

UNC-WRRI-92-269

CLOUD POINT EXTRACTION AND PRECONCENTRATION PROCEDURES FOR  
ORGANIC AND RELATED POLLUTANTS OF STATE CONCERN

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July 1992

"The research on which this report is based was financed in part by the United States Department of the Interior, Geological Survey, through the North Carolina Water Resources Research Institute."

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Agreement No. 14-08-0001-G1580

Project No. 70108

USGS Project No. 08 (FY90)

## ABSTRACT

A new extraction and preconcentration procedure for organic compounds originally present in aqueous or solid matrices (soil, coal) based upon the unique properties (i.e. solubilization and phase separation ['clouding'] ability) of aqueous solutions of neutral surfactant micellar systems was evaluated. At low surfactant concentrations above the critical micelle concentration (CMC), typically below 15 wt%, micellar solutions of nonionic surfactants can exist as homogeneous isotropic liquid phases. Phase separation can be induced in this concentration range by varying the temperature. In many such phase separations, the single isotropic micellar phase separates into two isotropic phases, both of which contain surfactant but which differ in total surfactant concentration. In the surfactant micellar-rich phase will be concentrated any hydrophobic organic components originally present in the sample subjected to the phase separation step. The factors that influence both the phase separation behavior and extraction efficiency (concentration factor and percent recovery) for model test solutes (phenols and polycyclic aromatic hydrocarbons) were critically assessed. Preliminary results were also obtained for the extraction of organics from solid (soil) matrices using this approach. The results obtained in this study demonstrate the potential of this proposed micellar phase separation (or cloud point) extraction technique. The use of this cloud point extraction scheme appears to offer some significant practical advantages over existing extraction approaches for organic compounds.

(key words: extractions, preconcentration, nonionic surfactants, cloud point, phase separation, micelles, solubilization, phenols, pesticides, polycyclic aromatic hydrocarbons)

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## SUMMARY AND CONCLUSIONS

The results indicate that the proposed cloud point extraction technique is feasible, but more work is required in order to compare and contrast the general method with existing liquid-liquid extractions for different model classes of pollutants. The key findings (Frankewich 1992; Frankewich and Hinze 1992) include the following: First, a survey of several nonionic surfactants for use in the cloud point extraction technique indicated that Triton CF-21 (cloud point 38°C), C<sub>8</sub>E<sub>3</sub> (cloud point 10.6°C) and C<sub>7</sub>E<sub>3</sub> (cloud point 27.6°C) provided for the best extractions. The non-Triton surfactants are superior as an extractant medium since they do not possess an aromatic ring and thus have virtually no absorbance in the UV region which facilitates subsequent analyte analysis. In addition, useful extractions can be achieved using zwitterionic surfactants which had not been previously reported.

With respect to factors that influence the extent of extraction, the extraction concentration factor was found to increase as the temperature above the cloud point at which the separation is attempted is increased. This probably reflects mass transfer effects. However, the time spent in the bath at a certain temperature prior to analyses did not appreciably alter the extent of the extraction. There was noted a slight increase in the concentration factor with the time of centrifugation (i.e. longer times slightly improved the extraction). Based on phenolic test solutes, it appears that the ionic strength of the solution does not influence the extraction efficiency. As expected, the extraction efficiency does depend upon the solution pH for any ionizable solutes with the extraction efficiency greater for the neutral form of the analyte. Using optimized experimental results, it was found that essentially quantitative transfer of

hydrophobic organic solutes from the bulk aqueous to the surfactant-rich micellar phase is possible. This near quantitative extraction appears to occur for nonpolar organic solutes that bind to the micellar assembly with binding constants greater than, or equal to about  $1000 \text{ M}^{-1}$ .

Although much more work is required before this technique is recommended for field work, it appears that the proposed technique could offer possible advantages over traditional liquid - liquid extractions. These include the following: i) simplicity, safety (only a small volume of the nonvolatile 'extraction solvent' [i.e. the concentrated surfactant solution] is required which obviates the need for large volumes of flammable organic solvents now utilized in liquid - liquid extractions), ii) compatibility of the extracting solvent with HPLC (due to fact that the same nonionic surfactants can be utilized in micellar liquid chromatography), and iii) possible enhanced detection modes due to surfactant micelle effects (especially for luminescence detection) among others. The only difficulty encountered in the developmental work stemmed from the fact that the extractant phase (surfactant-rich phase) is almost too small (of course this is why one is able to achieve such high preconcentration factors). However, for real world samples, when one would have to scale-up in order to have enough extractable analyte to detect, this probably would not pose any difficulty.

Some work was aimed at testing the proposed micellar solubilization and cloud point extraction procedure for its ability to 'remove' analytes from solid matrices. Some success was achieved for the extraction of anthracene from coal samples. In addition, limited success was achieved using nonionic surfactant solutions for the extraction of some polycyclic aromatic hydrocarbons from spiked soil samples. However, further work is required in

these areas in order to optimize the systems and determine the feasibility of the approach for such applications. Since surfactant scrubbing of hazardous chemicals from soil has recently been proposed as a possible large scale decontamination approach (Chawla et. al. 1991), the ability to subsequently concentrate the organics in the surfactant-rich micellar phase using our cloud point extraction approach may prove to be very beneficial.

## RECOMMENDATIONS

Although further work is required in order to fully understand and design cloud point extraction systems for environmental work, the results of the present study indicate that the technique is viable and can be applied for the extraction and/or preconcentration of organic compounds from both aqueous and solid matrices. Specifically, the optimized cloud point extraction system developed in this work was demonstrated to function very well for the extraction of a mixture of chlorophenols as well as alkylbenzenes from a bulk aqueous solution. The general extraction approach should be applicable to other organic species. Further research aimed at comparing and contrasting the proposed cloud point technique to that of conventional liquid - liquid extractions is obviously required. It is recommended that separation scientists and environmental chemists consider use of such surfactant-mediated phase separation technique in lieu of the traditional liquid - liquid extraction procedure for the extraction and preconcentration of organic species.

## INTRODUCTION

In view of the carcinogenicity, co-carcinogenicity, and/or toxicity of many organic compounds, it is very important to be able to quickly and accurately monitor as well as control the concentration levels of organics in aqueous and solid matrices (Bjorseth 1983; Frei and Brinkman 1983; Straub 1988; Vo-Dinh 1989). The desorption/extraction and analysis of organic components in solid matrices or extraction/preconcentration of organics from aqueous samples represents one of the most difficult and challenging tasks for the analytical chemist. This is due to a number of factors, including the following: (1) the concentration of individual organic compounds of interest is frequently small; (2) in some cases, e.g. dated sediment cores, organisms, etc., sample amounts can be very limited; and (3) there is a problem in achieving 100% extraction efficiency with good reproducibility rapidly from such sample matrices. Additionally, extensive sample manipulation during the extraction/enrichment step(s) can lead to problems in ensuring adequate and constant recovery of the organic component(s).

Although several general procedures (i.e. Soxhlet extraction, homogenization/sonication procedures, shake-flask methods, etc.) have been described in the literature for the extraction of hydrophobic organic components in different matrices, all suffer limitations to different degrees in terms of recovery efficiency, reproducibility, volume of the extraction solvent required, processing time, and/or ease of use. Consequently, there is a continuing need for the development of alternative extraction/enrichment procedures which are safe, rapid, convenient, and accurate. In this report, a new general extraction/enrichment scheme based upon the solubilization and phase separation behavior of neutral surfactant micellar systems is described which should be applicable to many types of

organic species and have advantages over those techniques currently available to the water scientist, analytical chemist, and environmental scientist among others. The important experimental factors influencing this new extraction and preconcentration approach are identified and evaluated. Several examples of the successful utilization of the proposed procedure for the extraction/preconcentration of organics from aqueous or solid matrices are presented.

#### UNIQUE PHASE SEPARATION BEHAVIOR OF SURFACTANT MICELLES

Neutral surfactant systems have been utilized in some separation science applications, but to date there have been only limited reports concerning their use in extraction or preconcentration schemes (Scamehorn and Harwell 1989; Hinze and Armstrong 1987; Hinze et.al. 1989). Aqueous solutions of neutral (i.e. nonionic or zwitterionic) surfactants can form micellar assemblies (Figure 1) in which a certain number of surfactant molecules aggregate to form an assembly possessing a central core region comprised of their long alkyl (or alkylaryl) hydrocarbon chains with their more polar polyethyleneoxide (or zwitterionic) headgroups extending outward and interacting with the bulk water (Fendler 1982). Table 1 lists some properties of representative neutral surfactants utilized in this study.

Aqueous solutions of neutral surfactants have two particularly important properties (i.e. their solubilization ability and phase separation behavior) that can be exploited in order to develop a new viable extraction - preconcentration technique. First, it is well known that micellar aggregates in water can solubilize and bind hydrophobic solute molecules that are typically insoluble or only sparingly soluble in bulk water (Attwood and Florence 1983). For example, whereas the solubility of pyrene and anthracene in water are in the 0.1-0.6 micromolar range, their

Figure 1. Schematic representation of one-half of a Triton X-100 micellar aggregate based upon calculations for (a) spherical, (b) oblate, and (c) prolate micelle models (taken from Robson and Dennis 1977).

