (Kile

and Chiou, 1989), solubilizing ability of a micelle is usually expressed by a thermodynamic constant referred to as the partitioning coefficient, K_m.

Kile and Chiou (1989) expressed K^k_m as the ratio of the apparent solubility of PCB (total dissolved PCB) in surfactant solution to its intrinsic solubility in water:

$$K^k_m = S/S_w = (1+C_{mn}K_{mn}+C_{mic}K_{mic}) \quad (2.1)$$

where S = apparent solubility of the solute in the surfactant solution, g/L;

S_w= intrinsic solubility of the solute in pure water, g/L;

C_{mn}= concentration of the surfactant as monomers, g/L;

C_{mic}= concentration of the surfactant as micelles, g/L;

K_{mn}= partition constant of the solute between water and monomers, $K_{mn}= S'_{mn}/S_w$.

Here S'_{mn} expresses the mass of solute partitioned into a unit mass of monomers;

K_{mic}= partition constant of the solute between water and micelles, $K_{mc}= S'_{mic}/S_w$.

Here S'_{mc} expresses the mass of solute partitioned into a unit mass of micelles;

Edwards *et al.* (1991) defined molar solubility ratio (MSR) as the ratio of moles of solute dissolved per mole of surfactant. The partitioning of a solute between water and

surfactant can be expressed by the thermodynamic coefficient K^e_m, related to MSR as follows (Hayashe and Hayano, 1977):

$$MSR=(S-S_{cmc})/(C-CMC) \quad (2.2)$$

$$K^e_m=X_m/X_a$$

$$=MSR/[(1+MSR)S_{cmc}V_w] \quad (2.3)$$

where C= surfactant concentration, M

S= total apparent solubility of solute at C > CMC, M;

S_{cmc}= apparent solubility of solute at CMC, M;

X_m= mole fraction of solute in micellar pseudophase;

X_a= mole fraction of solute in aqueous pseudophase;

V_w= molar volume of water, 0.0181 L/mole at 25 °C.

Jafvert, *et al.* (1994) described K^j_m as follows:

$$K^j_m= (S-S_{cmc})/[S_{cmc}(C-CMC)]$$

$$= MSR/ S_{cmc} \quad (2.4)$$

where S, S_{cmc}, C, CMC, and MSR are the same as defined in Equation 2.2.

Thus, K^e_m and K^j_m are correlated as follows:

$$K^j_m = K^e_m (1+MSR)V_w \qquad (2.5)$$

The partitioning coefficient K_m can be correlated to the activity coefficient (τ) of the solute and K_{ow} , its octanol/water partitioning coefficient. Using the relationship proposed by Bolden *et al.* (1983) for a solute in equilibrium between aqueous and micellar pseudophases

$$\tau_a X_a = \tau_m X_m \exp(- P_L \nu_A/RT) \qquad (2.6)$$

where τ_m and τ_a are solute activity coefficients in micellar and aqueous pseudophases, respectively;

P_L= Laplace pressure acting across the curved micelle-water interface;

ν_A= molar volume of solute;

R and T are gas constant, J K^{-1} mol^{-1}, and temperature, K, respectively.

Valsaraj and Thibodeaux (1989) derived a relationship between K^e_m and K_{ow}:

$$K^e_m = K_{ow}\tau_0 * \frac{V_0^*}{V_w} \exp(-\frac{P_L \nu_A}{RT}) \qquad (2.7)$$

where τ_o*= activity coefficient of solute in octanol;

V_o* = molar volume of octanol saturated with water;

V_w = molar volume of water saturated with octanol;

K_{ow}= octanol/water partitioning coefficient.

Using Equation 2.4, Jafvert *et al.* (1994) derived a similar relationship between K^j_m and K_{ow}:

$$K^j_m = K_{ow} V_s v_s v^*_w / (v_o v_w) \qquad (2.8)$$

where v_o= volume fraction of solute in octanol phase;

v_s= volume fraction of solute in micelles in dilute solutions;

v^*_w= volume fraction of solute in octanol-saturated water phase;

v_w= volume fraction of solute in distilled water;

V_s= molar volume of surfactant.

Linear relationships between $\log K_m$ and $\log K_{ow}$ was derived by Valsaraj and Thibodeaux (1989), Edwards *et al.* (1991).

Chlorophenol Partitioning between Micellar and Aqueous Pseudophases. Chlorophenols are less hydrophobic than PCBs. Studies of chlorophenols are always carried out in

unsaturated solutions. Distribution of chlorophenols between the micellar and aqueous pseudophase in such solutions can be estimated using a linear solvation energy relationship (LSER) given in Equation 2.9. The micelle-water partitioning coefficient, K^j_m, can be determined in units of M^{-1}(Quina *et al,* 1995; Abraham, 1987, 1993):

$$\log K^j_m = c + a\Sigma\alpha_2 + b\Sigma\beta_2 + p\pi_2 + rR_2 + v(V_x/100) \qquad (2.9)$$

where: $\Sigma\alpha_2$, $\Sigma\beta_2$, π_2, R_2, and V_x ($cm^3\ mol^{-1}$) are parameters to account for solute hydrogen bond acidity, hydrogen bond basicity, dipolarity, excess molar refraction, and molar volume, respectively;

a, b, p, r, and v are the system dependent coefficients corresponding to $\Sigma\alpha_2$, $\Sigma\beta_2$, π_2, R_2, and V_x, respectively;

c is a constant.

Location of CACs inside Micelles Location of a solubilized molecule in a micelle primarily depend on the chemical structure of the molecule (Myers, 1991). In general, molecules of extremely hydrophobic compound such as hydrocarbons intimately partition inside the core of micelles; less hydrophobic compounds such as alcohols usually locate themselves in the interfacial region (palisades layer) between the core and outer layer of micelles. Hydrophilic organic compounds may reside only at the outer layer of micelles (Mukerjee , 1980; Myers, 1991).

Mukerjee (1971) proposed a theoretical model for determining the location of solutes inside a nonionic surfactant micelle. There are two possible loci of solubilization inside a micelle: the nonpolar hydrocarbon core and the surrounding polyoxethylene

mantle. The model assumes that the amount of the molecules solubilized in the core is proportional to the number of equivalents of surfactant alkyl chain moiety (C_R), while the amount of the molecules solubilized in the mantle is proportional to the number of equivalents of surfactant oxyethylene groups (C_{EO}). The total amount of molecules solubilized in the micellar pseudophase, S, is expressed by:

$$S = aC_{EO} + bC_R \tag{2.10}$$

or $$S/C_{EO} = a + bC_R/C_{EO} \tag{2.11}$$

where a and b are proportionality constants. They can be easily determined if S/C_{EO} and C_R/C_{EO} are linearly correlated.

The distribution, Y_n, of the solute between the mantle and core of a nonionic surfactant micelle can be expressed as

$$Y_n = aC_{EO}/bC_R = n(a/b) \tag{2.12}$$

where $n = C_{EO}/C_R$

If $Y_n = 1$, the solute is equally distributed between the core and the mantle of a surfactant micelle. If $Y_n < 1$, the solute prefers the core and if $Y_n > 1$, it prefers the mantle.

Mukerjee (1971) tested the model using several benzoic acid derivatives dissolved in different polyoxyethylene stearate (Myri-49, 51, 52, 53, and 59) solutions and found the results to fit the linear model well. Goldenberg *et al.* (1993) applied the same model

to a group organic compounds of different polarities dissolved in micellar solutions of several Triton surfactants (C_8PhEO_x, X= 9.5, 12.5, 16, and 30). Both nonlinear and linear models were needed to describe the solubility data. For nonlinear systems, the sites of solutes could not predicated using the model. Even for linear systems, the solubilization sites predicted by the model did not match those obtained from experimental methods such as UV and NMR. These results indicate that the location of solute inside micelle may not be predicated using simple models that do not consider factors such as micellar size, interactions between solute, surfactant, and water molecules. The location of a solubilized molecule inside a micelle can also be determined using analytical techniques such as UV, fluorescence, NMR, X-ray diffraction, and ESR (Attwood and Florence, 1983; Lopes *et al.* 1992; Goldenberg *et al.* 1993). To date, almost no information exists in the literature regarding the location of PCBs and chlorophenols inside surfactant micelles though this type of information is useful in understanding the fate of such chemicals in photochemical and other reactions.

2.1.3 Solubilization of CACs by Surfactant in Soil Suspensions

Solubilization of soil-bound CACs by surfactants is a complicated process that has been extensively studied over the past two decades (Hutzinger *et al.*, 1974; Sawhney, 1986; Jafvert *et al.*, 1995). However, only the issues related to application of surfactant washing to soils contaminated with CACs are addressed in this report.

McDermott, *et al.* (1989) were able to extract in excess of 95% of soil-bound PCBs (Aroclor 1260) from an artificially contaminated soil (1 g PCB/kg soil) using a 1%

sodium dodecylbenzenesulfonate (SDBS) in a laboratory-scale four-stage countercurrent soil washing system. The PCBs in the wash water were further reduced to 1.8 μg/L, approximately the solubility of Aroclor 1260, by precipitation using $CaCl_2$. Abdul and co-workers (1991, 1992) evaluated the effectiveness of an alcohol ethoxylate surfactant (Witconol SN70) for washing PCBs from a contaminated field soil. Using surfactant concentrations ranging from 5 to 20 g/L, 50 to 86 % of the Aroclor 1248 (1728 g/kg) were washed off of the contaminated soil in a laboratory column after 20 pore volume of the surfactant solution was applied in single passes (no recycle). A surfactant concentration of 10 g/L was found to be most effective. It was postulated that lower concentrations resulted in fewer micelles in solution into which soil-bound PCBs could partition, and higher concentrations resulted in elevated adsorption of surfactant on the soil which led to pore clogging and changes in soil surface chemistry thereby decreasing PCB mobilization.

Based on their laboratory experiment, Abdul and co-workers (1992) conducted a field test of the surfactant-washing process for desorbing PCBs from a contaminated soil. During 70 days of washing, 5,375 gallons of a 0.75% aqueous surfactant solution were applied at the site at an average rate of 77 gal/day. A total of 10,981 gallons of leachate were recovered at an average rate of 157 gal/day (including 80 gal/day of ground water). A total of 1.6 kg of PCBs (10% of the initial mass) with a maximum concentration of 65 mg/L was extracted from the site. *In-situ* surfactant washing was able to mobilize PCB

from the contaminated soil although recovery was less than that obtained in the laboratory.

In addition to synthetic surfactants, biosurfactants can successfully enhance removal of CAC pollutants from soils. Dyke *et al.* (1993) used partially purified rhamnolipid produced by *P. aeruginosa* UG2 to enhance desorption of 2,2',5,5'CB, 3,3',4,4',5,5'CB, and PAHs sorbed to soil. They found that removal of PCBs depended upon the type of soil, equilibration time, and concentration of biosurfactant. Using a 5 g/L biosurfactant solution for soil washing, recoveries of 43 and 69% of 2,2',5,5'CB and 3,3',4,4',5,5'CB were achieved in a silty loam soil. Approximately 20% of the biosurfactant became bound to the soil. For a sandy loam soil, recoveries of the two test PCB congeners were about 55% each. Recovery of 2,2',5,5'CB from the silty loam soil using biosurfactant was 7.6 times higher than that recovered using the anionic surfactant SDS, but only 0.8 times higher than that recovered using a polyoxyethylene glycol surfactant (Witconol SN70). Shi (1995) reported that a purified biosurfactant (rhamnolipid R1, 96% pure) solution at 4 g/L, removed 85% of 4,4'CB from a laboratory contaminated soil (1.73 mg PCB/kg soil) after 3 batch washes. Sorption of the biosurfactant to the soil was 4.55 mg/g soil.

2.2 MATERIALS AND METHODS

2.2.1 Materials

Surfactants Five surfactants, Brij35, polyoxyethylene 10 lauryl ether (POL (10)), polyoxyethylene 6 lauryl ether (POL (6)), Triton X-100 (TX100), and sodium dodecyl sulfate (SDS), obtained from Sigma Chemical Co., were used without further purification. SDS was the only anionic surfactant used while the others were nonionic.

CACs. Three PCB congeners (99.7% pure): 2,2'-dichlorobiphenyl (2,2'CB), 2,2',4,4'-tetrachlorobiphenyl (2,2',4,4'CB), 2,2',4,4',6,6'-hexachlorobiphenyl (2,2',4,4',6,6'CB), and one commercial PCB mixture (technical grade Aroclor 1242), were used. All PCBs were obtained from Ultra Scientific and used as received. Additionally, 2-chlorophenol (2CP) was used. 2CP was purchased from Fisher Scientific Company and further purified by chromatography on a Chromatotron (Model 7924T, Harrison Research) eluting with dichloromethane. After purification, the 2CP was found to be > 99.5 % pure by gas chromatography (GC) (HP 5890 series II) with a flame ionization detector (FID). All solvents used in the study were GC or HPLC grade. The characteristics of the surfactants and CACs used in the study are listed in Table 2.1.

2.2.2 Methods

Surface Tension Surface tension of test solutions was measured at ambient temperature (22± 1 °C) using a tensiometer (Tensiomat Model 21, Fisher Scientific Co).

Solubilization of PCBs by Surfactants All solubilization experiments were carried out at room temperature (22 ± 1 °C). While duplicate samples were used to determine

Table 2.1. Characteristics of surfactants and CACs

Compound	Chemical formula	MW	HLB[a]	
Brij35	$C_{12}H_{25}(OCH_2CH_2)_{23}OH$	1198	22.2	
POL(10)	$C_{12}H_{25}(OCH_2CH_2)_{10}OH$	626	17.9	
POL(6)	$C_{12}H_{25}(OCH_2CH_2)_6OH$	450	16.6	
TX100	$C_{14}H_{21}(OCH_2CH_2)_{9.5}OH$	624	18.7	
SDS	$CH_3(CH_2)_{11}OSO_3Na$	288	51.4	
			Solubility[b] (M)	$\log K_{ow}$[b]
2,2'CB	$C_{12}H_8Cl_2$	223.1	4.48×10^{-6}	4.9
2,2',4,4'CB	$C_{12}H_6Cl_4$	292.0	3.08×10^{-7}	5.9
2,2',4,4',6,6'CB	$C_{12}H_4Cl_6$	360.9	1.94×10^{-9}	7.0
Aroclor 1242	$C_{12}H_{6.92}Cl_{3.08}$[c]	260.3[c]	1.22×10^{-6}	4.7
2CP	ClC_6H_4OH	128.6	0.182[d]	2.17[d]

[a]Hydrophile-lipophile balance, calculated using Davies and Rideal equation.(Myers, 1992).

[b]Aqueous solubility and octanol/water partitioning coefficient (K_{ow}) of Aroclor 1242 are according to Mackay *et al.* (1992), the others are from Shiu and Mackay (1986).

[c]Average molecular formula and molecular weight determined by its Cl content, 42% by weight (see section 2.3.3 in this chapter).

[d]Shiu *et al.* (1994).

solubilities in surfactant solutions, aqueous solubilities were determined in triplicate. Excess pure PCB crystals were added to 25 mL glass centrifuge tubes containing 8-10 mL surfactant solutions (0 – 4.0 g/L) prepared in deionized (DI) water. The amount of crystals added was at least five-fold greater than the amount required to saturate the surfactant solutions. To determine aqueous solubility, PCB crystals were added to 8-10 mL of DI water and mixed for 3 days in an end-over-end rotor. The solution was then centrifuged at 10,000 rpm (7280 x g) for 30 minutes. A 1-mL aliquot, carefully collected from mid-depth of the supernatant layer, was transferred to 15-mL glass tube containing 4 mL of hexane. To prevent emulsion formation during mixing, 0.3 g of a silica-based powder, tC_{18} (Waters, Inc.), was then added in experiments involving nonionic surfactants. For experiments involving anionic surfactants, 0.3 g of an anionic exchange resin, QMA (Waters, Inc.) was used instead. The samples were then mixed for 30 minutes in a reciprocal shaker followed by centrifugation for 10 minutes at 1,000 rpm (168 x g). The hexane phase was carefully collected, suitably diluted, and analyzed for PCB by GC (Shimadzu: Model GC-14A) equipped with an electron-capture detector (ECD) and a DB-1 capillary column (0.25 mm id, 30 m long) (J & W Scientific Inc.). The GC column temperature was programmed as follows: It was initially held at 60 °C for 2 minutes, then raised to 180 °C at a rate of 10 °C/min. and thereafter to 225 °C at a rate of 6 °C/min. After 14 minutes at 225 °C, the temperature was further raised to 280 °C at a rate of 5 °C/min and held constant for 13.5 minutes. The PCB concentration in a sample was determined by comparing with standard PCB congeners. 2,2',3,3',4,5,6,6'-octachlorobiphenyl was used as the internal standard (Ultra Scientific) in all GC analyses. No attempt was made to establish detection limits for the PCB congeners. However, all test PCBs with concentrations greater than 0.01 mg/L in hexane could be identified by GC using 1 μL injection.

To estimate extraction efficiency, a 2 mL surfactant solution saturated with PCB was extracted with hexane as follows. Known amounts of PCB dissolved in ether were added to 15-mL test tubes. The amount of PCB added ranged from 90 to 110% of that needed to saturate the surfactant solution. Having vaporized ether by gently purging with N_2, 2 mL of surfactant solution was added. Then the tubes were capped with Teflon lined cap and shaken for 3 days. PCB in the surfactant solution (2 mL) was then extracted with 8 mL of hexane. 0.6 g of tC_{18} (or QMA in the case of anionic surfactants) was used. The PCB extracted in the hexane phase was analyzed by GC. The ratio of the total recovered PCB to the total added was taken as a measure of extraction efficiency. The extraction efficiency of all PCB-surfactant solutions tested, save for 2,2',4,4'CB-POL(6) and 2,2',4,4'CB-SDS solutions, was greater than 90%. The extraction efficiency of 2,2',4,4'CB-POL(6) was between 67 and 87%, and that for 2,2',4,4'CB-SDS between 78 and 95%.

The aqueous solubilities of PCB determined by the "centrifugation method", described above, and the "filtration method" were compared using 2,2',4,4'CB as the test compound. After mixing for 3 days, the aqueous solutions of 2,2',4,4'CB were filtered through three different filtering media: silver (0.45 μm), Teflon (0.20 μm), and polycarbonate (0.20 μm). After discarding the first 4 mL of the filtrate, the remainder (4 mL) was collected and analyzed in the same fashion as that used in the "centrifugation method." To estimate loss of dissolved PCB due to adsorption on the filter paper, a submicellar POL(10) solution with a 2,2',4,4'CB concentration nearly equal to its

aqueous solubility was filtered through a fresh filter paper. The difference in PCB concentration before and after filtration was taken as an estimate of the loss of dissolved PCB due to adsorption on filter paper.

Solubilization of 2CP by Surfactants Two surfactants, Brij 35 and SDS, at concentrations of 0.1 and 4.0 g/L, were used to prepare solutions of 2CP. To prepare a 0.1 g/L solution of 2CP in surfactants, 19.8 μL of pure 2CP liquid (density: 1.2634 g/mL) was added with a syringe to a 250 mL flask containing 200 mL of standard surfactant solutions. The total volume of the solution was made up to 250 mL with the standard surfactant solution. All solutions were prepared without pH manipulation, or degassing, unless otherwise stated. The solutions were stirred overnight with a magnetic stirrer before use.

The concentration of 2CP in surfactant solution was determined with a HP1090 liquid chromatograph (LC) (Hewlett Packard, Inc.) equipped with a Hypersil ODS column (id x length = 2.1mm x 200 mm, C_{18} with particle size 5 μm). The solvent ratio of acetonitrile:water (CH_3CN:H_2O) was linearly changed from 20:80 to70:30 over a period of 16 minutes. To protonate hydroxyl groups of the products, the eluent water was preadjusted to pH 2.0 with H_2SO_4. All samples were analyzed in duplicate. The detection limit of 2CP by HPLC was 0.02 mg/L for 0.5 μL injection.

Surfactant Solubilization of Soil-Bound PCBs To study the feasibility of mobilizing PCB from contaminated soils with surfactants followed by UV-irradiation of the soil wash, a

clayey soil and a sandy soil obtained from PCB contaminated sites were chosen. Following air-drying, the soils were screened through US standard sieve no. 35 (0.50 mm) and the fraction passing was stored in an amber glass bottle at 4 °C. The PCB contents of the soils were determined by Soxhlet extraction (EPA method 3541). 2.5 g soil was extracted with 50 mL of a 1:1 (v/v) hexane:acetone mixture in a Soxhlet extraction apparatus (Soxtec, Model HT1043, Perstorp Analytical Inc.). The total PCB concentration in the clayey and the sandy soil were found to be 11.73 and 0.318 mg/g, respectively.

Surfactant solubilization of soil-bond PCB was conducted in batch experiments. 1 g of screened soil was mixed with 20 mL of POL(10) solution (0-4 g/L) in 25 mL glass centrifuge tubes for various time periods. At the end of mixing, the samples were centrifuged at 10,000 rpm (7280 x g) for 30 minutes. 1 mL aliquots of supernatant were extracted with hexane and analyzed for dissolved PCB using the method described in Section 2.2.2 All samples were prepared and analyzed in duplicates.

2.3 RESULTS AND DISCUSSION

2.3.1 Aqueous Solubility of 2,2',4,4'CB

The solubility of 2,2',4,4'CB in deionized water was determined using both centrifugation and filtration methods (Table 2.2). The aqueous solubility of 2,2',4,4'CB

Table 2.2. Comparison of aqueous solubility of 2,2',4,4'CB determined by centrifugation and filtration methods[a]

Method		Solubility (mg/L)	Solubility (M)
Literature value (average)[b]		0.090 ± 0.030	$(3.08 \pm 1.03) \times 10^{-7}$
Centrifugation		0.0917 ± 0.0150	$(3.14 \pm 0.51) \times 10^{-7}$
Filtration:	Silver Filter (0.45 μm)	0.365 ± 0.251	$(1.25 \pm 0.86) \times 10^{-6}$
	Teflon Filter (0.20 μm)	0.472 ± 0.385	$(1.62 \pm 1.32) \times 10^{-6}$
	Polycarbonate Filter (0.20 μm)	0.0964 ± 0.0371[c]	$(3.30 \pm 1.27) \times 10^{-7}$

[a]Errors are reported as standard deviation
[b]Shiu and Mackay (1986)
[c]Dissolved 2,2',4,4'CB in filtrate = 0.0193 ± 0.0112 mg/L; dissolved 2,2',4,4'CB adsorbed on polycarbonate filter = 0.0771 ± 0.0259 mg/L

obtained in the current study using the centrifugation method agreed well with the value of 0.090 ± 0.030 mg/L or (3.08 ± 1.03) x 10^{-7} M reported by Shiu and Mackay (1986). Corrected for the loss of dissolved PCB due to adsorption, the values obtained using filtration through polycarbonate filters also agreed well with values reported by Shiu and Mackay (1986).

The minimum radius (r) of the particle which can be removed by centrifugation can be calculated from Equation 2.13 below (Hiemenz, 1986):

$$r^2 = \frac{4.5\eta \ln \frac{R_2}{R_1}}{\omega^2 (t_2 - t_1)(\rho_2 - \rho_1)} \qquad (2.13)$$

where R_1 and R_2 = radial positions of particle at time t_1 and t_2, respectively;

t_2-t_1= centrifugation time;

ω = angular velocity;

ρ_1 = density of the solution; ρ_2 = density of 2,2',4,4'CB;

η = viscosity of solution;

In this study, the values of the parameters in Equation 2.13 are as follows:

R_1= 5.5 cm; R_2 = 7.5 cm;

t_2-t_1= 1800 sec;

ω = 1047.2 sec^{-1};

$\rho_1 \approx \rho_w$ at 25 °C = 997 kg/m^3;

ρ_2 = 1090 kg/m^3 (Shiu and Mackay, 1986);

$\eta \approx \eta_w$ at 25 °C = 8.904 x 10^{-4} kg sec^{-1} m^{-1}.

The minimum average radius (r) of the 2,2',4,4'CB crystals that were removed by centrifugation is estimated to be 0.0823 μm which is much less than the pore size of the filters tested. Thus, the centrifugation method was found to be reliable.

Silver and Teflon filters yielded solubility values much greater than those reported. Conceivably, some of the micro-crystals passed through the 0.45 μm silver filter. The Teflon filter paper stretched in the filter holder and the pores might have been enlarged. The "centrifugation method" was used for measuring solubilities of PCB congeners in the remainder of this study.

2.3.2 Equilibration Time for PCB Solubilization by Surfactants

To determine the equilibriation time for PCB solubilization, the concentration of 2,2',4,4'CB dissolved in POL(10) and Brij35 was measured as a function of time. The results are shown in Figure 2.1. For the surfactant dosages studied, equilibrium was achieved after about 48 hours. However, the standard deviation of measured at 72 hours was smaller than that at 48 hour. PCB was allowed to equilibrate with surfactants for 72 hours in all solubilization experiments. These results agree well with that reported in the

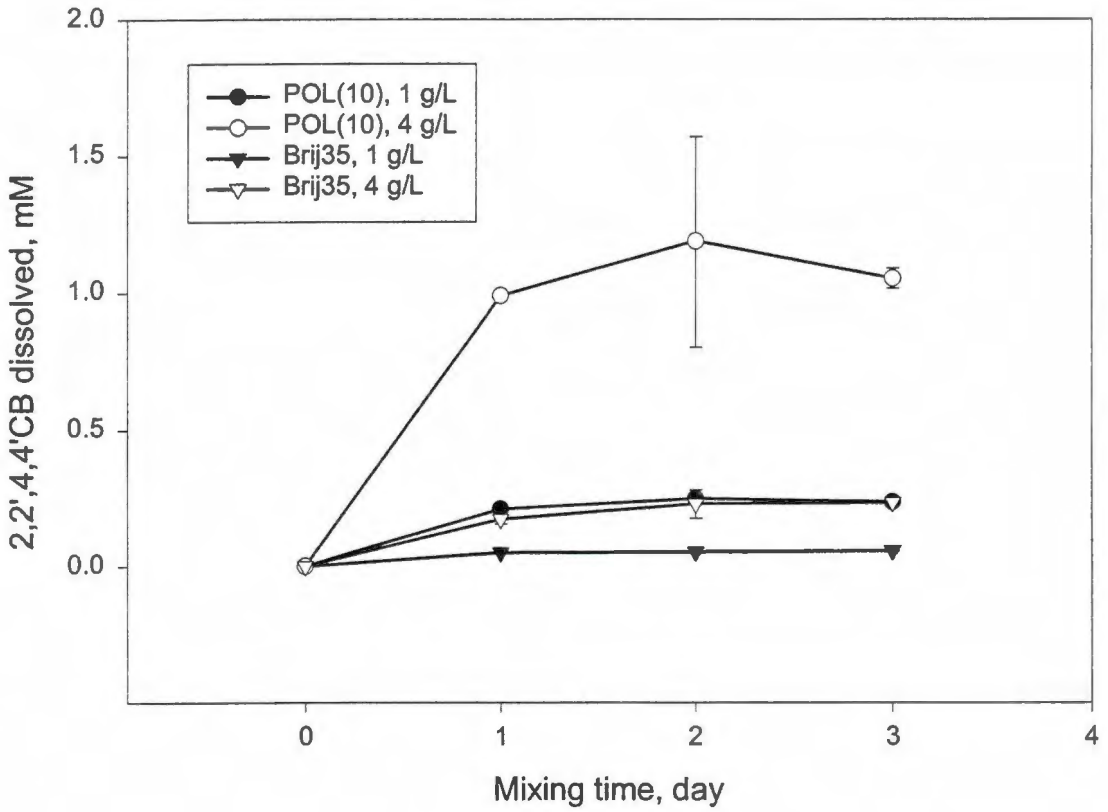


Figure 2.1 Determination of equilibrium time for 2,2',4,4'CB dissolution in surfactant solutions

literature. Dulfer *et al.* (1995) observed that 48 hours were required for PCB concentration to reach maximum in SDS solutions. Jafvert *et al.* (1994) used 48 hour to equilibrate PCB with nonionic surfactant solutions.

2.3.3 Determination of Solubility of Aroclor 1242

Until banned, Aroclors were extensively used worldwide. Under the experimental conditions used in the current study, 41 significant GC peaks were identified in Aroclor 1242 (Figure 2.2). In Figure 2.3a, the distribution of GC peaks of Aroclor 1242 dissolved in POL(10) (followed by extraction with hexane) are compared with that of Aroclor 1242 standard dissolved in hexane. Both the congener profile and the peaks for individual congeners were nearly identical in the two solutions. Statistical analysis of the data confirmed the similarity of the two congener profiles (Figure 2.3b). Further, the congener profile compared well with that reported by Frame *et al.* (1996). Thus, to determine the concentration of individual congeners, the weight distribution of congeners for Aroclor 1242 reported by Frame *et al.* (Table 2.3) was used in this study. The sum of concentration of all individual congeners was taken as the concentration of Aroclor 1242 in a given sample:

$$\sum [X]_s = \sum \frac{[X]_{std}}{[IS]_{std}} \frac{A_{ISstd}}{A_{Xstd}} \frac{A_{Xs}}{A_{ISs}} [IS]_s \qquad (2.14)$$

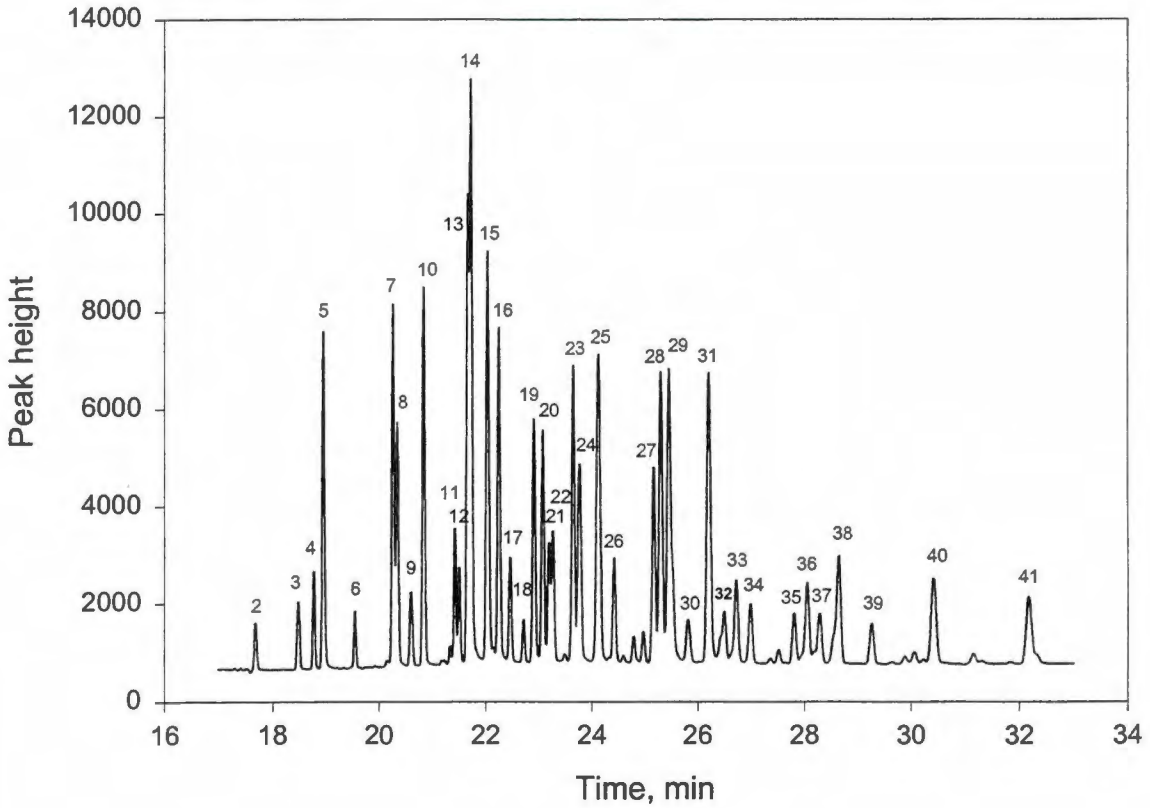


Figure 2.2 Gas chromatogram of Aroclor 1242 dissolved in POL(10) and extracted into hexane

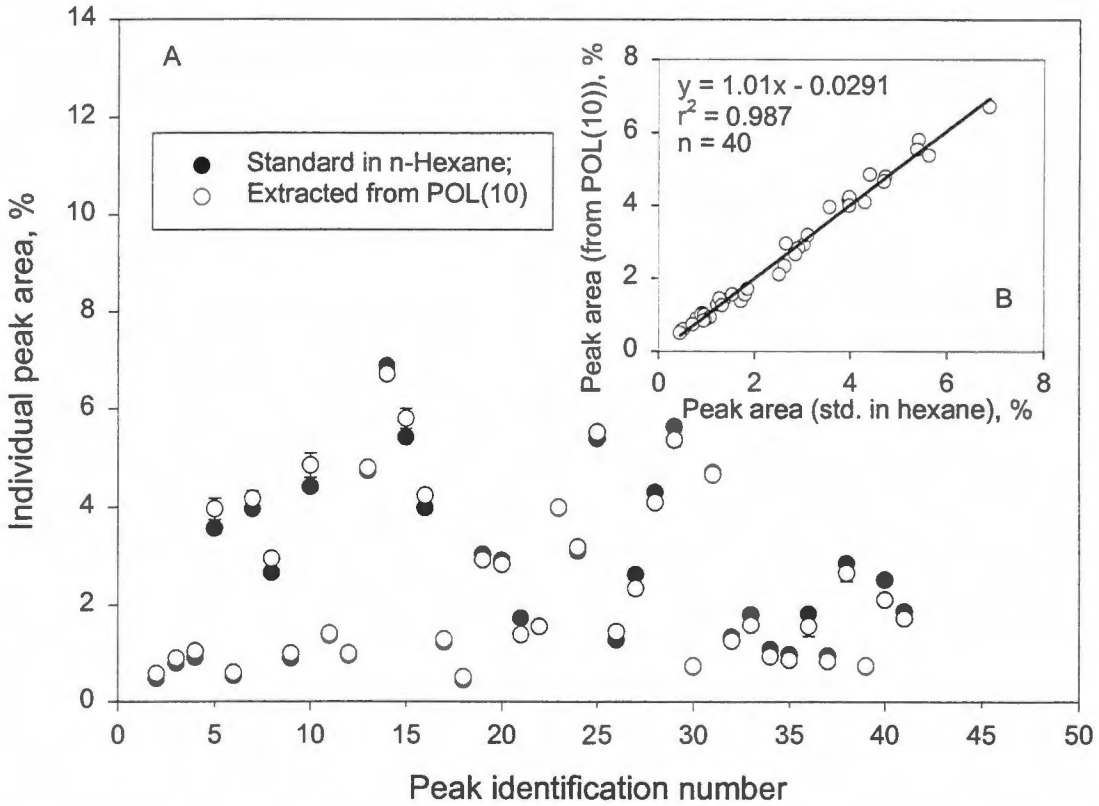


Figure 2.3 Comparison of GC peaks of Aroclor 1242 dissolved in POL(10) and in hexane

Table 2.3. Weight distribution of GC peaks in Aroclor 1242 (Frame *et al.*, 1996)

Peak no.[a]	PCB Congener	Weight (%)
2(5)	2,2'	2.74
3(6)	2,5	1.02
4(7)	2,3'	1.34
5(8)	2,4'	6.40
6(10)	2,2'6,	0.96
7(14)	4,4'; 2,2',5	10.17
8(15)	2,2',4	4.57
9(16)	2,3,6; 2,3',6	0.83
10(17)	2,2',3	5.14
11(21)	2,3',5	1.23
12(22)	2,3',4	0.89
13(23)	2,4',5	6.75
14(24)	2,4,4'	8.01
15(25)	2',3,4; 2,2',5,6'	6.28
16(26)	2,3,4'; 2,2',4,6'	2.88
17(27)	2,2'3,6	1.10
18(29)	2,2',3,6'	0.80
19(31.1)	2,2',5,5'	3.32
20(32)	2,2',4,5'	2.63
21(33)	2,2',4,4'	1.10
22(34)	2,2',4,5	1.48
23(37.2)	2,2',3,5'	3.26
24(38)	3,4,4'; 2,2',3,4'	3.32
25(39)	2,3,4',6	3.11
26(42)	2,2',3,3'	1.01
27(46.1)	2,4,4',5	1.60
28(47)	2,3',4',5	3.41
29(48.1)	2,3',4,4'; 2',3,4,5; 2,2',3',4,6	3.62
30(49)	2,2',3,6,4'	0.70
31(50)	2,3,4,4'	2.51
32(51)	2,2',3,3',6	0.76
33(53)	2,2',4,5,5'	0.88
34(54)	2,2',4,4',5	0.74
35(57.1)	2,2',3',4,5	0.72
36(58)	2,2',3,4,5'	0.78
37(59)	2,2',3,4,4'	0.71
38(61)	2,3,3',4',6	1.00
39(63)	2,2',3,3',4	0.69
40(69)	2,3',4,4',5	0.80
41(74)	2,3,3',4,4'	0.74

[a]Peak numbers assigned by Frame *et al.* (1996) are given in parentheses.

In this study,

$[IS]_{std} = [IS]_s$

and $[X]_{std} = [\text{total PCB}]_{std} \times wt\%$

$$\sum [X]_s = [\text{totalPCB}]_{std} \sum wt\% \frac{A_{ISstd}}{A_{Xstd}} \frac{A_{Xs}}{A_{ISs}} \qquad (2.15)$$

where $[X]_s$ and $[X]_{std}$ are the concentrations of peak X in sample and standard, respectively;

$[IS]_{std}$ and $[IS]_s$ are the concentrations of internal standard (2,2',3,3',4,5,6,6'CB) in sample and standard, respectively;

A_{ISstd} and A_{ISs} are peak areas of internal standard in standard and sample, respectively;

A_{Xstd} and A_{Xs} are peak areas of peak X for standard and sample , respectively;

$[\text{total PCB}]_{std}$ = total concentration of commercial PCB standard, Aroclor 1242;

wt% = weight percent of peak X in the commercial PCB, using the data given by Frame *et al.* (1996) (Table 2.3).

Assuming the general molecular formula of Aroclor to be $C_{12}H_{10-n}Cl_n$ and a 42% (w/w) chlorine content in Aroclor 1242, the molecular weight (MW) of Aroclor 1242 can be calculated as follows:

$$MW = 12 \times 12 + 1 \times (10 - n) + 35.5\ n \qquad (2.16)$$

and $$Cl\% = \frac{35.5n}{[12x12 + (10 - n) + 35.5n]}\% = 42\% \quad (2.17)$$

or,

$$n = 3.08$$

Thus, the nominal formula for Aroclor 1242 is $C_{12}H_{6.92}Cl_{3.08}$ with a corresponding molecular weight of 260.3.

