

# Application of $L_3$ Sponge Phase in Extraction of Polycyclic Aromatic Hydrocarbons

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*Application of  $L_3$  sponge phase as an extractant in extraction of polycyclic aromatic hydrocarbons (PAHs) from aqueous solution were studied systematically at 25°C with three nonionic surfactants, Tergitol 15-S-5, LE-203 ( $C_{12}E_3$ ), and Brij 30 ( $C_{12}E_4$ ). The transition temperatures of the coexisting  $W + L_3$  phases of these surfactants could be regulated with the addition of proper salting-out electrolytes and short-chain alcohols. The low viscosities of these  $L_3$ -phase extractants, ranging from 10 to 40 mPa s, make it not difficult for separation of these extract-containing  $L_3$  phases from the coexisting water ( $W$ ) phases. Compared to the conventional cloud-point extraction techniques, a relatively larger preconcentration factor with satisfactory recovery efficiency of PAHs are achieved in such  $L_3$ -phase extraction procedure. For example, a preconcentration factor as much as ca. 200 was achieved in 0.2 wt % Tergitol 15-S-5 solution added with 5.6 wt % NaCl. In general, a higher preconcentration factor is attained with a decrease in surfactant concentration and/or with increasing concentrations of additives employed in this work. © 2007 American Institute of Chemical Engineers AICHE J, 53: 1450–1459, 2007*

**Keywords:** extraction,  $L_3$  phases, nonionic surfactant, polycyclic aromatic hydrocarbon, cloud-point extraction

## Introduction

The environmentally benign surfactant-based extraction techniques have become more and more attractive,<sup>1–9</sup> since water is commonly employed as the main solvent in contrast to the massive use of volatile organics in the conventional organic liquid–liquid extraction.<sup>10–12</sup> Among these surfactant-based extraction techniques, preconcentration procedures based on the clouding phenomena of surfactant solutions, called cloud-point extraction (CPE), prevail, in which surfactant aggregates, e.g. concentrated micelles, are used as the extraction media.<sup>4–9</sup> In general, the CPE process usually yields a preconcentration factor about a few tens.

The work mechanism of the CPE process is similar to the conventional liquid–liquid solvent extraction, which separates

the desired components by their different affinity in these two immiscible liquid phases.<sup>12</sup> There are several factors influencing the performance of the extraction process. These include selectivity and distribution coefficient of extraction solutes, i.e., the affinity of the solutes, loading capacity of solutes in extraction solvent, interfacial tension, density, etc.<sup>12</sup>

In CPE processes, hydrophobic extracts initially solubilized in the bulk micellar solution still tend to reside in the hydrophobic space of the concentrated micelles after cloud-point separation. In principle, if the phase volume of the concentrated micelles after cloud-point separation is relatively small, compared to the original bulk solution or the coexisting surfactant-lean phase, commonly referred as a water ( $W$ ) phase, the hydrophobic extracts are, thus, concentrated in the surfactant-rich phase, in which the hydrophobic extraction solutes are usually far yet to be saturated.<sup>4–8</sup>

As aforementioned, water, instead of the flammable and volatile organic solvents, is utilized in the CPE process,

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which offers many advantages for the CPE process, such as the process safety, lower cost, and operation easiness, over the conventional liquid–liquid extraction techniques.<sup>8</sup> Other advantages of the CPE processes, for instance, enhancement of preconcentration factor and recovery efficiency as well as minimization of extract loss, etc., are reported as well.<sup>8</sup> Moreover, insignificant effects of initial extract concentrations on the preconcentration factor and extraction efficiency were reported for the CPE techniques as well.<sup>8,13</sup>

Nonetheless, the surfactant-rich phase in a CPE process, where trace level of hydrophobic extraction solutes are concentrated, often consists of elongated micelles and may have even reached the phase boundary between the concentrated  $L_1$  micellar phase and mesophases, such as  $L_a$  lamellar phase. Consequently, it becomes very viscous to succumb to difficulty in its separation from the coexisting surfactant-lean phase. Instead, people start to search for different surfactant phases as extractants. Recently, idea of using bicontinuous microemulsions to extract compounds of interests from aqueous solutions have surfaced up.<sup>2,3</sup> Unfortunately, it is inevitable to include organic solvents to form microemulsions. For example, Tricoli et al.<sup>2</sup> and Castro-Dantas et al.<sup>3</sup> had to adopt 23.7 wt % tetradecane and significant amount of isoamyl alcohol, respectively, in the formulations of their bicontinuous microemulsions.