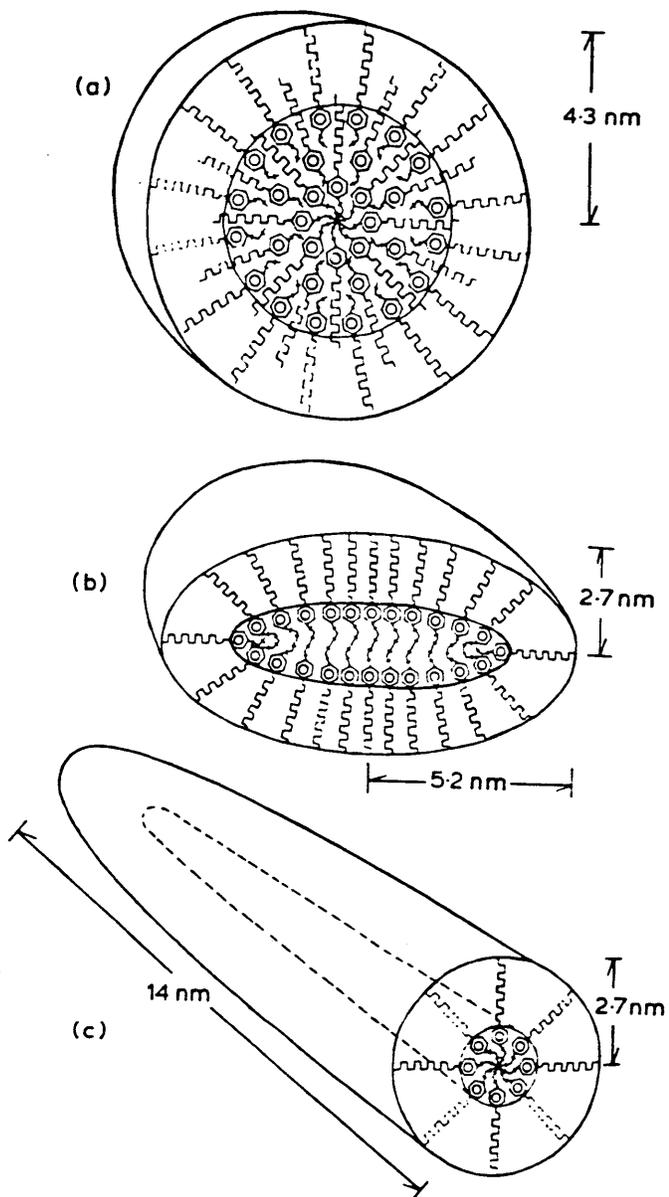


TABLE 1. Summary of Neutral Surfactants and Some of Their Properties

Surfactant Structure and Name (or Abbreviation)	CMC <sup>a</sup> , M	N <sup>b</sup>	Cloud Point <sup>c</sup> , °C
$\text{CH}_3 - \underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}} - \text{CH}_2 - \underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}} - \text{C}_6\text{H}_4 - (\text{OCH}_2\text{CH}_2)_x - \text{OH}$			
if x = 7-8, Triton X-114 (TX-114)	$3.5 \times 10^{-4}$	---	27.1
if x = 9-10, Triton X-110 (TX-100)	$2.0 \times 10^{-4}$	143	64.0
Triton CF-10	----	---	28.2
Triton CF-21	----	---	38.0
-----			
$\text{C}_9\text{H}_{19} - \text{C}_6\text{H}_4 - (\text{OCH}_2\text{CH}_2)_x - \text{OH}$			
if x = 7-8, PONPE-7.5	$8.0 \times 10^{-5}$	---	23.4
if x = 9-10, Igepal CO-610	----	---	30.0
if x = 10, Igepal CO-630	----	---	54.4
if x = 40, Nonidet P-40	----	---	48.8
-----			
$\text{CH}_3(\text{CH}_2)_y - \text{O} - (\text{CH}_2\text{CH}_2\text{O})_x - \text{H}$			
if y = 5, x = 3, C <sub>6</sub> E <sub>3</sub>	$1.0 \times 10^{-1}$	---	45.0
if y = 5, x = 5, C <sub>6</sub> E <sub>5</sub>	----	---	75.0
if y = 7, x = 5, C <sub>8</sub> E <sub>5</sub>	$9.0 \times 10^{-3}$	80	60.0
if y = 9, x = 5, C <sub>10</sub> E <sub>5</sub>	----	---	45.0
if y = 11, x = 4, C <sub>12</sub> E <sub>4</sub>	----	---	4.5
if y = 11, x = 5, C <sub>12</sub> E <sub>5</sub>	$6.0 \times 10^{-5}$	160	31.0
if y = 11, x = 6, C <sub>12</sub> E <sub>6</sub>	$6.8 \times 10^{-5}$	110	50.0
if y = 11, x = 7, C <sub>12</sub> E <sub>7</sub>	$6.9 \times 10^{-5}$	---	65.0
if y = 11, x = 8, C <sub>12</sub> E <sub>8</sub>	$7.1 \times 10^{-5}$	90	77.0
if y = 11, x = 23, C <sub>12</sub> E <sub>23</sub>	$1.0 \times 10^{-4}$	40	>90.0

<sup>a</sup>Critical micelle concentration in water at 25.0° C.    <sup>b</sup>Micellar aggregation number, i.e. number of monomer surfactant molecules per micelle assembly.

<sup>c</sup>Cloud point temperature of a 1.0%(w/v) aqueous solution of the surfactant. Data experimentally determined or taken from (Hinze 1987 or DeGiorgio 1985).

solubility can easily be increased to the 10 millimolar range by the presence of micelles (Almgren, Grieser and Thomas 1979). The amount of solute solubilized and bound to the micellar aggregate in an aqueous solution is typically proportional to the surfactant concentration up to a limiting value.

In view of their superior solubilizing power, the addition of a known volume of a surfactant micellar-containing solution to either a given volume of an aqueous sample solution or a given mass of a solid sample provides micelles capable of binding and concentrating (in the former) or desorbing and then binding (in the latter) in the micellar entity the organic species which was originally present in the aqueous or solid sample. For the extraction technique for solids, an aqueous concentrated neutral surfactant micellar solution is merely contacted with or passed through the solid sample containing the organic component(s). The organic solute(s) present are desorbed and solubilized into the micelles in the bulk solution which then are further enriched (as will be described shortly) by the phase separation behavior of the surfactant solution. The desorption process is thought to be similar to the molecular mechanism reported for solubilization of water-insoluble solids by micellar solutions, which involves direct micelle diffusion to and from the surfactant-modified solid surface, in series with interfacial steps including adsorption and desorption of the micellar-organic solute species (Chan, Evans and Cussler 1976; Shaeiwitz 1987).

A significant advantage of this bulk micellar extraction technique is that once the initial 'extraction' from the solid matrix has been performed, the organic component(s) now present in the extractant micellar solution can be further enriched and preconcentrated prior to final quantitation or

workup (as can be any organic species originally present in an aqueous borne sample to which a small amount of a concentrated surfactant micellar solution has been added). This preconcentration is made possible by the phase separation ability of micellar solutions (DeGiorgio 1985; Nilsson, Lindman and Laughlin 1984; Attwood and Florence 1983). Aqueous solutions of neutral surfactant micellar compositions can exhibit so-called critical phenomena and clouding upon temperature alteration. That is, upon increasing the temperature of such isotropic aqueous micellar solutions, a critical temperature is eventually reached at which the aqueous solution suddenly becomes turbid (cloud point) due to the diminished solubility of the surfactant micelles present in the bulk water. After some time interval (which can be speeded up by centrifugation), demixing into two transparent liquid phases occurs (i.e. formation of a wet surfactant-rich micellar phase in equilibrium with almost pure water with some surfactant molecules). Any organic species present which can bind and partition to the micellar entity will be extracted into and thus concentrated in the small volume element of the surfactant-rich micellar phase. This property forms the basis of the surfactant micelle phase separation or cloud point extraction technique which is schematically depicted in Figure 2.

A plot of the data of the temperature required for clouding vs. surfactant concentration typically exhibits a minimum in the case of nonionic surfactants (or maximum in the case of zwitterionics) in its coexistence curve, with the temperature and surfactant concentration at which the minimum (or maximum) occurs being referred to as the critical concentration and temperature, respectively (Figure 3). This type of behavior is exhibited by nonionic surfactants, such as those given in Table 1, as well as others not shown, i.e. nonionic polymers, n-alkylsulfinyl-

Figure 2. Simplified schematic representation of the proposed cloud point extraction scheme using a nonionic surfactant micellar system.