2.3.4 Characterization of PCB Solubilization

The solubilities of 2,2'CB, 2,2',4,4'CB, 2,2',4,4',6,6'CB and Aroclor 1242 in POL(10) are compared in Figure 2.4. The solubility of Aroclor 1242 was considerably higher than that of any of the three individual congeners. All three PCB congeners were the solids (crystals) at room temperature whereas Aroclor 1242 was a liquid state at room temperature. Hence, from thermodynamic considerations, the solid solutes (2,2CB, 2,2',4,4'CB, and 2,2',4,4',6,6'CB) would have lower solubilities than the liquid solute (Aroclor 1242) (Mackay et al., 1992). The solubility of 2,2',4,4'CB in three different nonionic POE surfactants are compared in Figure 2.5. Given that the hydrocarbon chain length of the surfactants were the same, the solubility appeared to be inversely related to e HLB of the surfactants or the POE chain length. Atwood and Florence (1983) reported an inverse relationship between solubility and HLB for other compounds. For POE

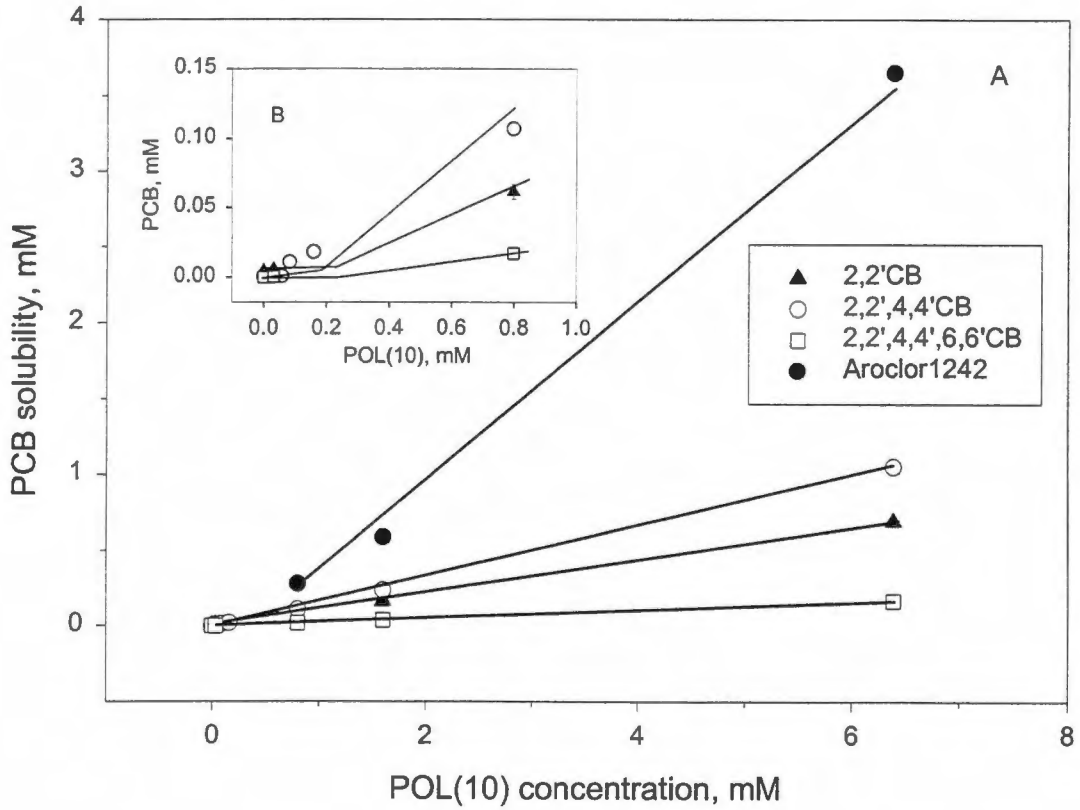


Figure 2.4 Solubility of different PCB congeners in POL(10) solution

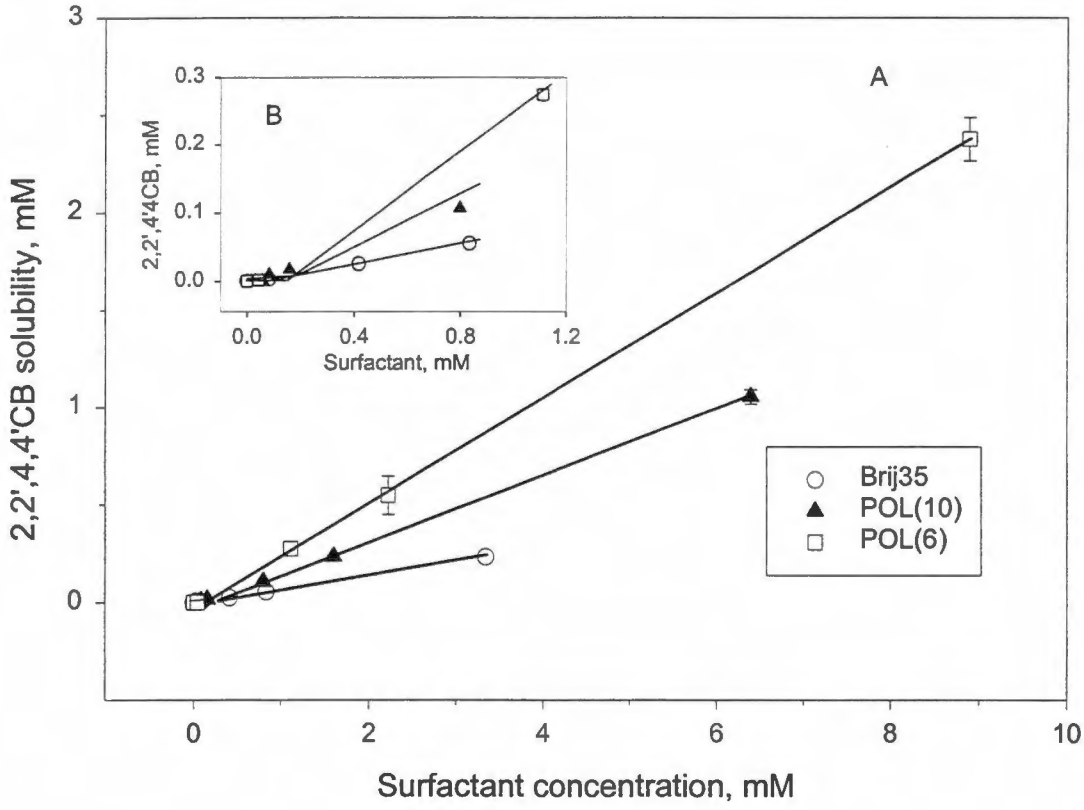


Figure 2.5 Solubility of 2,2',4,4'CB in different nonionic surfactant solutions

surfactants, increasing POE chain length will result in decreasing aggregation numbers and increasing micellar inner polarity (Saito *et al.*, 1985) and consequently, decreasing. apparent solubilities of hydrophobic compounds in micellar solutions. Figure 2.6 shows a comparison of the solubility of 2,2',4,4'CB in TX100 (nonionic) and SDS (anionic). Clearly, nonionic surfactants are superior to ionizable ones in solubilizing hydrophobic compounds. The PCB solubilization in surfactant solutions is further characterized by CMC, MSR, and K_m.

Critical Micelle Concentration (CMC) At sub-micellar dosages of surfactant, the solubility of the PCBs increased only by a factor of 2 to 3 of their aqueous solubilities (Figures 2.4 -2.6). However, at supra-CMC dosages the apparent solubility increased sharply and linearly. The increase in solubility was linear both at the sub- and supra-micellar dosages. The intersection of the two straight lines was taken as the solubility of PCB at the CMC of surfactant, S_{cmc}. The CMC values determined from solubilization were compiled in Table 2.4. It is worthwhile to note that most often commercial POE surfactants are mixtures of homologs with identical hydrophobic moiety (R) but polydisperse distribution of hydrophilic oxyethylene (EO) (Edwards *et al.*, 1991, Myers, 1992). Consequently, a precise determination of CMC from solubility data is often difficult. For comparison, CMC values determined from surface tension measurements (Figure 2.7), in the absence of PCBs, are included in the Table 2.4. The dosage at which surface tension became invariant was taken as the CMC. Except for Brij35 and TX100

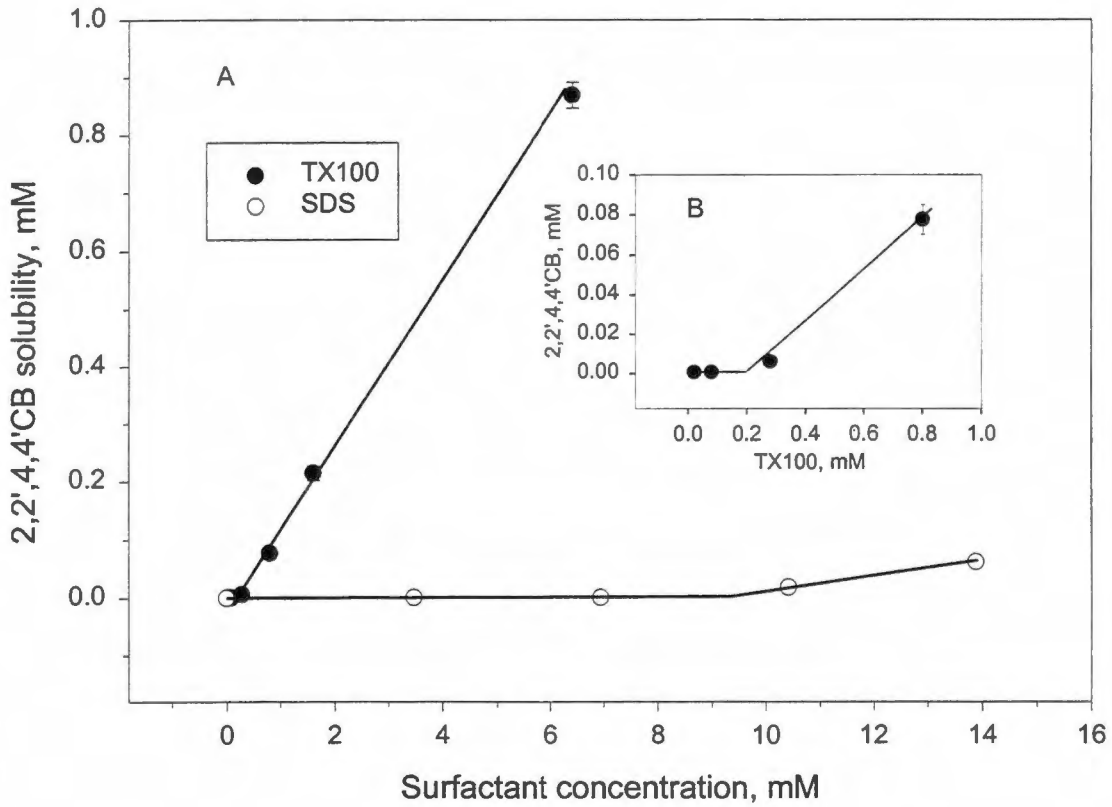


Figure 2.6 Solubility of 2,2',4,4'CB in TX100 and SDS solutions

Table 2.4. CMC determined from solubility and surfactant measurements

Surfactant	PCB	$CMC_{solubility}$ (M)	$CMC_{surface\ tension}$ (M)
POL(6)	2,2',4,4'CB	1.57×10^{-4}	6.82×10^{-5}
POL(10)	2,2'CB	2.46×10^{-4}	8.39×10^{-5}
POL(10)	2,2',4,4'CB	1.98×10^{-4}	8.39×10^{-5}
POL(10)	2,2',4,4',6,6'CB	2.41×10^{-4}	8.39×10^{-5}
Brij35	2,2',4,4'CB	9.55×10^{-5}	1.93×10^{-4}
TX100	2,2',4,4'CB	1.97×10^{-4}	2.71×10^{-4}
SDS	2,2',4,4'CB	9.33×10^{-3}	8.06×10^{-3}

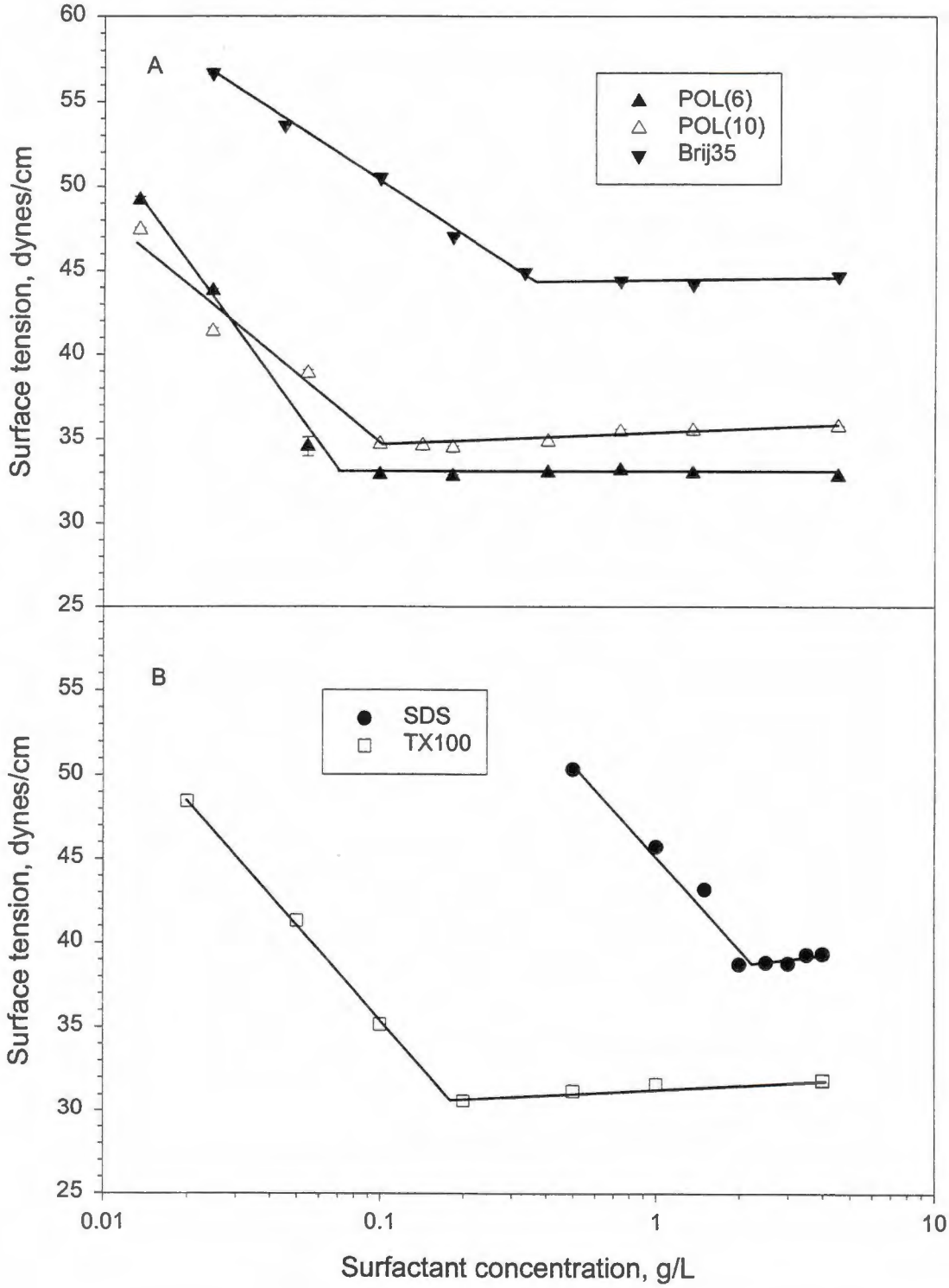


Figure 2.7 Determination of critical micelle concentration (CMC) from surface tension measurement

solutions with 2,2',4,4'CB present, the CMC values based on solubility were always greater than those based on surface tension. Seemingly, presence of hydrophobic solutes tends to lower CMC of some surfactants. Edwards *et al.*, (1991) reported a $CMC_{solubility}$ of Triton X-100 based on PAH solubility that was nearly an order of magnitude less than the $CMC_{surface\ tension}$. In fact, they reported solubility-based CMCs that were always less than the surface tension based CMCs.

Molar Solubility Ratio (MSR) and K^e_m By definition, MSR (Eq. 2.2) is the slope of the linear relationship between PCB solubility and surfactant dosage above CMC. The micelle-water partitioning of a PCB congener is given by the thermodynamic equilibrium constant K^e_m. As shown in Eq 2.3, K^e_m can be calculated from the experimental value of MSR. The MSR and K^e_m values for the PCB-surfactant systems studied are listed in Table 2.5.

In a descending order of solubilities (MSR) of 2,2',4'4' CB, the surfactants can be arranged as POL(6)>POL(10)>TX100>Brij35>SDS. Likewise, in a descending order of K^e_m values, the surfactants can be arranged as TX100>POL(6)>POL(10)>Brij35>SDS. MSR and K^e_m values for nonionic surfactants were considerably larger than those for anionic surfactants. In a descending order of solubilities in POL (10), the PCB congeners can be arranged as 2,2',4,4'CB>2,2'CB>2,2',4,4',6,6'CB.

Table 2.5. MSR and K^e_m

Surfactant	PCB	S_{cmc} (M)	MSR	log K^e_m
POL(6)	2,2',4,4'CB	1.88×10^{-6}	0.271 ± 0.004	6.80
POL(10)	2,2'CB	5.56×10^{-6}	0.112 ± 0.002	6.00
	2,2',4,4'CB	1.55×10^{-6}	0.170 ± 0.001	6.71
	2,2',4,4',6,6'CB	2.83×10^{-8} [a]	0.0272 ± 0.0005	7.71
	Aroclor 1242		0.617 ± 0.031	
Brij35	2,2',4,4'CB	3.06×10^{-6}	0.0708 ± 0.000	6.08
TX100	2,2',4,4'CB	6.72×10^{-7}	0.140 ± 0.003	7.04
SDS	2,2',4,4'CB	1.06×10^{-6}	0.0126 ± 0.000	5.81

[a] Estimated by assuming that both 2,2',4,4',6,6'CB and 2,2',4,4'CB have the same ratio of S_{cmc}:S_w (aqueous solubility) = 3.95.

Relationship Between K^e_m and K_{ow}. For a given surfactant-CAC system, a linear relationship between K^e_m and K_{ow} has been reported (Valsaraj and Thibodeaux, 1989; Edwards *et al* 1991). A similar relationship between K^e_m and K_{ow} was established in the current study (Figure 2.8). The relationships between K^e_m and K_{ow} are summarized in Table 2.6.

2.3.5 Location of PCB Molecules inside Micelles.

Equations 2.11 and 2.12 (Mukerjee, 1980) were applied to determine the intra-micellar location of 2,2',4,4'CB in various ethoxylate surfactants: POL(6), POL(10), and Brij35. The plot of C_R/C_{EO} versus S_{mic}/C_{EO} defined in Equation 2.11 was used to construct Figure 2.9. To calculate C_R and C_{EO}, each CH_2CH_2 (expressed as R) or CH_2CH_2O (expressed as EO) unit was assumed to represent one equivalent. Contrary to prediction made by Mukerjee's model, a nonlinear relationship resulted in the concentration range of 0.5 to 4.0 g/L of POL(10). Thus, this model failed to predict the solubilization sites. Similar nonlinear relationships for the solubility of other hydrophobic compounds in nonionic surfactant solutions were reported by Goldenberg *et al.* (1993).

To determine the location of PCB inside micelles, UV-VIS spectra of 2,2',4,4'CB were examined in 4 g/L solution of POL(10), n-hexane, 1,2-dimethoxyethane (DME), and 4 g/L solution of polyethylene glycol (MW = 400) (PEG-400) as shown in Figure 2.10. 2,2',4,4'CB was insoluble in PEG-400 as demonstrated by its UV-VIS spectra (not

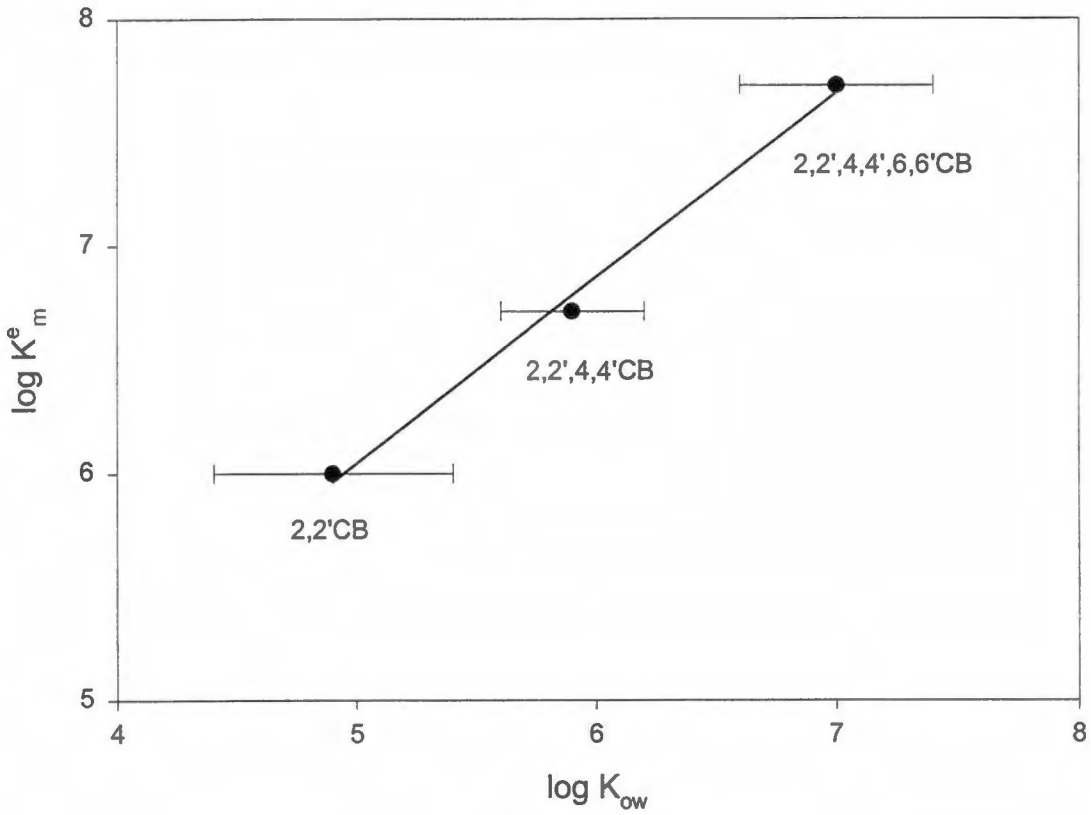


Figure 2.8 Correlation of log K^e_m and log K_{ow} for three PCB congeners dissolved in nonionic surfactant (POL(10)) solutions

Table 2.6. Relationship between K^e_m and K_{ow}.

Surfactant	Relationship of K^e_m and K_{ow}	References
SDS	$\log K^e_m = 0.847 \log K_{ow} + 1.09$	Valsaraj and Thiboeaux, 1989
SDBS[a]	$\log K^e_m = 0.865 \log K_{ow} + 0.92$	Valsaraj and Thiboeaux, 1989
HTAB[b]	$\log K^e_m = 0.782 \log K_{ow} + 1.56$	Valsaraj and Thiboeaux, 1989
TX100	$\log K^e_m = 0.791 \log K_{ow} + 1.98$	Edwards *et al.*,1991
POL(10)	$\log K^e_m = 0.815 \log K_{ow} + 1.97$	This study

[a]SDBS: sodium dodecyl benzene sulfonate.
[b]HTAB: hexadecyltrimethylammonium.

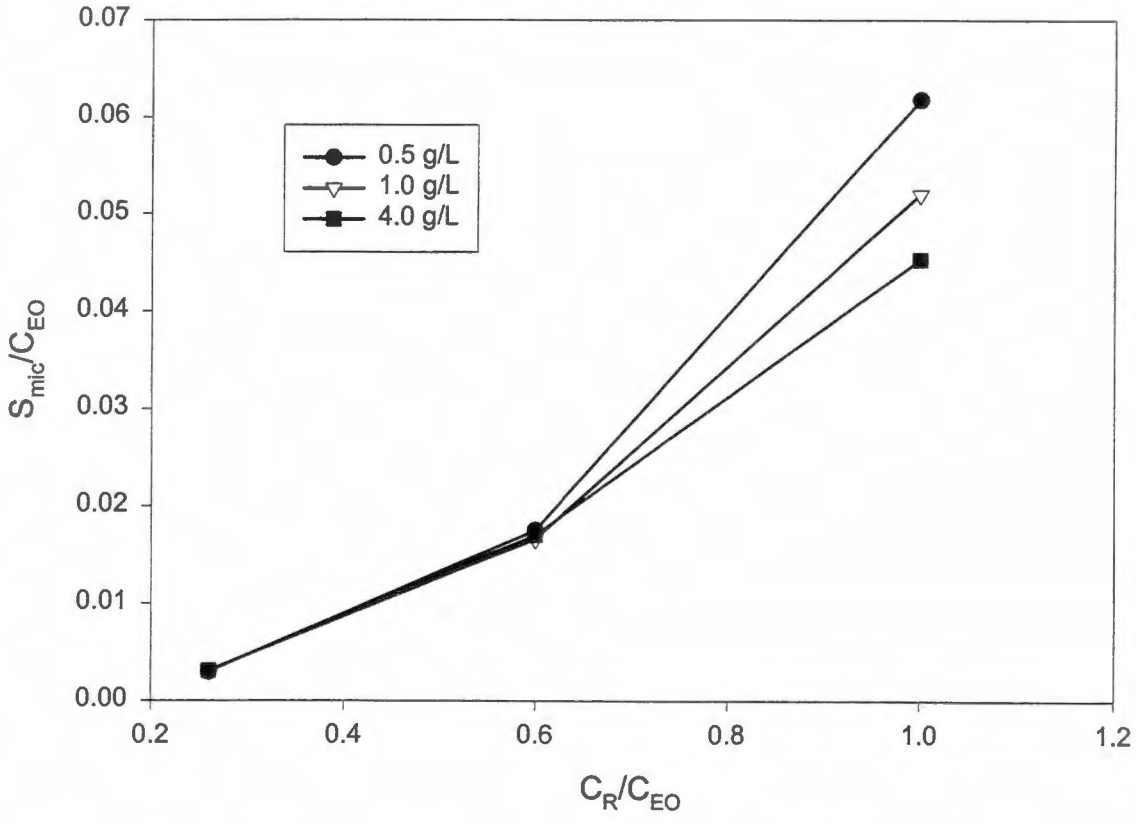


Figure 2.9 Micellar solubilization of 2,2',4,4'CB in polyoxyethylene lauryl ether surfactant solutions according to Mukerjee's model

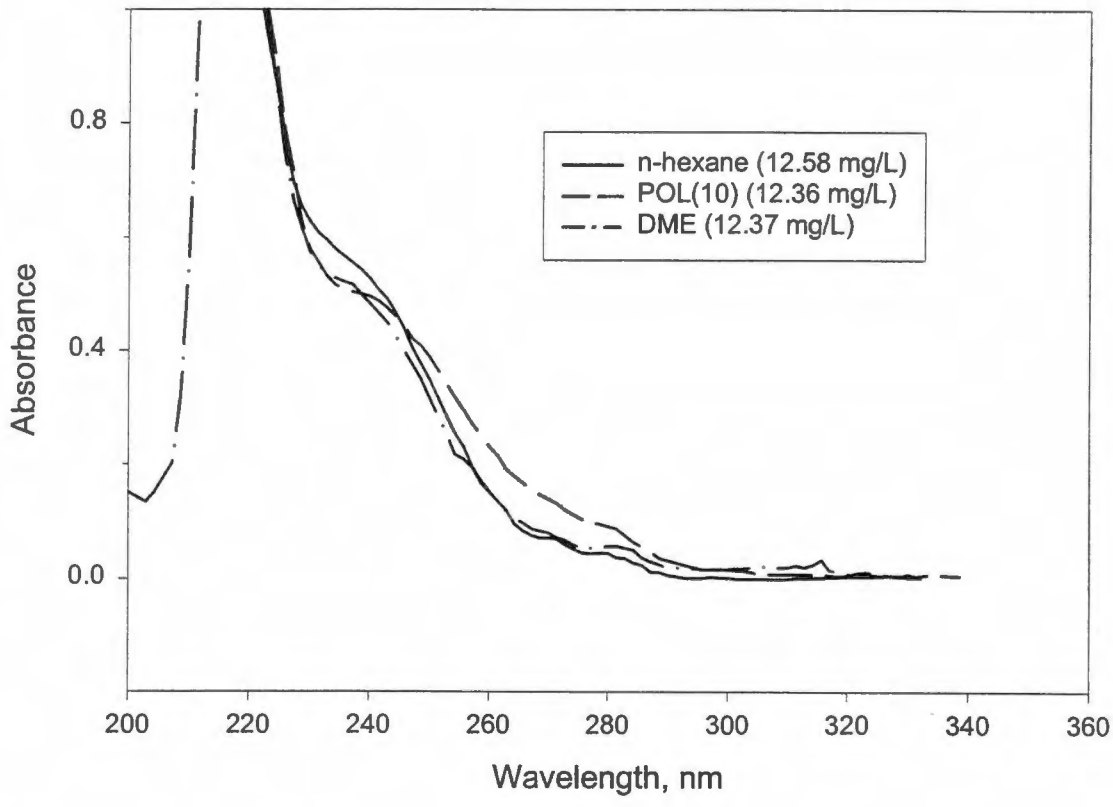


Figure 2.10 UV-VIS spectra of 2,2',4,4'CB in different solutions

shown on Figure 2.10) which overlapped with the X-axis. The spectra of 2,2',4,4'CB in *n*-hexane, DME, and POL(10) were similar. Particularly in the region of wavelength < 230 nm, the spectra in *n*-hexane and POL(10) overlapped. These results revealed that the environment surrounding the 2,2',4,4'CB molecules inside the micelles was similar to that of 2,2',4,4'CB in hexane or DME. Therefore, the possible locus of 2,2',4,4'CB inside the micelle is the hydrophobic core (hydrocarbon chain) and its vicinity (part of the polyoxyethylene chain near the core).

2.3.6 Distribution of 2-Chlorophenol Between Water and Surfactant Micelles

The linear solvation energy relationship (LSER), given in Equation 2.9, allows calculation of the micellar pseudophase incorporation coefficient, K^j_m in units of M^{-1} (Quina *et al.*, 1995):

$$\log K^j_m = c + a\Sigma\alpha_2 + b\Sigma\beta_2 + p\pi_2 + rR_2 + v(V_x/100) \qquad (2.9)$$

In Equation 2.9 , $\Sigma\alpha_2$, $\Sigma\beta_2$, π_2, R_2, and V_x ($cm^3\ mol^{-1}$) are the parameters that account for, respectively, hydrogen bond acidity of solute, hydrogen bond basicity of solute, dipolarity, excess molar refraction, and molar volume. a, b, p, r, and v are the system dependent coefficients for $\Sigma\alpha_2$, $\Sigma\beta_2$, π_2, R_2, and V_x, respectively. c is a constant. Literature values for these parameters (Abraham, 1987, 1993) and coefficients (Quina *et al.*,1995) are listed in Table 2.7.

Table 2.7. Parameters and coefficient of LSER applied to surfactants and 2CP

Surfactant	**c**	**a**	**b**	**p**	**r**	**v**
Brij35	-1.39	1.62	-3.83	-0.37	1.63	3.65
SDS	-0.62	-0.08	-1.84	-0.57	0.32	3.25
Solute		$\Sigma\alpha_2$	$\Sigma\beta_2$	π_2	$\mathbf{R_2}$	$\mathbf{V_x}$
2CP		0.32	0.31	0.88	0.853	89.75

The micelle-water partitioning coefficient, K^j_m, (Quina *et al.*,1995) is identical to K^j_m (Jafvert *et al.*, 1994) given by:

$$K^j_m = (S\text{-}S_{cmc})/[S_{cmc}(C\text{-}CMC)] \qquad (2.4)$$

The terms S, S_{cmc} , C, and CMC have been defined earlier. At 4 g/L of POL(10), (C-CMC) values were 3.18×10^{-3} M and 5.83×10^{-3} M for Brij35 and SDS, respectively.

The molar solubility ratio (MSR), molar partitioning coefficient, K^e_m, and micellar occupancy number, N_{occ}, defined as the average number of 2CP molecules partitioned into each micelle, can be related to K^j_m as follows:

From Equation 2.4,

$$MSR = (S\text{-}S_{cmc})/(C\text{-}CMC)$$
$$= K^j_m S_{cmc} \qquad (2.18)$$

and from Equation 2.5

$$K^e_m = \frac{K^j_m}{V_w(MSR+1)} \qquad (2.19)$$

and $$N_{occ} = \frac{(S - S_{cmc})N_{aggr}}{(C - CMC)}$$
$$= MSR\, N_{aggr} \qquad (2.20)$$

N_{aggr} is the micelle aggregation number, i.e., the average number of surfactant molecules in each micelle. The molar volume of water, V_w, is 0.0181 M^{-1} at 25 °C and N_{aggr} has a value of 40 and 62, respectively, for Brij35 and SDS (Kalyanasundaram, 1987).

Estimates of K^j_m, S_{mic}, S_{aq}, $(S-S_{cmc})/S$, MSR, K^e_m, and N_{occ} obtained from Equations 2.19-2.20 are listed in Table 2.8. All of these values are greater for Brij 35 than those for SDS indicating that Brij35 micelles are more effective than SDS in associating with 2CP molecules.

2.3.7 Solubilization of PCB from Soil Using POL(10)

The GCs of the PCB washed from a clayey soil and a sandy soil are shown in Figure 2.11 and 2.12. Of the two, the sandy soil had a relatively larger weight fraction of highly chlorinated congeners though the total concentration of PCB in the clayey soil (11. 73 mg/g soil) was considerably greater than that in the sandy soil (0.318 mg/g soil). However, both congener profiles closely resembled that of Aroclor 1248. Thus, the weight percent data of GC peaks given by Frame *et al.* (1996) for standard Aroclor 1248 (Table 2.9) was used for estimating the total concentration of PCBs in the soil washings using the method discussed in section 2.3.3.

The results of solubilization of PCB from the two soils are shown in Figure 2.13 and 2.14. Further, the results of surfactant washing are summarized in Table 2.10. For the clayey soil, small amounts of PCB could be solubilized at a POL(10) dosage of 1 g/L or

Table 2.8. K^j_m, S_{mic}, S_{cmc}, MSR, K^e_m, and N_{occ} values for 2CP (0.1 g/L) in 4.0 g/L of POL(10) estimated by LSER

Surfactant	K^j_m (M^{-1})	S_{mic} (M^{-1})	S_{cmc} (M^{-1})	S_{mic}/S (%)	MSR	K^e_m	N_{occ}
Brij35	191	2.94×10^{-4}	4.84×10^{-4}	37.8	0.0924	9660	3.70
SDS	29.6	1.15×10^{-4}	6.63×10^{-4}	14.8	0.0196	1604	1.22

[a] $S_{mic} = S - S_{cmc}$

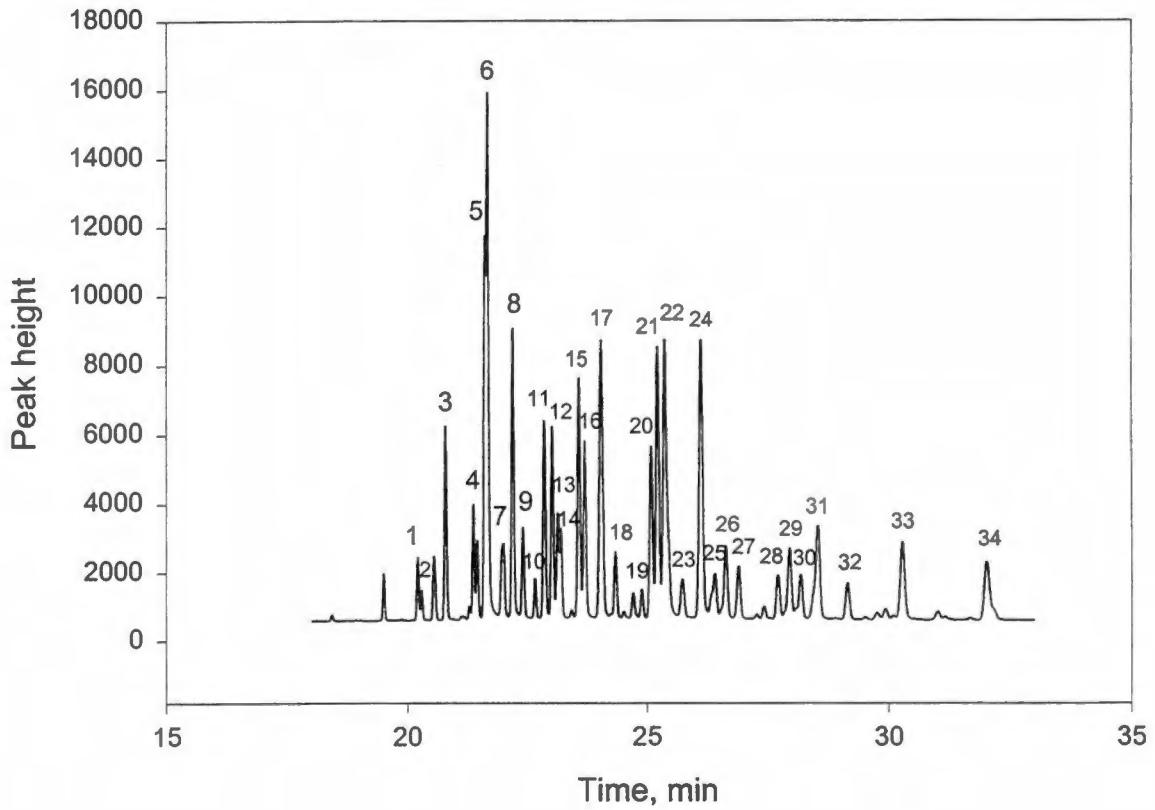


Figure 2.11 Gas chromatogram of PCBs in clayey soil washing solution

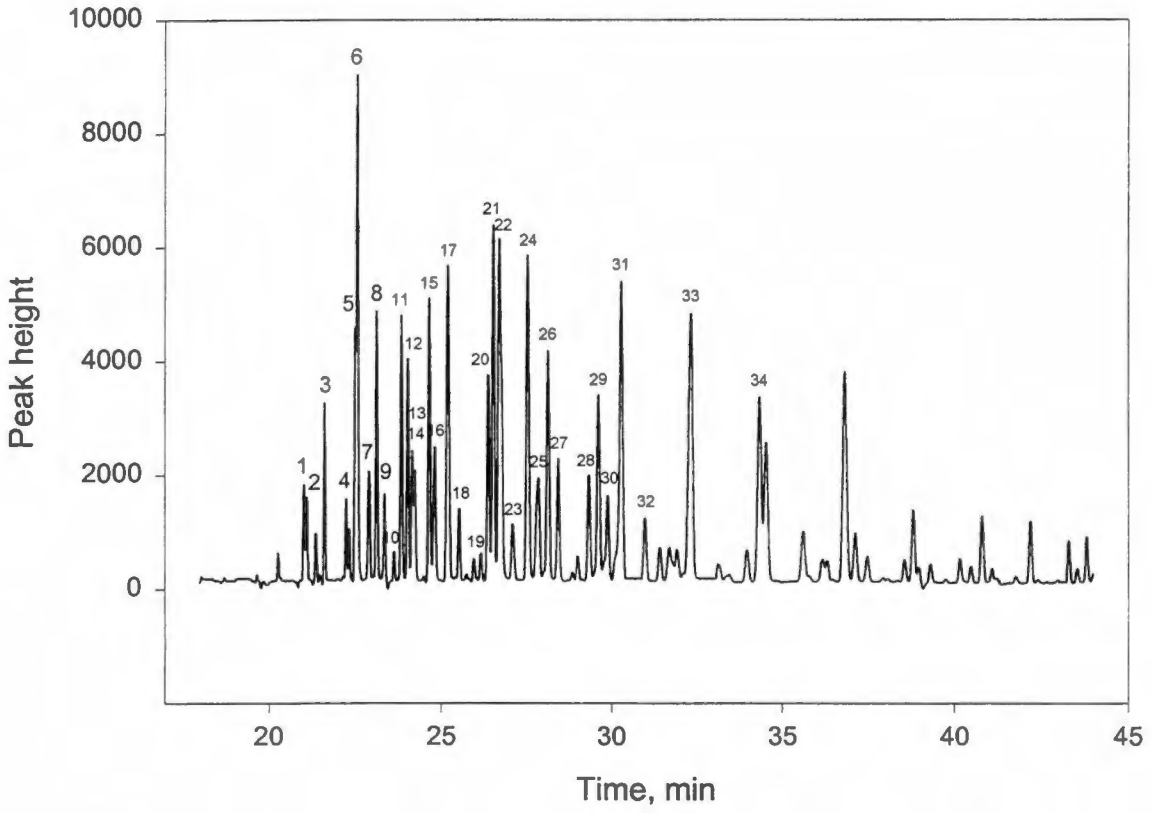


Figure 2.12 Gas chromatogram of PCBs in sandy soil washing solution

Table 2.9. GC profile of Aroclor 1248 for identification and quantitation of PCB congeners in POL(10) soil washing solutions

Peak No.[a]	PCB Congener	Weight Percent (%)
1 (14)	2,2',5; 4,4'	2.95
2 (15)	2,2',4	1.22
3 (17)	2,2',3; 2,4',6	1.62
4 (21)	2,3',5	0.77
5 (23)	2,4',5	4.76
6 (24)	2,4,4'	6.09
7 (25)	2,3,3'; 2,3',4'; 2,2',5,6'	2.78
8 (26)	2,3,4'; 2,4,2',6'	1.60
9 (27)	2,2',3,6	1.17
10 (29)	2,2',3,6'	0.84
11 (31.1)	2,2',5,5'	5.91
12 (32)	2,2',4,5'; 2,2',3,5	4.59
13 (33)	2,2',4,4'	2.55
14 (34)	2,2',4,5	2.19
15 (37.2)	2,2',3,5'	5.00
16 (38)	3,4,4'; 2,2',3,4'; 2,3,3',6	2.91
17 (39)	2,2',3,4; 2,3,4',6; 2,3',4',6	6.10
18 (42)	2,2',3,3'	1.18
19 (45)	2,3,4',5	0.78
20 (46.1)	2,4,4',5	4.50
21 (47)	2,3',4',5	7.55
22 (48.1)	2,3',4,4'; 2,2',3,5',6	9.63
23 (49)	2,2',3,4',6	0.83
24 (50)	2,3,3',4'; 2,3,4,4'	5.34
25 (51)	2,2',3,3',6; 2,2',3,5,5'; 2,2'3,4,6'	1.06
26 (53)	2,2',4,5,4'; 2,2',3,5,4'	2.07
27 (54)	2,2',4,4',5	1.76
28 (57.1)	2,2',3',4,5	1.05
29 (58.1)	2,2',3,4,5'; 2,3,4,4',6	1.35
30 (59)	2,2',3,4,4'	1.25
31 (61)	2,3,3',4',6	2.73
32 (63)	2,2',3,3',4	0.85
33 (69)	2,3',4,4',5; 2,2',3,4',5',6	2.35
34 (74)	2,3,3',4,4'; 2,2',3,3',4,6'	1.82

[a]PCB congeners in the soil-washing solution were identified and quantified by comparison with standard Aroclor 1248. (After Frame *et al.*, 1996). Peak numbers assigned by Frame *et al.* are given in parentheses.