Another alternative to amend this issue is to utilize another isotropic surfactant-rich phase utilizing water as the major components but still having fluidic nature, i.e.  $L_3$  sponge phase.<sup>1,14,15</sup> In general, the bicontinuous  $L_3$  phase possesses smaller phase volume and could provide quite a good hydrophobic affinity to trace hydrophobic solutes, instead of the concentrated  $L_1$  phase in the CPE process. Hence, better extraction and preconcentration performance is expected by using the  $L_3$  sponge phase. More importantly, as water is still used as the main solvent, the aforementioned advantages of the CPE processes are, therefore, anticipated in such an innovative  $L_3$  extraction technique.

A proof-of-principle using the  $L_3$  sponge phase to extract a trace amount of hydrophobic solutes from aqueous solutions was previously demonstrated with the use of a slightly hydrophobic nonionic surfactant Tergitol 15-S-5.<sup>1</sup> In the present article, outcomes from more detailed investigations on the application of the  $L_3$  sponge phase in extraction of trace amounts of 10 kinds of polycyclic aromatic hydrocarbons (PAHs), having two to five fused rings, simultaneously from aqueous solutions conducted systematically at 25°C with three different nonionic surfactants, Tergitol 15-S-5, LE-203 ( $C_{12}E_3$ ), and Brij 30 ( $C_{12}E_4$ ) are summarized. In view of the fact that such a preconcentration and extraction procedure does not involve the clouding phenomena of micellar solutions, but the phase change from the  $L_3$  phase to the coexisting  $W + L_3$  phases, it may not be adequate to refer it as the CPE process. Instead, the  $L_3$ -phase extraction process is called.

The  $L_3$  sponge phase is an isotropic bicontinuous phase and exists at a temperature relatively higher than the  $L_1$  phase.<sup>14–16</sup> A decade-long dispute on its phase structure was settled not until the early 1990s.<sup>17–19</sup> In general, it was firstly believed that such a  $L_3$  phase only appears in the phase diagrams of certain nonionic surfactants, for example,  $C_mE_j$  ethoxylated alcohols.<sup>14–16</sup> Nowadays, more evidences show its universal existence in many ionic surfactants as well. It possesses a bicontinuous structure with surfactant bilayer films connected over

macroscopic distances.<sup>16</sup> The  $L_3$  phase often exists in dilute surfactant solutions. In spite of the bicontinuous phase, the  $L_3$  phase often exhibits interesting nature of flow birefringence under shear,<sup>18,19</sup> and a Newtonian behavior and moderate viscosities even at relatively high volume fractions.<sup>16</sup>

This bicontinuous structure of  $L_3$  phase provides more hydrophobic space available than the discontinuous hydrophobic domain in the concentrated  $L_1$  phase, i.e. the main extraction media used in the CPE processes. Consequently, it gives a higher hydrophobic affinity to the hydrophobic extracts and leads to a higher preconcentration factor.<sup>9,12,20</sup> In addition, the phase volume of  $L_3$  phase is generally smaller than that of  $L_1$  phase, leading to a higher preconcentration factor. Moreover, such an isotropic  $L_3$  phase, known to possess quite fluidic nature, greatly facilitates the phase separation and eases the operation of the surfactant-based extraction process, compared to those of the CPE process.