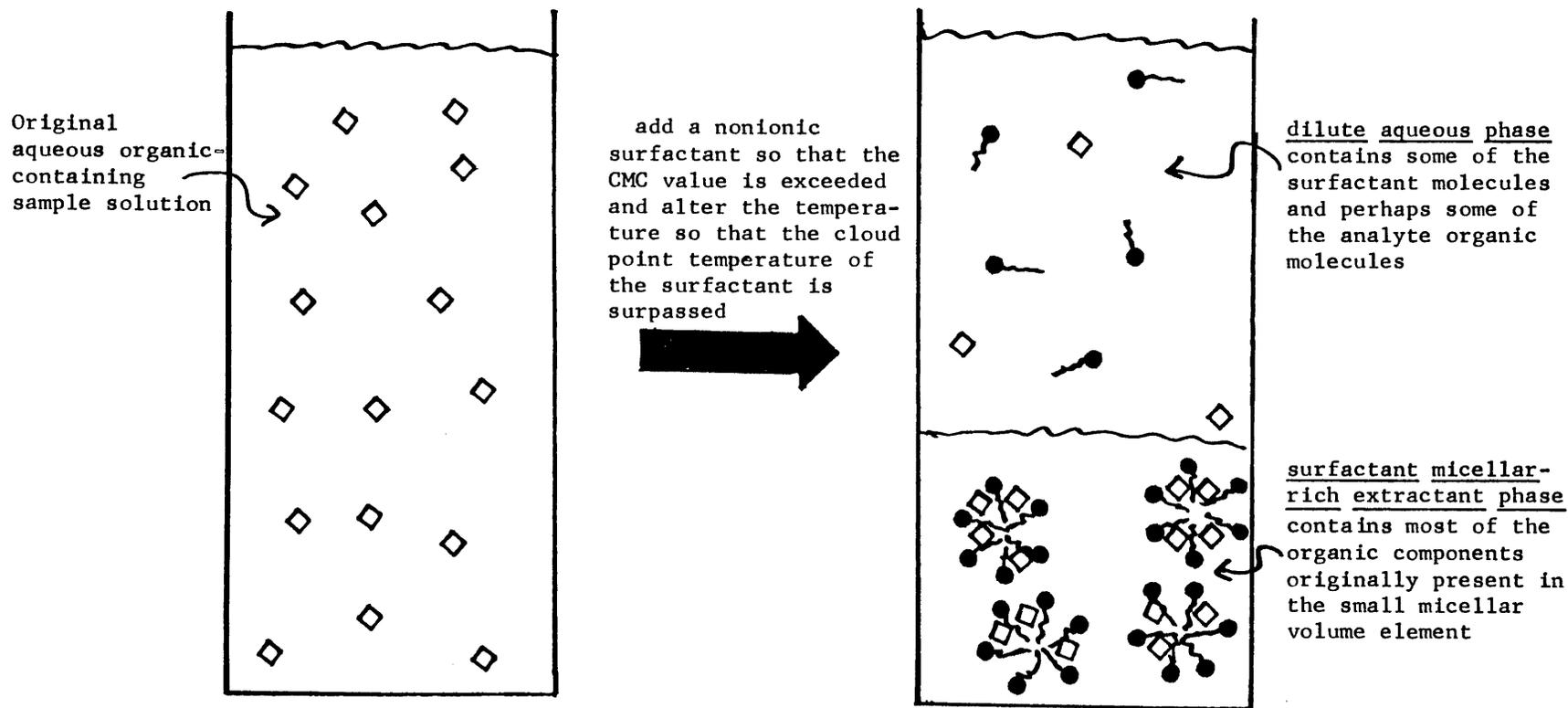
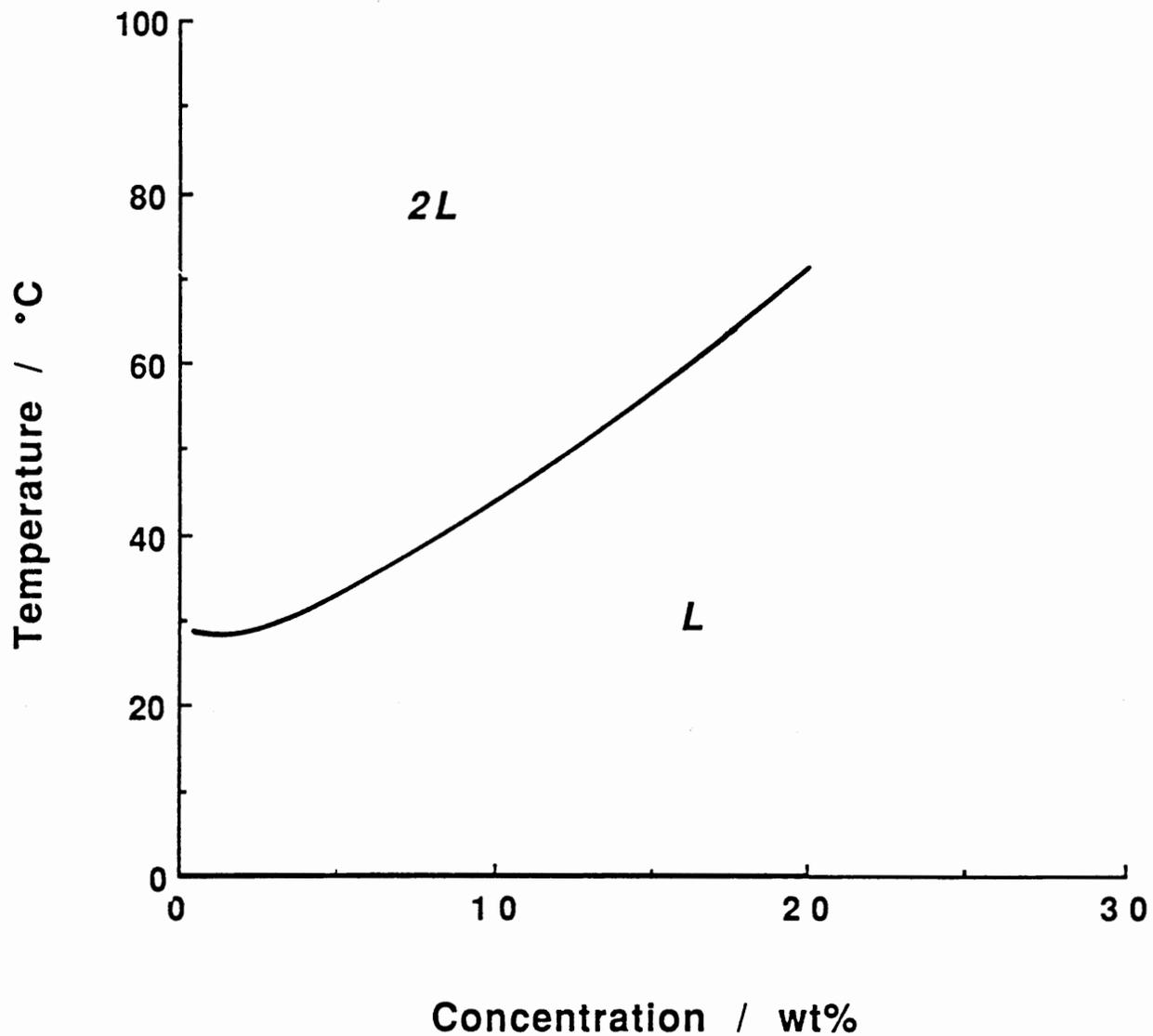


Figure 3. Typical phase diagram of an aqueous nonionic surfactant solution: L refers to the single isotropic solution region whereas 2L indicates the region where two isotropic phases co-exist.



alcohols, hydroxymethyl or ethyl celluloses, dimethylalkylphosphine oxides, or most commonly, alkyl (or aryl) polyoxyethylene ethers (general classes of Tweens, Spans, Igepals, Tritons, Brijs, etc.). Likewise, certain zwitterionic surfactant solutions can also exhibit critical behavior in which an upper rather than lower consolute boundary is present (Nilsson, Lindman and Laughlin 1984; Saitoh and Hinze 1991).

Previously, metal ions (as metal chelate complexes) have been extracted and enriched from aqueous media using such a cloud point extraction approach with nonionic surfactants (Watanabe 1982). Extraction efficiencies in excess of 98% for such metal ion extractions were achieved with enrichment factors in the range of 45-200. In addition to metal ion enrichments, this type of micellar cloud point extraction approach has been reported to be useful for the separation of hydrophobic from hydrophilic proteins both originally present in an aqueous solution along with a preconcentration of the former proteins (Bordier 1981).

## EXPERIMENTAL SECTION

### Instrumentation

The liquid chromatograph (Waters Associates, Milford, MA) consisted of two Model 510 pumps, U6K injector, Model 680 controller, and Model 481 or 484 Lambda-Max LC spectrophotometric detector (14 uL cell, 1-cm pathlength). The detector response was monitored with a Fisher Recordall Series 5000 strip chart recorder. The stainless steel columns utilized--either 4.6 mm x 10 cm (Advanced Separation Technologies, Whippany, NJ) or 4.6 cm x 25 cm (IBM)--were packed with 5 micron C-18 spherical material. Unless otherwise indicated, the mobile phase flow rate was 1.00 ml/min at room temperature.

The gas chromatographic system consisted of a basic Hewlett Packard 5890A gas chromatograph equipped with flame ionization and thermal

conductivity detectors and a 3392 A integrator. Either a 10 m x 0.25 mm Chiraldex (betacyclodextrin permethylated hydroxypropyl) GC capillary column (Advanced Separation Technologies, Whippany, NJ) or stainless steel packed column were utilized. The carrier gas was helium. It is important to note that one must use a precolumn packed with C-18 or similar material in front of the analytical column in order to protect the analytical column from becoming coated with surfactant. Such precolumns for GC had previously been described in the literature in work relating to the analysis of lipid extracts (Hopper 1987).

Spectral measurements were made on a Varian Cary 219 spectrophotometer while an Aminco-Bowman spectrofluorimeter was employed for all luminescence measurements. In all cases, 1-cm pathlength quartz cells were utilized. A Corning Model 135 pH/ion meter was used for all pH measurements.

#### Materials

The nonionic surfactants utilized in this work (Table 1) were all commercially available products and obtained from either Aldrich (Milwaukee, WI) or Sigma (St. Louis, MO) Chemical Companies. The materials were utilized as received without any further purification. The zwitterionic surfactants, C9-APSO<sub>4</sub> and C10-APSO<sub>4</sub>, were prepared by mixing the appropriate alkyldimethylamine with trimethylene sulfate in dry acetone and heating gently as reported in the literature (Nilsson, Lindman and Laughlin 1984). The phenolic, aniline, and polycyclic aromatic hydrocarbon test solutes were obtained from Aldrich, Sigma, and/or Fisher Scientific (Raleigh, NC) Companies. In all cases, the stated purities were > 97%. A premium standard coal sample (200 mesh) was kindly provided by Professor Fawzy S. Sadek (Winston-Salem State University, Winston-Salem, NC). Certified reference spiked soil materials (PCBs in soil) were obtained from

Environmental Resource Associates (Arvada, CO). Standard acid (HCl) or base (NaOH) solutions utilized for pH adjustments were obtained from Fisher Scientific Company. All other reagents/solvents used were of the best commercial grade available.

### Procedures

**Cloud Point, Phase Diagram, and Phase Ratio Determinations.** The phase behavior (cloud point) for each surfactant system under different experimental conditions was determined by observing the temperature required for the onset of turbidity upon heating or clarification upon subsequent cooling of an aqueous solution of the surfactant in a small test tube that was placed in a controlled temperature Haake (Berlin, Germany) water or aluminum block dri-bath. Typically, the cloud points reported were the average of three separate determinations which were in good agreement.