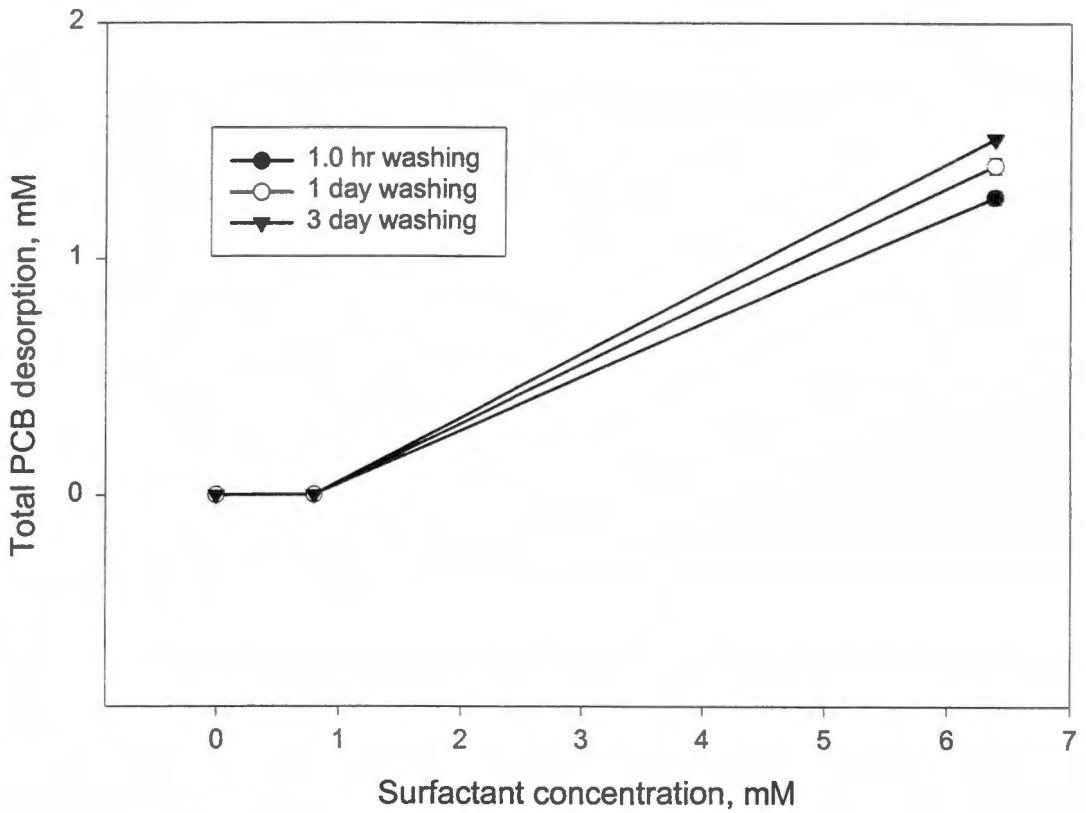


Figure 2.13 Desorption of PCBs from a clayey soil

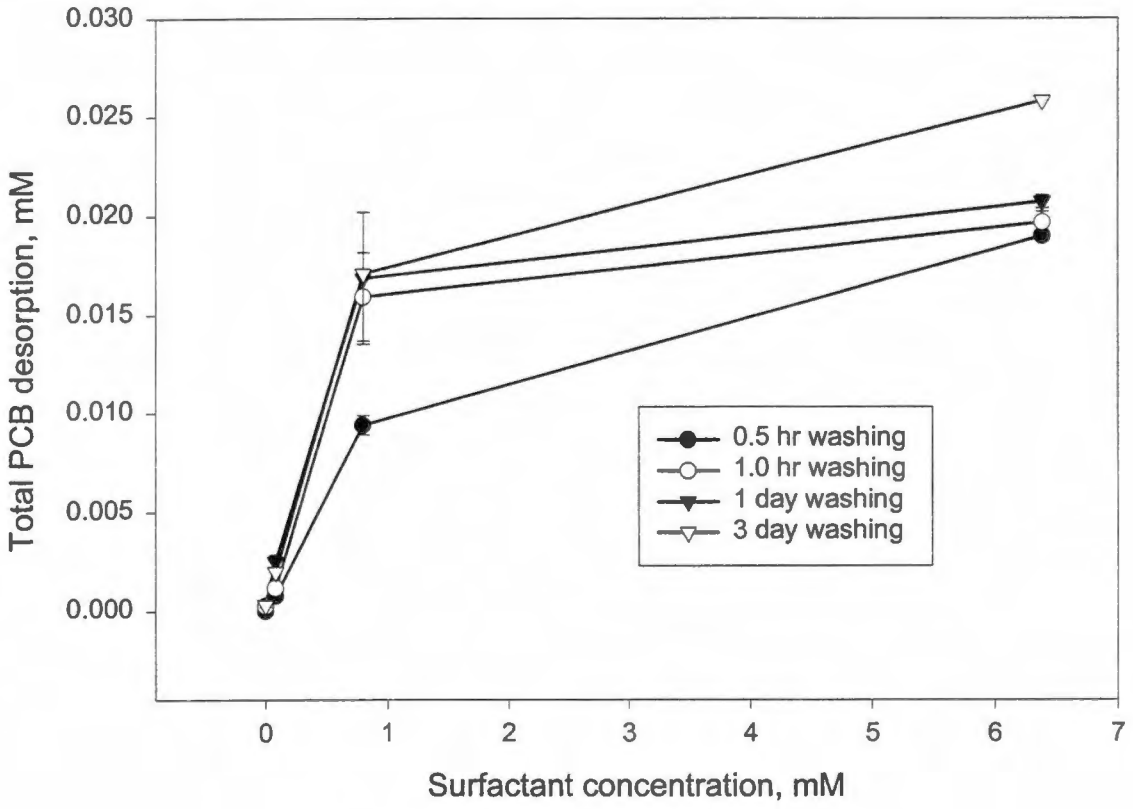


Figure 2.14 Desorption of PCBs from a sandy soil

Table 2.10. Summary of surfactant washing of PCB contaminated soils using 4 g/L POL(10)

Soil	PCB in soil[a] (mg/g soil)	PCB removal[b] (%)	Loss of POL(10) (%)
Clayey	11.73	74	14[c]
Sandy	0.318	47	4[c]

[a] Determined by Standard Soxhlet extraction (EPA Method No 3541)

[b] Based on Soxhlet extractable PCBs

[c] Adsorption losses are based on an initial aqueous concentration of 4 g/L of POL(10) and a mixing period of 3 days.

less, regardless of the duration of washing. At 4 g/L of POL(10), the highest dosage studied, about 8.7 mg PCB/g soil was solubilized in 3 days yielding a washing solution having 1.5 mM Aroclor 1248 based on an average molecular weight of 288.1. This represents 74% removal of Soxhlet-extractable PCBs in the original soil. By comparison, 60% removal of total PCB could be achieved in 1 hour, a decrease of only 14%. A large fraction of the soil-bound PCBs could be washed off of the sandy soil at POL(10) dosage of 1 g/L. At a POL(10) dosage of 4 g/L, 0.149 mg PCB could be solubilized /g soil. Or, 47% removal of Soxhlet-extractable PCB was accomplished. Figure 2.14 shows that, depending on the surfactant concentration applied, increasing duration of washing could increase the amount of PCB mobilized from soil.

The residual surfactant concentration during soil washing was also monitored. At a dosage of 4 g/L, 14% (0.56 g/L) of the surfactant was lost on the clayey soil while only 4% (0.16 g/L) surfactant was lost on the sandy soil after 3 days of washing. The relatively large portion of surfactant lost on clayey soil resulted in less surfactant being available to desorb PCB from the soil. This may partly explain the relatively small degree of PCB mobilization observed in the clayey soil.

2.4 SUMMARY

The solubility of PCBs was greatly enhanced at surfactant concentrations above the CMC. Nonionic surfactants were superior to anionic surfactants in solubilizing PCBs.

For POL(10), K^e_m and K_{ow} for various CACs were related as log K^e_m = 0.815log K_{ow} + 1.966. The UV spectra of 2,2',4,4'CB dissolved in different solvents revealed that the PCB molecules are possibly located at the micellar core or its vicinity. For 2CP dissolved in surfactant solutions, LSER indicated that more 2CP molecules were associated with Brij35, a nonionic surfactant, than those with anionic SDS. This information is important in understanding the fate of CACs in photochemical reactions.

CHAPTER 3

SURFACTANT-ENHANCED PHOTOLYSIS OF POLYCHLORINATED BIPHENYLS (PCBs)

3.1 BACKGROUND

Polychlorinated biphenyls (PCBs) are ubiquitous environmental pollutants that are generally recalcitrant to biodegradation, but they are photodegradable. Most PCBs have weak absorption bands that partially overlap solar spectrum in the ultraviolet (UV) region at wavelengths above 280 nm (Hutzinger *et al.*, 1974). The loss of PCBs in natural water due to solar radiation has been estimated to be of the order of 10 to 1000 g /km^2/year (Bunce *et al.*, 1978a). Photodegradation is an important process of PCB decomposition in the environment (Safe *et al.*, 1976, Sawhney, 1986). Artificial lights with wavelengths less than 280 nm are absorbed strongly by PCBs and are therefore useful in decontaminating PCB-containing waste waters. Literature is replete with reports of studies of photodegradation of PCBs, either by sunlight or by artificial light, conducted over the last three decades. Only studies on the photochemistry of PCB in water, organic solvents, surfactant solutions, as well as in soil suspensions are reviewed here.

3.1.1 UV Spectra and Conformation

UV spectrum of biphenyl shows two important absorption maxima: one at λ_{max} = 202 nm (molar extinction coefficient (ε) = 44,000), referred as the 'main band'; and the other at λ_{max} = 242 nm (ε = 17,000), referred as the 'κ band' (MacNeil *el al.*, 1976, Hutzinger *et al.*1974). The κ band is attributed to the conjugation between two phenyl rings. The characteristics of UV absorption by PCBs depend on the number and location of chlorine substitutions, especially the degree of substitution at the *ortho* (2, 2', 6, and 6') positions. MacNeil *et al.* (1976) examined 29 PCB congeners. It was observed that the κ band of 2-chlorobiphenyl (2CB) slightly shifted to shorter wavelengths (blue shift) with concomitant decrease in ε and the κ band of PCBs with two or more *ortho* chlorine atoms exhibits further blue shift; the observed decrease in ε of the κ band was remarkable. The shift and the intensity of reduction of the κ band were due to hindered interaction at the *ortho* position. Other studies showed that biphenyl has a non-coplanar conformation at ground state, so do its *meta-*, *para-* and *ortho-* derivatives (Bunce, 1982). According to spectroscopic and quenching data, dihedral angle of biphenyl between the two rings is 20-25° in solutions (Wagner, 1967). *Ortho* substituents causes a more twisting of the ground state due to steric interaction and κ band blue shift results; molecular orbitals of the ground and excited states overlap to a lesser degree. Using a semi-empirical AM1 model (Nevalainen and Kolehmainen, 1994) and *ab initio* model (McKinney *et al.* 1983), the dihedral angle of minimum energy conformation was calculated to be 41-42° for ground states of all PCBs with no *ortho* chlorine. The dihedral

angles for mono and multi *ortho* substituted PCB were ca. 60° and 90°, respectively. The rotational barrier at planar configuration for biphenyl and mono-*ortho* substituted PCBs are ca. 2.2 and 7.2 kcal/mol, respectively (Nevalainen and Kolehmainen, 1994). Biphenyl and PCB tend to be planar in the excited state (Bounce, 1982). This planar conformation must be accomplished by steric compression, especially at *ortho* positions. Hence, energy of the excited state is raised, especially for the PCBs with *ortho* chlorine, so further blue shift is observed. For PCBs with all four *ortho* chlorines, the steric compression is so severe that their excited states could be twisted, the κ band may vanish, and other low intensity bands may be observed in the range of 270-280 nm (Hutzinger *et al.*, 1974; MacNeil *et al.*, 1976). Similar increases in absorbance in the near UV region (about 300 nm) for the other highly chlorinated PCBs have been observed (Draper *et al.*, 1987).

3.1.2 Chlorine Substitution and Photochemical Activities

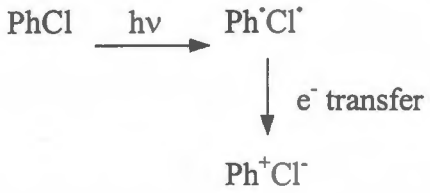
The chlorine content of the biphenyl ring influences photochemical activity of PCBs. Experiments showed that PCBs with higher chlorine content undergo photolysis faster than those with lower chlorine content (Hutzinger *et al.*, 1974; Sawhney, 1986; Draper *et al.*, 1987). PCB congeners with *o*-chlorines are most vulnerable to photochemical attack; they are usually lost preferentially to non-*ortho* chlorines (Ruzo *et al.*, 1974a, b; Safe *et al.*, 1976; Bunce, 1982). *Ortho* substituent raises the energy of the excited state and provides the extra energy for C-Cl homolytic scission. Mono *ortho*-substitued congeners are more rapidly photodegraded than di*ortho*-substituted congeners (Bunce *et al.*, 1978; Lepine *et al.*, 1991). Loss of the last *ortho* chlorine from a PCB

molecule may relieve the steric compression much better than loss of one of the two *ortho* chlorines in the planar excited state. Possibly, highly *ortho* substituted PCBs are twisted in the excited state decreasing extra energy of the excited state needed for C-Cl scission. Chlorine substitution at the *meta-* or *para* position has little effect on the photolysis of *ortho* chlorine-bearing PCBs of low chlorine content (Bunce, 1982). However, substitution at the *meta-* and *para* positions of highly chlorinated congeners attenuates photoreactivity of *ortho* chlorine (Lepine *et al*, 1991).

3.1.3 Mechanisms of PCB Photolysis

In general, dechlorination followed by hydrogen abstraction is believed to be the major photochemical reaction of PCBs while hydroxylation and isomerization may also occur as minor reactions (Hutzinger *et al.*, 1974; Pagni and Sigman, in press). Photoproducts (less chlorinated PCB congeners and chloride ion) may retard photolysis in some cases (Bunce *et al.*, 1978b; Orvis *et al.*, 1991). The literature on the photochemistry of PCB in water, organic solvents, and surfactant solutions are discussed below.

Mechanism of Photolysis in Water. Photochemical decomposition of PCBs in the environment depends largely on the aquatic and surface photochemistry of these chemicals. A superior solvent for reactions involving ions, water facilitates photochemically induced heterolysis reaction, as illustrated below (Hutzinger *et al.*, 1974; Pagni and Sigman, in press):



$Ph^{\bullet} + H_2O \longrightarrow PhH + HO^{\bullet}$ (endothermic)

$Ph^{+} + H_2O \longrightarrow PhOH + H^{+}$ (exothermic)

where: Ph = less chlorinated biphenyl

Dechlorinated and hydroxylated products were identified when di-, tri-, and tetrachlorobiphenyls were photolyzed in aerated water containing small amounts of CH_3OH (0.3-2 mL/L) (Crosby and Moilanen, 1973). Additionally, traces of 2-chlorodibenzofuran (0.2%) was also identified as a product of photolysis of 2-chlorobiphenyl (2CB) and 2,2',5,5'-tetrachlorobiphenyl. Using deuterium instead of hydrogen, Bunce (1978b) demonstrated that when 2CB was photochemically dechlorinated to biphenyl in acetonitrile/water mixture (CH_3CN/H_2O) (v:v= 4:1), both CH_3CN and H_2O acted as H-atom sources. However, CH_3CN contributed more H atoms than H_2O did due to its much smaller C-H dissociation energy, 94 kcal/mol compared to 119 kcal/mol for the dissociation of O-H. Photolysis of 2CB in aerated water led to the formation of 2-hydroxybiphenyl (2HB) with a quantum yield of 2.1×10^{-2} while photolysis of 4-chlorobiphenyl (4CB) under identical experimental conditions yielded trace amounts of 4-hydroxybiphenyl (4HB) with a quantum yield of only 2.5×10^{-4}. 4CB was relatively inactive in water; it also appeared to inhibit photolysis of other PCBs (Bunce *et al.*, 1978b). Seemingly, 4CB acted as an internal filter preventing more reactive PCBs from

absorbing light (Pagni and Sigman, in press). Dulin *et al.* (1986) reported that photolysis of 2CB in CH_3CN (10-25%)/H_2O mixture formed 2HB, four 2HB-derived products, and 2-$CH_3C(O)NHC_{12}H_9$, a product which can only arise from an aryl cation. Humic acid had no effect on the reaction rate.

While photolysis of 4CB in aerated water yielded only 4HB, in degassed water equal amounts of 4HB and 3HB were formed; no biphenyl was detected (Moore and Pagni, 1987). Further, it was observed that 3HB was formed as a result of hydroxylation of 3CB, a product of 4CB undergoing isomerization. Photolysis of radiolabelled 2CB in degassed water yielded 2HB only. Photolysis of radiolabelled 3CB under same condition afforded four different products: 2HB, 4HB, 3HB, and a small amount of biphenyl. Seemingly, dechlorination, hydroxylation, and isormerization led to the formation of these products. Adding Cl^- to 4CB in water rich CH_3CN/H_2O mixture retarded its hydroxylation presumably due to the common ion effect (Orvis *et al*, 1991).

Commercial PCB mixtures, Aroclor 1232 and 1268, are photodegradable. The highly chlorinated congeners in these mixtures are preferentially photolyzed. Loss of PCBs in natural waters has been estimated to be 10 to 1000 g km^{-2} y^{-1} (Bunce *et al.*, 1978).

Mechanisms of Photolysis in Organic Solvents. Because of the extremely low solubility of PCBs in water, many studies on photochemistry have been conducted in organic solvents, mainly alkanes and alcohols.

Being non-polar, alkanes are incapable of solvating ions and therefore photochemistry of PCB in alkanes always involve free radical reactions (Bunce, 1982; Pagni and Sigman, in press). The reaction is initiated by homolytic scission of a C-Cl bond to form a chlorine atom and a carbon-centered radical. Based on the results of quenching experiments with dienes or O_2, it is generally agreed that the homolysis occurs in the triplet excited state because of the high efficiency of intersystem crossing (ISC) of PCBs (Wagner, 1967; Ruzo *et al.*, 1974). The carbon-centered radical and chlorine atom will react with the solvent to yield less chlorinated biphenyls and HCl, respectively (Ruzo *et al.*, 1974a, b; Bunce, 1982):

$$PhCl \xrightarrow{h\nu} {}^1PhCl^*$$

$${}^1PhCl^* \xrightarrow{isc} {}^3PhCl^*$$

$${}^3PhCl^* \longrightarrow Ph^{\cdot} + Cl^{\cdot}$$

$$Ph^{\cdot} + RH \longrightarrow PhH + R^{\cdot}$$

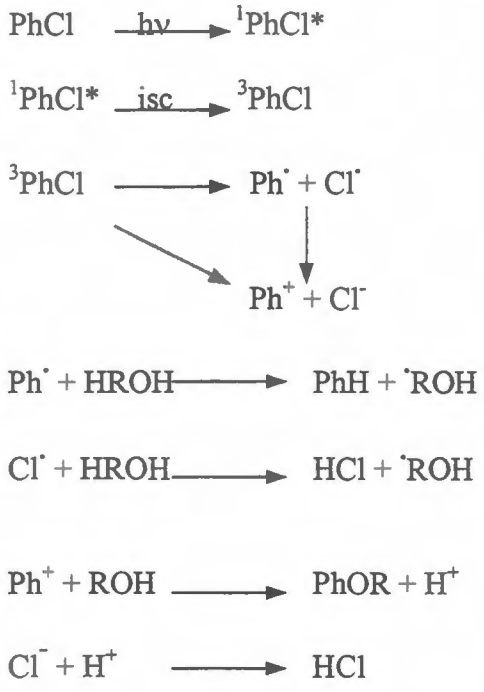
$$Cl^{\cdot} + RH \longrightarrow HCl + R^{\cdot}$$

Where Ph = biphenyl; RH = alkane;

As predicted by the mechanism above, photolysis of various PCBs dissolved in hexane mainly lead to the stepwise formation of dechlorinated congeners (Table 1). However, a minor product, cyclohexyl-PCB (<6%), was also identified when PCBs were

photolyzed in cyclohexane, presumably formed by the recombination of a PCB radical and a cyclohexane radical (Lepine, 1992a, b).

Alcohols, especially the ones with low molecular weights, are akin to water in solvating ions. Their weak C-H bonds are able to donate H atoms to carbon-centered radicals. Thus, the photochemistry of PCBs in alcohols always involve both homolytic and heterolyic mechanisms, as shown below:



Photolysis of PCBs in methanol and propanol resulted in less chlorinated PCBs as well as methoxylated PCB derivatives (Crosby and Moilanen, 1973; Nordbolm and Miller, 1974; Ruzo, 1974a, b; Hawarl *et al.*, 1992). These results coincide with the proposed mechanism.

Photodegradation in Surfactant Solutions. Surfactants are effective in enhancing solubility of PCBs in water and also mobilizing soil-bound PCBs by decreasing interfacial tension (Chapter 2). They also have the potential to enhance PCB photolysis. They may serve as H-atom sources, like the naturally occurring water soluble organics, and enhance dechlorination of PCB while minimizing side reactions such as hydroxyl substitution (Epling, *et al.*, 1988; Kalyanasundaram, 1987; Ramamurthy, 1986). Additionally, at dosages above the critical micelle concentration (CMC), surfactant micelles may impose a localized "cage effect" which favor PCB photolysis. The hydrocarbon-like micellar core or the "cage" favors partitioning of the hydrophobic PCB molecule while the polar photoproducts such as chloride ion are expelled. Thus, the common ion effect is eliminated and PCB molecules can react with surfactant (H-atom source) longer at a higher local concentration within the "cage".

Hashimoto and Thomas (1991) studied the photochemistry of biphenyl and 4CB dissolved in anionic (sodium dodecylsulfate (SDS)) and cationic (cetyltrimethylammonium bromide) micellar solutions using two step excitation (laser pulse) technique. Irradiation of the test compounds at upper triplet state showed no evidence of carbon-chlorine bond scission. Instead, photo-ionization of the test compounds was observed. Enhanced photodechlorination of seven PCBs in CH_3CN/H_2O (v:v = 9:1) solution containing NaBH occurred in the presence of anionic (sodium dioctyl sulfsuccinate (SdiS)) or non-ionic (Brij58) micelles (Epling and Florio, 1986; Epling *et al.*, 1988). O_2 had little effect on photolysis. Two competing mechanisms of

dechlorination were possible: (1) hydride directly attacking the excited state of chlorobiphenyl and (2) photoinduced electron transfer from BH_4^- to the chlorobiphenyl excited state.

Guillet (1991) reported that a water-soluble polymer, poly(sodium styrensulfonate-*co*-2-vinylnaphthalene) (PSSS-VN), while solubilizing PCBs also catalyzed their photolysis. Photolysis of 2,2',3,3',6,6'CB and several commercial PCB mixtures (Aroclor 1242, 1248, and 1254) dissolved in this polymer solution led to the formation of less chlorinated biphenyls (Sustar *et al.*, 1992; Guillet, 1991); no hydroxybiphenyls were produced (Nowakowska *et al.* 1991). The reaction was faster in polymer solutions than in water alone and was retarded while purged with O_2. Further study on fluorescence quenching suggested a photoinduced electron transfer mechanism in which PCB radical anion was involved (Nowakowska *et al.* 1991).

Photolysis of PCBs in Soil Suspensions. An innovative approach to remediating PCB-contaminated soils may involve surfactant-washing of soils followed by photolysis of surfactant wash water. Two parameters are of paramount importance in such an application: attenuation of light by suspended particles and possible heterocatalytic reactions at the particle surface.

Miller and Zepp (1979) examined the effect of suspended sediment upon the photolysis rate of dissolved pollutants in several natural water bodies. They found photolysis rates within the photic zone to be generally more rapid in low turbidity waters

than in clear waters, by a factor of up to 1.8 in clay suspensions. Scattering effect was suggested as being responsible for the observed rate enhancement. Light attenuation due to the presence of colloidal particles in natural waters was attributed to two independent mechanisms: scattering and adsorption.

Photochemistry at the surface of soil particles may mimic that at the surface of TiO_2 which involves electron transfer and free radical reactions. Occhiucci and Patacchiola (1982) demonstrated dechlorination of PCBs adsorbed on montmorillonite, a clay mineral. Draper *et al.* (1987) reported that irradiation of a concrete surface contaminated with Aroclor 1260 (81 ± 31 μg/100 cm^2) resulted in 47% degradation in 21 hours. In soil slurries, with TiO_2 added, 2 hour irradiation with UV and sunlight resulted in up to 77% degradation of PCBs (Chiarenzelli *et al.*, 1995; Zhang *et al.*, 1993). Similarly, Hawarl *et al.* (1992) reported that photolysis of soil extracted Arcolor 1254 in alkaline 2-propanol led to effective dechlorination, especially when phenothiazine, a sensitizer, was added.

In general, PCBs in soils can be effectively destroyed by UV irradiation. The cost of soil treatment was estimated to be \$120-250/m^3 for rate of 1 m^3 of soil per day using a 100 kW system (Wekhof, 1991).

All the PCB researches reviewed in the section are summarized in Table 3.1.

Table 3.1. Summary of PCB photodegradation in different solvents.

PCB	Photoproducts/ Mechanism	Solvent	Wavelength (nm)	Authors and year
4CB[a] (10^{-5}-10^{-6} M)	3-HB[b] /isomerization and heterolysis	H_2O (N_2)[c]	300	Moore & Panni, 1987
	4-HB /heterolysis			
2CB ($2.15x10^{-5}$ M)	2-HB /heterolysis and secondary photolysis	H_2O		Orvis *et al*, 1991
3-CB (2.18×10^{-5} M)	Biphenyl /homolysis 2-CB and 4CB/isomerization 3-HB/ heterolysis	H_2O		
4CB	common ion effects/triplet excited state	H_2O/CH_3CN(80:20 = v:v) with Cl^-		
4CB	4-hydroxylbiphenyl			
2,4CB	hydroxylated product	H_2O/CH_3OH(0.3-2ml/L)	sunlight	Crosby & Moilanen, 1973
2,5CB	hydroxylated and reduced products			
3,4CB	none			
4,4'CB	hydroxylated and reduced products			
2,4,5CB	none			
2,2',3,3'CB	hydroxylated and reduced products			
2,2',4,4'CB	none			
2,2',5,5'CB	hydroxylated and reduced products 2-chlorodibenzofuran(0.2%)[d]			
2,4CB, 2,4,6CB, and 2,2',5,5'CB	photodegradation(Φ=0.0037-0.25)	H_2O/CH_3CN(v:v =1:4)	254	Bunce *et al.*, 1978
Aroclor 1232	photodegradation (Φ=0.036)		300	
Arcolor 1268	photodegradation (Φ=0.16)			

Table 3.1. Summary of PCB photodegradation in different solvents (continued)

PCB	Photoproducts/ Mechanism	Solvent	Wavelength (nm)	Authors and year
2CB(8^{-10} -10^{-6} M)	2-HB and Cl^-/((Φ=0.2-0.29)	H_2O/CH_3CN(10-25%)	230-410	Dulin *et al.*, 1986
	2-HB, 2-$CH_3C(O)NHBP$, and Cl^-	H_2O/CH_3CN(10-25%) /humic acid (5 mg/L)		
4CB(10^{-5}M)	4-HB and Cl^-	H_2O/CH_3CN(10%)		
2,3',4,4'CB, 2,2',4,5,5'CB, 1996	dechlorination	H_2O/DEA [e] (1 mg/L)	sunlight	Lin *et al.*, 1995,
2,3,3',4',6CB, 2,3',4,4',5CB, 2,2',3,4,4',5 (0.100 mg/L) Arocloer 1254	(k_1=0.07-0.2 hr^{-1}, Φ = 2.6 –7.5 x 10^{-4})[f]		(simulated)	
4,4'CB (1.0x10^{-3} M)	4CB(Φ=0.002)/	methanol(N_2)	310	Nordblom & Miller 1974
	4CB(Φ=0.002)	2-propanol(N_2)		
	4CB	2-propanol+2%CF_3CO_2H		
	4CB	Dierhyl ether		
	trace 4CB and unidentified products	hexane or cyclohexane		
2,2',4,4' CB (0.005M)	4.4' CB, 2,4,4' CB and trace 4CB /dechlorination/homolysis(triplet) trace 2,4,4' trichloro 2' –methoxybiphenyl and trace DCMB[g]/heterolysis	methanol	300	Ruzo *et al*, 1974a,b
2,2'.5.5' CB (0.005M)	2,5,3' CB, 3.3' CB, trace 3 CB TCMB[h] and trace DCMB chlorohydroxybiphenyls	methanol dioxane-water		
2,2',3,3' CB (0.005M)	2,3,3' CB and 3,3' CB TCMB and trace DCMB	methanol		
2,2',6.6' CB (0.005M)	2,2',6 CB, and 2,2'CB trace TCMB	methanol		

Table 3.1. Summary of PCB photodegradation in different solvents (continued)

PCB	Photoproducts/ Mechanism	Solvent	Wavelength (nm)	Authors and year
3,3',4,4' CB (0.005M)	3,4,4'CB, 4,4'CB, and TCMB	methanol		
3,3',5,5'CB (0.005M)	3,3',5 CB	methanol		
2,2',4,4'CB, 2,2'.5.5' CB, 2,2',3,3' CB, 2,2',6.6' CB, 3,3',4,4' CB, and 3,3',5,5'CB	Tri- and Di- chlorobiphenyls /stepwise dechlorination	cyclohexane		
2,2',4,4'CB	(Φ =0.10, ε^i = 140)	cyclohexane	300	Draper *et al.*, 1987
2,2',3,3'CB	(Φ =0.007, ε = 116)			
2,2',5,5'CB	(Φ =0.010, ε = 120)			
2,2',6,6'CB	(Φ =0.006, ε = 30)			
3,3',5,5'CB	(Φ =0.002, ε = 1410)			
3,3',4,4'CB	(Φ =0.005, ε = 6740)			
4CB	(Φ =0.004, ε = 120)	CH_3CN/H_2O(v:v = 4:1)	254	
2,4CB	(Φ =0.22, ε = 25)			
2,4,6CB	(Φ =0.25, ε = 7)			
2,2',5,5'CB	(Φ =0.017, ε = 30)			
2,2',3,3',4,4',5,5',6,6'CB	(Φ >0.21, ε = 1200)			
Arcolor 1232	(Φ =0.036, ε = 60)			
Arcolor 1268	(Φ =0.16, ε = 770)			
4,4'CB (1 g/L)	4CB	hexane	300	Ruzo *et al*, 1972
3,3',4,4'CB (1 g/L)	3,4,4'CB, 4,4'CB			
2,2',5,5'CB	chlorobenzenes 3CB, 3,3'CB 2,2',5CB, 2,3',5CB	hexane	xenon	Miao *et al.*, 1996

Table 3.1. Summary of PCB photodegradation in different solvents (continued)

PCB	Photoproducts/ Mechanism	Solvent	Wavelength (nm)	Authors and year
2,2',4,4',6,6'CB (12.5 g/L)	dechlorination dechlorination and hydroxlation	hexane methanol	310	Safe & Hutzinger, 1971
2,2',5,5'CB (4 mg/L) 3,3',4,4'CB (4 mg/L) 2,2',4,5,5'CB (4 mg/L) 2,3',4,4',5CB (4 mg/L) 2,2',3,4,4',5'CB (4 mg/L) 2,2',4,4',5,5'CB (4 mg/L) 2,2',3,4,4',5,5'CB (4 mg/L) 2,2',3,4,4',5',6'CB (4 mg/L)	not detected 3,4,4'CB, 3,3'4CB 2,3',4',5CB, 2,3'4,5CB, 2,2',4,5'CB, 2,2',5,5'CB 3,3',4,4CB, 2,3',4,4'CB, 3,4,4'CB, 3,3',4CB 2,3',4,4',5CB, 2,3,3',4,4'CB, 2,2',4,4',5CB, 2,2',3,4,4'CB, 2,2'3,4,5'CB, 3,3',4,4'CB 2,3',4,4',5CB, 2,2',4,4'5CB, 2,2',4,5,5'CB, 3,3',4,4'CB, 2,3',4',5CB, 2,3',4,5CB, 2,3,4,4',5,5'CB, 2,3,3',4,4',5CB, 2,2',4,4',5,5'CB, 2,2',3,4,4'5'CB 2,2',3,4',5,5'CB, 3,3',4,4',5CB, 2,3',4,4',5CB 2,2',4,4',5CB, 2,3',4,5,5'CB, 2,2',4,5,5'CB 2,3',4,4',5,5'CB, 2,3,3',4,4',5CB, 2,2',4,4',5,6'CB, 2,2',3,4',5',6CB, 2,2',3,4,5',6CB, 2,2',4,4',6CB, 2,2',4,5',6CB, 2,2',4,4',5CB, 2,2',4,5,5'CB, 2,2',3,5',6CB, 2,3',4,4',6CB	cyclohexane	300	Lepine *et al*, 1991
2,2',4,5CB, 2,4,4',5CB, 2,3',4,4',5CB, 2,2',3,4',5'CB(4mg/L)	trace cyclohexyl-PCB(<6%) /triplet/homolysis	cyclohexane(N_2)	300	Lepine *et al*, 1992a
Arcolor 1254 (4 mg/L)	trace cyclohexyl-PCB	cyclohexane(N_2)	sunlight	Lepine *et al*, 1992b
4CB (1 x10^{-3} M)	dechlorination/slow	CH_3CN/H_2O (v:v=1:1) /amine[j]/zinc protoporphyrin	visible light	Epling *et al*, 1991

Table 3.1. Summary of PCB photodegradation in different solvents (continued)