In general, on the phase diagrams of  $C_mE_j$  nonionic surfactants in water, heating up micellar solutions at proper surfactant concentrations at first reaches the aqueous solubility limit of micelles at the lower consolute curve, i.e. the cloud-point temperature, at which nonionic surfactants are not hydrophilic enough any more to interact with water, because of diminishing H-bond formation.<sup>14–16,21</sup> Consequently, surfactant solutions are spinodally decomposed into  $W + L_1$  coexisting phases and turn cloudy and. With a further heating, the same system would generally undergo the phase transition, following the phase sequence as  $L_2$ ,  $W + L_2$ ,  $L_3$ ,  $W + L_3$ , and eventually  $W + L_2$  coexisting phases.<sup>14–16</sup>

Notably, the conventional CPE techniques mainly utilize the phase transition from a single micellar phase ( $L_1$ ) into the coexisting  $W + L_1$  phases. As aforementioned, in a CPE process, given that the apparent solubilities of these hydrophobic extracts by the micelles are much greater than their aqueous molecular solubilities, hydrophobic solutes originally incorporated in the micelles will avoid entering the water phase and, instead, reside preferentially in the concentrated  $L_1$  micellar phases after cloud-point phase separation. Consequently, hydrophobic extracts are extracted and concentrated. Likewise, similar principle also works in the  $L_3$ -phase extraction process, as employed and studied in this work.

As mentioned previously, since the saturated solubilities of these hydrophobic extracts in extraction media are, in general, not reached in the CPE and the  $L_3$ -phase extraction processes, the extraction performance is mainly determined by the volume ratio of the surfactant-rich phase, in which most extracts are found after phase separation, to the coexisting water phase.<sup>12,20</sup> Proper electrolytes and short-chain alcohols are often added to salt out water from the surfactant-rich phase in an attempt to decrease the phase volume of the surfactant-rich phase.<sup>1,16,21</sup> Moreover, addition of these salting-out agents could reduce the phase transition temperature as well, so that extraction and preconcentration processes could be possibly carried out at a lower temperature, e.g. at ambient temperature at 25°C.

In this work, additive effects of electrolytes, such as NaCl,  $Na_2SO_4$ , and  $Na_3PO_4$ , as well as alcohols, ranging from *n*-butanol to *n*-hexanol, to the  $L_3$ -based extraction process were studied. They all show in different extents the salting-out effects, namely to decrease the phase volume of the surfactant-rich phase and the phase-transition temperature, so that

good extraction performance and operations at ambient conditions could be satisfactorily achieved. However, for experimental convenience and to attain the ambient operational conditions, in addition to three electrolytes, only *n*-pentanol among three alcohols initially examined was chosen, because *n*-butanol is too weak to effectively serve these purposes and *n*-hexanol is too strong to precisely adjust the phase transition temperature among all three surfactants studied, which may jeopardize the reliabilities of our investigation on the effect of the phase transition temperature to the performance of the  $L_3$ -phase extraction process.

The viscosities of the obtained  $L_3$  phases were found in the range between 10 and 40 mPa s, an order of magnitude less than the viscosities of the concentrated  $L_1$  phase used in our previous CPE studies, in which similar nonionic surfactants were used.<sup>13,22</sup> More importantly, a preconcentration factor as high as ca. 200 was found. The strategy to acquire a larger preconcentration factor is successfully demonstrated with a decrease in surfactant concentration and/or with increasing concentrations of slating-out additives employed in this work. The details in the  $L_3$ -based extraction process are contained in this report.

## Materials and Methods

### Materials

Three readily biodegradable nonionic surfactants were used in this work. They are Tergitol 15-S-5 and Brij 30 (C12E4), both purchased from Sigma, and LE-203 (C12E3) as a gift from the En Hou Polymer Chemical Ind. (Taiwan). Both Brij 30 and LE-203 are commercial blends of polyethylene glycol dodecyl ethers having averaged EO numbers of 4 and 3, respectively. In contrast to Brij 30 and LE-203 as primary ethoxylated alcohols, Tergitol 15-S-5 is a mixture of species with secondary ethoxylated alcohols located at various positions along a linear hydrocarbon chain having 11–15 carbon atoms and with an average ethylene oxide number of 5. Selected properties of these surfactants are tabulated in Table 1.