The volumes of the respective surfactant-rich and aqueous phases upon phase separation were measured using calibrated glass tubes. In these determinations, the surfactant solution was placed into a small test or NMR tube and the tube allowed to sit in a constant temperature bath for specified periods of time prior to measurement of the respective phase volumes.

**Micellar Cloud Point Extraction of Organics from Aqueous Samples.** The typical procedure for the batch extraction optimization experiments consisted of preparation of an aqueous 1.0% (w/v) solution of the surfactant under consideration (at appropriate pH or ionic strength conditions). To an aliquot (5.00 or 10.00 ml) of this surfactant micellar solution in a test or centrifuge tube was added the appropriate volume of a concentrated stock solution of the organic analyte so that the final analyte concentration was  $5 \times 10^{-5}$  M. After shaking to mix, this solution was placed in a

constant-temperature bath which was adjusted to a temperature above the cloud point of the surfactant. The solutions were allowed to stand in the constant temperature bath for a specified time until the layers separated (gravity procedure) or placed in a centrifuge and centrifuged at 9,000 rpm for a specified time to speed-up the phase separation (centrifugation procedure). After phase separation was achieved, an aliquot of each of the separated phases was taken and analyzed for its organic analyte content. Typically, the analysis was performed by UV spectrophotometry, fluorescence, and/or high performance liquid chromatography (HPLC). In a few instances, gas chromatographic (GC) analysis was performed. Solute absorption or fluorescence was monitored at specified wavelengths and the concentration in the respective separated phases was determined from standard calibration curves.

It might be mentioned that for the extraction of organics from a real-world aqueous sample, the following procedure would be followed: First, to a given volume of the organic-containing water sample would be added a small aliquot of concentrated standard surfactant solution so that with respect to the total volume, the critical micelle concentration of the surfactant employed would be exceeded. The rest of the procedure would be as outlined above except that the volumes required would be dependent upon the initial organic solute present. That is, if very low levels of an organic pollutant were present, then a larger initial volume (i.e. 50 or 100 ml) of the aqueous solution to be extracted would be required.

The organic solute partitioning from the aqueous to the surfactant micellar-rich phase in such batch extractions can be described by the typical distribution coefficient,

$$D = [\text{solute}]_m / [\text{solute}]_w, \quad (\text{eq. 1}),$$

where  $[\text{solute}]_m$  is the final organic solute concentration in the surfactant micellar-rich phase and  $[\text{solute}]_w$  is the same solute's final concentration in the separated bulk aqueous phase. Various means can be utilized to describe the extent of the extraction process. The extraction factor is

$$E = D (V_m / V_w), \quad (\text{eq. 2}),$$

where  $D$  is the previously defined partition coefficient and  $V_m/V_w$  is the volume ratio, i.e.  $V_m$  equals the volume of the surfactant micellar-rich extractant phase and  $V_w$  represents the volume of the bulk aqueous phase.

The fraction of organic solute extracted is given by

$$p = D / [D + (V_w / V_m)] \quad \text{or} \quad = E / (1 + E). \quad (\text{eq. 3}).$$

The percent extracted, % Ext, merely equals to 100p. In most of the optimization experiments, the relative degree of extraction was calculated and utilized to monitor the effect of changes in the experimental procedure upon the cloud point extraction process. The degree of extraction was calculated as 100 times the difference in the concentration of the organic solute in the aqueous phase before and after the extraction divided by its initial concentration or

$$\text{Degree of extraction} = 100 ([\text{solute}]_i - [\text{solute}]_f) / [\text{solute}]_i. \quad (\text{eq. 4}).$$

**Extraction of Organics from Soil Matrices.** The organic-containing soil samples were either purchased commercially or prepared in-house as described in the literature (Coover, Sims and Douchette 1987). The spiked soil samples were prepared in a 125 mL Erlenmeyer flask by adding 5 ml of a standard concentrated stock solution (dissolved in a volatile solvent such as methylene chloride or acetone) of the polyaromatic hydrocarbon under consideration to 10 or 20 grams of the soil. After mixing the PAH solution with the soil, the solvent was allowed to evaporate prior to subjecting the sample to the cloud point extraction.

The batch cloud point extractions of the soil samples were conducted as follows. First, 5.0000 (or 10.0000) grams of the organic contaminated soil samples were contacted with 100.0 (or 200.0) ml of an aqueous nonionic surfactant (1.00% or 2.00% w/v) solution in a large centrifuge tube. These solutions were initially agitated by manual shaking and then by rotation using a Roto Torque rotator at room temperature for 12 hours, allowed to sit undisturbed for 6 hours and then centrifuged. An aliquot of the clear solution above the soil was then taken and analyzed for its organic solute content prior to being subjected to the cloud point extraction as previously described (micellar cloud point extraction of organics from aqueous solutions section). The solubilization solution or cloud point extracts were analyzed by reversed phase LC using a C-18 stationary phase column and acetonitrile - water mobile phase with detection at 254 nm. Since the original organic PAH concentration was known, the percent recovery for the initial solubilization step, cloud point and extraction step, and overall solubilization/extraction process could be calculated in the usual manner.

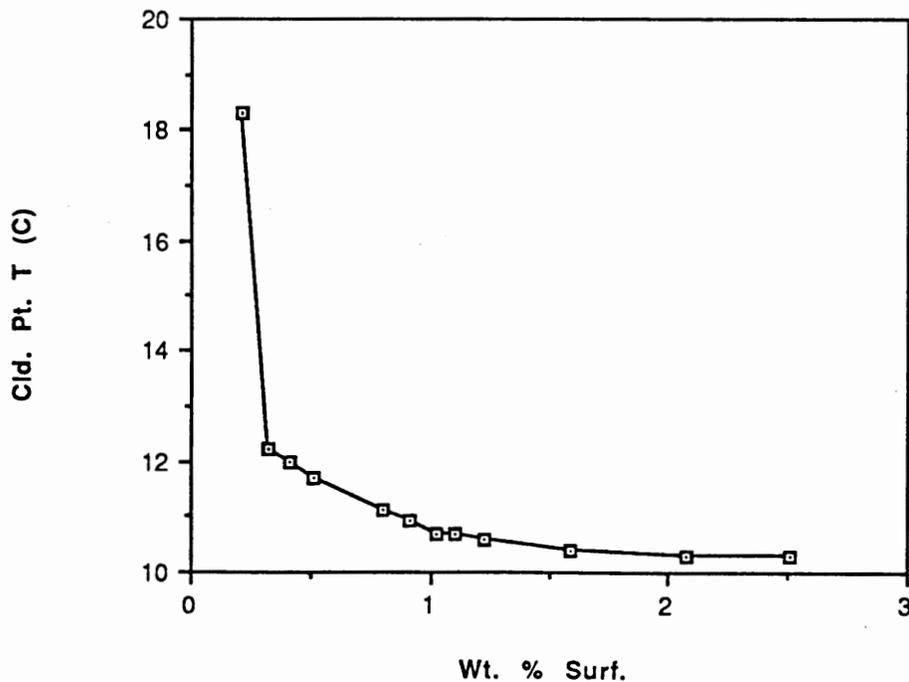
**Coal Extraction.** A 0.05 gram portion of the premium coal sample was poured into 10.00 ml of the appropriate aqueous surfactant solution, heated to a specified temperature for 5 (or 10) minutes and stirred for the given time interval. Following filtration to remove the solid coal, the solution was subjected to the phase separation extraction procedure and a 20 microliter aliquot of the surfactant-rich extractant phase was taken and injected for HPLC analysis. In order to identify the component(s) extracted, pure standards of different polycyclic aromatic hydrocarbons were also injected and their retention times determined under identical chromatographic conditions (Saitoh and Hinze 1991).

## RESULTS AND DISCUSSION

### Cloud Point Behavior

Table 1 summarizes cloud point temperatures for some of the common neutral surfactant systems examined in this work. The cloud point temperatures are in good agreement with available literature values (DeGiorgio 1985; Hinze 1987; Binana-Limbelle, et al 1991). As can be seen, the cloud points can vary from well below room temperature ( $4.5^{\circ}\text{C}$ ) to near  $100^{\circ}\text{C}$  depending upon the specific nonionic surfactant employed. Figure 4 illustrates the typical profile observed for the dependence of the cloud point temperature of the nonionic surfactant  $\text{C}_8\text{E}_3$  as a function of the solution surfactant concentration.

Figure 4. Dependence of the cloud point temperature of  $\text{C}_8\text{E}_3$  as a function of the surfactant concentration.



It is important to stress that the presence of additives (organic species, salts, organic solvents, ionic surfactants) can alter (i.e. either lower or raise) these cloud point temperatures. For example, as shown in Table 2, the addition of other surfactants typically raises the cloud point of nonionic surfactants. According to the literature, added inorganic salts can either lower or raise the cloud point (see Tokiwa and Matsumoto 1975; Attwood and Florence 1983; Binana-Limbelle, et al 1991). Thus, the preconcentration of thermally labile organic species using this approach would pose no problem since one could select a surfactant system already itself possessing (or manipulate the experimental conditions so that) a desired low cloud point temperature is achieved. In many instance, the presence of polar organic solutes can result in a lowering of the cloud point temperature (refer to Table 2, data for  $C_{12}E_6$  in the presence of 4-hydroxybenzoic acid methyl ester). Other phenolic compounds (phenol, cresols, xylenols) have been reported to give similar results (Donbrow and Azaz 1976). Hence, the presence of the organic solute(s) to be extracted using this procedure can alter the normal cloud point temperature of the surfactant.