PCB	Photoproducts/ Mechanism	Solvent	Wavelength (nm)	Authors and year
4,4CB (7×10^{-4} M)	4CB (86% yield)	CH_3CN/H_2O (v:v=1:1) /amine/methylene blue		
2CB	dechlorination ($\Phi = 0.28$)	CH_3CN/H_2O (v:v=9:1) /$NaBH_4$/SdiS[k] (0.06M)	254	Epling *et al.*,1988
4CB	dechlorination ($\Phi = 0.030$)	CH_3CN/H_2O (v:v=9:1) / $NaBH_4$/SdiS (0.06M)		
	dechlorination ($\Phi = 0.097$)	H_2O/ $NaBH_4$ / Brij58 (0.13M)		
4,4'CB	dechlorination ($\Phi = 0.10$)	H_2O/ $NaBH_4$ /Brij58 (0.13M)		
2,2',4,4'CB	dechlorination ($\Phi = 0.30$)	CH_3CN/H_2O (v:v=9:1) / $NaBH_4$/SdiS (0.06M)		
2,2',5,5'CB	dechlorination ($\Phi = 0.125$)	CH_3CN/H_2O (v:v=9:1) / $NaBH_4$/SdiS (0.06M)		
2,3,3',4,5,6CB	dechlorination ($\Phi = 0.51$)	CH_3CN/H_2O (v:v=9:1)		
2,2',4,4',6,6'CB	dechlorination ($\Phi = 0.94$)	CH_3CN/H_2O (v:v=9:1) / $NaBH_4$/SdiS (0.06M)		
3CB, 4CB, 4,4CB, 2,2',5,5'CB	degradation ($\Phi = 0.013–0.14$)	CH_3CN/H_2O (9:1) / $NaBH_4$	low presure Hg lamp	Epling *et al*, 1986
4,4CB, 1,3,5'CBCB	dechlorination (53–74%)	CH_3CN/H_2O (1:1) /Et_3N(amine, 0.02M) /Protoporphyrin IX (0.003M)	visible light	Epling *et al*, 1991

Table 3.1. Summary of PCB photodegradation in different solvents (continued)

PCB	Photoproducts/ Mechanism	Solvent	Wavelength (nm)	Authors and year
2,2',4,4'CB	dechlorination	Surfactant/TiO_2	254	Shi *et al.*, 1994
BP, 4CB, 4BB, 4,4'BB	triplet excitation	SDS[l] and CTAB[m]	xenon lamp	Hashimoto & Thomas, 1991
Aroclor 1254	degradation	H_2O/acetone (trace)	xenon lamp	Lin *et al.*, 1996
2,2',3,3',6,6'CB	2,2',3,3',6CB, 2,2',3,5',6CB, 2,2',3,6,6'CB, 2,2',3,5'CB, 2,2',5,5'CB,2,2',5,6CB, 2,2',3,6'CB,2,3',5CB,2,2',6,6'CB,2,2',3CB, 2,2',5CB,2,2',6CB,2CB	H2O/PSSS-VN[o] (2 g/L)	280	Nowakowska *et al*, 1991
Arcolor 1254 (40 mg/L)	photodechlorination	$H_2O(N_2)$	sunlight	Sustar *et al*, 1992
(20 mg/L)	photodechlorination	hexane (N_2)	(simulated)	
(20 mg/L)	photodechlorination	H_2O (N2)/PSSS-VN (2g/L)		
Arcolor 1248 (1 mg/L)	photodechlorination	H_2O (N2)/PSSS-VN(0.6g/L)		
Arcolor 1242 (1 mg/L)	photodechlorination	H_2O (N2)/PSSS-VN(0.6g/L)		
Arcolor 1260 (81±31 ug/100cm2)	47% degradation in 2 hr	concrete surface	fluorescence lamp	Draper, *et al.*, 1987
Aroclor 1248 (32 mg/L)	77 % degradation in 2 hr	H_2O/clay(0.2 g/L)/TiO_2	sunlight	Zhang *et al.*, 1995
	27 % degradation in 2 hr	H_2O/sediment (0.2 g/L)/TiO_2		
PCB in sediment (31 mg/L)	77% degradation in 24 hr	H_2O/sediment/TiO_2		Chiarenzelli *et al.*, 1995
PCB in sediment (228 mg/L)	55% degradation in 24 hr	H_2O/sediment/Al_2O_3		

Table 3.1. Summary of PCB photodegradation in different solvents (continued)

PCB	Photoproducts/ Mechanism	Solvent	Wavelength (nm)	Authors and year
Aroclor 1254 (1000 mg/L)	25% dechlorination in 20 hr 3,3'CB, 2,3',5CB	2-propanol/NaOH	sunlight	Hawarl *et al.*, 1992
	100% dechlorination in 4 hr	2-propanol/HaOH/PT[p]		
	100% dechlorination in 0.5 hr	2-propanol/NaOH	254	
	100% dechlorination in 1 hr	2-propanol/NaOH/PT[p]	350	
Soil Extraction/Aroclor 1254 (730 mg/L)	not detected	2-propanol/NaOH	350	
	100% dechlorination in 2 hr	2-propanol/NaOH/PT[p]	350	
	100% dechlorination in 55 hr	2-propanol/NaOH	254	
	30% dechlorination in 20 hr	2-propanol/NaOH/PT[p]	sunlight	
	100% dechlorination in 20 hr	2-propanol/NaOH/PT[p]	sunlight	
PCB soil (mg/kg soil)	85% degradation in 0.5 hr	spray SDS (10 g/L)	pulsed UV	Wekhof, 1991

[a] CB: chlorobiphenyl
[b] HB: hydroxylbiphenyl
[c] Deoxygenated with N_2
[d] Yield of product
[e] Diethylamine
[f] First order rate constant
[g] Dichlorodimethoxybiphenyl
[h] Trichlorodimethoxybiphenyl
[i] Extinction coefficient, measured at 290 nm for tetrachloro PCBs and at 300 nm for others
[j] Et3N, 0.2M
[k] Sodium dioctyl sulfosuccinate
[l] Sodium dodecylsulfate
[m] Cetyltrimethylammonium bromide
[g] Poly(sodium styrenesulfonate-co-2-vinylnaphthalene)
[p] Phenothiazine

3.2 MATERIALS AND METHODS

3.2.1 Materials

One non-ionic surfactant, polyoxyethylene (10) lauryl ether (POL (10)), and one anionic surfactant, sodium dodecyl sulfate (SDS), obtained from Sigma Chemical Co., were used as received for all experiments. Five PCB congeners (99.7% pure), 2,2',4,4'-tetrachlorobiphenyl (2,2',4,4'CB), 2,4,4'-trichlorobiphenyl (2,4,4'CB), 4,4'-dichlorobiphenyl (4,4'CB), 4-chlorobiphenyl (4CB), biphenyl, and a commercial PCB mixture, Aroclor 1242, were also used without further purification. All PCB congeners were obtained from Ultra Scientific Co. The characteristics of the surfactants and PCBs are listed in Table 3.2. 1,2-dimethoxyethane (DME) (99.7% pure, Sigma Chemical) was used without further purification. All other solvents used in the study were GC or HPLC grade.

3.2.2 Methods

Solutions of PCBs in POL(10) were prepared in 150 mL centrifuge bottles using the method used for PCB solubilization experiments (Chapter 2). After centrifugation and suitable dilution, the supernatants of PCB-POL(10) (4 g/L) solutions were transferred for photolysis without pH adjustment, aeration, or degassing unless otherwise mentioned. All the PCB-POL(10) solutions in 5 mL quartz tubes (id = 10 mm), except the Aroclor 1242-POL(10) solution, were irradiated in a Rayonet photoreactor fitted with a merry-go-round

Table 3.2. Characteristics of surfactant and PCBs used for photolysis

Compound	Chemical formula	MW	CMC (M)[a]	HLB[b]
POL (10)	$C_{12}H_{25}(OCH_2CH_2)_{10}OH$	626	8.39×10^{-5}	17.9
SDS	$CH_3(CH_2)_{11}OSO_3Na$	288	8.06×10^{-3}	51.4
			Solubility (M)[c]	$\log K_{ow}$[c]
Biphenyl	$C_{12}H_{10}$	154.2	4.54×10^{-5}	3.9
4CB	$C_{12}H_9Cl$	188.7	6.36×10^{-6}	4.5
4,4'CB	$C_{12}H_8Cl_2$	223.1	2.68×10^{-7}	5.3
2,4,4'CB	$C_{12}H_7Cl_3$	257.5	6.21×10^{-7}	5.8
2,2',4,4'CB	$C_{12}H_6Cl_4$	292.0	3.08×10^{-7}	5.9
Arolor 1242	$C_{12}H_{6.92}Cl_{3.08}$[d]	260.3[d]	1.22×10^{-6}	4.7

[a]Critical micellar concentration, determined by surface tension measurement (Chapter 2)
[b]Hydrophile-lipophile balance, calculated using Davies and Rideal equation.(Myers, 1992).
[c]Aqueous solubility and Octanol/water partitioning coefficient (K_{ow}) of Aroclor 1242 were reported by Mackay *et al.* (1992); those for the others were reported by Shiu and Mackay (1986).
[d]Nominal formula and molecular weight of Aroclor 1242 determined from its Cl content, (42% by weight) (see section 2.3.3 in Chapter 2).

unit. 300 mL of Aroclor 1242-POL(10) solution (Aroclor 1242 = 210.5 mg/L; POL(10) = 4 g/L) was transferred into a quartz vessel (id x length = 4 cm x 32 cm) and irradiated at the center of the photoreactor. To study the behavior of 2,2',4,4'CB in its excited state, solutions of 2,2',4,4'CB in POL(10) were first purged with ultra pure N_2 (degassed) and O_2 (aerated) separately for 1 hour before being UV irradiated. The incident UV light intensity was measured using a radiometer (Model 97503, Cole-Parmer Instrument Co.). The measurements were performed at positions where the samples were located. Since the 5 mL-quartz tubes were evenly placed in the merry-go-round unit, four different test tube positions were evenly selected to obtain an estimate of the average incident light intensity. At each of the four positions, four measurements were taken with the UV sensor facing in four different directions: one toward to the center and one toward away from the center of the photoreactor, the other two were facing away each other and perpendicular to the other two directions. The output of the UV-lamps at 245 nm, an average of all measurements made, was 7.48×10^{-5} einsteins m^{-2} sec^{-1}. To estimate the loss of UV light intensity due to absorption by the wall of the quartz vessels, similar measurements were carried out again with the quartz tube overlapped on the sensor. It was found that 10% of the UV light was lost when it passed through the quartz tube. Thus, the light intensity reaching the sample was 6.73×10^{-5} einsteins m^{-2} sec^{-1}. For the Aroclor 1242 solution, the average irradiance of the UV lamp, measured at the surface of the quartz vessel in a similar manner, was 9.59×10^{-5} E m^{-2} sec^{-1} at 254 nm. The net light intensity reaching the sample was 90% of that incident on the surface of the quartz cell or 8.63×10^{-5} E m^{-2} sec^{-1}. The PCB remaining in solution was determined as a function of time. PCBs and products of photolysis were analyzed using a GC-ECD and a GC

(HP5890)-MS (HP5989B). The analytical details of these measurements can be found in Chapter 2. The GC-MS was equipped with a HB-5 column (0.45mm id, 30 m long). The column temperature of the GC was programmed as follows: It was initially held constant at 70 °C for 1 minute, then raised to 150 °C at a rate of 10 °C/min, and at a rate of 2 °C/min thereafter to 230 °C. Finally, the temperature was further raised at a rate of 10 °C/min to its final value, 280 °C, where it was held constant for 15 minutes. The PCB concentration was calculated by comparing with PCB standards. 2,2',3,3',4,5,6,6'-octachlorobiphenyl (2,2',3,3',4,5,6,6'CB) (Ultra Scientific) was used as the internal standard for GC-MS analysis. The identities of the products were confirmed by matching their retention times and mass spectra with those of standards.

The concentration of chloride in photolyzed solutions was measured by using a chloride selective electrode (Model Orion 96-17): 3 mL of the photolyzed sample was placed in a 22-mL glass vial and measured immediately. The chloride concentration was determined by comparing with chloride standards prepared by dissolving KCl in POL(10) (4 g/L). In addition, the chloride concentration was occasionally verified by a colorimetric method (Iwasaki *et al.*, 1952). The stock solutions of Hg^{2+} and Fe^{3+} used in developing the colored complex of chloride were prepared as follows. The Hg^{2+} stock solution was prepared by dissolving 0.3 g of $Hg(SCN)_2$ (99 % pure, Sigma Chemical) into 100 mL of 95% ethyl alcohol. The Fe^{3+} stock solution was prepared by dissolving 6 g of $NH_4Fe(SO_4)_2 \cdot 12H_2O$ (99.2% pure, Sigma Chemical) in 100 mL of 35.1 % nitric acid solution. Both Fe^{3+} and Hg^{2+} solutions were shaken on an end over end rotor for 10 days before use. After suitable dilution of the test solution, 1 mL aliquots were mixed

with 0.1 mL of Hg^{2+} stock solution and 0.2 mL of Fe^{3+} stock solution, allowed 10 minutes for color development and absorbance measured at 460 nm with a UV-VIS spectrophotometer (Beckman DU-70). The detection limits for Cl^- by both the electrometric and colorimetric methods were ~ 0.05 mg/L.

The POL(10) concentration was colorimetrically measured at 620 nm using standard methods (American Public Health Association, 1989) without any pretreatment of samples. The cobalt reagent used in the test was prepared by carefully dissolving 36 g $Co(NO_3)_2.6H_2O$ and 240 g NH_4SCN in 1000 mL deionized (DI) water. 1 mL test sample was mixed with 3 mL cobalt thiocyanate reagent and 8 mL methylene chloride (CH_2Cl_2) in 15 mL glass tube by shaking for 10 minutes. After centrifuging at 1,000 rpm for 5 minutes, 1.2 mL from the CH_2Cl_2 phase was placed in a quartz cuvette and the absorbance of the solution was measured at 620 nm using a UV-VIS spectrophotometer (Beckman DU-70).

To study the efficiency of photolysis in turbid suspensions, surfactant washing solutions were prepared as follows. One g of screened (US sieve no. 35) PCB contaminated soil was shaken for 3 days with 20 mL of 4 g/L surfactant solution (POL (10) or SDS). The resulting suspension was either settled by gravity for different time periods or centrifuged for 30 min at 10,000 rpm (7280 x g). Thus, suspensions having various turbidities were obtained. The nephelometric measurements of turbidity were made using a turbidimeter (Model 2100A, HACH Chemical Co). The samples were then irradiated in the Rayonet photoreactor and the PCBs in solution were measured as a

function of time. The characteristics of soils used in the study can be found in Chapter 2.

All UV-VIS spectra of PCBs were measured using a Beckman Spectrophotometer (DU-70) in 1-cm path quartz cell against the same solution without PCBs.

3.3 RESULTS AND DISCUSSION

3.3.1 UV-VIS Absorbance of PCB Solutions

The UV-VIS absorbance of suitably diluted solutions (POL(10) and DME) of the test pure PCBs are shown in Figure 3.1 and the absorbance characteristics are summarized in Table 3.3. The main band and κ band of biphenyl in POL(10) were at 204 and 250 nm, respectively (Figture 3.1A). One chlorine substitution at the *para* position of the biphenyl (4CB) caused a bathochromic (red) shift of the κ band. Two chlorine substitutions at both *para* positions (4,4'CB) pushed bathochromic shift further. However, with one chlorine substituted at the *ortho* position of 4,4'CB, as in 2,4,4'CB, caused a hipsochromic (blue) shift of the κ band (Figure 3.1B). Additional *ortho* substitution, as in 2,2',4,4'CB caused further hipsochromic shift such that the κ band was no longer discernible. The observed κ band shift with progressive *o*-chlorine substitution into PCBs dissolved in POL(10) agreed well with published literature (MacNeil *et al.*, 1976). The shift of the κ band, and ultimately its disappearnce, was attributed to the *ortho* chlorines increasing the barrier to free rotation of the two phenyl rings, resulting in a loss

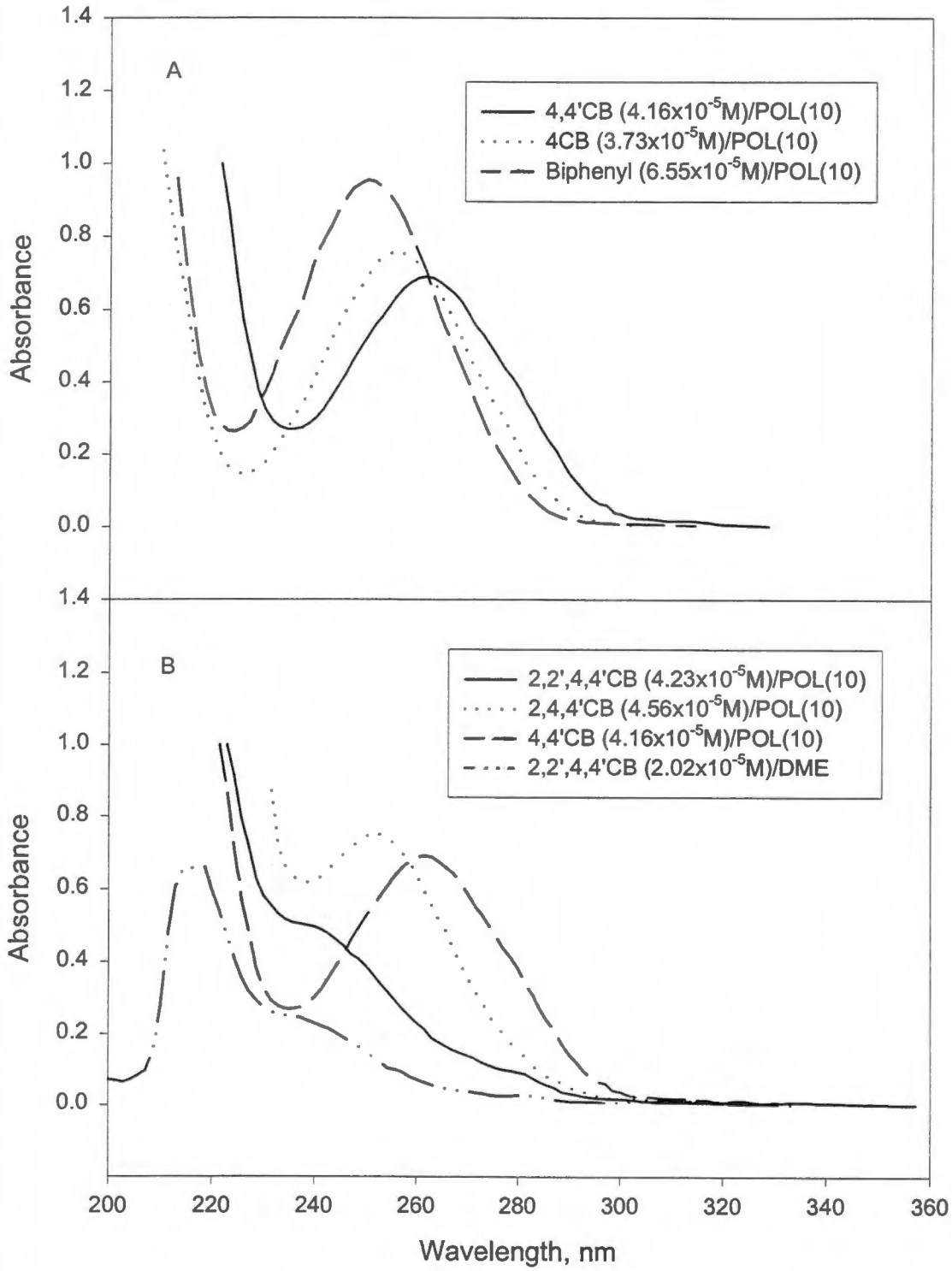


Figure 3.1 UV-VIS spectra of PCBs dissolved in POL10 (4 g/L) and DME

Table 3.3. Characteristic UV-VIS absorbance of PCB solutions

PCB	main band λ(nm)			κ band λ(nm)/ε (M^{-1} cm^{-1})		
	POL(10)	hexane[a]	DME	POL(10)	hexane[a]	DME
Biphenyl	204	202		250/14641	242/17000	
4CB		199		256/20371	253/20500	
4,4'CB	210	200		262/16354	258/22900	
2,4,4'CB	218	205		252/16413	250/14800	
2,2',4,4'CB	208	207(206)	218	236/11812[b]	220(235)/29400(29400)[b]	233/12394

[a] Values in parentheses were measured in n-hexane in the study, others were in cyclohexane (MacNeil *et al.*, 1976)
[b] Estimated at shoulder

of conjugation (coplanarity) of the two rings at the excited state (MacNeil *et al.*, 1976). The wavelength (λ) for κ band were always greater in POL (10) solutions than in cyclohexane (Table 3.3). Further, the λ and molar extinction coefficient (ε) of the κ band of 2,2',4,4'CB in POL(10) and DME solutions were very close, indicating a similar conformation of the PCB molecule in both solutions. It was also observed that the main band of the PCBs had similar shifting trends as that of the κ band (Table 3.3). That the absorption spectra in organic solvents (cyclohexane and DME) and in POL(10) solutions were similar implies that the interactions between PCB and the three solvents must also be similar. Thus, the photochemistry of PCB in POL (10) solution should mimic that in organic solvents.

Changes in UV-VIS spectra of PCBs during photolysis are illustrated in Figure 3.2 to 3.7. Save 2,4,4'CB, the spectra for all PCBs exhibited isosbestic points. No isosbestic point was observed for 2,4,4'CB which was transformed to 4,4'CB very fast (< 1 min) and no spectrum could be measured (Figure 3.5). For the spectra of PCBs without *ortho* chlorines (Figure 3.2 to 3.4), the maximum intensity of the κ band decreased without shifting during the initial period of photolysis. However, the maximum of the κ band of 4,4'CB shifted blue later ($\geq$ 5 min.). For PCBs with *ortho* chlorines (Figure 3.5 to 3.7), there was a red shift first, followed by decreasing intensity of the κ band, similar to that observed in non-*ortho* chlorinated PCBs. This would suggest a possible stepwise dechlorination with preferential removal of the *ortho* chlorine atoms.

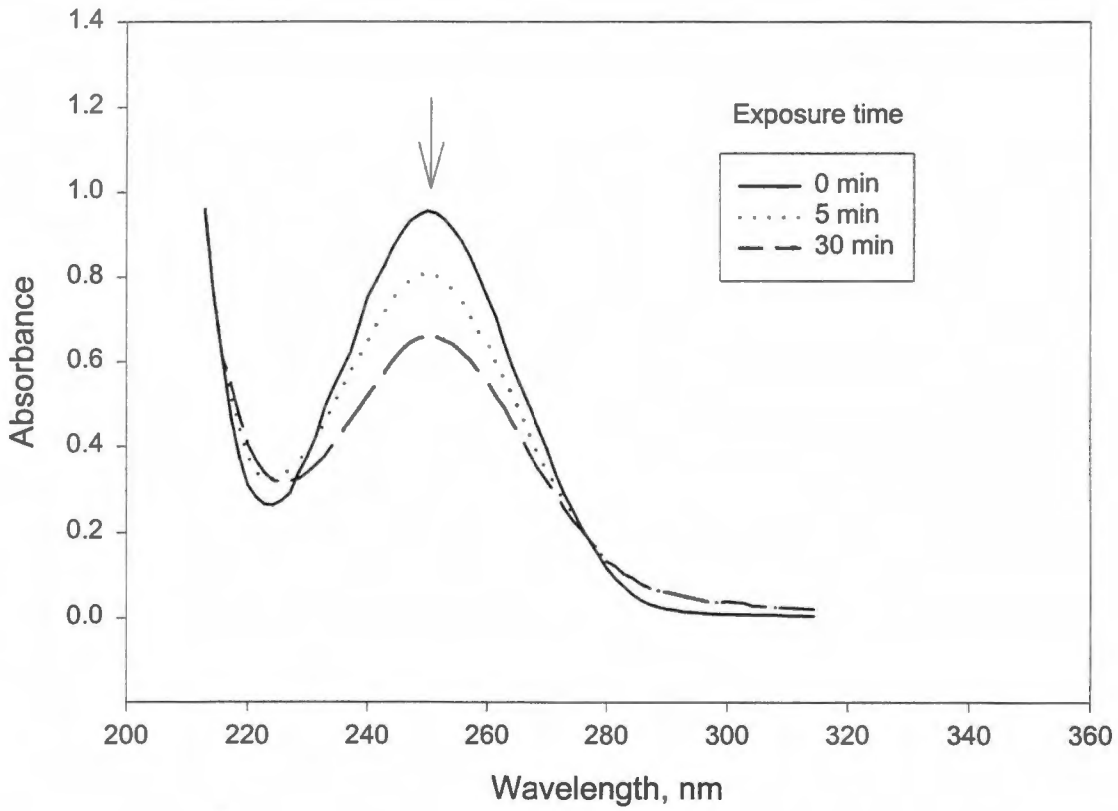


Figure 3.2 UV-VIS spectra of photolysis of biphenyl in POL(10) (4 g/L)

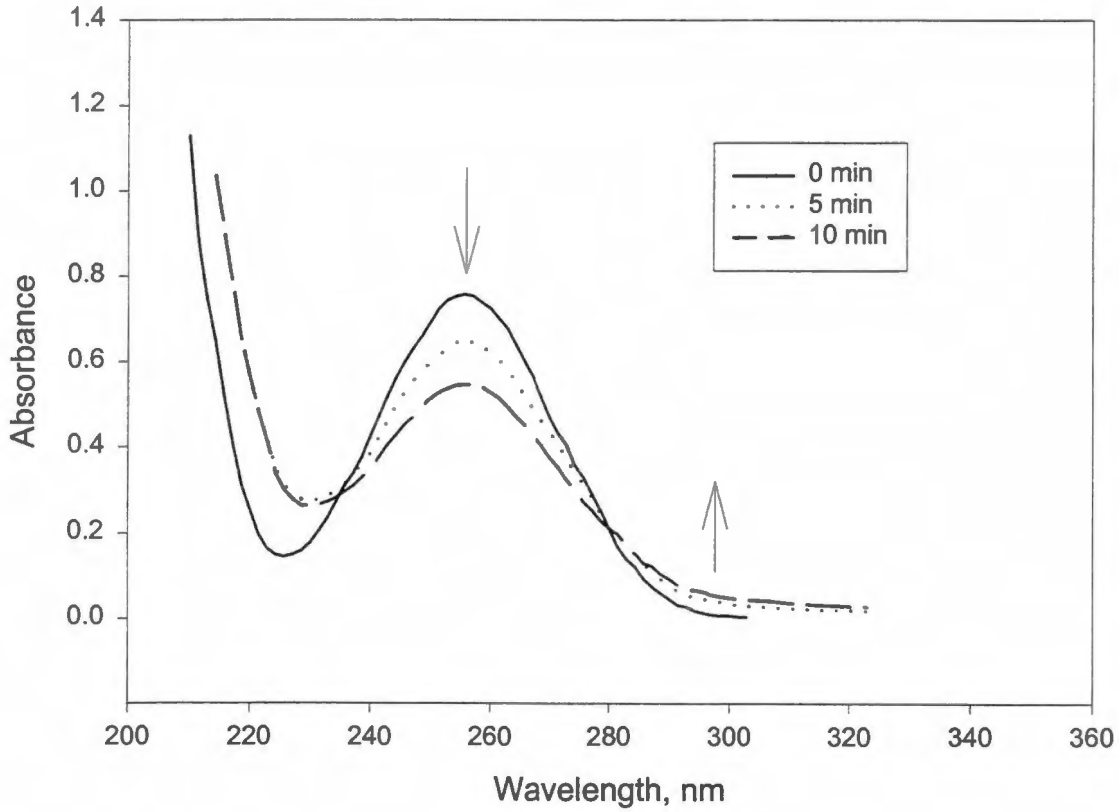


Figure 3.3 UV-VIS spectra of photolysis of 4CB in POL10 (4 g/L)

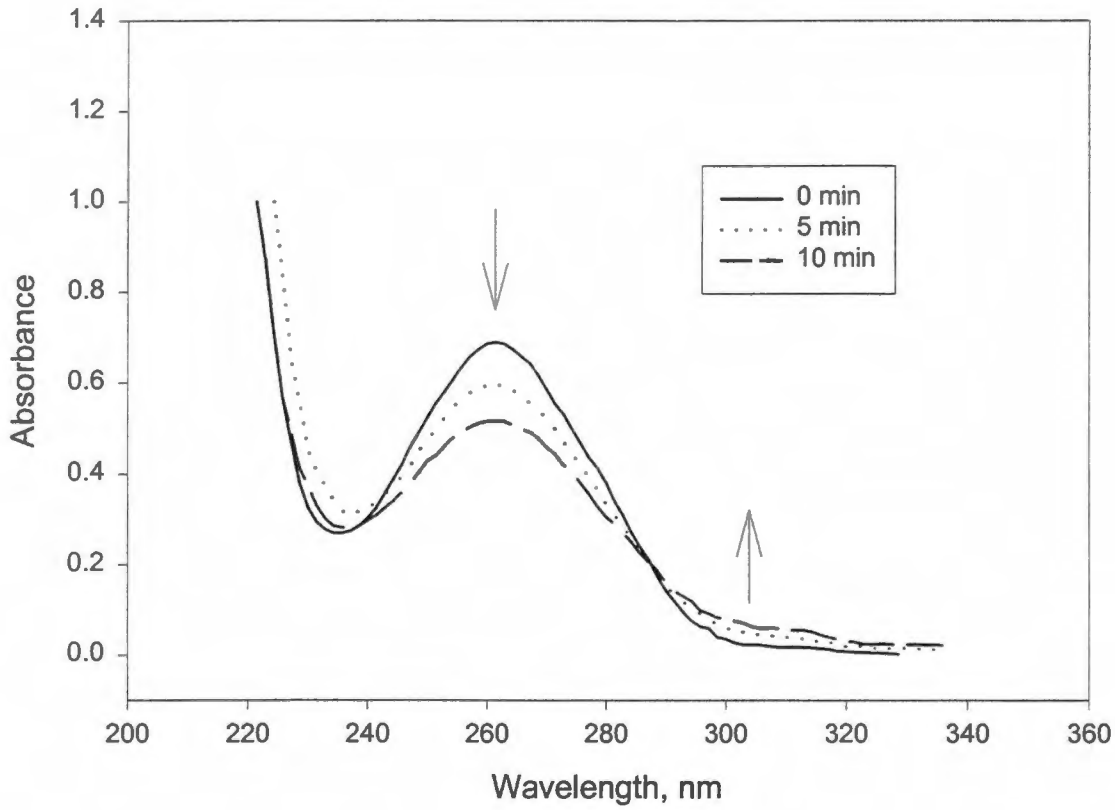


Figure 3.4 UV-VIS spectra of photolysis of 4,4'CB in POL10 (4 g/L)

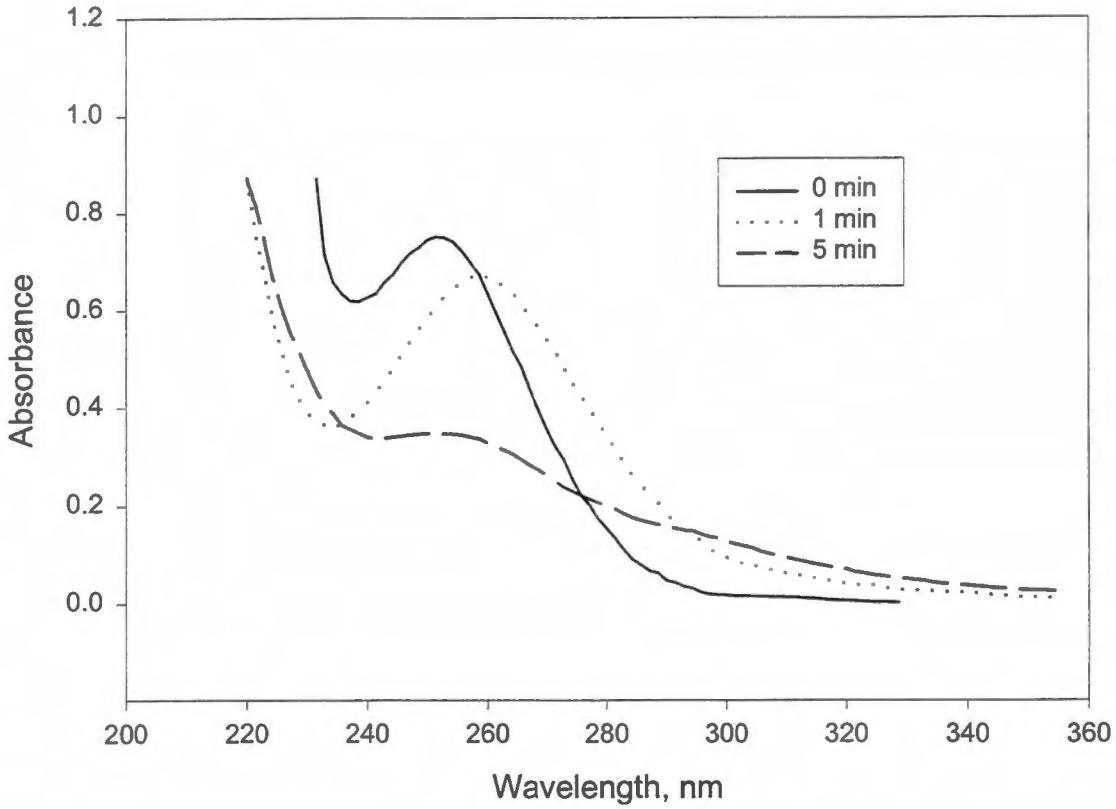


Figure 3.5 UV-VIS spectra of photolysis of 2,4,4'CB in POL10 (4 g/L)

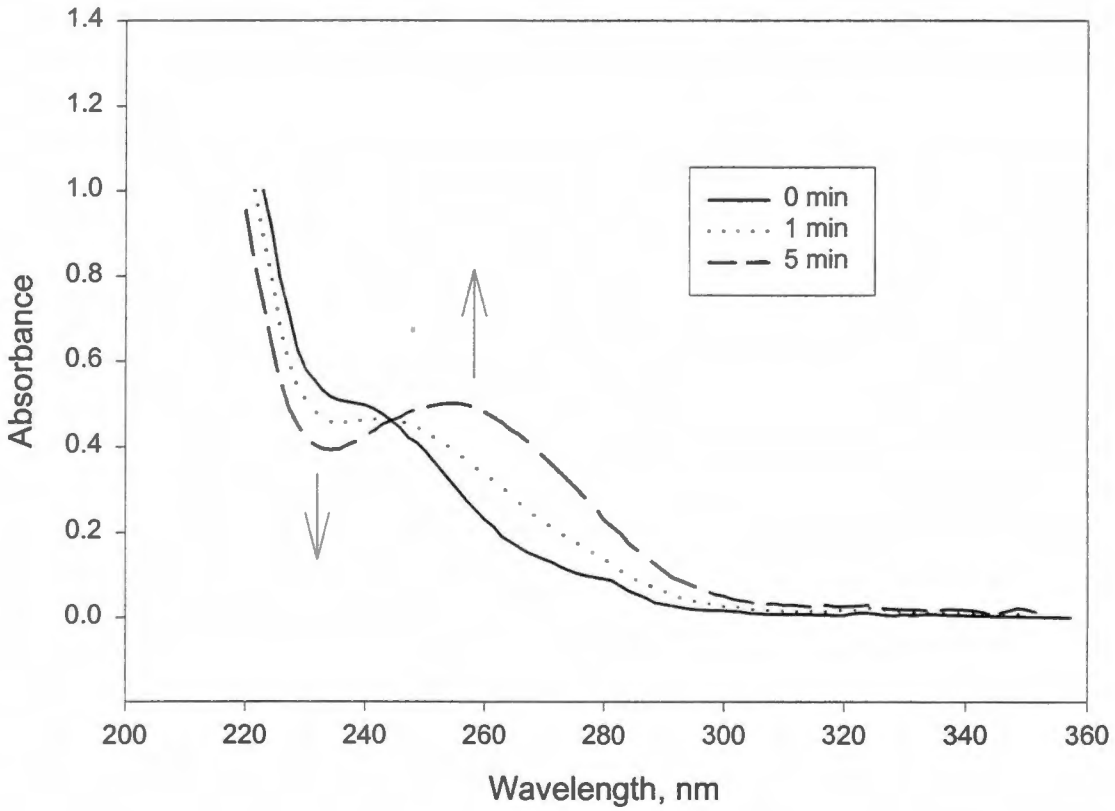


Figure 3.6 UV-VIS spectra of photolysis of 2,2',4,4'CB in POL10 (4 g/L)

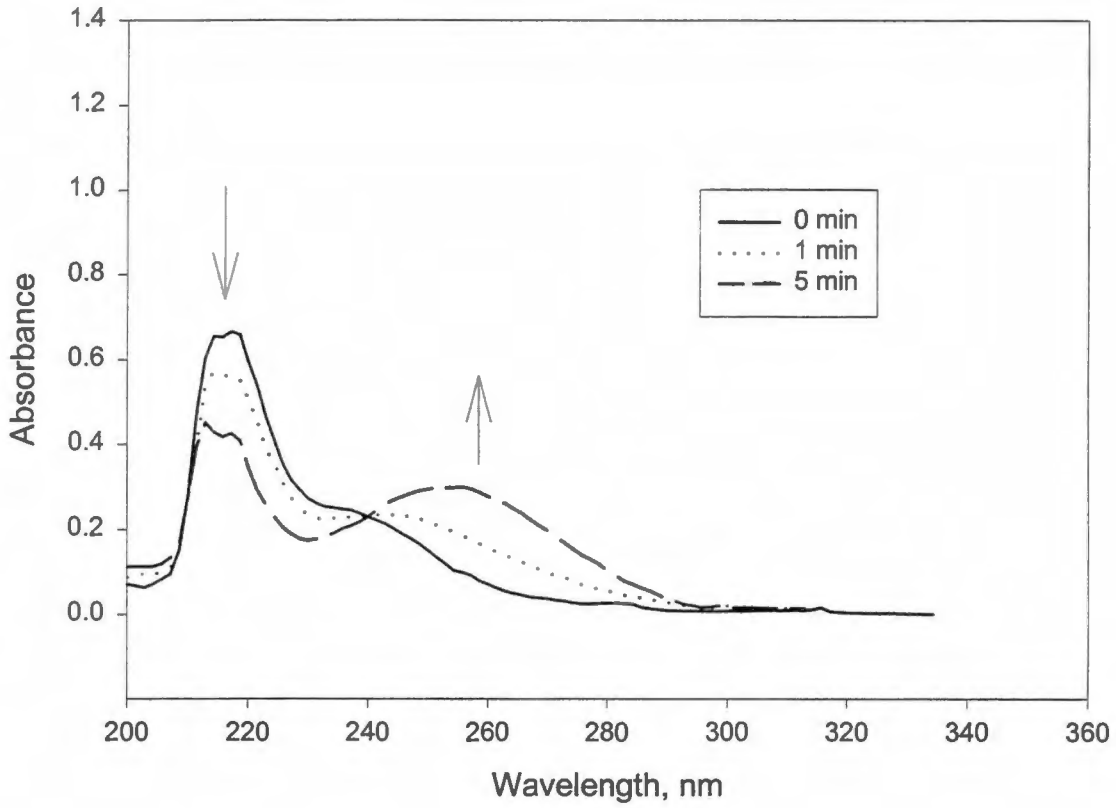


Figure 3.7 UV-VIS spectra of photolysis of 2,2',4,4' in DME

3.3.2 Photolysis Rates and Quantum Yields

The concentrations of biphenyl, 4CB, 4,4'CB, 2,4,4'CB, and 2,2',4,4'CB in 4 g/L POL(10) solution are plotted as a function of photolysis time in Figure 3.8, 3.9, 3.10, 3.11, and 3.12, respectively. The concentrations of 2,2',4,4'CB are plotted as a function of time in deoxygenated (N_2-purged) and oxygenated POL(10) solutions in Figure 3.13A and 3.13B, respectively. Additionally, Figure 3.14 illustrates the photolysis of 2,2',4,4'CB in 1,2-dimethoxyethane (DME). The initial absorbance (λ = 254 nm) of all PCBs solutions in Figures 3.8 through 3.14 was much greater than 2, i.e., all incident light was absorbed by the solutions. Consequently, the initial photolysis reaction should obey a zero-order kinetics (Leifer, 1988):

$$C_o = C_t + k_0 t \qquad (3.1)$$

where: C_o and C_t = concentration of PCB at time zero and t, respectively, M

k_0 = zero order rate constant, M min^{-1}

t = time, min

To minimize error due to competitive absorption of light by photoproducts, the initial photolysis rate constants (k_0) were calculated for the initial period of irradiation (t = 1 min) (Table 3.4). The standard error of the estimated k_0 values are also listed in Table 3.4. The initial rate constant (k_0) ranged from 1.10×10^{-5} to 3.35×10^{-4} M min^{-1} for the