Analytical reagent grade of polycyclic aromatic hydrocarbons (PAHs) were purchased from Fluka and Aldrich. These PAHs include naphthalene (Nph), acenaphthene (Acp), fluorine (Flr), anthracene (Ant), phenanthrene (Pnt), fluoranthene (Fla), pyrene (Pyr), benz[a]anthracene (Baa), benzo[a]pyrene (Bap), and perylene (Pel). Table 2 lists their selected physicochemical properties. Reagent grade of sodium chloride, sodium sulfate, sodium phosphate, and *n*-pentanol, as well as HPLC-grade acetonitrile, were purchased from Fluka, Sigma, and Mallinckrodt. Deionized water from a Milli-Q purification system (Millipore, USA) having resistivity greater than 18.2 MΩ cm was used in preparing samples and mobile phase for HPLC analysis. All reagents were used as received.

### Apparatus

The PAH concentrations in extract and water phase were determined using a Shimadzu HPLC system consisting of a LC-10AT pump, an ERC-3415α degaser, a Rheodyne 7725i injector with a 20 μL sample loop, a column oven, an SCL-10A system controller, and an SPD-10A UV/vis detector with detection wavelength mainly set at 254 nm. Particularly, a second detection wavelength at 220 nm was set to quantify acenaphthene and naphthalene better, which do not absorb strongly at 254 nm. PAH concentrations were obtained using the Shimadzu Class-VP software. The stationary phase was a Tosoh C18 reverse phase column (Model ODS-100S, 250 × 4.6 mm<sup>2</sup>, 5 μm) connected with an Alltima C18 guard column (7.5 × 4.6 mm<sup>2</sup>, 5 μm; supplied by Alltech, Deerfield, IL). Gradient elution was employed to enhance separation of PAH peaks. The programming of the gradient elution is shown as Figure 1. Figure 2 exhibits a typical chromatograph of these PAH mixtures with detection wavelength set at 254 nm. The overall flowrate of the mobile phase was always maintained at 1 mL/min.

Determination of phase-transition temperatures of surfactants in aqueous solutions was carried out in a water-bath with a good temperature control within 0.1°C (Model B-403L, Firstek, Taiwan). A Nikon Optiphot-2 optical microscope with crossed polarizers was employed in the penetration scan experiments to observe the phase sequences of surfactants in aqueous solutions at 25°C.<sup>1,25</sup> Preconcentration processes of PAHs were carried out in a 556-L incubator (Model RI-550, Firstek Scientific, Taiwan), which provides a temperature variation within 0.15°C and several electric sockets. The solutions containing surfactants, PAHs and additives were mixed on an end-to-end rotary mixer in the incubator (Model LD-76, Labinco B.V., Netherlands).

Viscosity measurements of  $L_3$  coacervate phases were performed using capillary viscometers in a temperature-controlled water bath. Anhydrous glycerol and deionized water were used as references. No kinetic correction was applied, since the elution times of the samples were always greater than 6 min.

### Experimental procedures

Preconcentration of PAHs by  $L_3$  phases were carried out at 25°C. Hence, it has to ensure that the transition temperature between  $L_3$  phase and  $L_3 + W$  phases is below 25°C. The phase transition temperature was determined by visual observation with crossed polarizers and/or by optical microscopy equipped with crossed polarizers, along with the information available on the phase diagrams of surfactants.<sup>1,14,15</sup>

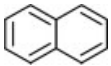
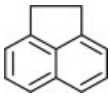
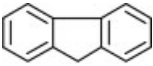
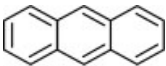
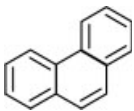
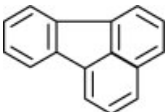
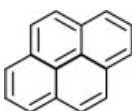
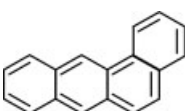
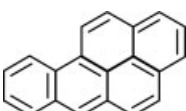
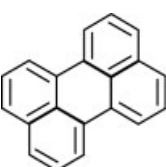
Appropriate amounts of solutions, ca. 10–50 mL, containing mixtures of all 10 PAH species together in presence of surfactants and additives, were stored in the incubator at 25°C for 48 h. The surfactant solutions with PAHs and addi-