#### Factors Influencing the Cloud Point Extraction of Organic Test Solutes from Aqueous Solutions

A series of experiments was performed in order to determine which factors influence the extent of extraction of the model test solutes, phenol (P) [ $pK_a$  9.92, water solubility 0.71 M] and 4-chlorophenol (4-CP) [ $pK_a$  9.37, sparingly soluble in water], from an aqueous solution using the cloud point extraction procedure. These two solutes were selected for study because they are polar and exhibit some solubility in water. Thus, they do not completely partition to the micellar phase and one can determine the

TABLE 2. Additive Effects upon Cloud Point Temperature of Some Nonionic Surfactant Systems

Surfactant	Additive	Cloud Point, °C
Brij-30 (C <sub>12</sub> E <sub>4</sub> ) (1.1 % w/v)	none	ca. 1.6
	+ 3 mM CTAC <sup>a</sup>	> 85.0
	+ 5 mM SB-12 <sup>b</sup>	4 - 7
	+ 1 mM NaLS <sup>c</sup>	79.0
PONPE-7.5 (4.0 % w/v)	none	19.0
	+ 3 mM CTAC	51.0
	+ 1 mM NaLS	44.5
	+ 3 mM Brij-35 (C <sub>12</sub> E <sub>23</sub> )	27.0
C <sub>12</sub> E <sub>6</sub> (5.0 mM)	none	52.6
	+ 1 mM methylparaben <sup>d</sup>	48.0
	+ 3 mM "	43.6
	+ 6 mM "	36.3

<sup>a</sup>Refers to the surfactant, hexadecyltrimethylammonium chloride.

<sup>b</sup>Refers to the surfactant, dodecyldimethylammonio propane sulfonate.

<sup>c</sup>Refers to the surfactant, sodium dodecylsulfate.

<sup>d</sup>Refers to 4-hydroxybenzoic acid methyl ester.

dependence of the extraction parameters upon changes in the experimental conditions in order to gauge the important factors influencing the extraction process. Our preliminary screening results had indicated that hydrophobic solutes, such as anthracene, pyrene, benzopyrenes, etc., are not good model solutes for such optimization studies because they completely partition and bind to the surfactant micellar phase. Thus regardless of the exact extraction conditions, nearly 100% extraction efficiencies are often observed for such hydrophobic polycyclic aromatic hydrocarbons.

The experimental factors examined included solution pH, ionic strength and temperature at which the extraction is carried out, the nature (i.e. surfactant type, chain length, hydrophobicity, etc.) and concentration of the surfactant present, and timing of the extraction and centrifugation

steps among others.

First, the relative effect of the method utilized in order to achieve the phase separation (gravity or centrifugation) in the extraction procedure was examined. The results (Table 3) based upon use of two nonionic surfactants indicate that the extent of extraction did depend upon the method of phase separation employed. However, there are no general trends evident as the gravity method proved best if the surfactant Triton CF-21 was utilized in the cloud point extraction while the centrifugation method proved best in the case of Nonidet P-40 as surfactant. Thus, in subsequent studies, the centrifugation procedure was utilized to facilitate the phase separation since it is much more rapid and convenient compared to the gravity approach. The latter gravity approach would probably be of use in applications for the purification of large volumes of organic-contaminated water.

A brief study was conducted to determine the effect of the time spent at the separation temperature (i.e. the equilibration time prior to centrifugation and analysis of the two separated phases) upon the extraction

TABLE 3. Estimate of the Cloud Point Extraction Effectiveness as a Function of the Method utilized to achieve the Phase Separation

Surfactant	Method	Extent of Extraction <sup>a</sup>	
		Phenol	4-Chlorophenol
Triton CF-21	Gravity	26.7%	53.6%
	Centrifugation	15.2%	40.1%
Nonidet P-40	Gravity	3.0%	7.1%
	Centrifugation	5.3%	17.3%

<sup>a</sup>Conditions: Gravity phase separation conducted at 50°C, centrifugation separation conducted at 60-65°C with 5-minute bath and centrifugation times.

parameters. Results obtained for equilibration times of 1, 5, and 10 minutes for the two surfactants mentioned above revealed no appreciable differences within experimental error in the degree of extraction of phenol or 4-chlorophenol. Thus, equilibration times in the range of 1 to 5 minutes appear to be adequate for the extraction of these phenolic compounds. Table 4 presents data on the effect of the centrifugation time upon the extraction parameters. As can be seen, both the concentration factor and extent of extraction generally increase as the centrifugation time is increased from 1 to 10 minutes. These results are probably the result of the fact that longer centrifugation time results in a smaller, more concentrated hydrophobic surfactant micellar-rich extractant phase. Thus, a centrifugation time of 5.0 minutes is recommended for such cloud point separations.

Next, the effect of nonionic surfactant structure upon the extraction efficiency and relative concentration factor were determined. Table 5 summarizes the data for five randomly selected nonionic surfactants possessing an aromatic ring. As can be seen, the use of either Triton CF-10 or CF-21 resulted in the most efficient extractions using the proposed cloud point extraction procedure. Although these aromatic nonionic surfactants yielded fairly good extraction parameters, a problem with their general utilization in separation science stems from the fact that the absorption of their aromatic moiety limits or precludes the use of the popular 254 nm detection wavelength for monitoring the extracted analyte concentration. In addition, luminescence detection modes could also be unfavorably impacted due to quenching by the aromatic group. Thus, a study was conducted in order to evaluate the general effectiveness of aliphatic nonionic surfactants for the cloud point procedure since their use would obviate this difficulty

TABLE 4. Dependence of the Cloud Point Extraction Efficiency upon the Centrifugation Time Step in the Procedure<sup>a</sup>

Surf.	Time(min)	Conc. Factor <sup>b</sup>		Extraction Extent (%)	
		phenol	4-Cl-phen	phenol	4-Cl-phen
CF-21	1.0	33.33	75.13	15.39	58.28
	5.0	32.10	81.64	32.76	79.32
	10.0	35.96	83.58	-	-
NP-40	1.0	6.64	17.49	-	-
	5.0	7.68	21.09	35.11	67.47
	10.0	8.94	23.14	-	-

<sup>a</sup>Conditions: Equilibration time of 1 minute in a 60-65° C constant temperature bath prior to centrifugation at that same temperature.

<sup>b</sup>Conc. factor refers to the relative concentration factor as calculated by taking the ratio of the [solute] in the surfactant phase after extraction to [solute] in the aqueous solution prior to extraction.

TABLE 5. Effect of Different Alkylaryl Nonionic Surfactants upon the Cloud Point Extraction Parameters

Surfactant	% Concentration		Extraction Extent (%)	
	phenol	4-chlorophenol	phenol	4-chlorophenol
Triton X-114	19.6	46.4	21.6	48.1
POENPE - 7.5	15.3	42.3	17.7	44.0
Nonidet P-40	8.5	24.3	11.3	27.0
Triton CF-10	54.4	59.9	54.7	60.5
Triton CF-21	31.5	64.1	32.1	64.4

with subsequent spectral detection modes.

The effect of variation of the alkyl chain of a homologous series of nonionic surfactants upon the extraction parameters (extent of the extraction and relative concentration factor) were evaluated. The results are presented in Figure 5. It is observed that the extent of extraction (Fig. 5A) slightly increased to a maximum value and then decreased with an increase in the number of methylene groups present. However, there was a dramatic decrease in the relative concentration factor (Fig. 5B) as the surfactant became progressively more hydrophobic. This latter result is thought to be due to the fact that the phase ratio (i.e. ratio of the volume of the surfactant micellar-rich extractant phase to that of the bulk aqueous phase) becomes larger with increases in the number of methylene groups present in the surfactant. For example, this phase ratio increases from 0.0250 for  $C_{10}E_5$  to 0.0382 for  $C_{14}E_5$ .

The influence of variation of the number of ethylene oxide units in the surfactant molecule was next examined. The results, presented in Figure 6, show that both the extent of extraction (Fig. 6A) and concentration factor (Fig. 6B) decreased as the number of ethylene oxide units was increased. Taken together, the results from Figures 5 and 6 suggest that a nonionic surfactant possessing a relatively short alkyl chain length and small number of ethylene oxide units might prove superior for the proposed cloud point extraction technique. Thus, extraction parameters were determined using the nonionic surfactants,  $C_8E_3$  (cloud point  $10.6^{\circ}C$ ) and  $C_7E_3$  (cloud point  $27.6^{\circ}C$ ), in the extraction procedure. The results are presented in Table 6. As can be seen, the extraction parameters obtained were essentially comparable to those obtained for the alkylaromatic nonionic surfactants (Table 5). As previously noted, although use of some of the Triton CF

Figure 5. Dependence of the Extent of Extraction (A) and Relative Concentration Factor (B) of Phenol and 4-Chlorophenol as a Function of the Alkyl Chain Length of the Surfactant,  $C_xH_{2x+1}-(OCH_2CH_2)_5-OH$ , Utilized in the Cloud Point Extraction.