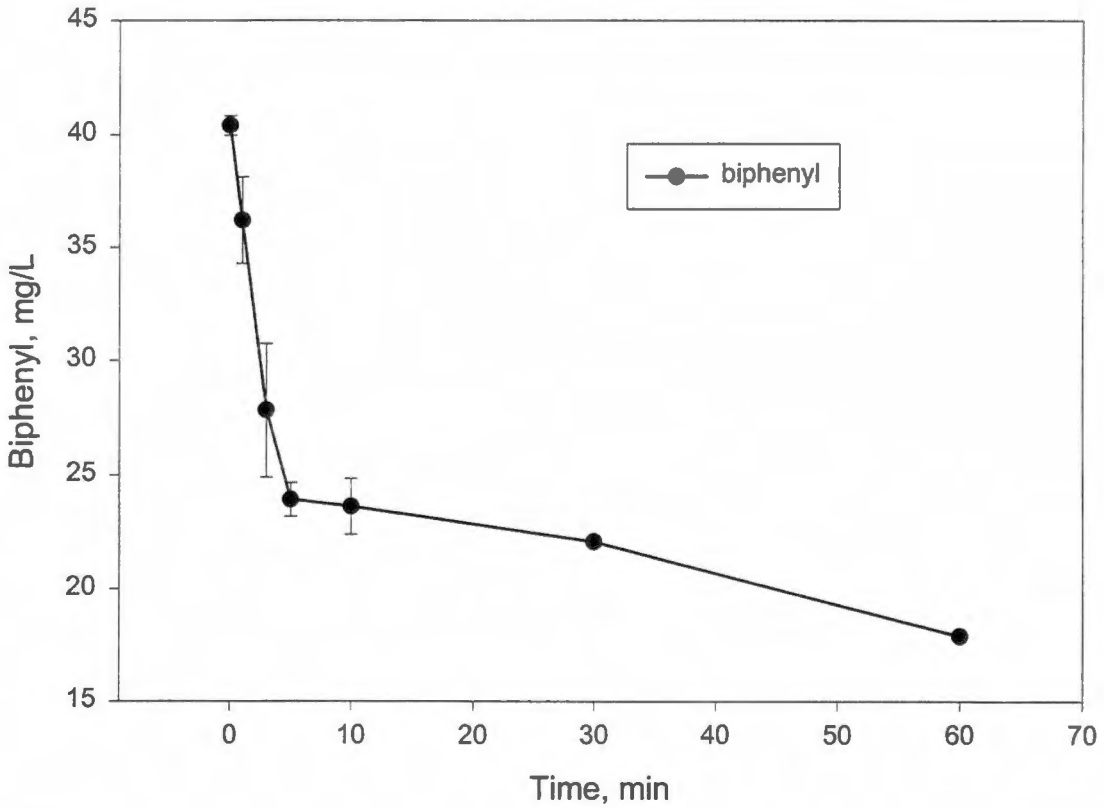


Figure 3.8 Concentration of biphenyl in POL(10) at various photolysis time

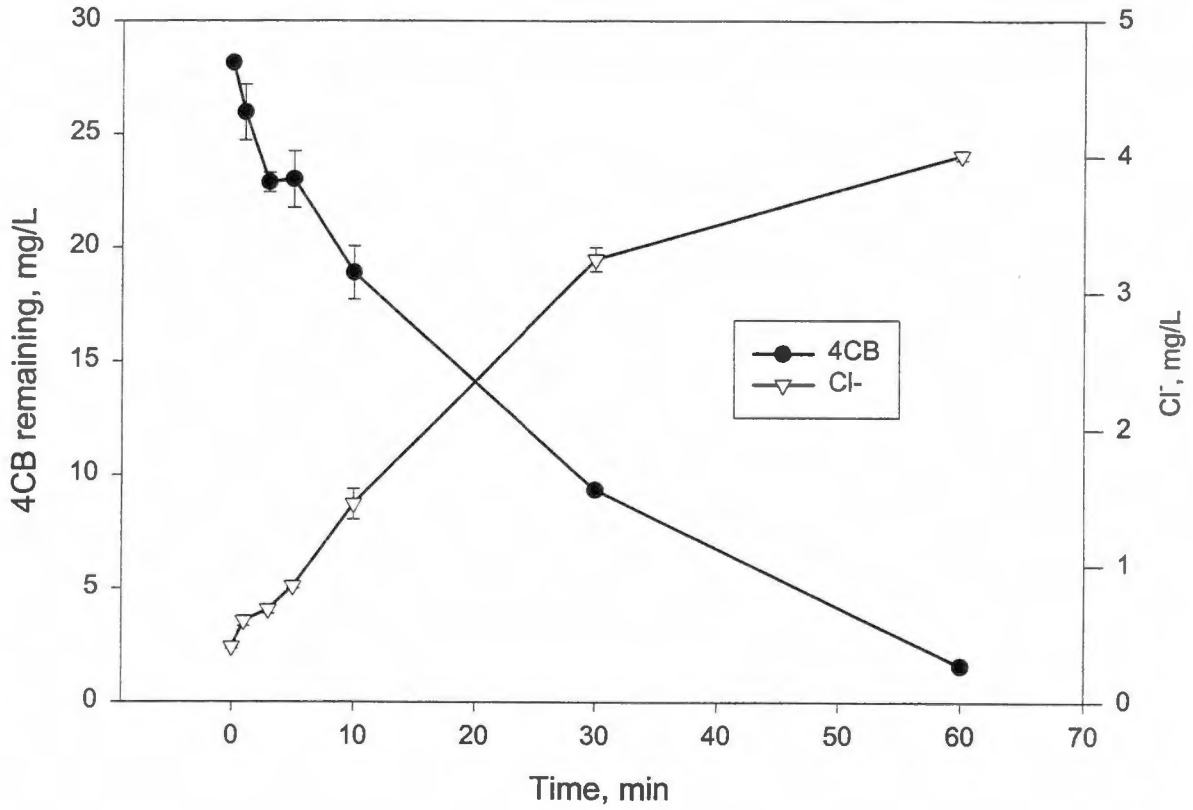


Figure 3.9 Concentration of of 4CB and its photoproduct (Cl^-) in POL10 solution at various photolysis time

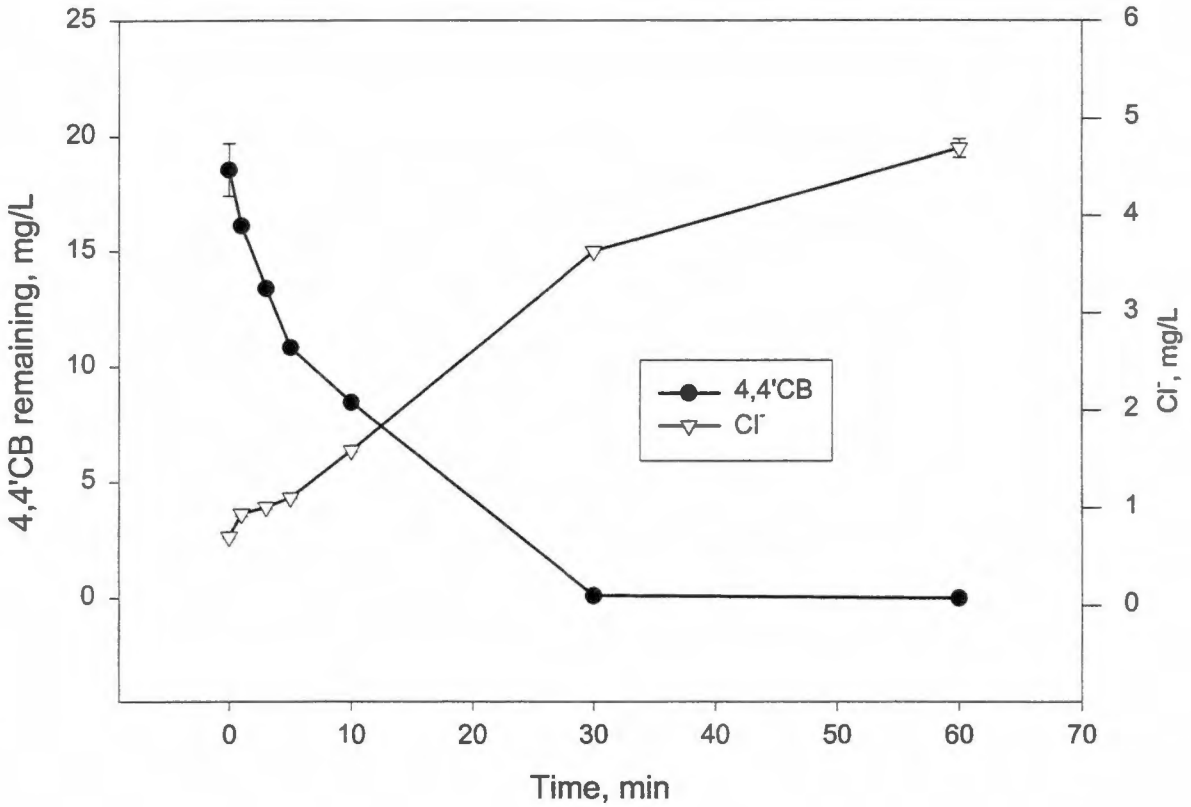


Figure 3.10 Concentration of 4,4'CB and its photoproduct (Cl^-) in POL10 solution at various photolysis time

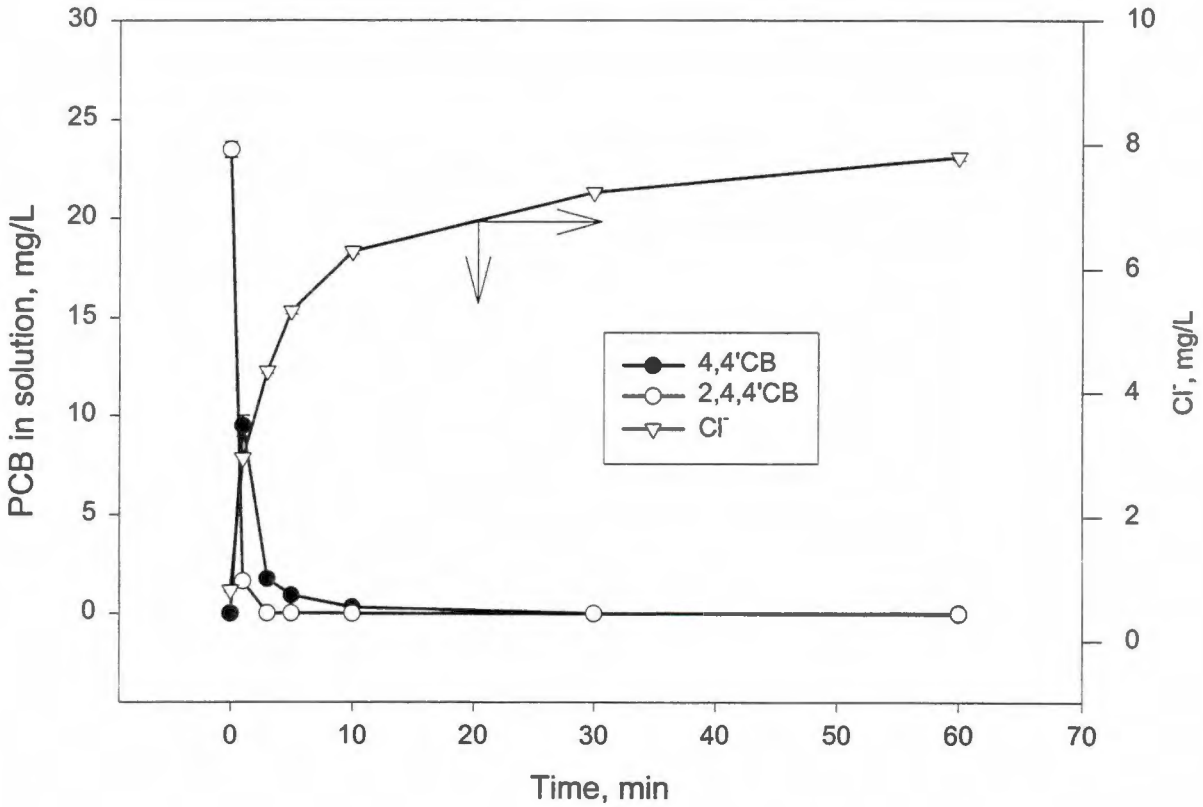


Figure 3.11 Concentrations of 2,4,4'CB and its photoproducts (4,4CB and Cl^-) in POL(10) solution at various photolysis time

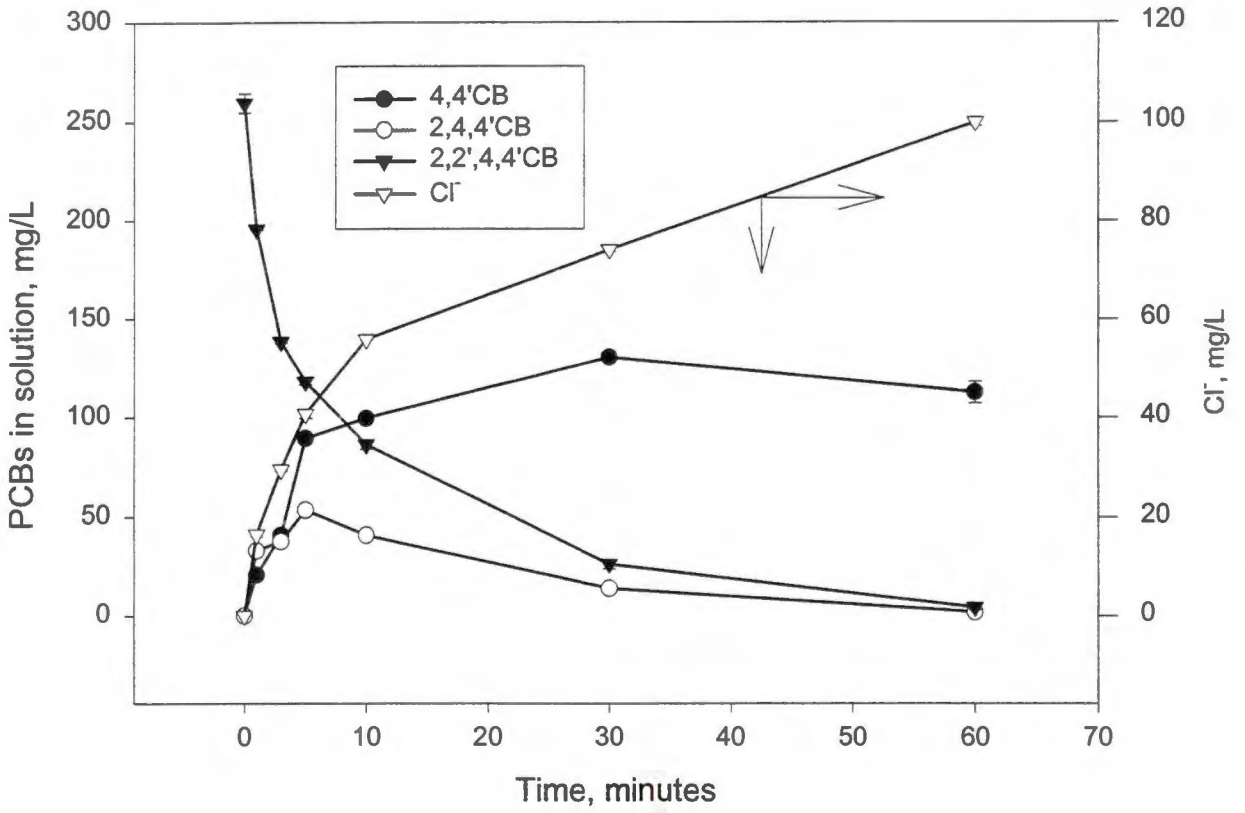


Figure 3.12 Concentrations of 2,2',4,4'CB and its photoproducts (2,4,4'CB, 4,4'CB, and Cl-) in POL(10) solutions at various photolysis time.

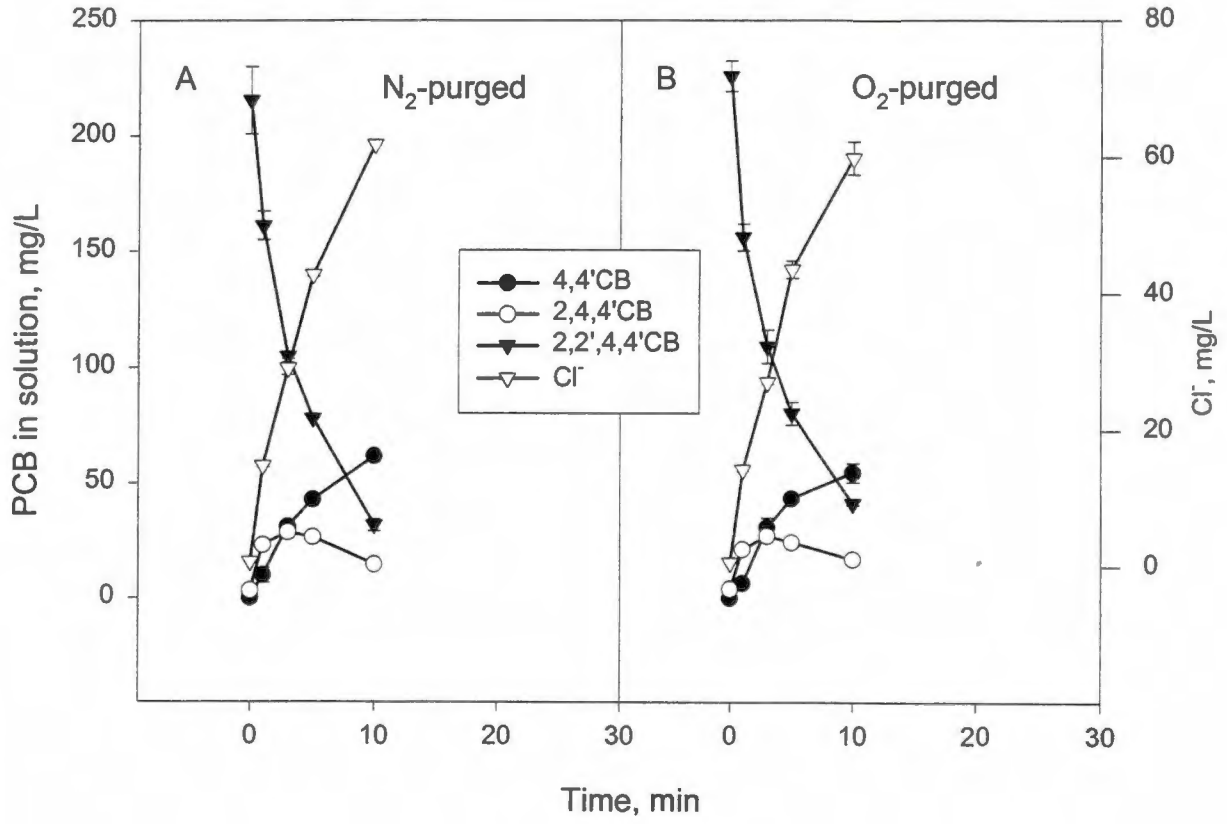


Figure 3.13 Comparison of photolysis of 2,2',4,4'CB in POL10 (4g/L) in oxygenated and deoxygenated solutions: concentrations of 2,2',4,4'CB and its photoproducts (2,4,4'CB, 4,4'CB, and Cl^-) at various photolysis time

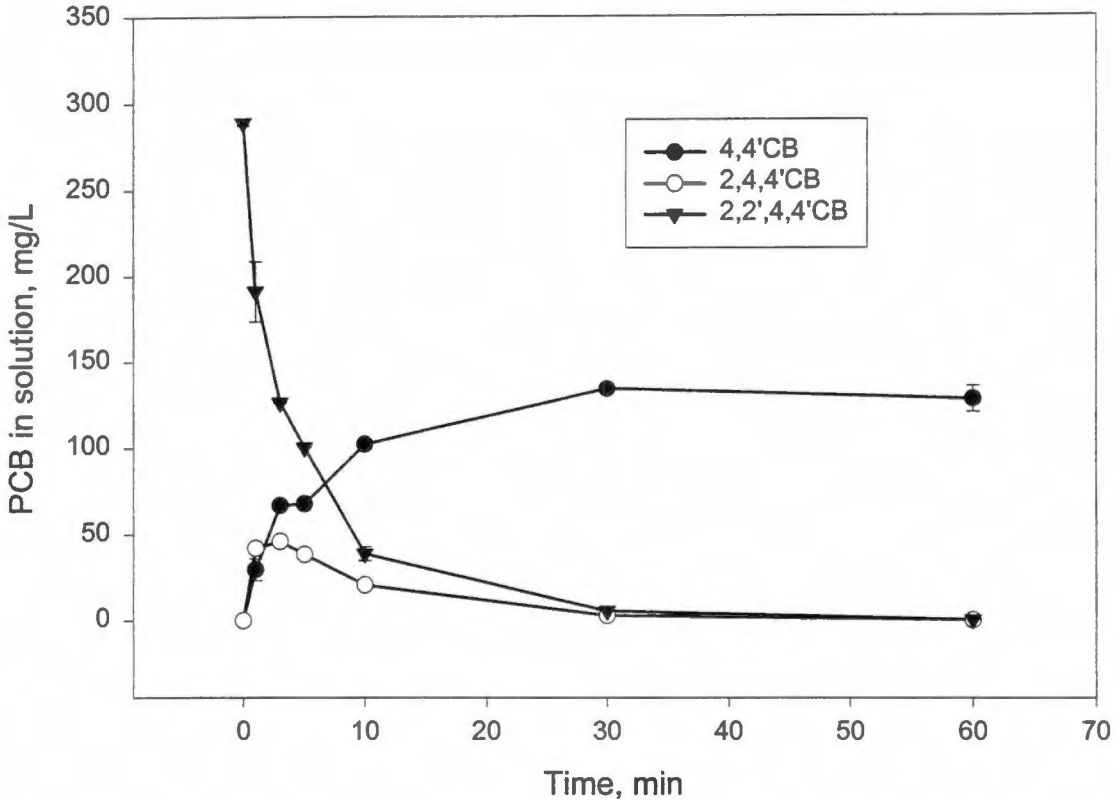


Figure 3.14 Concentrations of 2,2',4,4'CB and its photoproducts (2,4,4'CB and 4,4'CB) in DME at various photolysis time

Table 3.4. Initial photolysis rate and quantum yield of PCBs

PCB/Solution	Rate, $k_0 \times 10^5$ ($M\ min^{-1}$)	Quantum Yield, Φ Φ_1 (This Study)	Φ_2 (Literature)[b]	Φ_1/Φ_2
Biphenyl/POL(10)[a]	2.72 ± 1.27	0.0168 ± 0.0079		
4CB/POL(10)	1.16 ± 0.65	0.0072 ± 0.0040	0.0090	0.78
4,4'CB/POL(10)	1.10 ± 0.52	0.0068 ± 0.0033	0.0010	6.80
2,4,4'CB/POL(10)	8.47 ± 0.16	0.0524 ± 0.0010	0.014	3.74
2,2',4,4'CB/POL10	21.9 ± 0.17	0.1356 ± 0.0103	0.10	1.36
/POL10/N_2[c]	18.6 ± 5.43	0.1153 ± 0.0337		
/POL10/O_2[d]	23.9 ± 3.30	0.1481 ± 0.0187		
/DME	33.5 ± 6.05	0.2072 ± 0.0375		

[a] Concentration of POL(10) = 4 g/L
[b] In CH_3CN/H_2O (v:v=9:1) (Epling *et al.*, 1988)
[c] After purging with N_2
[d] After purging with O_2.

solutions tested. In a descending order of k_0, the surfactant solutions of PCB with no pretreatment can be arranged as 2,2',4,4'CB>2,4,4'CB>biphenyl>4CB>4,4'CB. Because the range of k_0 values of deoxygenated and oxygenated solutions of 2,2',4,4'CB in POL (10) nearly overlapped each other, the differences in the values themselves were considered statistically insignificant. However, k_0 for the photolysis of 2,2',4,4'CB in DME, a good donor of H-atoms, was 50% greater than that in POL (10). The corresponding quantum yields (Φ) at λ = 254 nm can be calculated as follows (Zepp, 1978, Leifer, 1988):

$$\Phi = k_0 / [I_{o\lambda} (A/V)] \qquad (3.2)$$

where, $I_{o\lambda}$ = average irradiance of incident light at 254 nm, (einsteins m^{-2} sec^{-1}).

= 6.73×10^{-5} einsteins m^{-2} sec^{-1} (this study)

k_0 = zero order rate constant, (sec^{-1})

A/V = (exposed area : volume of sample) (m^{-1}), A/V = 400 m^{-1} (this study).

The quantum yields of PCBs in POL(10) solutions ranged from 0.00719 to 0.136. In a descending order of Φ values, the PCBs can be arranged as 2,2',4,4'CB>2,4,4'CB>biphenyl>4CB>4,4'CB. Again, there was no significant difference in quantum yields of 2,2',4,4'CB among POL(10) solutions, regardless of their oxygen contents. However, the quantum yield of 2,2',4,4'CB in DME was higher relative to that in POL (10).

Based on the k_0 and Φ values, it appears that PCB photodegradation in POL (10) solution is directly related to the number of *ortho* chlorine atoms that a congener has. The photolysis of PCBs with no *ortho* chlorines, 4CB and 4,4'CB for example, was extremely slow. This corresponds well to results reported for PCB photolysis in organic solvents (Hutzinger *et al.*, 1974; Lepine *et al.*, 1991). The quantum yields reported in the literature (Φ_2) for 4CB, 4,4'CB, 2,4,4'CB and 2,2',4,4'CB in CH_3CN/H_2O solutions ranged 0.001-0.10 (Table 3.4) (Epling *et al.*, 1988). By comparison, save 4CB, the quantum yields (Φ_1) of the same PCB congeners in POL(10) were 36-580% greater (Table 3.4). Clearly, surfactant promotes photolysis.

3.3.3 Products and Mechanism

In this study, the appearance of free chloride ion in solution was taken as the evidence for PCB dechlorination. Chloride was measured electrochemically, using a chloride ion selective electrode, as well as colorimetrically (Iwasaki *et al.*, 1952) (Figure 3.15). As shown in Figure 3.15b, the results obtained using the two methods agreed well. All subsequent measurements of chloride were made electrochemically. Chloride resulting from the dechlorination of 4CB, 4,4'CB, 2,4,4'CB and 2,2',4,4'CB are shown in Figure 3.9 to 3.13. In Figures 3.11 and 3.12, stepwise formation of less chlorinated congeners are also shown along with chloride. 2,4,4'CB and 4,4'CB were identified as the products of stepwise dechlorination of 2,2',4,4'CB as shown in by the gas chromatogram (Figure 3.16) and GC-MS (Figure 3.17). The concentration of photoproducts are shown as a function of time in Figure 3.12. After one minute, total

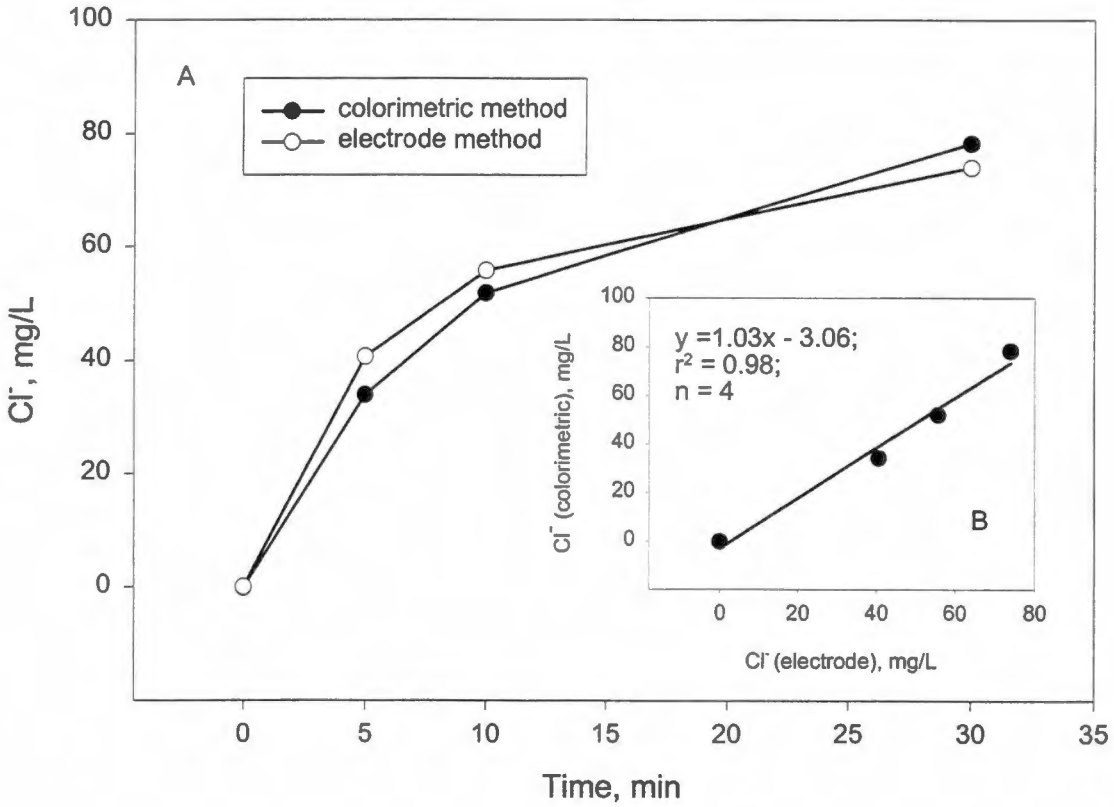


Figure 3.15 Comparison of two methods for Cl^- monitoring

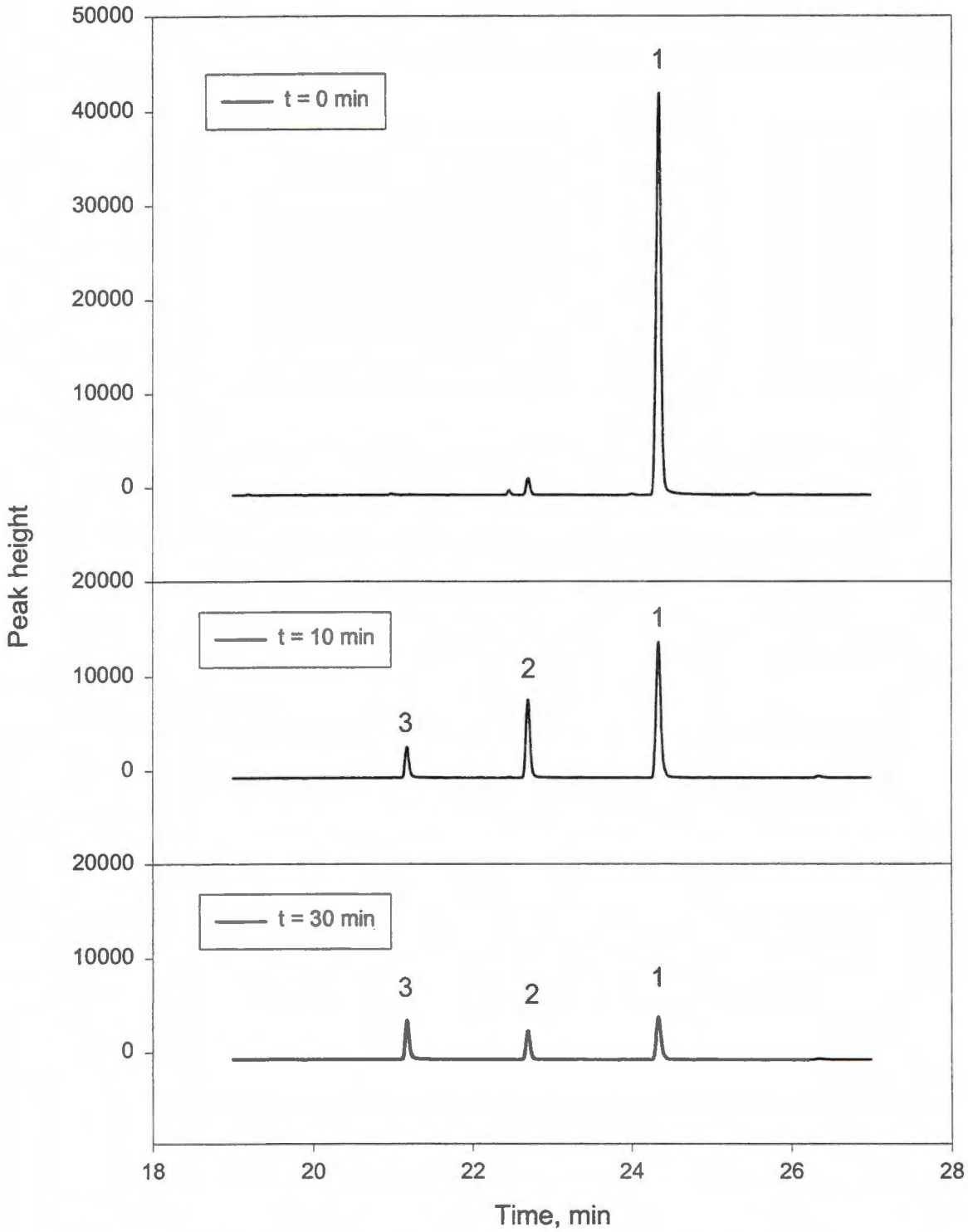


Figure 3.16 Gas chlormatogram of 2,2',4,4'CB and photoproducts
peak: No.1: 2,2',4,4'CB; No.2: 2,4,4'CB; No.3: 4,4'CB

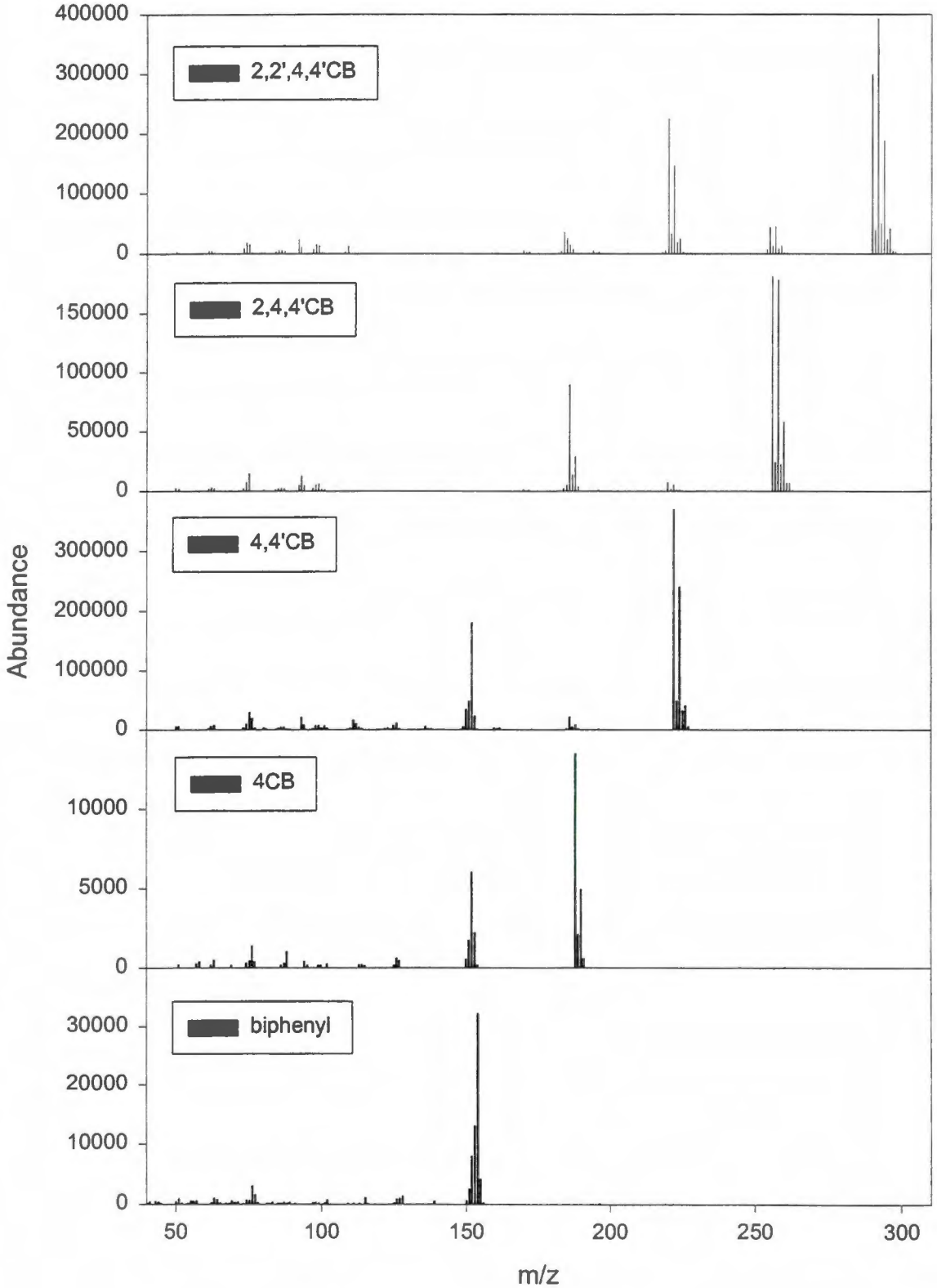


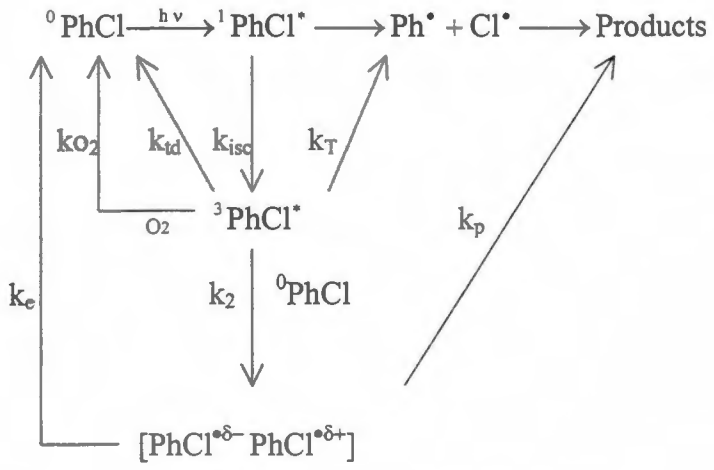
Figure 3.17 Mass spectra of 2,2',4,4'CB and its photoproducts

measured PCB (2,2',4,4'CB, 2,4,4'CB, and 4,4'CB) accounted for 95.4% of the initial amount of 2,2',4,4'CB photolyzed. In the same time period, 16.53 mg/L of free chloride ion was measured, which accounted for 98.2 % of total Cl^- expected if 2,2',4,4'CB were to be converted to 2,4,4' and 4,4'CB. Save a mere 4.6% of the initial 2,2',4,4'CB that remained unaccounted for, 2,2',4,4'CB was nearly completely dechlorinated. After 60 minutes, the recovered total PCBs in solution accounted for 59% of the initial amount of 2,2',4,4'CB while the measured chloride accounted for 84.4% of the expected chloride mass. Similarly, 4,4'CB, identified as the photoproduct of 2,4,4'CB, was plotted as a function of time in Figure 3.11. The recovered 4,4'CB and 2,4,4'CB, after 1 min of photolysis accounted for only 54% of the initial 2,4,4'CB. The major photoproducts of 4,4'CB could not be identified and remained unaccounted for, and hence the unsatisfactory mass balance. In the same time period, free chloride in solution was found to be 2.94 mg/L, which accounted for only 35.3% of the expected amount. After 60 minutes, 2,4,4'CB was completely degraded (no PCBs detected), the total measured Cl^- (7.8 mg/L) was 71.9% of the expected amount. Photolysis of 4CB and 4,4'CB showed the same trend (Figure 3.9 to 3.10). Free Cl^- recovered after 1 min, expressed as percent of that expected was initially low (29-35%). After 60 minutes, it increased to 67-72%. For all PCBs tested, only traces of 4CB and biphenyl were found (GC-MS) in the photolyzed solutions. Further quantitative analysis of concentrated samples of photolyzed 4,4'CB solutions revealed that after 5 min irradiation of a 84 μM solution, 48.5 μM of the initial 4,4'CB remained in solution and 2.07 μM of 4CB was produced. Thus, 5.8% (2.07/(84-48.5) x 100%) of the degraded 4,4'CB was converted to 4CB while no biphenyl could be detected. After 30 min, 4.15 μM biphenyl and no 4CB and 4,4'CB were found

in solution. Thus, 4.9% (4.15/84) of the degraded 4,4'CB was converted to biphenyl. In a descending order of the rate constant, these compounds can be arranged as biphenyl>4CB>4,4'CB (Section 3.3.2). Thus, only small amounts of 4CB and biphenyl may form when 4,4'CB is photolyzed. However, the recovery of Cl^- was much less than predicated during the initial period of photolysis. Partially dechlorinated products, in addition to 4CB, might have formed initially which were later converted to biphenyl. It has been reported that photolysis of PCB in cyclohexane formed cyclohexyl-PCB (Lepine *et al*, 1992a, b) and other unidentified complexes (Nordblom and Miller, 1974); photolysis in methanol resulted in the formation of methoxylated PCB (Ruzo *et al.*, 1974a, b). The surfactant molecule is somewhat similar to hexane and methanol. Thus, 4CB-surfactant could conceivably result in the formation of chlorinated complexes upon UV irradiation. Such compounds are difficult to extract in hexane for GC analysis, especially when silica based $^tC_{18}$ (Waters, Inc.) is used to separate surfactant from PCBs during extraction. Also these complexes could conceivably be further dechlorinated to a surfactant-biphenyl complex. Though these compounds could not be identified in the present study, the 4CB- and biphenyl-like UV-VIS spectra observed after prolonged irradiation of 4,4'CB, 2,4,4'CB, and 2,2',4,4'CB (Figure 3.4 to 3.7) indirectly supports the hypopersis that 4CB-surfactant and biphenyl-surfactant complexes may form during photolysis. Continuous increase in the recovery of Cl^- observed in the present study, indicates that such intermediates can be further dechlorinated. Attempts to identify products from the photolysis of biphenyl failed, even when samples were acidified to pH 1.0 before extraction.