**Table 1. Chemical and Physical Properties of Surfactants\***

Surfactant	Abbreviation	Formula	Molecular Weight	HLB	Density at 20°C	Structure
Tergitol 15-S-5	T-S-5	C <sub>12-14</sub> H <sub>25-29</sub> (OCH <sub>2</sub> CH <sub>2</sub> ) <sub>5</sub> OH	415 g/mol	10.6	0.965 g/mL	Secondary ethoxylated alcohols
Brij 30 (C <sub>12</sub> E <sub>4</sub> )	B-30	C <sub>12</sub> H <sub>25</sub> (OCH <sub>2</sub> CH <sub>2</sub> ) <sub>4</sub> OH	362 g/mol	9.7	0.946 g/mL	Primary ethoxylated alcohols
LE-203 (C <sub>12</sub> E <sub>3</sub> )	LE-203	C <sub>12</sub> H <sub>25</sub> (OCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> OH	318 g/mol	8.3	N/A	Primary ethoxylated alcohols

\*Data provided by suppliers.

**Table 2. Chemical and Physical Properties of Polycyclic Aromatic Hydrocarbons (PAHs)**

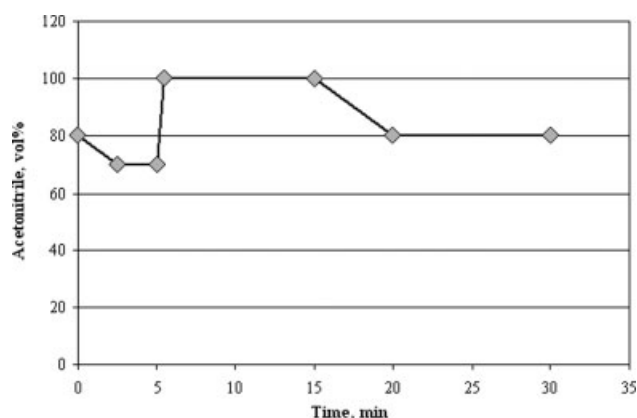
PAHs	Abbreviation	Structure	Formula	log $K_{ow}$ <sup>*</sup>	Aqueous Solubility <sup>†</sup> at 25°C
Naphthalene	Nph		C <sub>10</sub> H <sub>8</sub>	3.36	31.70 mg/L
Acenaphthene	Acp		C <sub>12</sub> H <sub>10</sub>	4.01	3.93 mg/L
Fluorene	Flr		C <sub>13</sub> H <sub>10</sub>	4.21	1.98 mg/L
Anthracene	Ant		C <sub>14</sub> H <sub>10</sub>	4.53	0.073 mg/L
Phenanthrene	Pnt		C <sub>14</sub> H <sub>10</sub>	4.57	1.29 mg/L
Fluoranthene	Fla		C <sub>16</sub> H <sub>10</sub>	5.08	0.26 mg/L
Pyrene	Pyr		C <sub>16</sub> H <sub>10</sub>	4.92	0.135 mg/L
Benz[a]anthracene	Baa		C <sub>18</sub> H <sub>12</sub>	5.67	0.014 mg/L
Benzo[a]pyrene	Bap		C <sub>20</sub> H <sub>12</sub>	6.11	3.80 × 10 <sup>-3</sup> mg/L
Perylene	Pel		C <sub>20</sub> H <sub>12</sub>	6.14	4.00 × 10 <sup>-4</sup> mg/L

\*From Ref. 23.

†From Ref. 24.

tives were prepared outside and, subsequently, mixed on the rotary mixer, set at 20 rpm, within the incubator for 2 h. Initial PAH concentrations spiked in the solutions were 600 ppb, but 60 ppb only for benz[a]anthracene (Baa), benzo[a]pyrene (Bap), and perylene (Pel). Our preliminary results

show that the phase separation of  $L_3 + W$  coexisting phases can be mostly completed within 12 h. That is, complete phase separation of surfactant solutions in this work could be achieved within 48 h after mixing. In practice, the equilibrium time for complete phase separation could be greatly



**Figure 1. Time program of mobile phase, consisting of acetonitrile and water, employed in gradient elution of PAH mixtures in this work.**

Flow rate of mobile phase is 1 mL/min.

shortened with application of centrifugal force to the surfactant solutions containing these PAH mixtures.<sup>1</sup>

Afterward, 20  $\mu$ L aliquot from the surfactant-rich phase, i.e.  $L_3$  phase appearing as the top phase, was withdrawn and injected directly without any dilution to the HPLC. The reported values in this work were the average from a triplicate measurement in, at least, two independent runs under the same experimental conditions. In addition, PAH concentrations remained in the water phase after phase separation was too small to yield any significant measure.