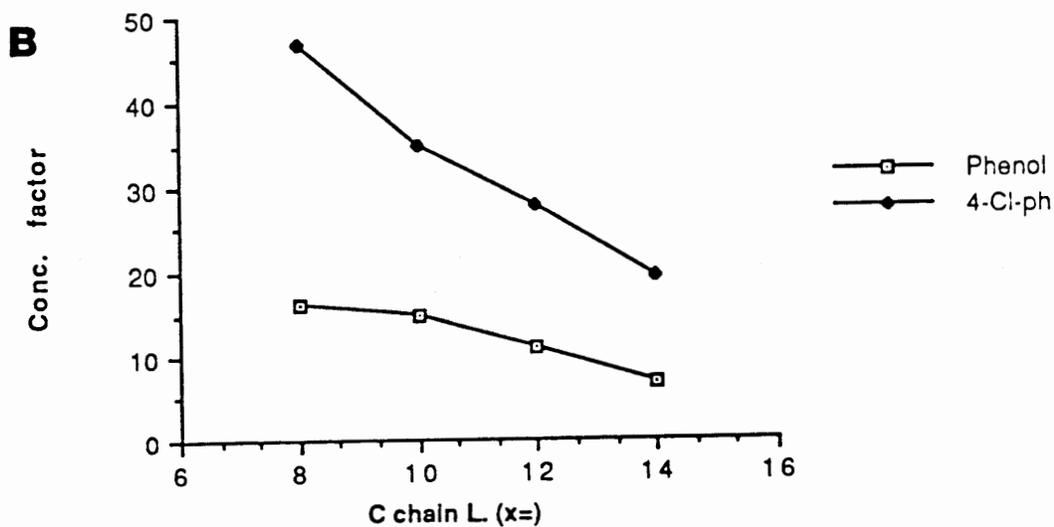
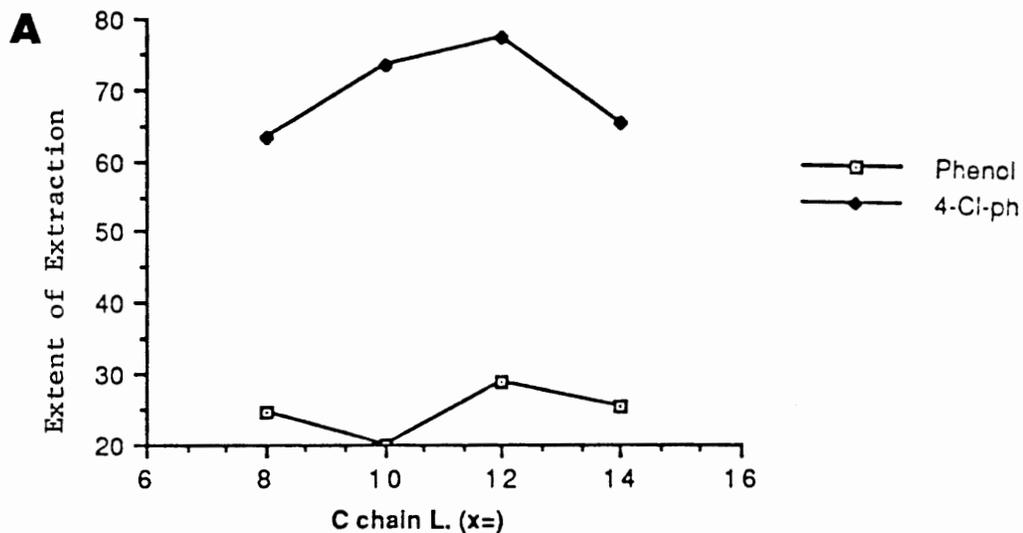
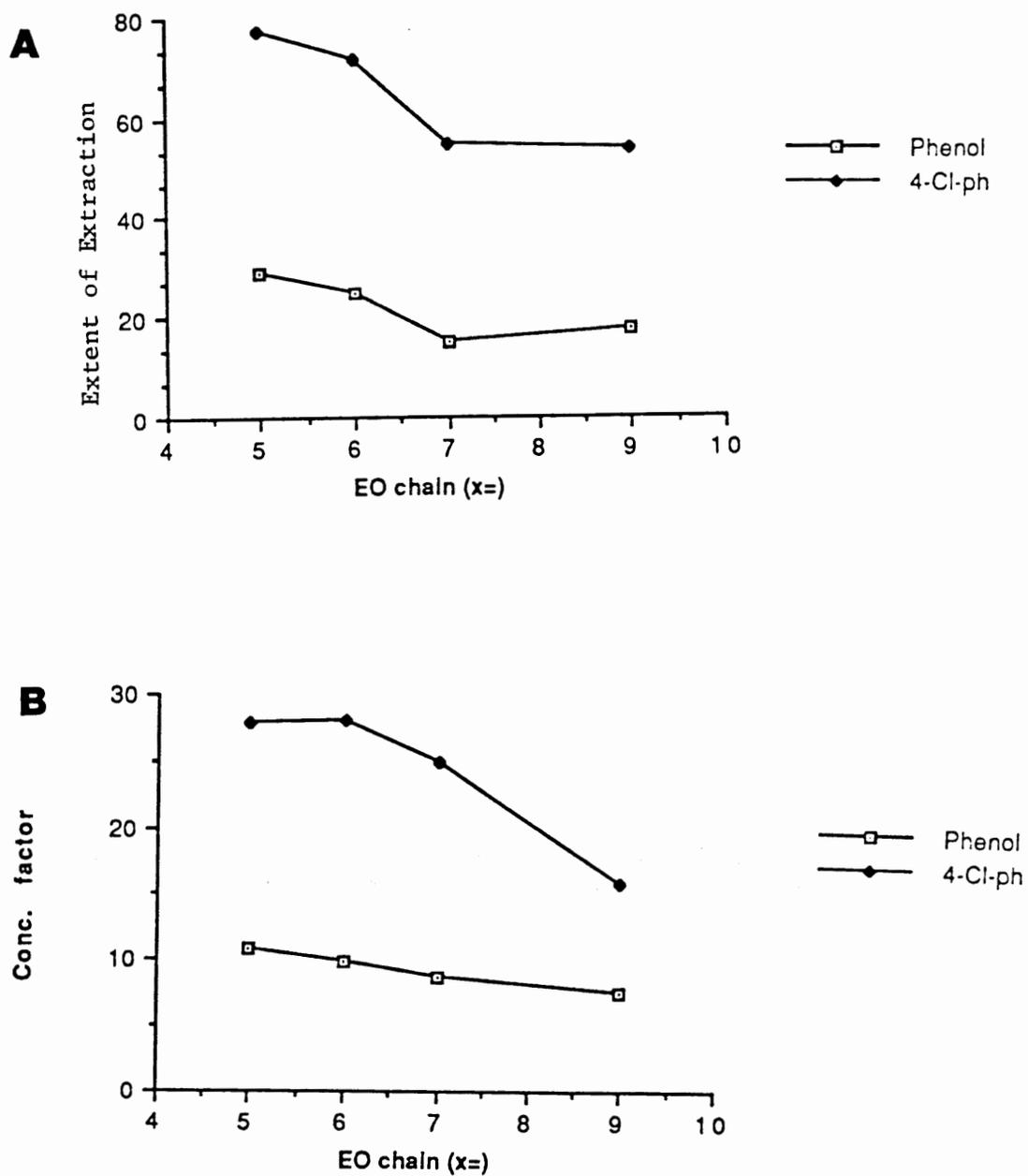


Figure 6. Dependence of the Extent of Extraction (A) and Relative Concentration Factor (B) of Phenol and 4-Chlorophenol as a Function of the Number of Ethylene Oxide Segments of the Nonionic Surfactant,  $C_{12}H_{25}-(OCH_2CH_2)_x-OH$ , Utilized in the Cloud Point Extraction.



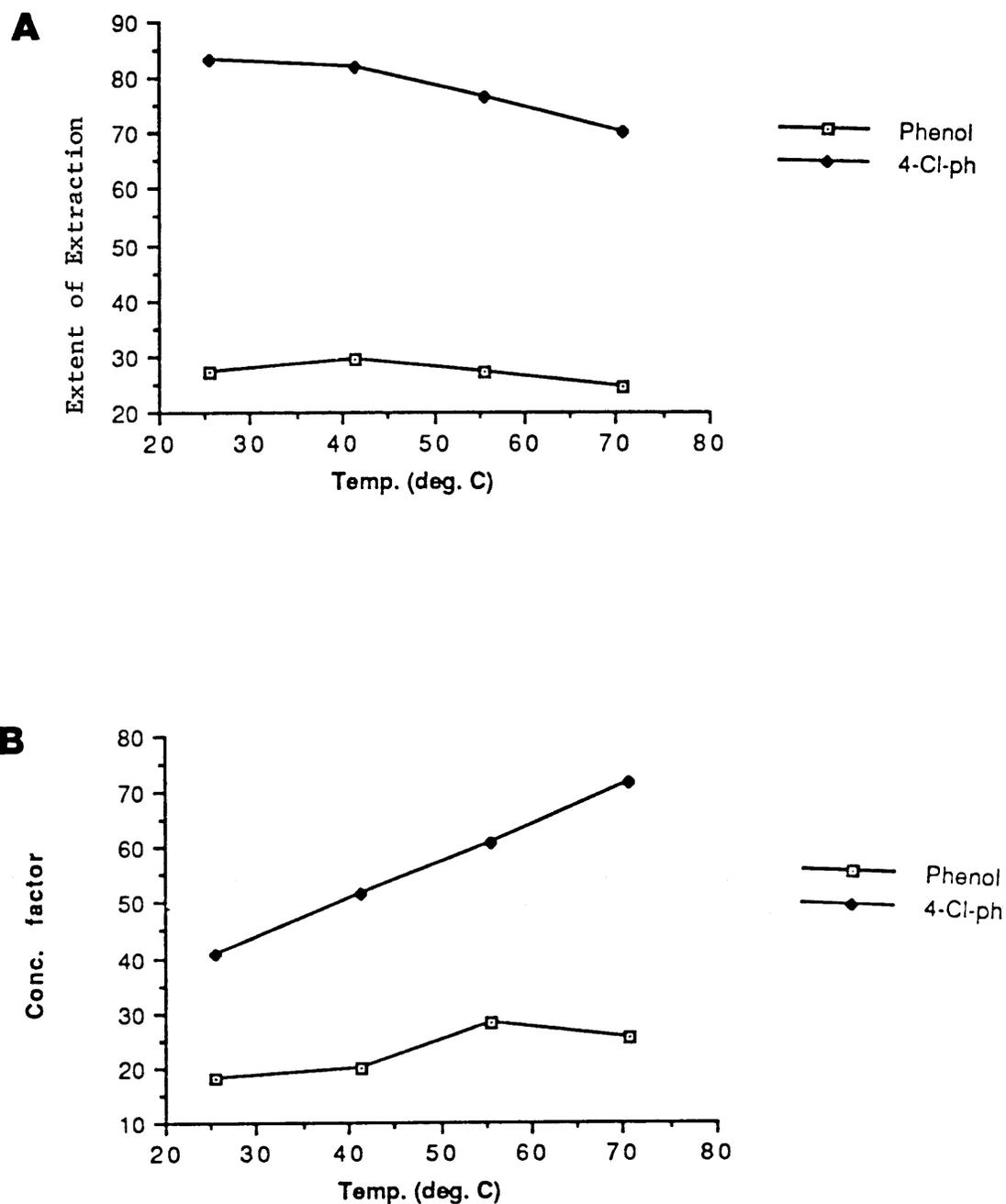
surfactants resulted in somewhat better extractions, their general use would limit ultraviolet and fluorescence detection modes since their aromatic moiety would absorb/luminesce and thus interfere with the detection/quantitation of the extracted organic compound(s) of interest.