Excitation of the PCB Molecule: To investigate the exited state of PCBs, solutions of 2,2,4,4'CB in POL(10) were deoxygenated (N_2 purging) and oxygenated (O_2 purging) in separate experiments before being photolyzed. The results are shown in Figure 3.13 and Table 3.4. The variation range (average value $\pm$ standard deviation) of the data points obtained in the two experiments overlapped according to either PCB degradation, Cl^- generation (Figure 3.13) or the reaction rate constant (k_0) and quantum yield (Φ_1) (Table 3.4), suggesting no statistically significant difference in the results between the two experiments. Since O_2 quenches triplet states, these results would indicate that 2,2',4,4'CB photodechlorination follows fission of C-Cl at singlet state (^{1}PhCl), similar to that of chloroaromatics in H_2O/CH_3CN (Dulin *et al.*,1986). Freeman *et al.* (1991) reported that singlet fragmentation was responsible for 2-6% of the product composition of pentachlorobenzene in acetonitrile at 254 nm. On the other hand, based on the observed high efficiency of intersystem crossing (ISC) and retardation of the reaction rate (k_t) in oxygenated solutions, triplet state has been suggested by others (Ruzo *et al* 1974 a, b; Bunce, 1978c, 1982) as the major reaction state of PCB in organic solvents, though there was an energy deficit for C-Cl scission at the triplet state (Bunce, 1978c, 1982). The energy deficit for C-Cl cleavage at the triplet state may be compensated by effective decomposition of PCBs (especially *ortho*-chlorobiphenyls) (Bunce, 1982), or may be overcome by the formation of a triplet excimer ($PhCl^{\bullet\delta-}$ $PhCl^{\bullet\delta+}$) via transfer of an electronic charge from the ground state of PCB (^{0}PhCl) to the excited triplet state (^{3}PhCl*) as observed in the photolysis of pentachlorobenzene in acetonitrile (Freeman *et al.*, 1991). There is little information available regarding the PCB excited state in micellar surfactant solutions. However, as discussed in Chapter 2, the PCB molecule in micellar

solutions has an environment similar to that in organic solvents. Thus, the excited states of PCB in micellar surfactant solutions are expected to be similar to that in organic solvents as shown in the following schemes (Bunce, 1982; Freeman *et al.*, 1991):



According to the scheme above, cleavage of C-Cl at singlet state may directly contribute to PCB photodechlorination. However, photolysis of PCB in organic solvents did not show evidence to support this hypothesis. It must be noted that under the test conditions of this research, oxygen trapped inside surfactant micelles may not have been completely purged. Thus, the conclusion made on the effect of oxygen on PCB photolysis is open to conjecture. Additional experiments using other quenchers or other methods to eliminate the O_2 trapped in micelles must be conducted to establish the excited state of the irradiated PCB in micellar solution.

Proposed Mechanism of Dechlorination Results obtained in this study supports stepwise dechlorination, *ortho* chlorine atoms being preferentially removed, followed by hydrogen

abstraction to be the mechanism of PCB (2,2',4,4'CB) photodegradation in surfactant solutions as illustrated in Figure 3.18. Once 4,4'CB is formed, further photolysis may lead to two different degradation pathways: (1) 4,4'CB may continue to undergo stepwise dechlorination until biphenyl forms; (2) after the cleavage of the C-Cl bond, it may react with the surfactant radical to form 4CB-surfactant adducts. The adducts can be further dechlorinated to biphenyl-surfactant adducts. However, substitution at the *ortho* position increases the dihedral angle. Not coplanar at the ground state, PCBs tend to be coplanar at the excited state. The bigger the molecule (atom) added, the larger is the dihedral angle and less stable is the product. Such electronic hindrance prevents big molecules such as surfactants from being added at the *ortho* position. Thus, PCB-surfactant adducts could not form at the *ortho* position.

3.3.4 Role of Surfactant

Surfactants may enhance photolysis in two ways: (1) by serving as H-atom donor (for abstraction) in dechlorination; (2) by providing more reaction opportunities between PCB and surfactant molecules inside the surfactant micelles (Ramamurthy, 1986; Kalyanasundaram, 1987; Epling *et al.*, 1988; Chu and Jafvert, 1994). Photolysis of PCBs leads to dechlorination followed by H abstraction. Thus, either water or surfactant or both may serve as H donors. Organic solvent has been reported as the major H donor when PCBs in the mixture of CH_3OH/H_2O are photolyzed (Nordblom and Miller, 1974; Orvis *et al*, 1991). Both the rate and quantum yield of photolysis were enhanced in POL(10) solutions relative to those in CH_3CN-rich solutions (Epling *et al*, 1988) (Table 3.4). For

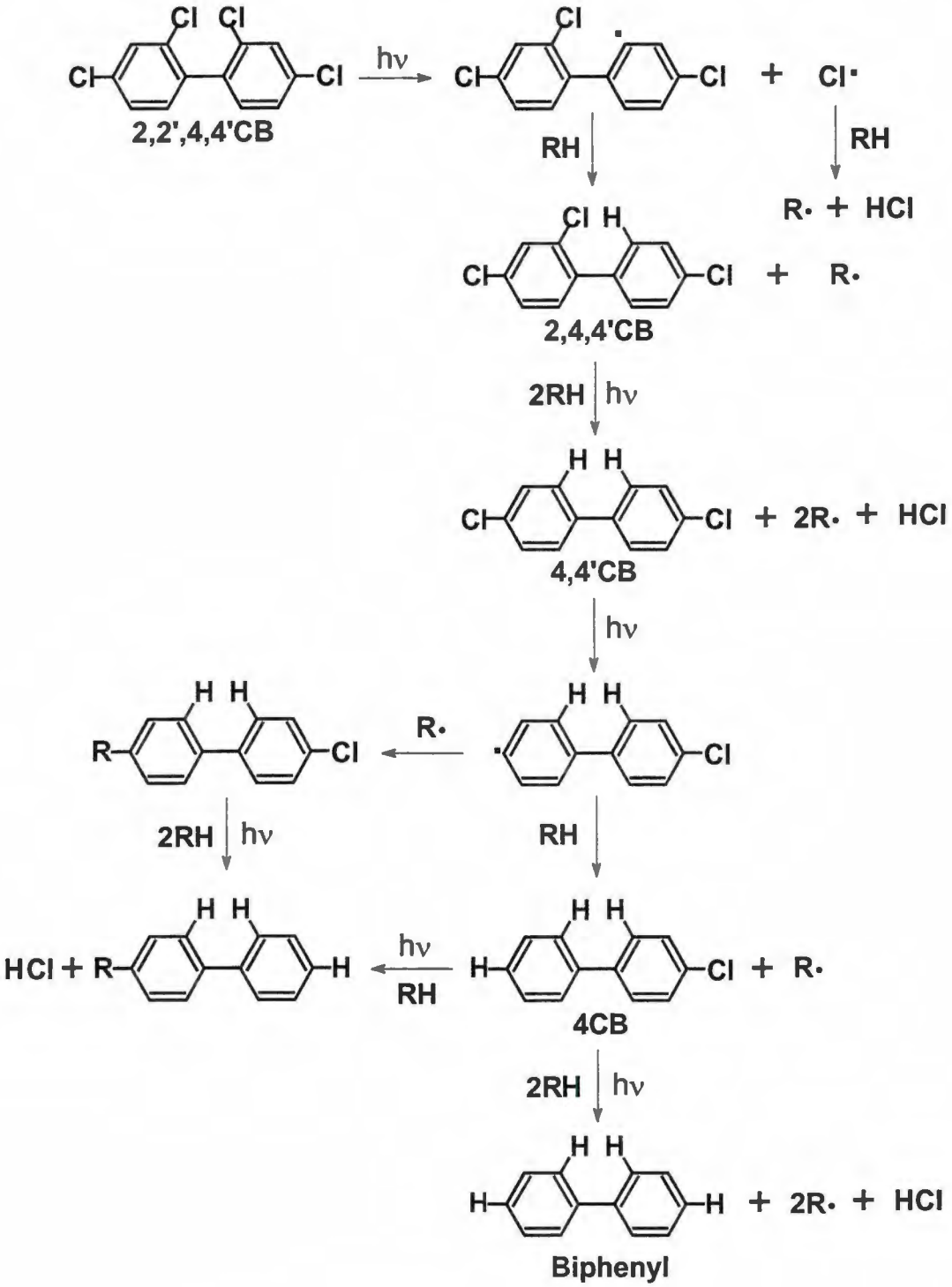


Figure 3.18 Mechanism of 2,2',4,4'CB photolysis

2,2',4,4'CB, the photolysis rate and quantum yield were further enhanced in DME, a very good H-donor. Since the DME molecule and the polyoxyetheylene chain of POL(10) are alike, it was concluded that POL(10) molecule was the major H donor.

In chapter 2, it was demonstrated that in micellar media, most PCB molecules partition into the micelles, greatly increasing the local PCB concentration within the micelles. Consequently, the reaction probability between PCB and surfactant (H donor) molecules increases. Further, the high hydrophobicity of the micellar core keeps the PCB molecule from escaping while excluding chloride ions from it. Thus, the reaction probability between PCB and surfactant molecules is further improved due to longer residence of PCB inside the micelle and also possible minimization of the potential Cl^- common ion effect (Orvis *et al.*, 1991). Only 8% of POL (10) was lost after 60 minutes of UV-irradiation (Figure 3.19).

3.3.5 Photolysis of Aroclor 1242 Solutions

Figure 3.20 shows the progress of photodegradation and photodechlorination of Aroclor 1242 dissolved in POL(10) micellar solution. PCB concentration remaining in solution was used to calculate the extent degradation and Cl^- appearing in solution was used to calculate the extent of dechlorination. During initial photolysis ($\leq$ 2 min), Cl^- concentrations measured by two methods, electrochemical and colorimetric, were close. However, later in the experiment, the colorimetric method yielded somewhat higher values than that obtained with the chloride selective electrode. Only colorimetrically

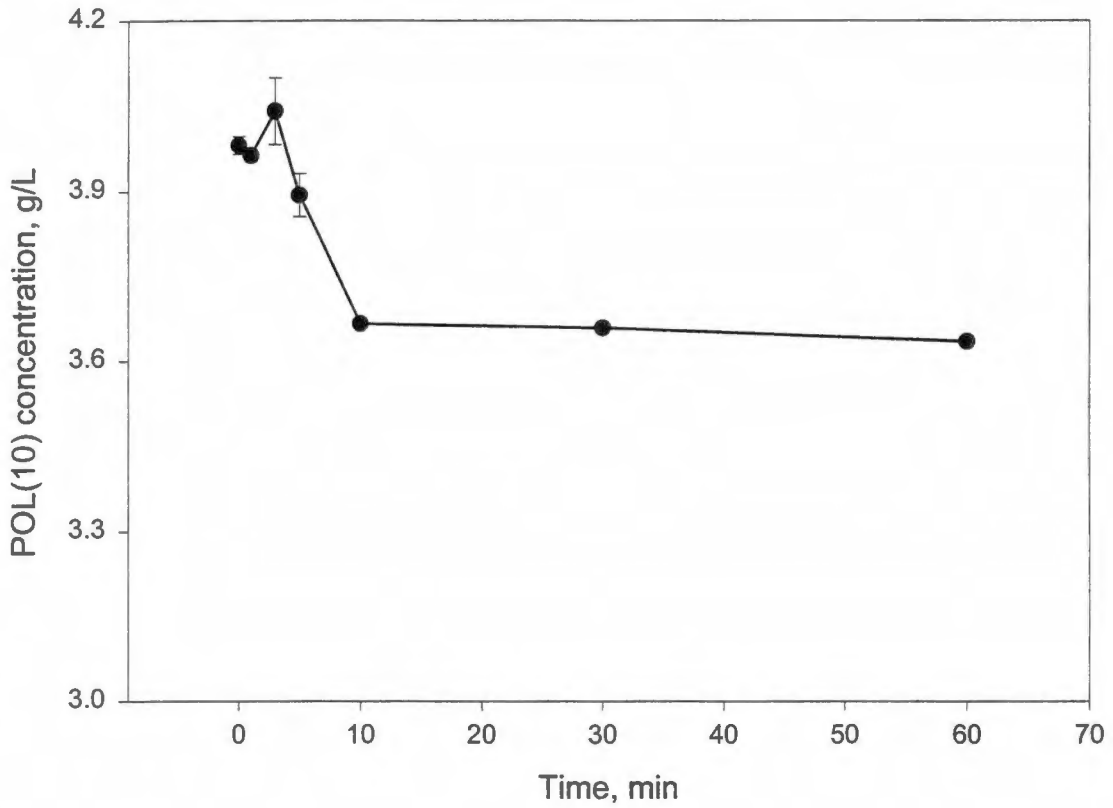


Figure 3.19 Photodegradation of POL(10) during photolysis of 2,2',4,4'CB

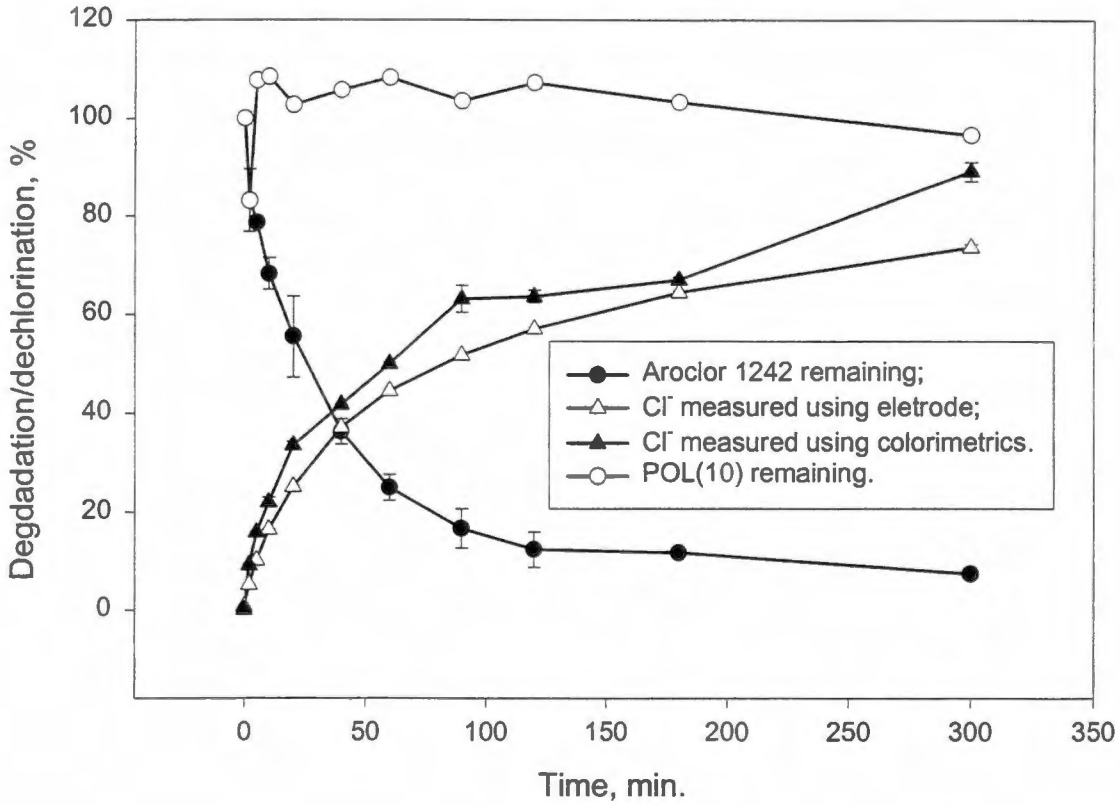


Figure 3.20 Photodegradatioon and dechlorination of Aroclor 1242 (210.7 mg/L) in POL10 (4g/L) solution. Cl^-: 88.49mg/L normalized as 100%

determined concentrations of chloride are used for discussions.

After 2 minutes of irradiation, 83.2% of the initial mass of Aroclor 1242 remained in solution, and 9.1 % of the total chlorine in Aroclor 1242 appeared in solution as Cl^-. Therefore, 92.3 % (83.2% + 9.1%) of the initial mass of Aroclor 1242 could be accounted for from a mass balance of PCB remaining in solution and the mass of PCB degraded, as represented by the mass of chloride appearing in solution. Further, of the 16.8 % of Aroclor 1242 degraded, the amount degraded through the dechlorination pathway was 9.1/16.8 = 54%. After 300 min., the amount of PCB degraded by dechlorination increased to 98.1%. Thus, dechlorination appears to be the major pathway for Aroclor 1242 degradation. Similar results were obtained for 2,2',4,4'CB photolysis. Literature is replete with such observations for PCB photolysis in organic solvents (Hutzinger *et al.*, 1974, Sawhney, 1986).

Since the absorbance (at 254 nm) of the PCB-surfactant solution was greater than 2, the solution was optically dense, i.e, it absorbed all of the incident light. Thus, initially ($\leq$ 2 min), photodegradation should followed a zero-order kinetics (Leifer, 1988) as shown in Equation 3.1.

Rearranging,

$$1- C_t/C_0 = (k_0/C_0)t \qquad (3.3)$$

where k_0/C_0= slope of the "Aroclor 1242 degradation (%) versus time" ($t \leq 2$ min.) curve.

From Figure 3.20, $(k_0/C_0) = (8.41 \pm 3.25)\ min^{-1}$ for $C_0 = 210.5$ mg/L (8.09×10^{-4} M)

And, the zero-order rate constant is

$$k_0 = (1.77 \times 10^{-2} \pm 0.68 \times 10^{-2})\ g/L\text{-}min \qquad (3.4)$$

$$= (1.13 \times 10^{-4} \pm 4.38 \times 10^{-5})\ M\ s^{-1}$$

The corresponding quantum yield was calculated as (Zepp, 1978; Leifer, 1988):

$$\Phi = k_0 / [I_{o\lambda}(A/V)] \qquad (3.2)$$

where, $I_{o\lambda}$ = flux of incident light at $\lambda = 254$ nm

$= 8.63 \times 10^{-5}$ einstein $m^{-2}\ s^{-1}$

k_0 = zero order rate constant (initial 2 min of photolysis) ($M\ sec^{-1}$) (Table 3.5)

A/V = (exposed area : volume of sample) = 102.6 m^{-1}.

The initial rate constant and corresponding quantum yield are shown in Table 3.5.

UV irradiation caused a decrease in total Aroclor 1242 concentration (Figure 3.20) and significantly changed the congener profile (Figure 3.21 and Table 3.6). After 40 min., the relative concentration of highly chlorinated congeners (peaks 34-41) decreased by more than 60%. Nine peaks (# 8, #14, #21, #27, #31, #37, #39, #40, and #41) were completely removed. Of these, #27 (2,4,4',5CB), #37 (2,2',3,4,4'CB), #39

Table 3.5. Initial photolysis rate and quantum yield for Aroclor 1242 in POL (10) Solution

Rate[a], k_0 ($M\ sec^{-1}$)	Quantum Yield[a], Φ
1.13×10^{-4}	0.0128

[a] Initial period (≤2 min)

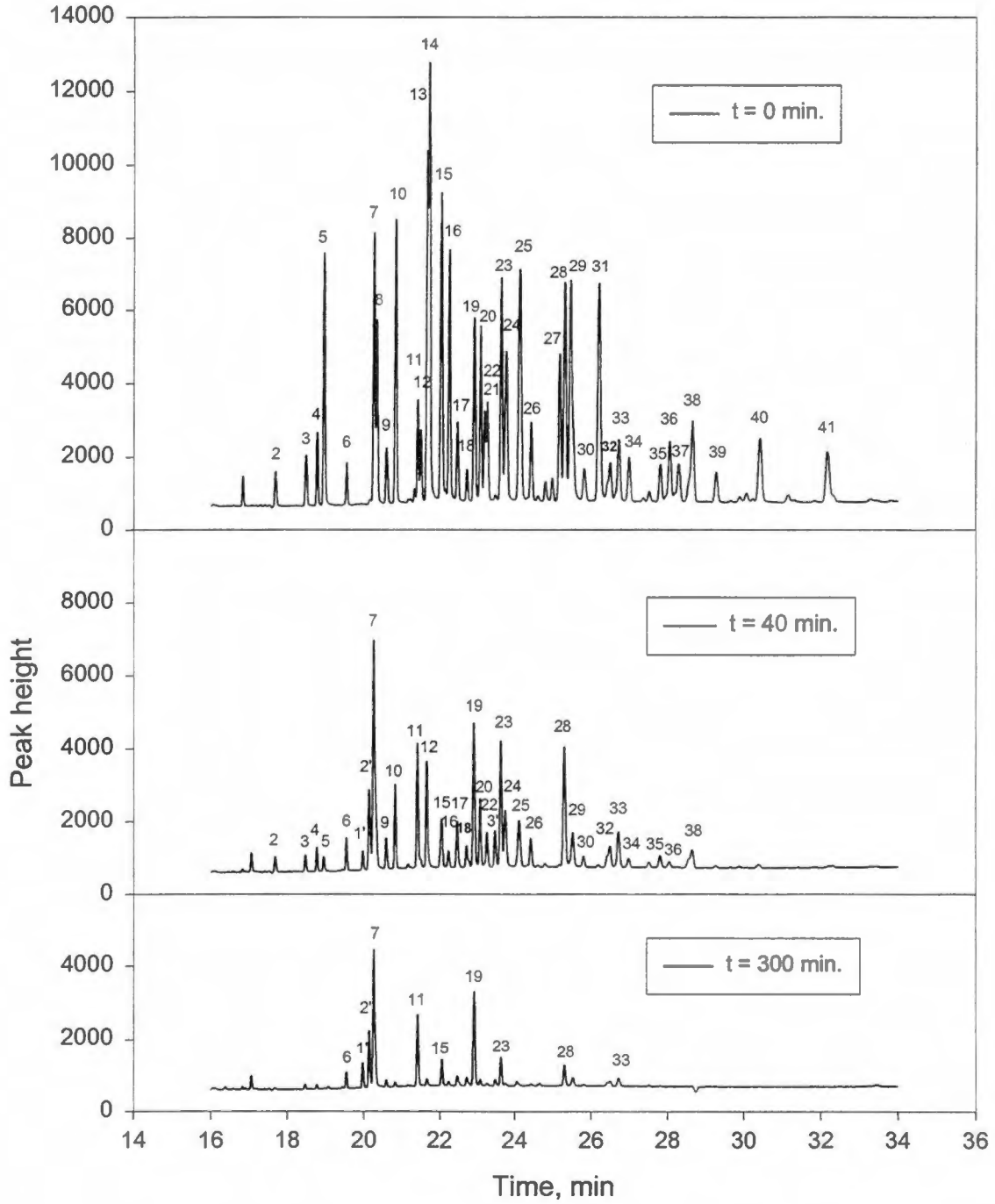


Figure 3.21 GC of photolyzed Aroclor 1242 in POL(10) (4 g/L) solution

Table 3.6. Photolysis of Aroclor 1242 in POL(10)

Peak no.[a]	PCB Congener (mg/L)	Weight (%)	Conc.[b]	Degradation, (%) 40 min	300 min
2(5)	2,2'	2.74	5.84	47.6	100
3(6)	2,5	1.02	2.13	67.4	100
4(7)	2,3'	1.34	2.79	61.7	100
5(8)	2,4'	6.40	13.27	93.3	100
6(10)	2,2'6,	0.96	1.94	1.52	68.6
7(14)	4,4'; 2,2',5	10.17	20.93	14.5	43.7
8(15)	2,2',4	4.57	9.42	100	100
9(16)	2,3,6; 2,3',6	0.83	1.74	38.5	100
10(17)	2,2',3	5.14	10.6	65.0	100
11(21)	2,3',5	1.23	2.63	-60.9	61.8
12(22)	2,3',4	0.89	1.90	88.1	100
13(23)	2,4',5	6.75	15.0	58.5	100
14(24)	2,4,4'	8.01	16.6	100	100
15(25)	2',3,4; 2,2',5,6'	6.28	13.4	79.6	91.7
16(26)	2,3,4'; 2,2',4,6'	2.88	6.13	92.2	100
17(27)	2,2'3,6	1.10	2.35	25.5	100
18(29)	2,2',3,6'	0.80	1.66	-3.29	100
19(31.1)	2,2',5,5'	3.32	7.23	0.30	48.7
20(32)	2,2',4,5'	2.63	5.52	50.2	100
21(33)	2,2',4,4'	1.10	2.31	100	100
22(34)	2,2',4,5	1.48	3.17	53.8	100
23(37.2)	2,2',3,5'	3.26	6.76	30.1	87.0
24(38)	3,4,4'; 2,2',3,4'	3.32	7.09	55.8	100
25(39)	2,3,4',6	3.11	6.69	76.1	100
26(42)	2,2',3,3'	1.01	2.21	56.5	100
27(46.1)	2,4,4',5	1.60	3.56	100	100
28(47)	2,3',4',5	3.41	7.56	30.9	93.7
29(48.1)	2,3',4,4'; 2',3,4,5; 2,2',3',4,6	3.62	7.73	83.9	100
30(49)	2,2',3,6,4'	0.70	1.51	67.3	100

Table 3.6. Photolysis of Aroclor 1242 in POL(10) (continued)

Peak no.[a]	PCB Congener (mg/L)	Weight (%)	Conc.[b]	Degradation, (%) 40 min	300 min
31(50)	2,3,4,4'	2.51	5.80	100	100
32(51)	2,2',3,3',6	0.76	1.29	28.8	100
33(53)	2,2',4,5,5'	0.88	1.37	31.1	100
34(54)	2,2',4,4',5	0.74	1.34	77.2	100
35(57.1)	2,2',3',4,5	0.72	1.37	61.5	100
36(58)	2,2',3,4,5'	0.78	1.56	95.2	100
37(59)	2,2',3,4,4'	0.71	1.66	100	100
38(61)	2,3,3',4',6	1.00	1.77	73.2	100
39(63)	2,2',3,3',4	0.69	1.46	100	100
40(69)	2,3',4,4',5	0.80	1.21	100	100
41(74)	2,3,3',4,4'	0.74	1.91	100	100

[a]Peak numbers assigned by Frame *et al.* (1996) are given in parentheses.
[b]Initial concentration of each GC peak, the total initial concentration is 210.5 mg/L.

(2,2',3,3',4CB), #40 (2,3',4,4',5CB), and #41 (2,3,3',4,4'CB) represent the most biorecalcitrant congeners reported in the literature (Bedard *et al.*, 1987). On the other hand, two peaks (#11 and #18) containing biodegradable congeners of 2,3',5CB and 2,2',3,6'CB showed increases (negative sign), and three new peaks (Nos. 1', 2', and 3') appeared after 40 min. These new peaks, #11, and #18 were either attenuated or disappeared completely upon further photolysis (Figure 3.21 and Table 3.6). Whereas highly chlorinated congeners (#34 and higher) were completely photodegraded in 300 min, these congeners were unable to completely biodegrade in 6 days by genetically engineered microorganisms (GEMs) (Shi *et al.*, in press). Compared to 4,4'CB (#7), congeners containing *o*-chlorines, 2,4,4'CB (# 14) and 2,2',4,4'CB (#21), were degraded relatively fast. After 40 min, the photolysis effciency (rate) significantly decreased (Figure 3.19 and Table 3.5).

The concentration of POL (10) during the 5-hr photolysis experiment remained relatively constant; less than 17 % of the surfactant was degraded by photolysis (Figure 3.20).

3.3.6 Photolysis of PCBs in Soil Washing Solutions

Samples of PCBs in POL(10)- and SDS-soil washing solutions were irradiated at 254 nm. Total concentration of mixed congeners in the soil washing solution is shown as a function photolysis time in Figures 3.22 and 3.23. Based on these data, "apparent" initial zero-order rate constant (k_0) and relative quantum yields (Φ) of initial photolysis

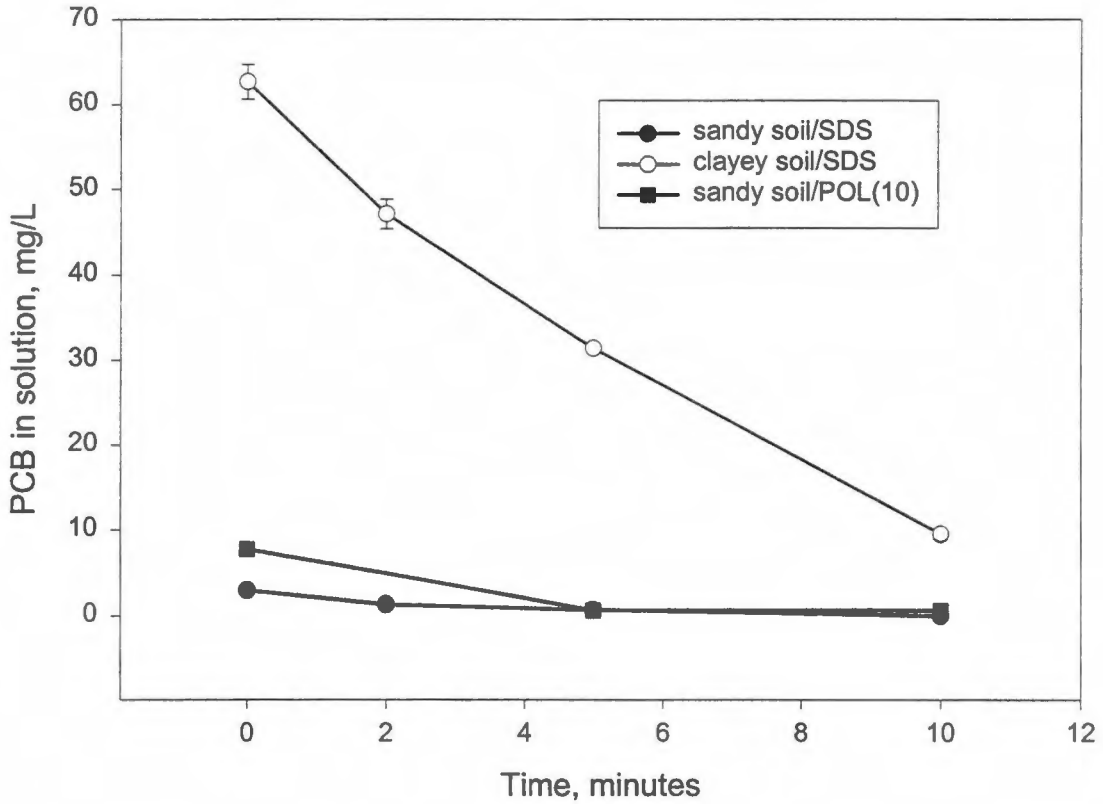


Figure 3.22 Photolysis of PCB in soil washing solutions (4 g/L surfactant, 6.5 NTU)

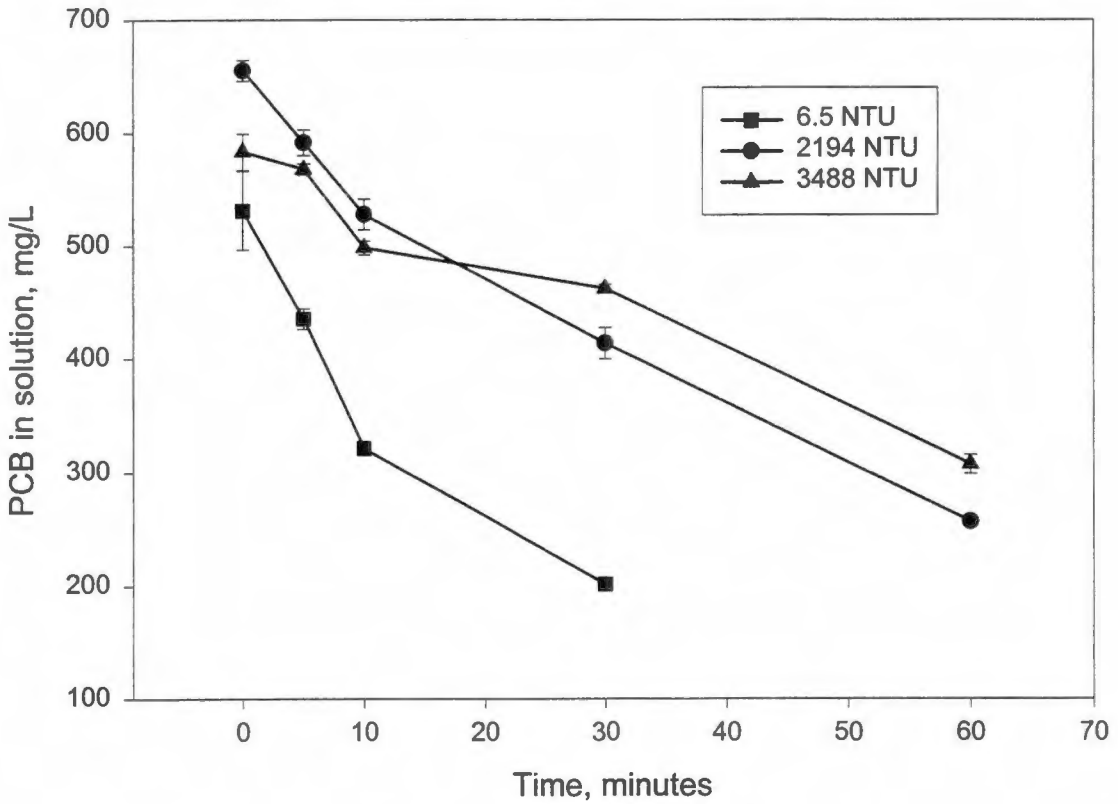


Figure 3.23 Photolysis of PCBs in turbid clayey soil washing solutions (4 g/L POL(10))

(t= 5 min) were estimated using Equations 3.1 and 3.2, respectively, (Table 3.7). For clayey soil washings with turbidity of 6.5 (NTU) (Amer. Pub. Health Assoc., 1985), 5-min photolysis resulted in 96 and 16 mg/L of total PCBs being degraded in POL(10) and SDS solutions, respectively. The "apparent" initial rate constants and quantum yields were 19.3 mg /L min^{-1} and $4.14x10^{-2}$ for POL(10) solution, and 6.2 mg/L min^{-1} and $1.33x10^{-2}$ for SDS solution, respectively. For sandy soil, almost all of the PCBs were degraded after 5 min of photolysis in both POL(10) and SDS solutions. The photolysis rate and quantum yield in POL(10) washing solution were 1.43 mg /L min^{-1} and 3.06 $x10^{-3}$, while for SDS washing solution they were 0.435 mg/L min^{-1} and $9.35x10^{-4}$, respectively.