The phase volume ratio,  $R_V$ , is defined as the ratio of volume of the surfactant-rich phase ( $V_S$ ) to that of the water phase ( $V_W$ ), i.e.  $R_V = V_S/V_W$ , whereas the preconcentration factor ( $f_C$ ) is defined as the ratio of the PAH concentration in the surfactant-rich phase ( $C_S$ ) to the initial PAH concentration in bulk solution before phase separation ( $C_0$ ), i.e.  $f_C = C_S/C_0$ . Therefore, the recovery efficiency of the PAH ( $R$ ) can be characterized as follows:

$$R = \frac{C_S V_S}{C_0 V_T} \times 100\% = f_C \left( \frac{R_V}{1 + R_V} \right) \times 100\% \quad (1)$$

where  $V_T$  is the total volume of bulk solution. For accuracy, the phase volume ratio,  $R_V$ , was measured using a 1 L volumetric flask.

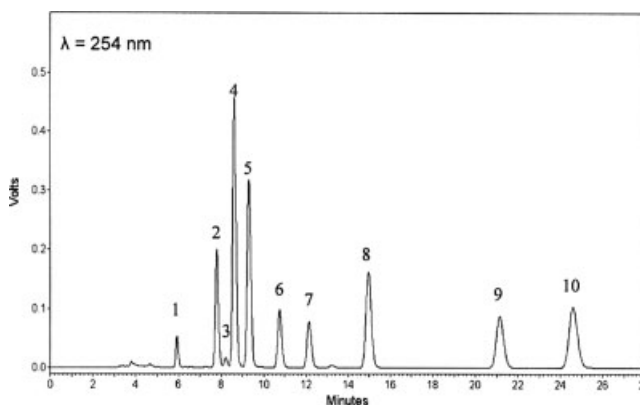
Solubility limits of PAH species in selected  $L_3$  phases at 25°C were measured by adding PAH mixtures in excess into the  $L_3$  phases contained in 15-mL screw-capped culture tubes. The test tubes were then agitated on the end-to-end rotary mixer in the incubator at 25°C. These samples were filtered through the cellulosic membrane syringe filters having pore size of 0.2  $\mu$ m to remove the fine particles for subsequent HPLC analysis. Owing to the very high PAH solubilities in these  $L_3$  phases, all samples had to be diluted with acetonitrile at 1000 times by volume. The PAH solubilities were measured every day from Day 3 to Day 5 and no significant variations in the measured PAH solubilities were observed. The relative standard errors of the measurements are mostly within 2%.

## Results and Discussion

In order to predict the extraction performance and conditions, investigations on the transition temperatures from the  $L_3$  sponge phase to  $W + L_3$  coexisting phases of surfactants were performed. Identification of the transition temperature is an interesting but laborious work, as details are contained in the supporting information of our previous report.<sup>1</sup>