TABLE 6. Cloud Point Extraction Efficiencies Obtained Via Use of  $C_8E_3$  and  $C_7E_3$  as the Nonionic Surfactants

Surfactant	Conc. Factor		% Concentration	
	phenol	4-chlorophenol	phenol	4-chlorophenol
$C_8EO_3$	$20.14 \pm 0.60$	$44.73 \pm 0.06$	$36.05 \pm 0.68$	$86.89 \pm 0.36$
$C_7EO_3$	$25.01 \pm 1.78$	$91.62 \pm 1.16$	$11.74 \pm 2.42$	$70.93 \pm 0.90$

The influence of the extraction temperature upon the extraction parameters was also investigated. The results are presented in Figure 7. While the degree of extraction (Fig. 7A) slightly decreased with temperature, the relative concentration factor (Fig. 7B) increased. These findings are in general agreement with a preliminary literature report (Gullickson, Scamehorn, and Harwell 1989) in which the influence of the extraction temperature upon the gravity cloud point extraction of hexanol or 4-t-butylphenol from water using Igepal CO-620 surfactant was examined. The increase in relative concentration factor could arise as a consequence of the fact that the phase volume of the surfactant micellar-rich extractant phase decreases with increased temperature. For the phenol extraction (Fig. 7B), there may be an optimum extraction temperature around  $55^{\circ}C$ . It had been previously been suggested that in some extractions there may be such an optimum temperature for the cloud point separation (Gullickson, Scamehorn and Harwell 1989).

Figure 7. Dependence of the Extent of Extraction (A) and Relative Concentration Factor (B) of Phenol and 4-Chlorophenol as a Function of the Extraction Temperature for the Cloud Point Extraction using  $C_8E_3$  as Surfactant.



A brief study to examine the effect of ionic strength upon the cloud point extraction technique revealed that within experimental error, there was no difference in the extraction parameters obtained at 0.00 and 0.10 M ionic strengths (Table 7). While the ionic strength does not seem to influence the extent of extraction, it does influence the cloud point temperature as has been reported in the literature. Also, the addition of an inert salt was found to be advantageous in the cloud point extraction of metal chelates since it increased the density of the bulk aqueous phase which facilitated the phase separation process (Watanabe 1982; Pramauro 1990). Thus, based upon such literature reports, the recommended procedure for the cloud point extraction of organics probably should include from 0.05 to 0.10 M added salt for this latter purpose.

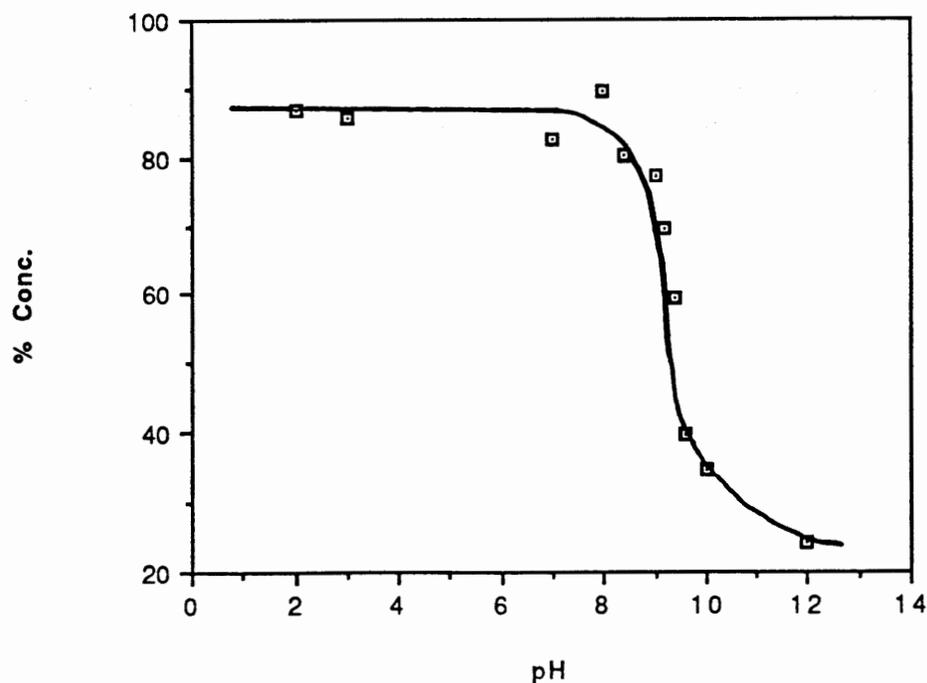
TABLE 7. Effect of Ionic Strength (Adjusted with NaCl) upon the Cloud Point Extraction Parameters using  $C_8E_3$  as the Nonionic Surfactant

Ionic strength	Conc. factor		% Concentration	
	phenol	4-chlorophenol	phenol	4-chlorophenol
0	26.12 ± 1.01	67.64 ± 0.15	13.50 ± 2.12	79.52 ± 0.26
0.10	25.71 ± 0.86	74.35 ± 4.77	15.10 ± 3.43	78.54 ± 0.97

It is well known from the micellar literature that for ionizable solutes, the charge state of the solute can greatly influence its extent of binding to a micellar assembly (Fendler 1982). The distribution of metal chelates in the two phases separated from the micellar solution of nonionic surfactants has been found to vary with the solution pH (see for instance, Watanabe et al 1987). Hence, it would be expected that the extraction parameters for the cloud point extraction of phenol would depend upon solution pH since it is a weak acid ( $pK_a$  9.92 in water alone). This is what

is observed in Figure 8 which presents the data for the pH profile for the cloud point extraction. The relative concentration factor remains essentially constant over the pH region 2 - 8 after which there is a drastic decrease in the amount of phenol extracted with further increases in the solution pH at which the extraction is conducted. This is due to the fact that phenol (ArOH) partitions and better binds nonionic surfactants than does the deprotonated phenolate anion (ArO<sup>-</sup>). Similar extraction vs. pH profiles are obtained for other phenolic compounds except that the pH values at which the extraction efficiency decreases are different due to the differences in their pK<sub>a</sub>'s. This means that one could engineer some selectivity into the extraction process by merely conducting the cloud point extraction at an appropriate pH value so that only one organic weak acid

Figure 8. Plot of the Dependence of the Relative Concentration Factor upon the Solution pH at which the Cloud Point Extraction is Conducted for 4-Chlorophenol as Analyte using C<sub>8</sub>E<sub>3</sub> as the Nonionic Surfactant.



species (out of several compounds originally present in the aqueous medium) is in its unionized state and thus preferentially extracted. In terms of practical extractions, the results mean that for a series of ionizable organic compounds of a particular family, the pH for the cloud point extraction should be such that all are in their neutral and not deprotonated forms. However, it should be mentioned that when using mixed surfactant systems, such as a cationic - nonionic surfactant combination, better extraction efficiency might result if the weak acid were in its anionic form due to the fact that the anionic conjugate base form would be electrostatically attracted to the cationic surfactant portion of the mixed surfactant micelle thus formed.

#### Some Practical Applications and Examples of Cloud Point Extractions

**Extraction of Organics from Aqueous Samples.** Table 8 summarizes data obtained in this work for the extraction of a mixture of chlorophenols as well as alkylbenzenes using the optimized cloud point extraction procedure with  $C_8E_3$  as the surfactant. As can be seen, good recoveries were obtained which are comparable to those reported in the literature for such compounds using a conventional organic solvent - aqueous extraction approach. In addition, Table 9 summarizes other data from our lab as well as that recently published in the literature concerning the removal and concentration of organic pollutants using the cloud point extraction technique. As can be observed in many instances, quantitative recoveries are possible for the indicated organic solutes. Likewise, other organic compounds should be amenable to similar concentration using the technique. For the more polar organic materials which are only partially removed, the use of mixed nonionic - ionic surfactant media may prove useful, as noted above.

TABLE 8. Summary of Data Concerning the Use of the Optimized Cloud Point Extraction Procedure for the Concentration of Organics from an Aqueous Solution

Organic Compounds Extracted	Surfactant System	% Extraction
4-Chlorophenol	1% C <sub>8</sub> E <sub>3</sub> /pH 3/40°C	88.3
2,4-Dichlorophenol		96.2
2,4,5-Trichlorophenol		97.8
2,3,5,6-Tetrachlorophenol		97.6
Pentachlorophenol		≥99.9
-----		
Benzene	1% C <sub>8</sub> E <sub>3</sub> /40° C	47.3
Toluene		77.1
p-Xylene		98.8
m-Xylene/Ethylbenzene		97.3
o-Xylene		99.5

TABLE 9. Summary of Data for the Cloud Point Extraction of Organic Species from Aqueous Sample Matrices

Organics Extracted	Surfactant System	% Recovery
<u>Phenolic Materials</u>		
Phenol and 4-Chlorophenol <sup>a</sup>	1% C <sub>8</sub> E <sub>3</sub> /40° C	30% / 80%
2,4-Dinitrophenol <sup>a</sup>	1% Triton X-100/68° C	87%
2,4,5-Tri-chloro, 2,3,4,5-tetra-chloro-, and pentachlorophenol <sup>b</sup>	0.5% C <sub>12</sub> E <sub>8</sub> + 0.5% C <sub>12</sub> E <sub>4.2</sub> pH 3.0 / 45° C	all 99.9+%
p-t-Butylphenol <sup>c</sup>	Igepal CA-520 / 40° C	97%
<u>Polycyclic Aromatic Hydrocarbons<sup>a</sup></u>		
Pyrene, Benzo[e]pyrene, Benzo[a]pyrene, Fluoranthene	Igepal CO-630 / 70° C	all 99.0+%
Fluoranthene	Triton X-100 / 65° C	ca. 80%
<u>PCB's:</u>		
3-Chlorobiphenyl, 3,3'-Dichlorobiphenyl <sup>b</sup>	0.5% C <sub>12</sub> E <sub>8</sub> + 0.5% C <sub>12</sub> E <sub>4.2</sub> pH 2.0 / 45° C	both 99%

<sup>a</sup>Data from this study. <sup>b</sup>Taken from (Pramauro 1990). <sup>c</sup>Taken from (Gullickson, Scamehorn, and Harwell 1989).