To investigate the effect of soil particles on photolysis, POL(10) soil (clayey) washing solutions containing different turbidities were irradiated (Figure 3.23). The initial (t < 5 min) photolysis rate constants and quantum yields are presented in Table 3.7. After 5 and 30 min of irradiation, nearly 18% and 62% of the PCB initially present in the soil washing solution containing a turbidity of 6.5 NTU was photolyzed, respectively. The photolysis of PCBs in the same soil washing solution decreased to 3% and 21% when the turbidity was 3488 NTU. The "apparent" initial rate constant and quantum yield were 19.3 mg /L min^{-1} and $4.14x10^{-2}$ in the solution with a turbidity of 6.5 NTU. As the turbidity of solution increased from 6.5 to 3488 NTU, both the rate constant and quantum yield decreased by 84%. However, when the turbidity of the solution increased to 2194 NTU, the rate and quantum yield only decreased by 34%. Since the solution with 6.5 NTU was prepared by centrifugation (7280 x g) for 30 min, particles with radius > 0.08

Table 3.7. Apparent initial photolysis rate constants (k_o) and quantum yields (Φ) of PCB in surfactant-soil washing solutions

Soil	Surfactant	Turbidity (NTU)[a]	PCB Conc.[b] (mg/L)	k_0[c] (mg/L min^{-1})	Φ[d]
Clayey	POL(10)	6.5	531.7	19.28±7.25	$4.14x10^{-2}$
		2194	655.7	12.76±2.93	$2.74x10^{-2}$
		3488	583.6	3.08±3.36	$6.62x10^{-3}$
	SDS	6.5	62.7	6.17±0.52	$1.33x10^{-2}$
Sandy	POL(10)	6.5	7.7	1.43±0.01	$3.06x10^{-3}$
	SDS	6.5	2.9	0.44±0.85	$9.35x10^{-4}$

[a]Nephelometric turbidity unit (American Public Health Assoc., 1985).
[b]After Frame *et al.* (1996)
[c]Initial (5 min.) rate constant (zero order).
[d]At 254 nm. After Zepp (1978).

μm was removed (see section 2.3.1). The solutions with 2194 and 3488 NTU were prepared by settling for 3 and 0.5 hours, respectively. Therefore, the increased turbidity from 2194 to 3488 NTU was contributed by relatively large particles. Thus, it seemed that smaller soil particles have less adverse effect on PCB photolysis than the larger particles. Therefore, satisfactory photolysis of PCBs may be achieved in moderately turbid waters. Conceivably, surfactant can be recycled in field applications, and, following small augmentation, can be reused.

It has been reported that the presence of colloidal particles may enhance rate of photolysis of dissolved pollutants in natural waters due to light scattering (Miller and Zepp, 1979). The quantum yields of biphenyl, 4CB, 4,4'CB, 2,4,4'CB, and 2,2',4,4'CB in POL(10) solution without soil particles ranged from 0.0068 to 0.1356 (Table 3.4). The average value of Φ for these congeners, 4.38×10^{-2}, was close to the observed value of Φ (4.14×10^{-2}) of the PCB mixture in the soil (clay) washing solution containing a turbidity of 6.5 NTU. Seemingly, the dissolved soil components that present a stable yellow color in the washing solution had only a minor effect on PCB photolysis.

The gas chromatograms of PCBs in soil washing solutions (POL(10)) with a turbidity of 6.5 NTU, before and after photolysis, are shown in Figure 3.24 and 3.25. The GC profile of the PCB congeners in soil washing solution was close to that of the Aroclor 1248 standard solution. Therefore, the major peaks were assigned numbers from 1 to 34, as in pure Aroclor 1248, and the Aroclor 1248 standard was used to identify and quantity the PCB congener(s) present in the soil washing solution using the method proposed by

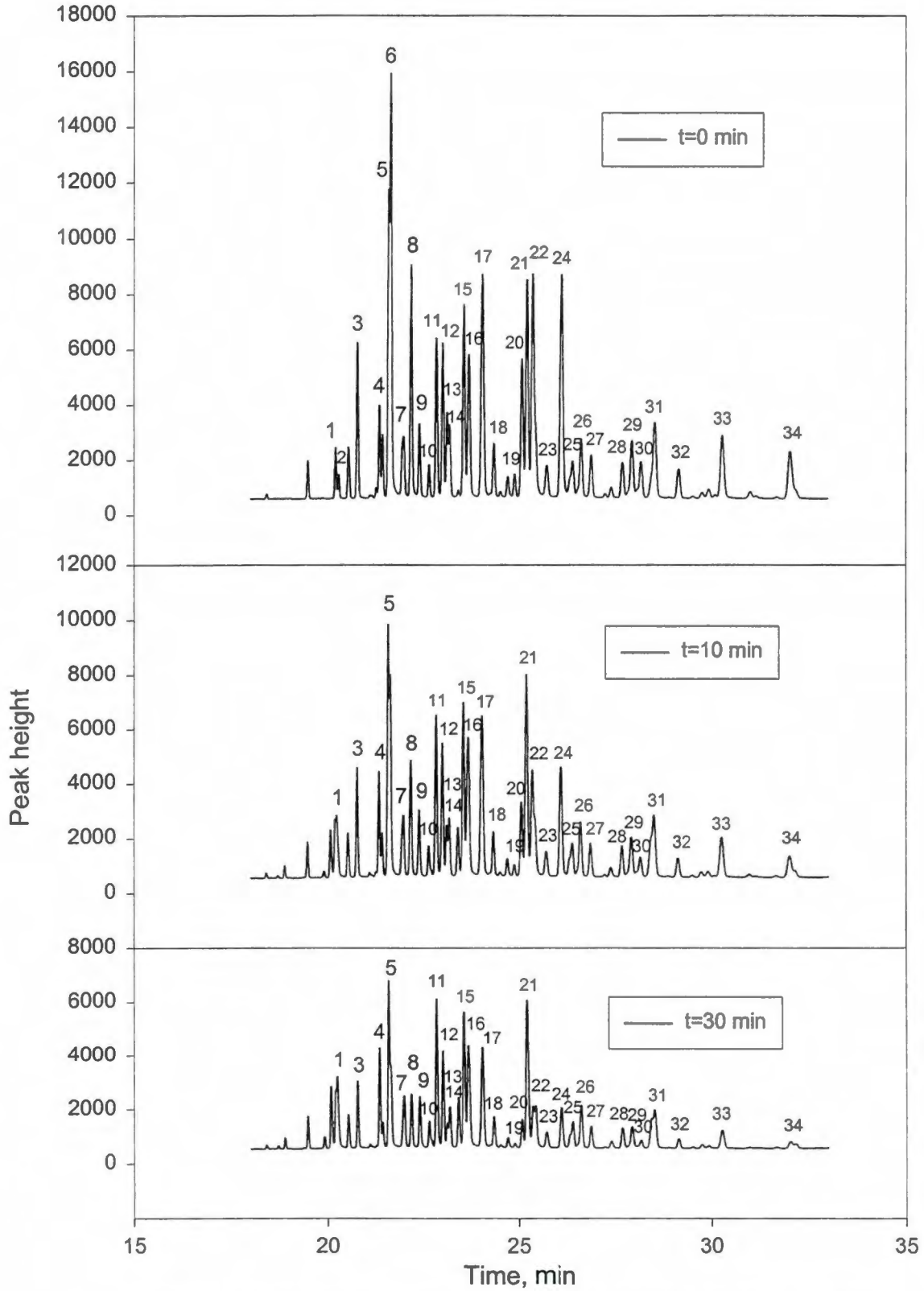


Figure 3.24 Gas chromatograms of PCBs in clayey soil washing solutions (4 g/L POL(10)) before and after photolysis

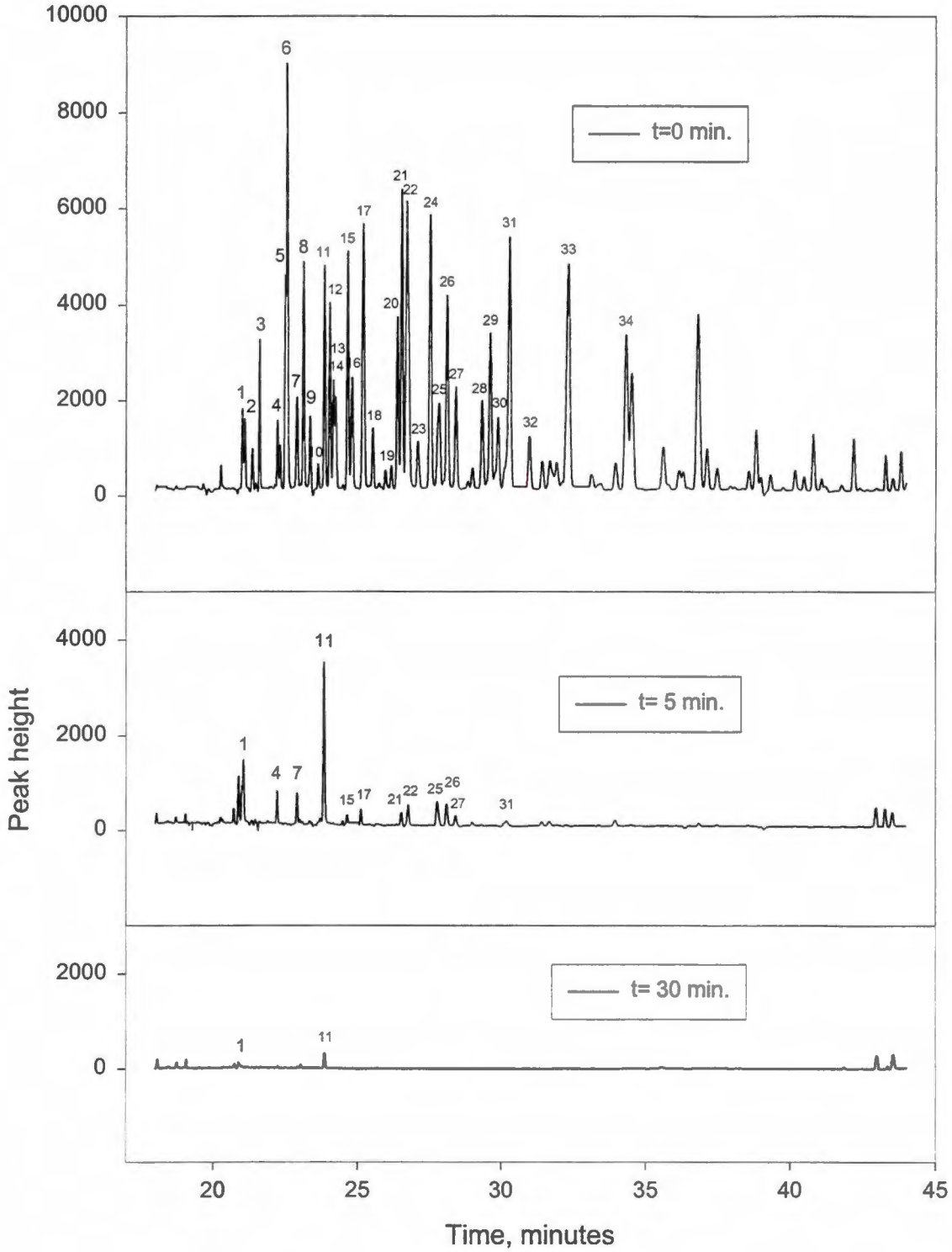


Figure 3.25 Gas chromatograms of PCBs in sandy soil washing solutions (4 g/L POL(10)) before and after photolysis

Frame *et al.* (1996) (Section 2.3.3). As shown in Figure 3.24 and 3.25, highly chlorinated congeners with large retention times tend to be photodegraded faster than those with less chlorine substitutions. Additional results of PCB photolysis in-clayey soil washings are summarized in Table 3.8. After 30 minutes of UV irradiation, all GC peaks (PCB congeners), except peak No.1 (4,4'CB), were 19.4% to 100% photolyzed. Peak 1 showed a net increase of 99%. Presumably, 4,4'CB is formed as a major byproduct of incomplete dechlorination of many highly chlorinated congeners such as 2,2',4,4'CB (peak No.13). Two peaks, peak No.2 (2,2',4CB) and peak No.6 (2,4,4'CB), were absent in the GC of the photolyzed washing solution. Presumably, these congeners were completely photolyzed. 2,2',4,4'CB and 2,4,4'CB degraded faster than 4,4'CB; this corresponds well with the results of photolysis of pure 2,2',4,4'CB in surfactant solutions (Section 3.3.2). Further, a significant decrease in both the concentration and mass (% weight) of congeners in peaks 27 to 34 indicated that highly chlorinated congeners (penta- and hexa-chlorobiphenyls) represented by these peaks were more photodegradable than the less chlorinated ones. Thus, photolysis of highly chlorinated congeners may benefit subsequent aerobic biodegradation of PCBs in an integrated two-step photolysis/biodegradation remediation scheme.

3.4 SUMMARY

Surfactants enhanced both the rate and quantum yield of photolysis of PCBs. The hydrophobic micellar core allows the reactants and intermediates to remain longer at higher local concentrations in a non-aqueous, solvent-like environment increasing the

Table 3.8. Photolysis of PCB congeners in POL(10) soil washing solution (6.5 NTU)[a]

Peak No.	PCB Congener	Concentration 0 min (mg/L)	(wt%)	30 min (mg/L)	(wt%)	Photolyzed (%)
1 (14)	4,4'	7.24	1.36	14.41	7.11	-99.0
2 (15)	2,2',4	3.07	0.58	0.00	0.00	100.0
3 (17)	2,2',3; 2,4',6	13.48	2.53	4.46	2.20	66.9
4 (21)	2,3',5	14.51	2.73	12.25	6.05	15.6
5 (23)	2,4',5	41.89	7.90	28.78	14.21	31.3
6 (24)	2,4,4'	83.50	15.74	0	0	100.0
7 (25)	2,3',4'; 2,2',5,6'	10.36	1.95	5.66	2.79	45.4
8 (26)	2,3,4'; 2,4,2',6'	18.81	3.55	3.51	1.73	81.3
9 (27)	2,2',3,6	6.79	1.28	3.78	1.87	44.3
10 (29)	2,2',3,6'	5.22	0.98	4.21	2.08	19.4
11 (31.1)	2,2',5,5'	24.67	4.65	17.02	8.40	31.0
12 (32)	2,2',4,5'	22.00	4.15	10.43	5.15	52.6
13 (33)	2,2',4,4'	13.00	2.45	2.83	1.40	78.2
14 (34)	2,2',4,5	9.55	1.80	4.54	2.24	52.5
15 (37.2)	2,2',3,5'	21.20	4.00	11.45	5.66	45.9
16 (38)	2,2',3,4'	19.82	3.74	12.74	6.29	35.8
17 (39)	2,3,4',6	30.17	5.69	10.82	5.34	64.1
18 (42)	2,2',3,3'	4.05	0.76	1.97	0.97	51.5
19 (45)	2,3,4',5	4.14	0.78	0.78	0.39	81.1
20 (46.1)	2,4,4',5	21.31	4.02	3.34	1.65	84.3
21 (47)	2,3',4',5	33.01	6.22	18.12	8.95	45.1
22 (48.1)	2,3',4,4'	42.37	7.99	9.43	4.65	77.8
23 (49)	2,2',3,4',6	3.36	0.63	1.35	0.67	59.7
24 (50)	2,3,4,4'	27.96	5.27	3.91	1.93	86.0
25 (51)	2,2',3,3',6	3.30	0.62	1.82	0.90	44.7
26 (53)	2,2',4,5,5'; 2,2',3,5,4'	6.24	1.18	3.45	1.70	44.7
27 (54)	2,2',4,4',5	5.24	0.99	2.21	1.09	57.8
28 (57.1)	2,2',3',4,5	3.14	0.59	1.47	0.72	53.4
29 (58.1)	2,2',3,4,5'	4.10	0.77	1.33	0.66	67.6
30 (59)	2,2',3,4,4'	3.03	0.57	0.58	0.29	80.7
31 (61)	2,3,3',4',6	8.88	1.67	2.74	1.35	69.1
32 (63)	2,2',3,3',4	2.64	0.50	0.76	0.38	71.1
33 (69)	2,3',4,4',5	6.55	1.24	1.64	0.81	75.0
34 (74)	2,3,3',4,4'	5.83	1.10	0.73	0.36	87.5

[a]PCB congeners in the soil-washing solution were identified and quantified by comparing with Aroclor 1248 standard. Peak numbers assigned by Frame *et al.* (1996) are given in parentheses.

probability of photolysis. Further, acting as a source of abstractable H atoms, surfactants promote dechlorination of PCBs. In surfactant solutions, stepwise dechlorination appears to be the major mechanism of photolysis of 2,2',4,4'CB and 2,4,4CB. *Ortho* chlorine was more photolabile than *para* chlorine. PCBs in surfactant soil-washing solutions can be effectively degraded, even in the presence of moderately high turbidities. Typically, the highly chlorinated congeners are likely to be more photodegradable. Therefore, surfactant washing followed by photolysis appears to be a viable technology for remediation of PCB contaminated soils.

CHAPTER 4

PHOTOLYSIS OF 2-CHLOROPHENOL DISSOLVED IN SURFACTANT SOLUTIONS

4.1 BACKGROUND

Widely used in pulp/paper and herbicide/pesticides industries, large quantities of 2-chlorophenol (2CP) have been introduced into the environment. It can be found in industrial effluents, soils, and finished drinking waters (Callahan *et al.*,1979; Suntio *et al.*, 1988; Beck *et al.*, 1995). Due to its recalcitrance to general biodegradation (Ettinger and Ruchhoft, 1950; Rochkind *et al.*, 1986; O'Connor and Young, 1996) and its potential to act as a precursor to the formation of more toxic compounds, such as highly chlorinated phenols formed during the disinfection of water and wastewater (Callahan *et al.*,1979), this xenobiotic compound adversely impacts environmental ecosystems and a presents a challenging problem in environmental restoration.

It was reported that photochemical transformation of 2CP played a major role in determining the fate of 2CP in aquatic environments (Boule *et al.*, 1982, 1984, 1987; Guyon *et al.*, 1982). 2CP undergoes different photochemical reactions depending on

reaction conditions, particularly the pH. At neutral or acidic pHs, where 2CP is not ionized, direct irradiation of aqueous 2CP can lead to the formation of cyclopentadienic acid and catechol, while under basic pH conditions photolysis of the anionic form of 2CP results in the formation of cyclopentadienic acid as the exclusive photoproduct (Boule *et al.*, 1984, 1987, 1982; Guyon *et al.*, 1982). It has been proposed that a ring contraction mechanism involving a Wolff rearrangement leads to the formation of cyclopetandienic acid and a hydroxyl substitution mechanism accounted for the catechol formation (Boule *et al.*, 1984, 1987, 1982; Guyon *et al.*, 1982). In basic solution (pH>9), the quantum yield of 2CP photoconversion is reported to be (0.30 ± 0.03), which is 10 fold higher than that in acidic solution (pH<5) (Boule *et al.*, 1987). Neither the product distribution nor the quantum yield is reportedly influenced by the presence of oxygen (Boule *et al.*, 1984, 1987).

Though photolysis of 2CP under laboratory conditions shows promise, its application to soil remediation may not be easy. Direct photolysis of contaminants in the subsurface is not feasible. Even in *ex situ* applications, both the rate and efficiency of photolysis may significantly decrease due to scattering of light and its absorption by naturally occurring substances. At concentrations above the CMC, surfactants can effectively desorb hydrophobic contaminants from soils (McDermott *et al.*, 1989; Abdul and Gibson, 1991; Abdul *et al.* 1992; Yeom *et al.*, 1996). Surfactants promote photodegradation by serving as hydrogen donor in abstraction reactions and thereby increase quantum yields even at sub-CMC dosages (Bunton, 1984; Ionescu and Nome,

1984; Pelizzetti *et al.*, 1984; Romsted, 1984; Ramamurthy, 1986; Kalyanasundaram, 1987; Epling *et al.*, 1988; Myers, 1992; Chu and Jafvert, 1994, Shi *et al.*, 1994). Because of the amphiphilic nature of the molecule and the hydrophobic core of the micelles, surfactants can modulate photodegradation reactions by various, micellar processes, such as cage effect, preorientation, localization, microviscosity, polarity, and counterion effects (Ramamurthy, 1986). Chu and Jafvert (1994) reported that for the photodechlorination of hexachlorobenzene (HCB), the decay quantum yield was about one magnitude greater in micellar surfactant solutions (Brij 35, 58, and Tween 20 and 80) than in water alone. It was observed that, in the presence of Brij 58 or SDS micelles, dechlorination of seven PCB congeners in acetonitrile/water (CH_3CN/H_2O) mixtures containing sodium borohydride (BH_4Na) was enhanced (Epling *et al.*, 1988). In the presence of surfactants, the quantum yields increased by a factor of 2.5 to 108, the increase being directly related to the degree of chlorination of the biphenyl molecule. Also, fewer side reactions were observed with surfactants present. Oxygen had little effect on the rate of photolysis. Shi *et al.* (1994) demonstrated that UV-irradiation (254 nm) of 2,2',4,4'CB in Triton X-100 with TiO_2 suspension resulted in 99% PCB degradation and 49% recovery of the total chlorine as chloride in 20 min.

Although photolysis of environmental contaminants in surfactant solutions has lately been the focus of a great many studies, data pertaining to the role of surfactant in photodegradation of environmental contaminants is scarce. 2CP was used as a model compound to study the photochemical behavior of chlorophenols in surfactant solutions.

4.2 MATERIALS AND METHODS

4.2.1 Materials.

2-chlorophenol, purchased from Fisher Scientific Company, was further purified by chromatography on a Chromatotron (Model 7924T, Harrison Research) using dichloromethane as the eluting solvent. A purity of > 99.5 % was achieved as measured by gas chromatography (HP 5890 series II) using a flame ionization detector (FID). The following chemicals, obtained from Aldrich Chemical Co., were used in the study without further purification: polyoxyethylene 23 lauryl ether (Brij 35), sodium dodecylsulfate (SDS) with a purity of 98%, phenol (>99% pure), catechol (>99% pure), and cyclopentanecarboxylic acid (>99%). The characteristics of the surfactants and 2CP are listed in Table 4.1. All solvents used in this study were HPLC grade. All other chemicals were regent grade and used as received.

4.2.2. Methods.

2CP (0.1 g/L) solutions for photolysis were prepared as described in section 2.2.2 for 2CP solubilization experiment. To determine the rate of 2CP photolysis, 350 μL of the prepared solution was pipetted into a quartz cell with 1 mm path length and closed with Teflon lined cap. The solutions were irradiated in a Rayonet photoreactor (model

Table 4.1. Characteristics of surfactants and 2CP

Name	Chemical Formula	MW	CMC (M)[a]	HLB[b]	N_{aggr}[c]
Brij35	$C_{12}H_{25}(OCH_2CH_2)_{23}OH$	1198	1.59×10^{-4}	22.2	40
SDS	$CH_3(CH_2)_{11}OSO_3Na$	288	8.06×10^{-3}	51.4	62

		Solubility (M)[d]	pK_a[d]	pK_a*[e]	log K_{ow}[d]
2CP	ClC_6H_4OH	128.6	0.182	8.5	2.6	2.17

[a] Determined by surface tension measurement at 22 ± 1 °C.
[b] Hydrophile-lipophile balance, calculated using Davies and Rideal eq.(Myers, 1992).
[c] N_{aggr}: aggregation number, i.e. average number of surfactant molecules per micelle (Kalyanasundaram, 1987).
[d] Average of the data listed by Shiu *et al.*, 1994.
[e] * Excited-state pK_a (Boule *et al.*, 1984)

RPR-100, Southern New England Ultraviolet) fitted with a merry-go-round unit. The maximum output (at 310 nm) of the low pressure mercury lamps was 2.32×10^{14} photons cm^{-2} sec^{-1}, and the total output (in the range of 250-370 nm) was 1.0×10^{16} photons cm^{-2} sec^{-1}. The photon flux was determined using an IL 700 photo radiometer (International Inc.). The 2CP remaining in solution was determined at various photolysis times using a HP1090 liquid chromatograph (LC) (Hewlett Packard, Inc.) equipped with a Hypersil ODS column (id x length = 2.1 x 200 mm, C_{18} with particle size 5 μm). The ratio of the CH_3CN:H_2O solvent was linearly changed from 20:80 to 70:30 over 16 min. The pH of the mobile phase H_2O was preadjusted to 2 using H_2SO_4 to protonate hydroxyl groups on the products. The concentration of chloride ion, generated from dechlorination of 2CP, was determined with a chloride selective electrode (Model Orion 96-17) and confirmed with a colorimetric method (Iwasaki *et al*, 1952). All samples were analyzed in duplicate.

Photolysis of 2CP for product identification was carried out using 80 mL of 2CP solutions placed in quartz tubes (id x length: 2.5 x 25 cm) with Teflon lined cap. After photolysis, samples were acidified to pH 2 using 100 μL 18.6% HCl, followed by three batch extractions with equal volumes of CH_2Cl_2. The CH_2Cl_2 fractions were combined in a flask and dried over 5-10 g anhydrous granular Na_2SO_4 (>99%, 10-60 mesh, E. M. Scientific). For samples containing surfactants, the CH_2Cl_2 fractions were further transferred into another flask containing 5-20 g of pre-dried silica gel (20-600 mash) to remove surfactants. Silica gel (20 g) was also used to avoid formation of emulsion in the SDS (4 g/L) solution during extraction for product identification. Quite possibly, this

large amount of silica gel interfered with the identification of OH-bearing products such as catechol and cyclopentadienecarboxylic acid which can strongly absorb to the slica gel surface. Finally, the extractions were passed through a glass wool filter (pore size 0.47 μm, Whatman), concentrated under vacuum, and redissolved in 1 mL of CH_2Cl_2 containing 1-naphthol (99%, Fisher Scientific Co.) as the internal standard for product analysis.

Photolysis products were identified by matching the GC retention time as well as the mass spectra of authentic compounds. Cyclopentanecarboxylic acid was used to quantitate the yield of cyclopentadienecarboxylic acid. A gas chromatograph-mass spectrometer (GC-MS) (GC: HP 5890 and MS: HP 5989B) with FID was used with the following temperature program: initial temperature was 50 °C for 1 min followed by a increase of 10 °C/min to 300 °C and isothermal elution for 10 minutes at 300 °C. Both the GC and GC-MS were equipped with a HP-1 capillary column (id x length 0.2 mm x 12 m). Due to the difficulty in separating 2CP from phenol produced, phenol was quantitatively determined in the presence of co-eluting 2CP by GC-MS using selected ion monitoring (SIM). The selected ion mass for 2CP and phenol were chosen as 128.0 and 94.0, respectively.

In this study, all UV-VIS spectra were measured by a Cary 4E UV-VIS spectrophotometer in 1 mm path length cells. Fluorescence was measured by a Fluorolog-

2 spectrofluorometer (Spex Industries, Inc) using 10 mm cells and right angle fluorescence collection.

4.3 RESULTS AND DISCUSSIONS

4.3.1 Characteristics of UV-VIS Absorbance and Fluorescence Emission

UV-VIS absorption spectra of 2CP and the lamp spectral profile are shown in Figure 4.1. At 0.1 g/L surfactant concentration (below the CMC), both the shape and intensity of the 2CP absorption spectra in both surfactant solutions were very similar to that in water. When the surfactant concentration was increased to the 4 g/L (>CMC), the spectra changed. In SDS solution, the absorption intensity decreased, although the spectral shape did not change whereas in Brij35 solution, the absorption intensity increased and the vibrational fine structure vanished, although the wavelength corresponding to the maximum absorbance (273 nm) did not shift. The changes in the 2CP spectra reflect the new molecular environment within the micelle and the partitioning of 2CP into the micelle. Using LSER, it was demonstrated earlier (chapter 2), that 2CP associated with surfactant micelles and the partitioning of 2CP into Brij35 micelles was greater than that into SDS.

The fluorescence quantum yield from the undissociated form of 2CP in water has been reported to be as low as $\Phi = 0.002$ (Boule *et al.*, 1982). In this study, fluorescence

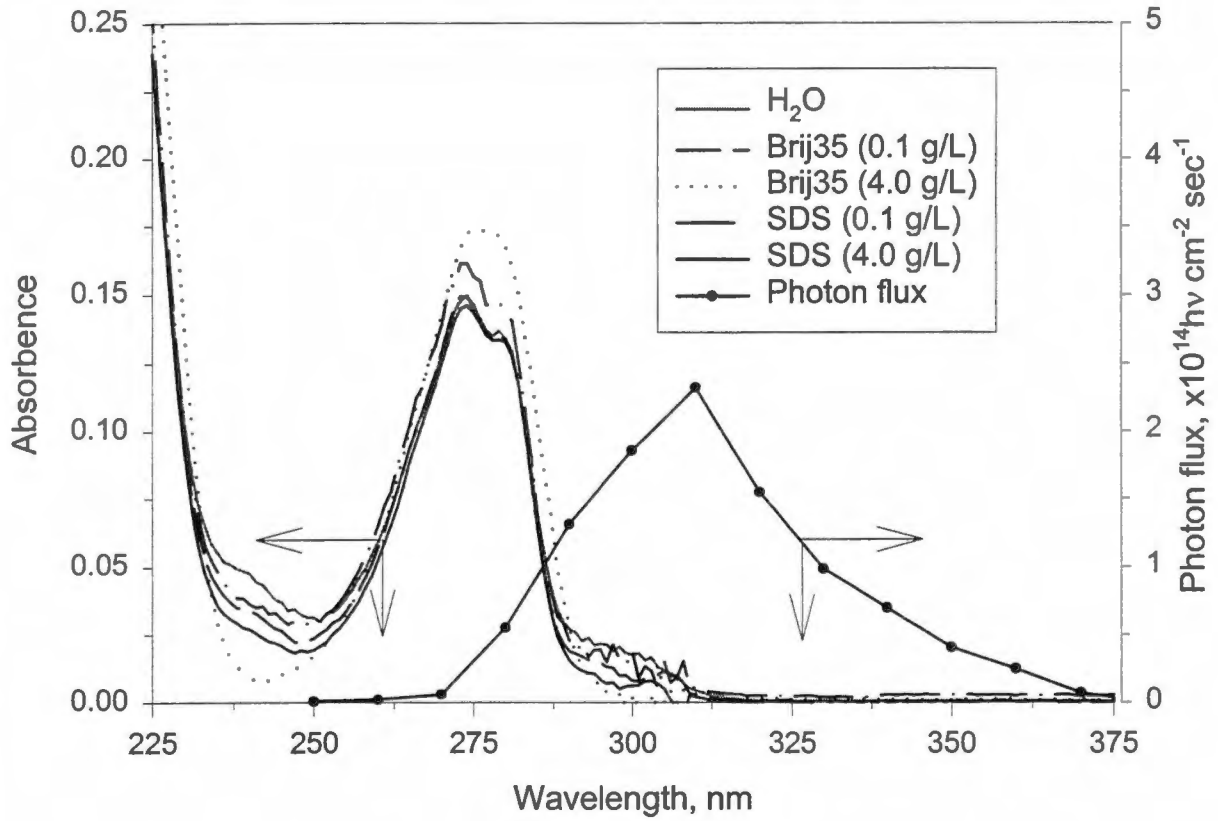


Figure 4.1 UV-VIS spectra of 2CP in water (pH 7.2), in surfactant solutions and UV lamp photon flux spectral profile.

from 2CP in any water or surfactant solution was not detectable, even when the aqueous solutions were adjusted to pH 2 using HCl.

Changes in the UV-VIS spectra of 2CP during photolysis are illustrated in Figure 4.2 and 4.3. The characteristics of 2CP spectra in water and Brij35 (0.1 g/L) solutions are very similar (Figure 4.2), and both exhibit isosbestic points. When the surfactant concentration was increased above the CMC (4 g/L), the spectra were different from what was observed for aqueous solutions. No isosbestic points were observed, and the maximum of the absorption band shifted blue as the reaction proceeded. These results suggest different photochemistry occurring in Brij35 micelles. Similar spectra were obtained for 2CP in SDS (Figure 4.3) as in Brij 35 solutions (Figure 4.2). Below CMC, the shape and intensity of the spectra were close to that observed in water and the isosbestic points could be identified. Increasing SDS concentration to 4 g/L resulted in the disappearance of isosbestic points. However, in SDS solution (4 g/L), no significant shift of the maximum absorption band occurred. Such spectral differences between SDS and Brij35 solutions at supra-CMC dosages indicate that more 2CP molecules partition into Brij35 micelles than in SDS micelles.

4.3.2 Photolysis Rates and Quantum Yields

2CP concentrations in the photolyzed water and surfactant solutions are plotted in the form of $\ln (C_o/C_t)$ as a function of time in Figure 4.4, where C_o and C_t represent the

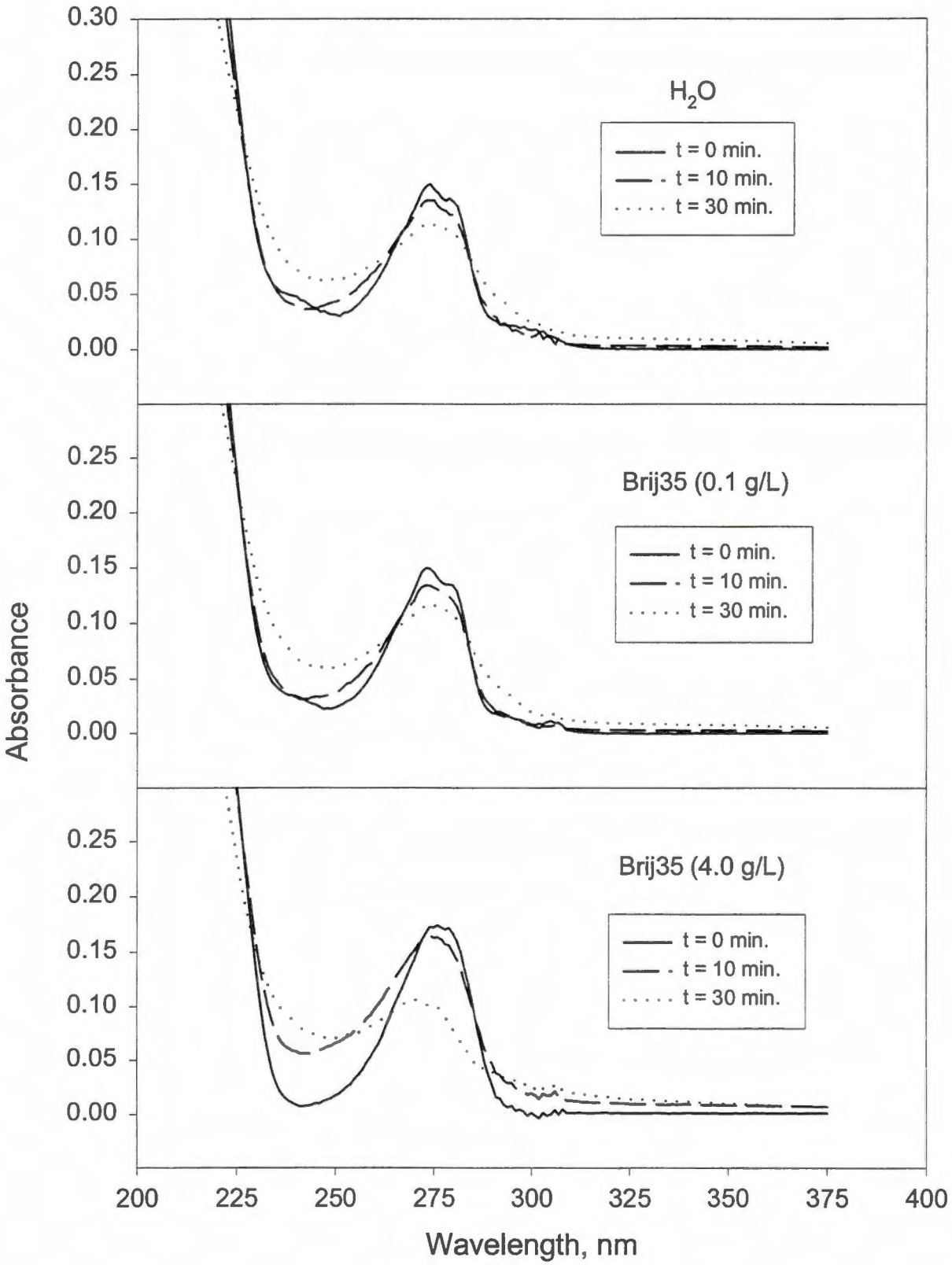


Figure 4.2 Comparison of UV-VIS spectra of 2CP in water and Brij35 solutions at various photolysis times

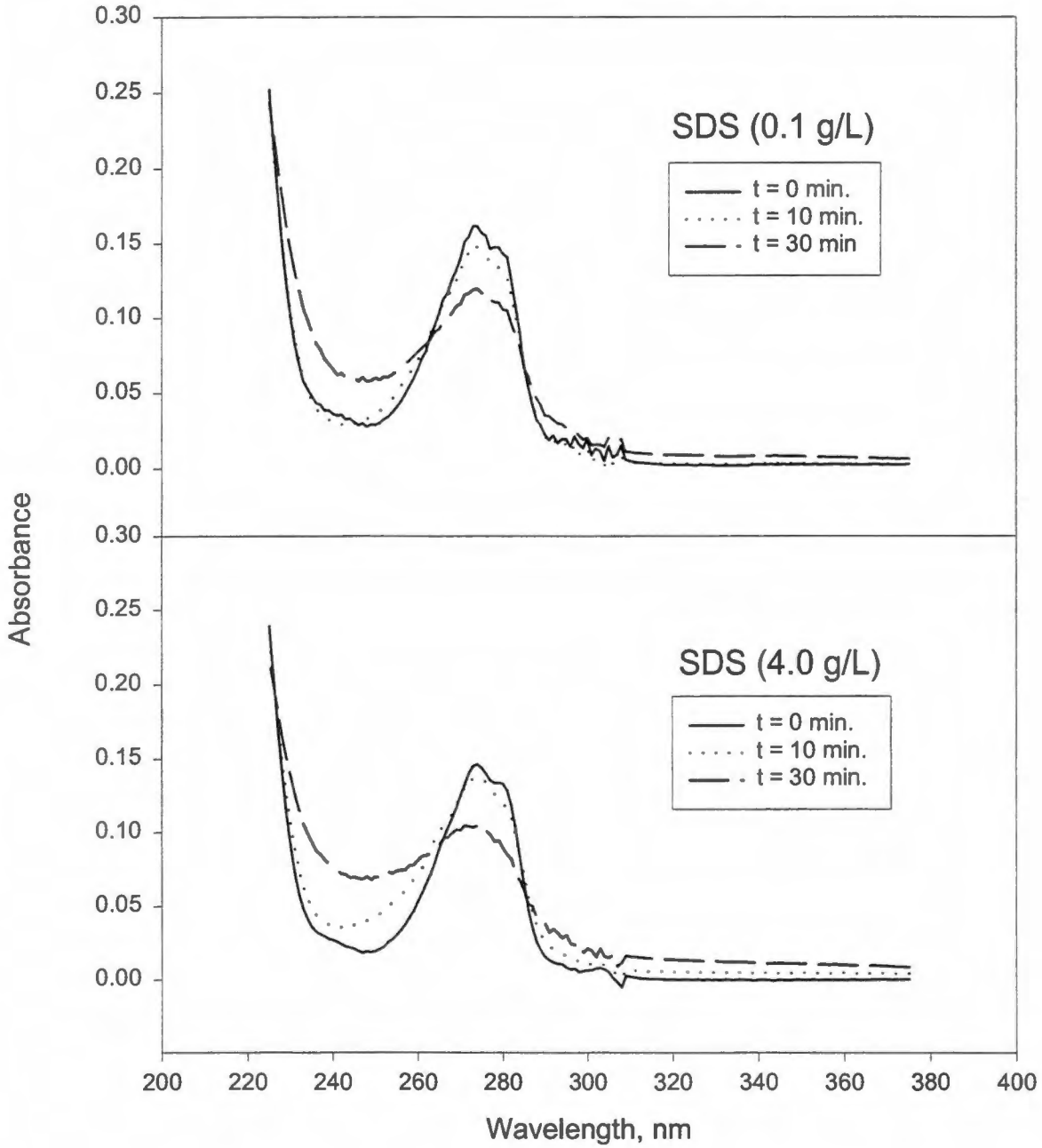


Figure 4.3 UV-VIS spectra of 2CP in SDS solutions at various photolysis times

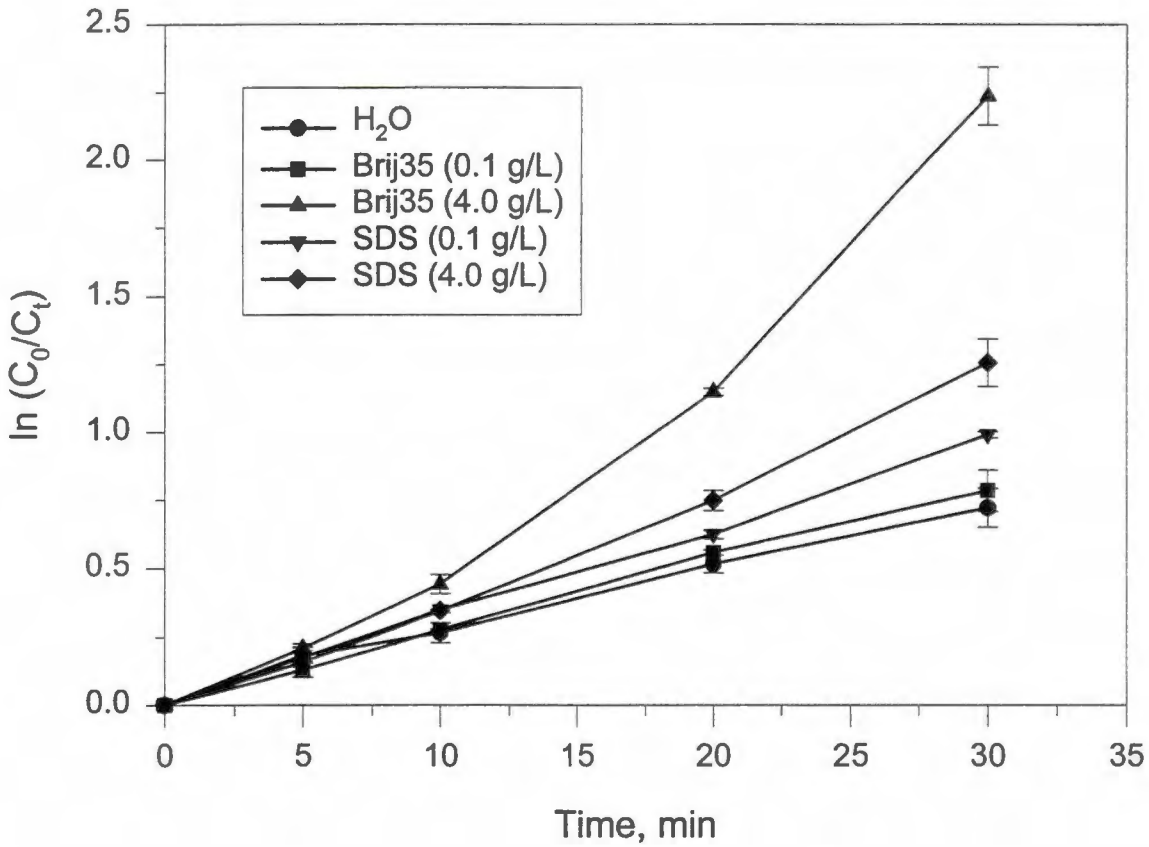


Figure 4.4 Photodegradation of 2CP (0.1 g/L) in water and surfactant solutions.