In addition, essentially quantitative extraction of a family of neutral solutes (i.e. pesticides) originally all present in a test mix solution was achieved. That is, a test mix of methoxychlor (present at a concentration of 50 picograms per microliter, pg/uL), endrin (40 pg/uL), endrin aldehyde (20 pg/uL), p-DDT (100 pg/uL), chloradane (20 pg/uL), lindane (10 pg/uL), aldrin (20 pg/uL), endosulfan (20 pg/uL), and chloropyrifos (30 pg/uL) was subjected to the cloud point extraction with a 1.2% (wt/v) solution of PONPE-7.5 conducted at 35°C and the two phases analyzed for their pesticide content. The GC analysis of the bulk aqueous phase remaining revealed no trace of any of the pesticides (at least at the detection limits of the electron capture detector employed) (Hinze et al 1990). The percent of these pesticide solutes extracted into the surfactant micellar-rich phase was greater than 99.9% for all solutes examined. Similar results have recently been reported (Pramauro 1990) for a similar cloud point extraction of some of these pesticides using a mixed nonionic surfactant (0.5% C<sub>12</sub>E<sub>8</sub> + 0.5% C<sub>12</sub>E<sub>4.2</sub>) system with the extraction conducted at 45.0°C.

**Extraction of Organics from Solid Matrices--Spiked Soil Samples.** Recently, the nonionic surfactant C10-12E7 has been reported to be useful for washing polychlorinated biphenyl from sandy soil materials (Abdul and Gibson 1991). In a batch cloud point extraction of commercially obtained PCBs in soil (Arochlor 1248 and 1254 samples) in which the mixed nonionic surfactants, PONPE-7.5 and Brij-35 (C<sub>12</sub>E<sub>23</sub>) were utilized, 88% of the PCBs was initially removed from the soil by solubilization in the mixed surfactant solution (this was prior to temperature alteration and its subjection to the cloud point extraction step). Of this 88%, approximately 81% subsequently was concentrated in the surfactant micellar-rich extractant phase upon the cloud point extraction step conducted at 45°C. Thus, the cloud point extraction

procedure not only effectively solubilizes and concentrates organics from solid samples, but also appears to offer a means to further the concentrated surfactant-enhanced wash solutions that have been utilized in such soil remediation process.

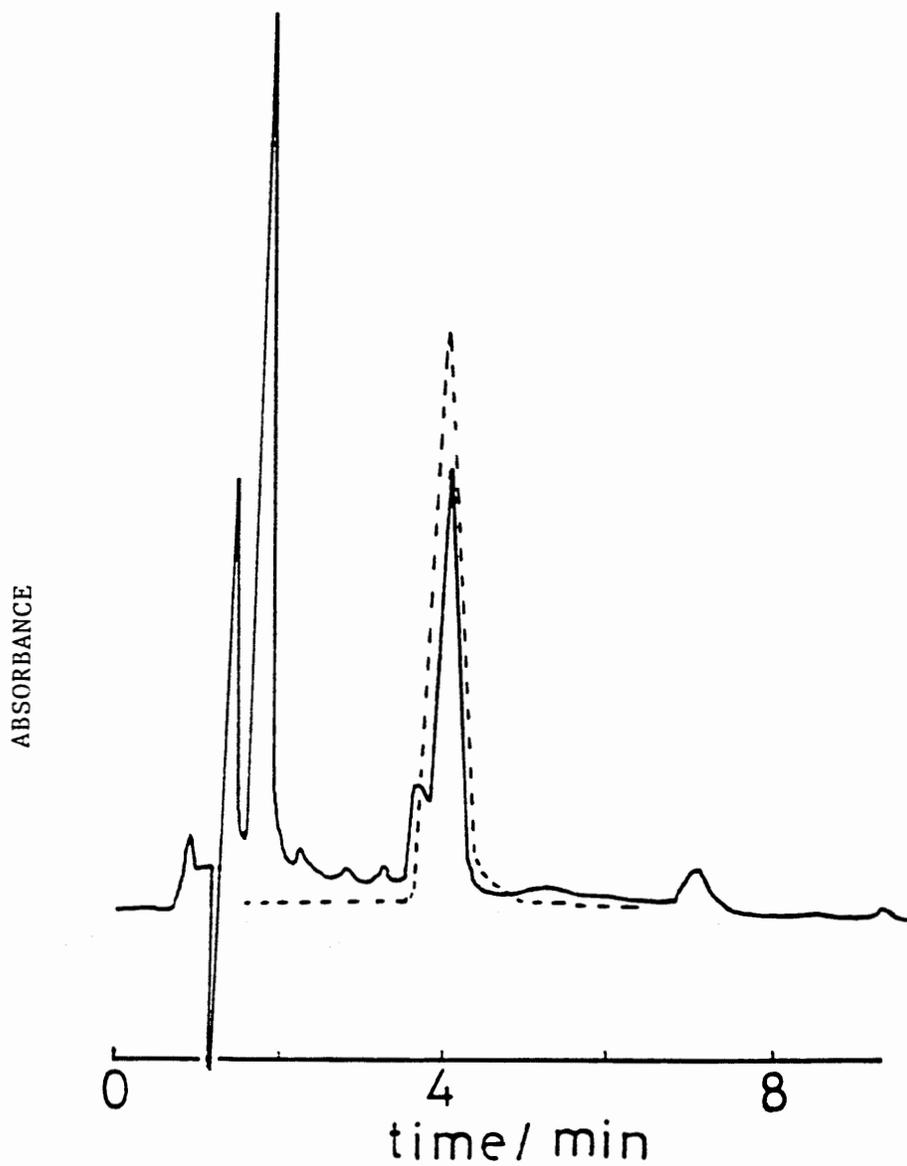
In addition, some soil samples spiked with anthracene or pyrene were examined. It was found that use of the mixed nonionic surfactants, Brij-30 ( $C_{12}E_4$ ) and Brij-35 ( $C_{12}E_{23}$ ), could initially desorb and remove approximately 68% anthracene and 76% pyrene from the soil. Subsequent cloud point extraction performed on the initial wash solution achieved roughly 80% recoveries of the polycyclic aromatic materials that were in the solution phase. This translates to an overall recovery of 55% pyrene and anthracene in the surfactant micellar-rich phase (i.e. 55% of the material originally present in the soil ended up in the extractant phase, with ca. 30% still in soil and ca. 15-20% in the bulk aqueous phase). It is important to stress that these are preliminary results and the systems have not been optimized. However, these results clearly show the potential of this cloud point extraction technique with respect to extraction of organics from solid matrices.

**Extraction of Organics from Solid Matrices--Coal Sample Extraction.** One potentially important finding arising from our comparison of nonionic and zwitterionic surfactants for utilization in the cloud point type extraction is that zwitterionic surfactants may prove better for extractions from solid matrices. This stems from the fact that aqueous solutions of zwitterionic surfactants exhibit an upper (rather than lower) consolute boundary, that is, they are cloudy due to the co-existence of two isotropic phases at low temperature and clarify at certain elevated temperatures at which only a single isotropic phase exists (Saitoh and Hinze 1991). The fact that the

zwitterionic surfactant system has its two-phase region at the lower temperature side might prove important with respect to convenience in attempted extractions from solid matrices. The extraction of hydrophobic materials from a solid sample often requires heating to improve mass transfer. For zwitterionic surfactant solutions, a clear homogeneous surfactant micellar solution will result at the required higher temperatures with the phase separation subsequently occurring when the solution is cooled back to room temperature. In this regard, Figure 9 shows the chromatogram obtained for the surfactant-rich phase following the cloud point extraction of a coal sample using the zwitterionic surfactant, 3-[nonyl-dimethyl-ammonio]propyl sulfate (C9-APSO<sub>4</sub>). Although the extraction system has not been optimized, it appears that some anthracene was extracted from the coal sample based upon a comparison of the retention times with pure standards. This ability to use zwitterionic surfactants for the extraction/preconcentration of hydrophobic species from solids may prove beneficial in such applications as pesticides in plants, polycyclic aromatic hydrocarbons in dusts or bio-mass samples, etc.

Although much more work is obviously required, the results to date indicate that the cloud point extraction technique is viable and could be applied for the extraction of organics from both aqueous or solid matrices. Further work to optimize the various systems and to compare and contrast the cloud point extraction with that of conventional liquid - liquid extractions is required. Such work is in progress in our laboratory.

Figure 9. Chromatographic trace of the HPLC Analysis of the Surfactant-rich Extractant Phase following the Cloud Point Extraction of an Argonne Premium Coal Sample with the Zwitterionic Surfactant C9-APSO<sub>4</sub>. The dotted line represents the chromatogram obtained following the injection of a standard anthracene solution.



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