2CP concentration at time zero and t, respectively. The graph demonstrates that during the initial photolysis period ($\leq$ 10 minutes), 2CP degradation, like that of 4-chlorophenol (Hwang *et al.* 1987), followed apparent first-order kinetics in all solutions except those above the CMC of both surfactants. At supra-CMC, the kinetics deviate from the first-order rate law at longer photolysis times. For comparison, the initial rates ($t \leq 10$ min.), characterized by the first-order rate constant k_1 (min^{-1}), are given in Table 4.2.

The absorbance of 2CP in water and surfactant solutions is less than 0.02 in the region of lamp emission-spectral profile (Figure 4.1, 4.2 and 4.3), indicating that light is weakly absorbed by these solutions (Leifer, 1988). The commonly used formula for calculating quantum yields in weakly absorbing solutions incorporates integrated photon flux values over specified spectral regions (usually ~ 10 nm) and average molar extinction coefficients over the same region (Hwang *et al.* 1987; Lyman *et al.*, 1982; Leifer, 1988). The lamp spectral profile in Figure 4.1 is not a plot of integrated light flux measured at 10-nm increments using a spectral radiometer having a 1 nm bandpass. Equation 4.1 was used to calculate 2CP degradation quantum yields. This equation is functionally equivalent to that previously given elsewhere (Hwang *et al.* 1987; Lyman *et al.*, 1982; Leifer, 1988):

$$\Phi = \frac{j k_1}{2.303 \sum I_i \varepsilon_i} \qquad (4.1)$$

Table 4.2. 2CP (0.1 g/L) initial photolysis rate and quantum yield

Solutions	Rate[a], k_1 (min^{-1})		Half-life, $t_{1/2}$ (min)		Quantum yield[a], Φ	
	Degradation	Dechlorination	Degradation	Dechlorination	Degradation	Dechlorination
H_2O	0.0285±0.0049	0.0222±0.0023	24.3	31.2	0.0548	0.0427
Brij35 (0.1 g/L)	0.0272±0.0009	0.0294±0.0026	25.5	23.6	0.0590	0.0638
Brij35 (4.0 g/L)	0.0438±0.0012	0.0394±0.0030	15.8	17.6	0.0867	0.0780
SDS (0.1 g/L)	0.0348±0.0001	0.0230±0.0018	19.9	30.1	0.0618	0.0408
SDS (4.0 g/L)	0.0339±0.0015	0.0289±0.0028	20.4	24.0	0.0866	0.0739

[a] Calculated using the data within 10-min photolysis

where: k_1: first order rate constant, sec^{-1};

I_i: the extrapolated flux of incident light (described below), photons cm^{-2} s^{-1};

ε_i measured molar absorptivity of 2CP at wavelength λ_I, M^{-1} cm^{-1};

j: unit converting constant, for k_1, I_λ and ε_λ in the given units, $j = 6.023 \times 10^{20}$.

The photon flux values were linearly extrapolated (to every 1 nm) between the measured points on the smooth profile (Figure 4.1) and multiplied by the measured 2CP ε values, and the summation was carried out as shown in Equation 4.1. Extrapolation of photon flux values between successively measured points can be made with good accuracy due to the broad and structureless nature of the spectral profile of the lamp. All of the light absorbed by the aqueous system is absorbed by the 2CP, and the path length of the light is assumed to be equal to the cell thickness of 1 mm. The calculated quantum yields of degradation are given in Table 4.2.

Photodechlorination of 2CP in water and surfactant solutions was confirmed by the production of free Cl^-. The chloride concentrations, measured electrochemically and colorimetrically, were within experimental error. The photochemical production of free chloride, measured electrochemically, is plotted in Figure 4.5. using Equation 4.2 (Moore and Pearson, 1981):

$$\ln = \frac{(C_\infty - C_0)}{(C_\infty - C_t)} = kt \qquad (4.2)$$

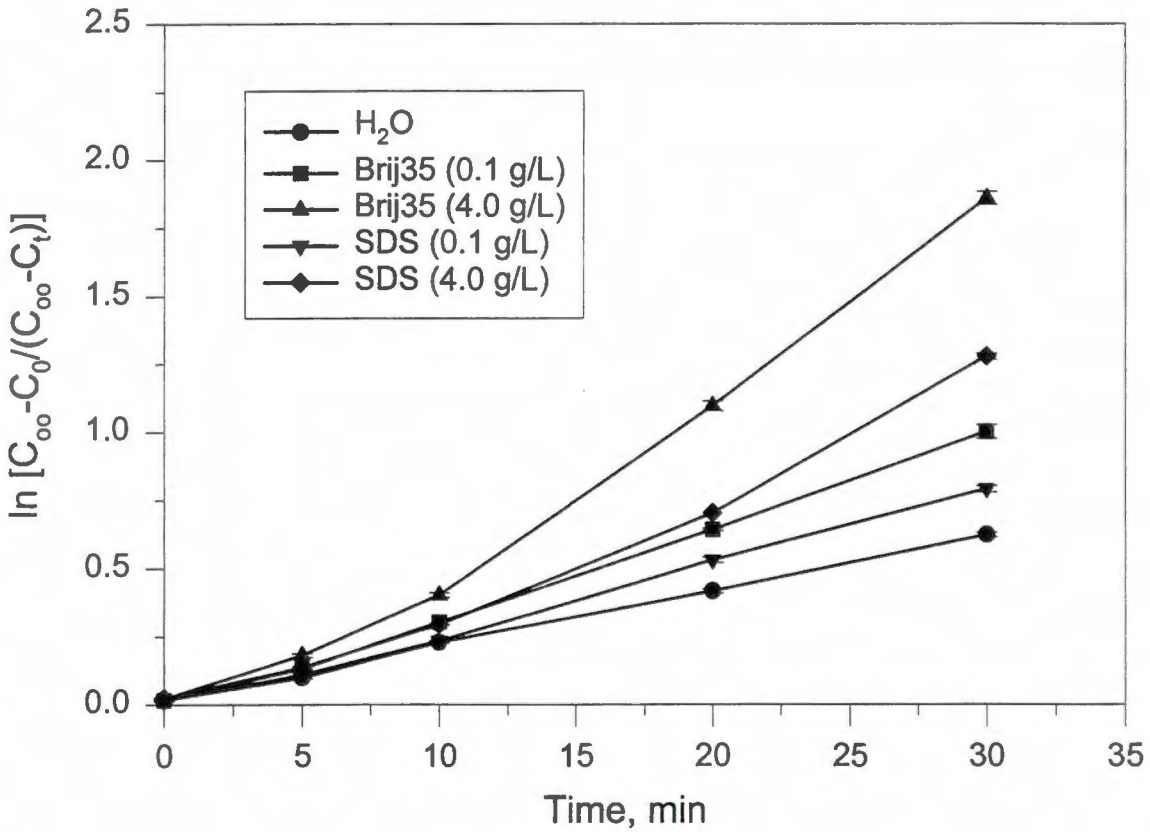


Figure 4.5 Chloride production from photodechlorination of 2CP (0.1 g/L) in water and surfactant solutions.

where: C_0: chloride concentration at time zero;

C_t: chloride concentration at time t;

C_∞: chloride concentration at infinite time, C_∞ is set equal to the initial concentration of 2CP.

Figure 4.5 demonstrates that chloride production followed a first-order rate law in water and surfactant solutions at concentration below the CMC. However, chloride production in micellar solutions of both Brij35 and SDS deviated from a simple first-order rate law at photolysis times exceeding 10 minutes. The initial rates (photolysis time $\leq$ 10 minutes) in these solutions can be approximated using the first-order rate law. The initial rate constants and quantum yields of dechlorination were calculated in the same fashion as for 2CP degradation and are given in Table 4.2.

In the absence of surfactants, the quantum yield in aqueous solution is close to the previously reported value (Boule *et al.*, 1984, 1987, and 1982). With surfactants present at sub-CMC concentrations, the initial rate and quantum yield of degradation are slightly enhanced in SDS solution. Increasing SDS concentration beyond 4 g/L (above the CMC) increases quantum yield although the rate of degradation does not significantly increase. This apparent discrepancy is accounted for by the change in absorption spectra for 2CP in 4 g/L surfactant concentrations (vide supra). In Brij35 solution, small changes in the degradation and quantum yields are also observed at surfactant concentration below the CMC; however, a sizable increase in the rate and quantum yields is observed above the

CMC (4.0 g/L surfactant). The initial modest degradation quantum yield enhancement at surfactant concentration below CMC appears to coincide with the presence of the surfactant molecules in solution, while the larger effect is observed for both surfactants upon the formation of micelles. All rates in 4.0 g/L surfactant solutions are enhanced and show deviation from first-order kinetics as the reaction proceeded.

To further study whether the observed acceleration could be also attributed to product-induced decomposition, 2CP photolysis was studied in the presence of added phenol. Solution of 2CP (0.1 g/L) in Brij35 (4 g/L) solutions with varied concentrations of added phenol (0-0.1 g/L) were irradiated, and the production of chloride was monitored (Figure 4.6). The initial dechlorination rate constants were determined according to Equation 4.2. As shown in Figure 4.7, 2CP initial dechlorination rate increased as the phenol concentration increased, confirming that the photoproduct, phenol, sensitizes 2CP decomposition (dechlorination).

The measured quantum yields of dechlorination are comparable to the quantum yields of degradation in all water or surfactant solutions examined, with the possible exception of 2CP in SDS below the CMC. Also, more than 90 percent of the initial mass of 2CP was accounted for from a mass balance of the 2CP remaining and the 2CP degraded (recovered as Cl^-). These results strongly suggest that degradation of 2CP mainly went through an initial dechlorination pathway. Similar results have been found in studies of the photolysis of HCB and PCBs in surfactant solutions (Chu and Jafvert,

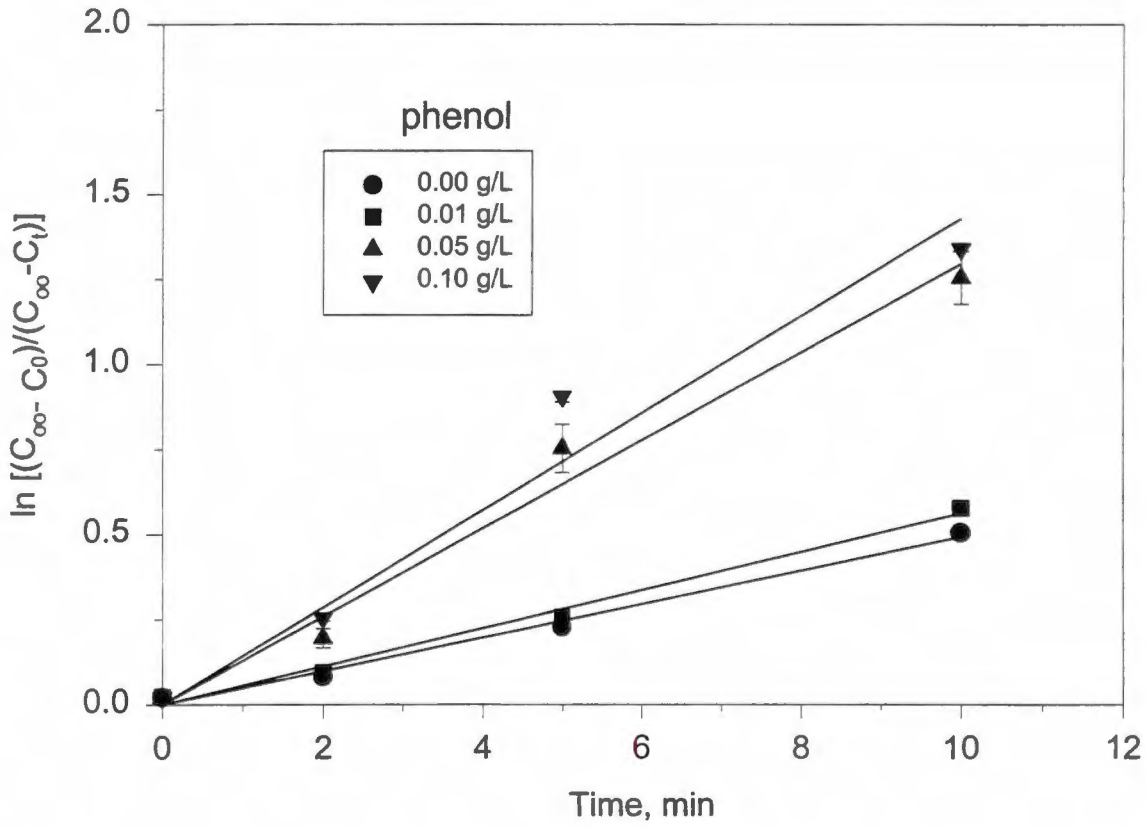


Figure 4.6 Chloride production from photodechlorination of 2CP (0.1 g/L) in Brij35 (4 g/L) sensitized by varying phenol concentrations.

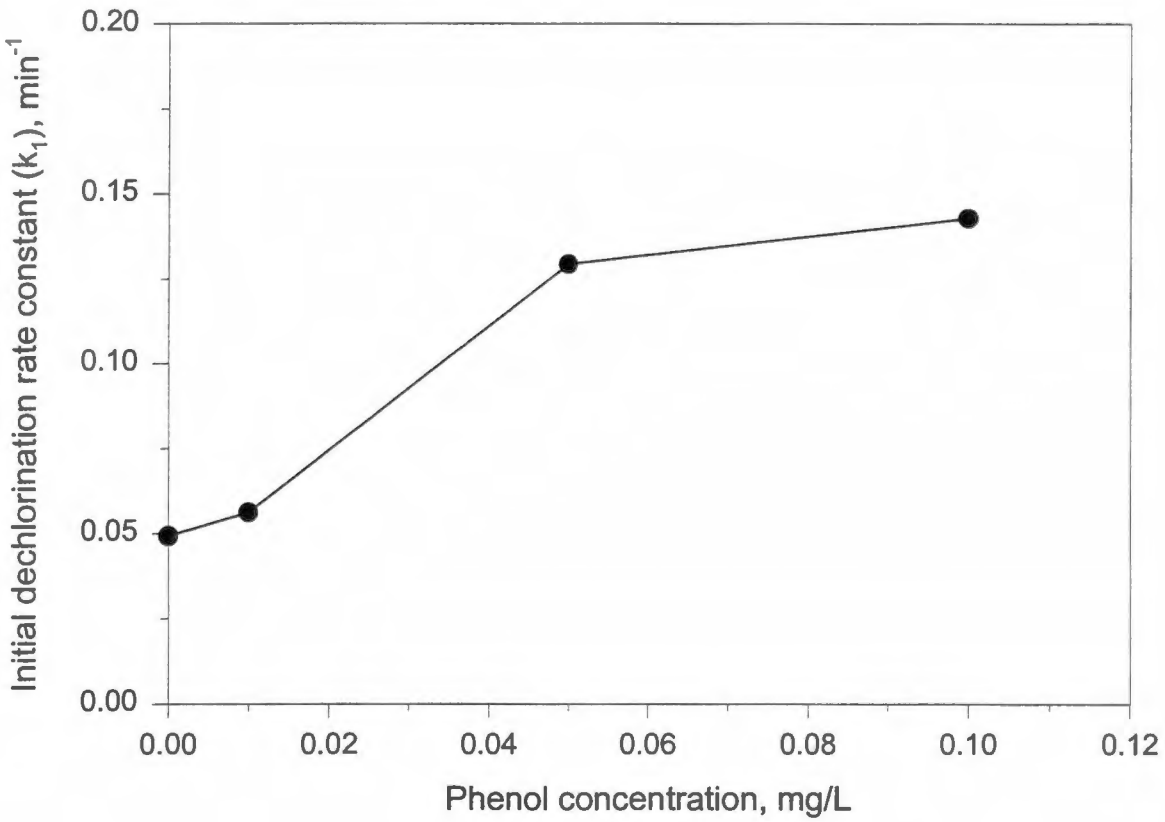


Figure 4.7 Effect of phenol (sensitizer) concentration on the initial photodechlorination rates of 2CP in Brij35 (4 g/L) solutions

1994, Epling *et al.*, 1988, Shi *et al.*, 1994). In SDS solution below the CMC, the degradation efficiency is greater than the dechlorination efficiency. This could be due to a non-dechlorination path; however, no products were identified to support this hypothesis.

4.3.3. Photolysis Products and Mechanism.

The photolysis products and their yields in water and surfactant solutions are listed in Table 4.3. In water solution (pH= 7.1) without surfactant, catechol and a cyclopentadienecarboxylic acid were the identified degradation products. The results agree with that reported by Boule *et al.* (1987, 1982) and Guyon *et al.* (1982), who propose that cyclopentadienecarboxylic acid results primarily from the 2CP anion undergoing a Wolff rearrangement. Catechol is thought to arise from a water nucleophilic displacement of chloride from the singlet excited state of 2CP. The mass balance (products plus remaining 2CP) was only 44 % in water (pH = 7.1), and the low yield may be due to partial photooxidization of these primary products (Boule *et al.*, 1987). In Brij35 and SDS solutions with concentrations at 0.1 g/L (< CMC), phenol was identified as a photoproduct in addition to catechol and cyclopentadienecarboxylic acid. The surfactant is thought to serve as the hydrogen atom source for the 2CP transformation to phenol, as proposed in Figure 4.8. The mechanism in Figure 4.8 suggests two pathways to phenol, one by C-Cl homolysis followed by free radical hydrogen atom abstraction and the second involving a triplet carbene mechanism requiring abstraction of two H atoms.

Table 4.3. 2CP photoproducts and transformation percentage

Solutions	Initial pH	Photolysis time (min)	Products	Transformation as degraded 2CP[a], %	Mass balance as initial 2CP[b], %
H_2O	7.1	30	Catechol	11.6	44
			Acid[c]	1.4	
Brij35 (4.0 g/L)	3.9	20	Phenol	56.0	90
Brij35 (0.1 g/L)	7.5	30	Catechol	16.3	86
			Acid[c]	1.7	
			Phenol	5.6	
SDS (4.0 g/L)	7.5	20	Phenol	3.0	24
SDS (0.1 g/L)	7.6	30	Catechol	21.7	45
			Acid[c]	7.1	
			Phenol	0.2	
DME	--	3	Phenol	45.0	80
25% DME	10	1	Acid[c]	38.7	58
			Phenol	1.0	
25% DME	2	1	Catechol	11.4	84
			Acid[c]	23.9	
			Phenol	31.2	

[a] Transformation = $C_{prod}/(C_0-C_t)$ x 100%, where C_{prod}, C_0, and C_t are the concentrations of product, 2CP at time zero, and 2CP at time t, (M), respectively.
[b] Mass balance = (C_t + sum of C_{prod})/C_0 x 100%.
[c] 1,3-Cyclopentadienecarboxylic acid.

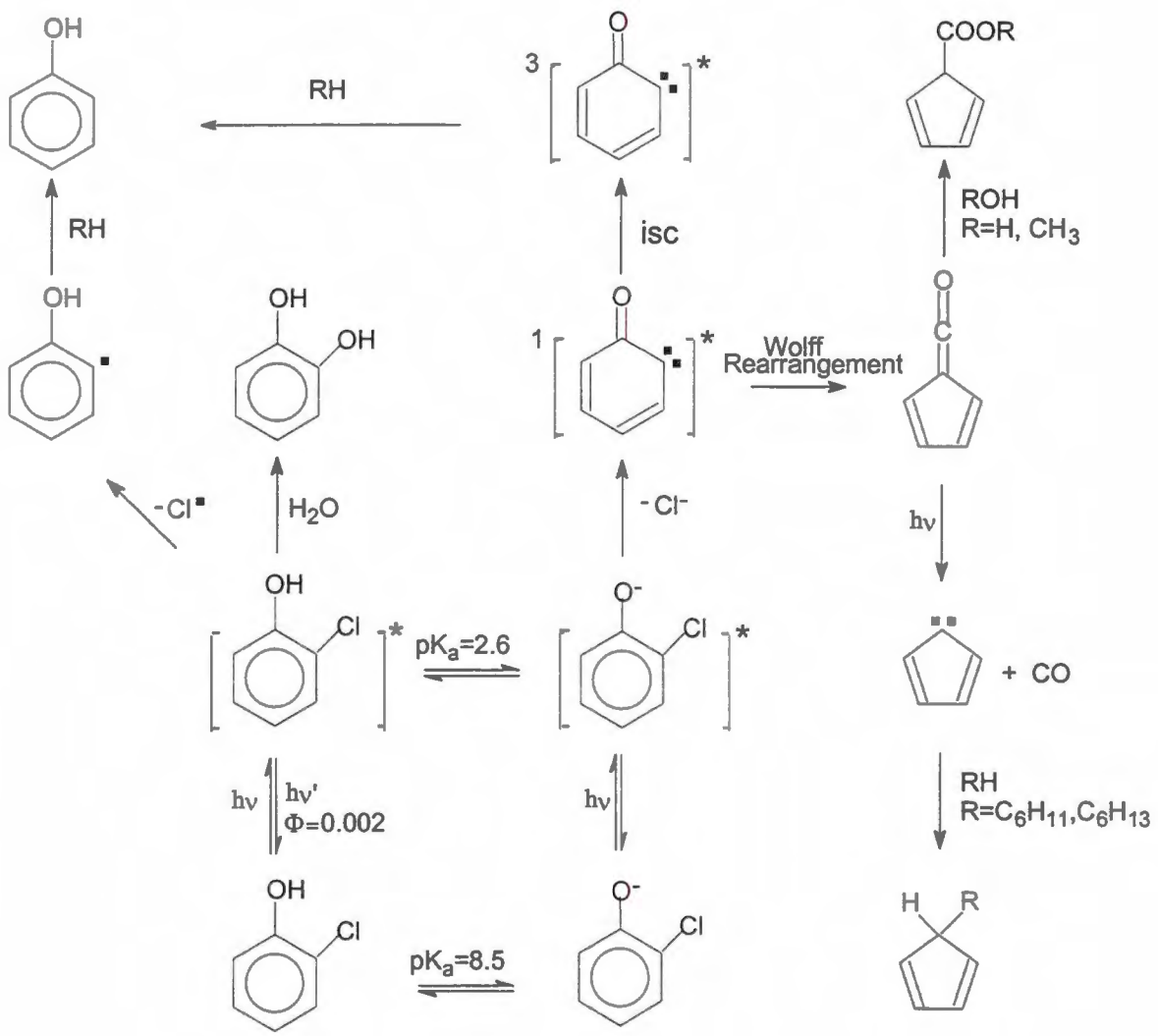


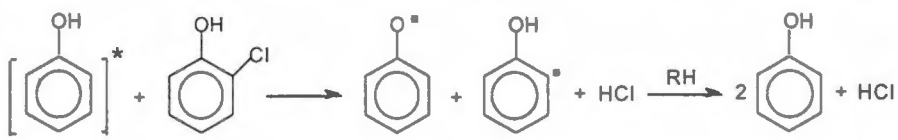
Figure 4.8 Mechanism of 2CP phototransformatiom

The carbene mechanism would require that intersystem crossing in the initially formed singlet carbene be kinetically competitive with the Wolf rearrangement. Product studies from 2CP photolysis in dimethoxyethane (vita infra) lend support to this proposed carbene-mediated mechanism of phenol formation. The mass balance was higher in the Brij35 surfactant solutions than in water (pH = 7.1). In solutions of Brij35 and SDS surfactants at 4 g/L (above CMC), phenol was the only observed product. Furthermore, it was found that the yields of phenol were greater at surfactant concentrations above the CMC than those below the CMC. Phenol yields and material balance were also found to be greater in Brij35 solutions than in SDS solutions. Increased yields of phenol in Brij35 and SDS micelles is consistent with 2CP solubilization within the micelles and phenol formation by a hydrogen atom abstraction reaction.

Upon photolysis, 80% (w/w) of 2CP in 99.9% pure dimethoxyethane (DME) (Aldrich Chemical Co.) was transformed to phenol. This result demonstrates that the polyoxyethylene (POE) functionality in Brij35 surfactants can serve as a good hydrogen source for 2CP transformation to phenol. Photolysis of 2CP in 25 % (v/v) solution (pH = 10, above the ground-state 2CP pK_a of 8.5) of DME in water reportedly yielded 38.7% (w/w) of cyclopentadienecarboxylic acid and only 1.0% (w/w) of phenol (Suntio *et al*, 1988, Shiu *et al.*, 1994). When the pH of the solution was reduced to 2 (below the 2CP singlet excited-state pK_a of 2.6), catechol (11.4 %) was formed along with phenol (31.2 %) and cyclopentadienecarboxyl acid (23.9%) (Boule *et al.*, 1984). Formation of catechol at a pH below the excited state pK_a of 2CP likely results from an excited-state

nucleophilic displacement of chloride by water, as discussed above. The observed high yield of phenol at pH = 2 and low yield of phenol at pH = 10 suggests that the major mechanism to phenol formation is through a free radical reaction (homolytic C-Cl scission or electron transfer sensitized decomposition). Formation of cyclopentadienecarboxylic acid at pH = 2 (below the 2CP singlet excited-state pK_a of 2.6) is attributed to rapid dissociation of the 2CP excited state.

Phenol has previously been suggested to sensitize the photodegradation of 2CP by a charge transfer dehalogenation reaction (Boule *et al.*, 1984):



The fact that the dechlorination rate of 2CP in Brij35 (4 g/L) was promoted by the presence of phenol confirmed the sensitizing action of phenol. At a 2CP concentration of 0.1 g/L, the occupation number (N_{occ}) for 2CP is calculated to be 3.7 in 4.0 g/L of Brij35 (Table 2.8). Similarly, N_{occ} values for various concentrations of phenol (0.01-0.1 g/L) in 4.0 g/L of Brij 35 containing 0.1 g/L of 2CP were calculated (Table 4.4). At the largest concentration of phenol used (0.1 g/L), the N_{occ} value was estimated to be 4.76, assuming that 2CP did not affect partitioning of phenol into micelles. These occupation numbers support the proposed sheme of enhancement 2CP photolysis by phenol via electron transfer sensitiztion. Further, at 0.1 g/L of 2CP in Brij35 (4 g/L), in rapidly forming and

Table 4.4. K^j_m, S_{cmc}, MSR, K^e_m, and N_{occ} for phenol in Brij35 (4.0 g/L) solutions containing 2CP (0.1 g/L)

Parameters[a] and Coefficients[a] of LSER[b]

Surfactant	**c**	**a**	**b**	**p**	**r**	**v**
Brij35	-1.39	1.62	-3.83	-0.37	1.63	3.65
Solute		$\Sigma\alpha_2$	$\Sigma\beta_2$	π_2	$\mathbf{R_2}$	$\mathbf{V_x}$
phenol		0.60	0.30	0.89	0.805	77.5

K^j_m, S_{cmc}, MSR, K^e_m, and N_{occ} Values

K^j_m	S		S_{cmc}	MSR	K^e_m	N_{occ}
(M^{-1})	(g/L)	(M^{-1})	(M^{-1})			
174	0.01	1.06×10^{-4}	6.82×10^{-5}	0.0119	9500	0.47
	0.05	5.31×10^{-4}	3.42×10^{-4}	0.0595	9073	2.3
	0.10	1.06×10^{-3}	6.82×10^{-4}	0.119	8591	4.7

[a]After Abraham (1987; 1993) and Quina *et al.*, (1995).
[b]Linear solvation energy relationship, Equation 2.9.

and dissociating micelles, phenol produced by photolysis can sensitize the decomposition of 2CP molecules occupying the same micelle.

To better understand the mechanism of 2CP photolysis, 2CP (0.1 g/L) was also photolyzed in cyclohexane, hexane and methanol. In each case, phenol was the minor product and cyclopentadiene derivatives were the major products. The cyclopentadiene derivatives of cyclohexane and hexane result from trapping cyclopentadienyl carbene. The carbene is formed by secondary photolysis of the cyclopentadienyl ketene, the product of the Wolff rearrangement. In methanol, as in water, the ketene is trapped by the nucleophilic solvent to give the cyclopentadienecarboxylic acid methyl ester.

An overall mechanistic description of the photochemical degradation of 2CP is given in Figure 4.8. Dissociation of chloride from 2CP excited anion results in the formation of a proposed carbene intermediate that can further undergo a Wolff rearrangement (Boule *et al.*, 1987) to form cyclopentadienyl ketene or intersystem cross to the triplet manifold, eventually leading to phenol production as discussed above. The ketene can undergo hydrolysis to form cyclopentandienecarboxyl acid in aqueous solution. In the absence of a good nucleophile, the ketene can be photolyzed to give cyclopentadienyl carbene. When C-H bonds are present in surfactants (Brij35 and SDS), or organic solvents (DME, methanol, and hexane), the cyclopentadienyl carbene undergoes a concerted insertion into the bond or abstract a hydrogen atom followed by

radical coupling to form a new covalent bond. In cyclohexane, the formation of cyclohexanone, dicyclohexyl ether, and cyclohexane as solvent-derived products was observed, which suggests that the cyclopentadienyl carbene is reacting from a triplet state.

The excited state of the undissociated 2CP can undergo a nucleophilic displacement of chloride by water to yield catechol. Phenol can be derived from the same excited state by homolytic scission of the C-Cl bond followed by hydrogen abstraction or by chloride elimination and deprotonation following electron transfer sensitization. The resulting radical leads to phenol production by hydrogen atom abstraction.

4.3.4. Role of Surfactants in Photolysis.

As discussed above, the surfactant seems to play two important roles in the enhancement of 2CP photolysis: (1) surfactant micelles supply a nonaqueous "cage" that retains phenol and catechol allowing for electron-transfer sensitized degradation of 2CP in a higher local concentration; (2) the polyoxyethylene chain and/or hydrocarbon chain of surfactant can act as the H source to allow for phenol production by reductive dechlorination of 2CP. When the concentration is below the CMC, a surfactant only serves as the H source.

4.4 SUMMARY

The photolysis of 2CP dissolved in surfactant solutions was studied. The initial degradation and dechlorination of 2CP followed a first-order rate law. Surfactants enhanced rates and quantum yields of 2CP degradation, particularly at surfactant concentrations greater than the CMC. Nonionic surfactant Brij35 enhanced photolysis to a greater extent than the anionic surfactant SDS. The greater enhancement in Brij35 is attributed to larger partitioning of 2CP into the micelles. Further study of 2CP photolysis in hexane, methanol, and dimethoxyethane suggested that surfactants can likely serve as a H source in phenol production following 2CP photolysis. Further, phenol appears to sensitize the photochemical decomposition of 2CP in micellar solutions by a charge transfer dehalogenation reaction. Two pathways for the phototransformation of 2CP in surfactant solutions are proposed: (1) The excited anionic form of 2CP may be converted to cyclopentadienecarboxylic acid by ring contraction via the Wolff rearrangement. It can also be converted to phenol if an H source is present; two H atoms must be abstracted per mole of the excited 2CP anion. (2) The excited undissociated form of 2CP may be converted to catechol via a nucleophilic displacement of chloride in the presence of water. In non nucleophilic solvents, the production of phenol may occur, presumably by hemolytic scission of the C-Cl bond followed by H abstraction, for example, from a surfactant. All 2CP photochemical reactions in surfactant solutions resulted in dechlorinated products which may be less toxic and easier to biodegrade.

CHAPTER 5

CONCLUSIONS

Surfactants are increasingly being used to enhance remediation of soils contaminated with hydrophobic organic contaminants. Transferring these contaminants, such as chlorinated aromatic compounds (CACs), from soils to solutions is the primary step in most remediation processes. Once mobilized from soils, the contaminants in micellar surfactant solutions can be treated by many different processes, photolysis among them. Surfactants can not only improve mobilization of CACs from contaminated soils, but also can enhance the CAC photolysis. In this study, dissolution and photolysis of chlorinated aromatic compounds (CACs), 2-chlorophenol, pure PCB congeners, and a commercial PCB mixture (Aroclor1242), were studied in surfactant micellar media. Based on the results obtained, the following conclusions could be drawn:

1. The solubility of pure PCB congeners and Aroclor 1242 was greatly enhanced by all surfactants tested, at concentrations above the CMC, nonionic surfactants being more effective than the anionic ones. For POL(10), the micelle-water partitioning coefficient K_m and the octanol-water partitioning coefficient K_{ow} for a group of PCB congeners with different *o*-chlorine substitutions, were related as:

$$\log K_m = 0.815 \log K_{ow} + 1.966.$$

2. A micellar/aqueous pseudophase partitioning model (Edwards *et al.*, 1991) was used to establish that the solubility enhancement was primarily because of partitioning of the PCB molecules into micelles. Further, the micellar/aqueous pseudophase partitioning coefficient (K_m) indicated that the mole fraction of PCB in micellar phase were 10^6 to 10^8 times greater than that in the aqueous pseudophase. The UV spectra of 2,2',4,4'CB dissolved in POL(10), DME, and n-hexane revealed that the PCB molecules were possibly located at the core of the nonionic surfactant micelle and its vicinity.

3. LSER was used to determine association of 2CP, a less hydrophobic solute, with micelles in unsaturated surfactant solutions. Thirty-eight percent of 2CP was associated with micelles in solutions of nonionic surfactant Brij 35 compared to only 15% in anionic surfactant SDS.

4. The rate and quantum yield of photolysis of CACs are always enhanced in the presence of surfactants, especially in micellar solutions. The micellar "cage" allows reactants and intermediates to remain longer at higher local concentrations in a non-aqueous, solvent-like environment, increasing their reaction probabilities. Further, acting as a source of H atoms that can be abstracted, surfactants promote dechlorination of CACs. Nonionic surfactants are better than anionic surfactants in promoting photolysis, especially at supra-CMC dosages. Stepwise dechlorination

appears to be the major photochemical mechanism for PCB photolysis in POL(10) solutions. *Ortho* chlorine is more vulnerable to photochemical attack than *para* chlorine; highly chlorinated congeners are likely to be more photodegradable.

5. Two pathways for the phototransformation of 2CP in surfactant solutions are proposed. The electronically excited anionic form of 2CP can either be converted to cyclopentadienecarboxylic acid through a ring contraction via the Wolff rearrangement or be converted to phenol if an H donor is present. The electronically excited undissociated form of 2CP leads to the formation of catechol via a nucleophilic displacement of chloride in the presence of water. In non nucleophilic solvents, the production of phenol occurs, presumably by hemolytic scission of the C-Cl bond followed by hydrogen abstraction. Further, phenol may sensitize phtodegradation of 2CP by a charge transfer dehalogenation.

6. A 4 g/L of POL(10) solution was used wash two contaminated soils, a clayey soil and a sandy soil. In 3 days, 74% and 47% of Soxhlet-extractable PCBs were removed from the clayey soil and the sandy soil, respectively. PCBs in the surfactant soil-washing solutions could be effectively photodegraded even in the presence of moderately high turbidities. An integrated treatment scheme comprising of surfactant washing and photolysis of washwater could be a viable technology for remediating PCB contaminated soils.

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