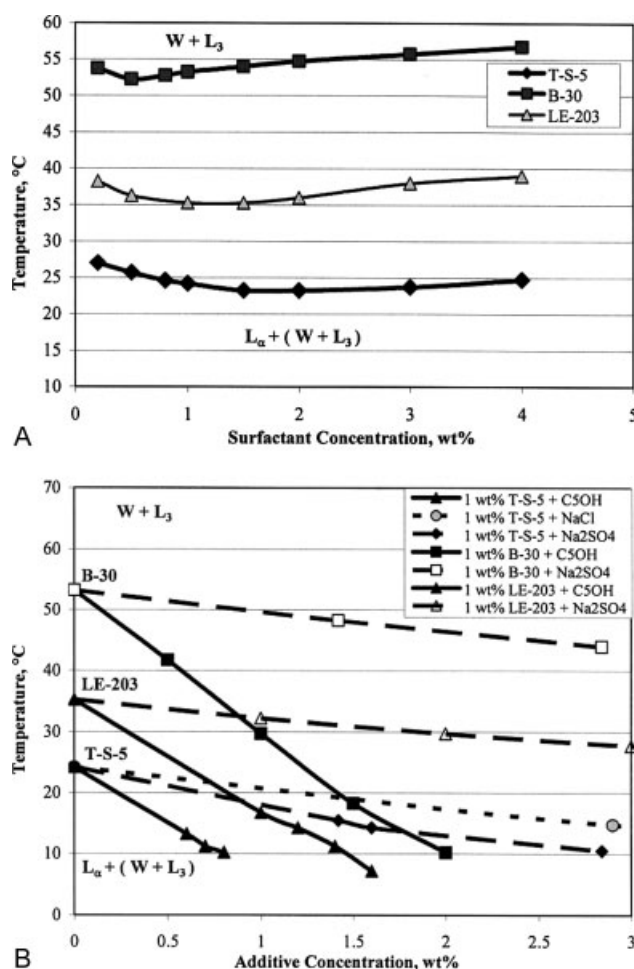
The transition temperatures from the  $L_3$ -phase dispersion to the  $W + L_3$  coexisting phases of Tergitol 15-S-5, LE-203 and Brij 30 slightly decrease and then increases with increasing surfactant concentrations, as shown in Figure 3a, which is consistent with previous reports.<sup>1,14,15</sup> Above each curve, surfactant solution separates into two distinct isotropic phases,  $W + L_3$  phases, in which  $L_3$  was used later as the surfactant-rich phase to extract trace amounts of PAHs from aqueous solution. A single  $L_3$  phase with a very narrow temperature window and the lamellar dispersion in water ( $W + L_\alpha$ ) can be found below each curve.<sup>1,14,15</sup> However, as these three non-ionic surfactants used are of commercial blends, surfactant solutions mainly exhibit as the dispersion of the lamellar phase in water at a temperature slightly below the transition temperature (Figure 3a). Moreover, the temperature required to induce formation of the  $L_3$  coacervate phase are still high, for instance 53°C for 1 wt % Brij 30 solution, so that external heating up surfactant solutions is necessary. To facilitate extraction procedures taking place at a lower temperature, e.g. 25°C in this work, various salting-out organic and inorganic additives were introduced into surfactant solutions.

Figure 3b indicates the effects of these additives in lowering the phase-transition temperature. For simplicity, the curves corresponding to  $\text{Na}_3\text{PO}_4$  are not shown here. As expected, the extent of added electrolytes and alcohols at the same additive concentration in decreasing this phase-transition temperature generally follows the order:  $\text{Na}_3\text{PO}_4 > \text{Na}_2\text{SO}_4 > \text{NaCl}$  and  $n$ -hexanol  $>$   $n$ -pentanol  $>$   $n$ -butanol. However, with addition of  $\text{Na}_3\text{PO}_4$  or  $\text{Na}_2\text{SO}_4$  to aqueous solutions containing LE-203 and Brij 30, white solid-like powder often precipitates out from surfactant-rich phase, presumably



**Figure 2. Chromatogram of PAH mixtures used in this work.**

Detection wavelength is set at 254 nm. (1) Naphthalene; (2) fluorene; (3) acenaphthene; (4) phenanthrene; (5) anthracene; (6) fluoranthene; (7) pyrene; (8) benz[a]anthracene; (9) perylene; (10) benzo[a]pyrene.



**Figure 3. Transition temperature from  $L_3$  sponge phase to  $W + L_3$  coexisting phases of surfactants: (A) Neat surfactant solutions; (B) effect of additives in 1 wt % surfactant solutions.**

the  $L_2$  solid phases, before the transition temperature can be brought down enough to the experimental temperature. Similarly, small amount of added *n*-hexanol could dramatically decrease the transition temperature, for example, a 46°C temperature drop with addition of only 0.8 wt % *n*-hexanol to 1 wt % Brij 30 solution. Considering experimental convenience, NaCl and *n*-pentanol are chosen as main additives in

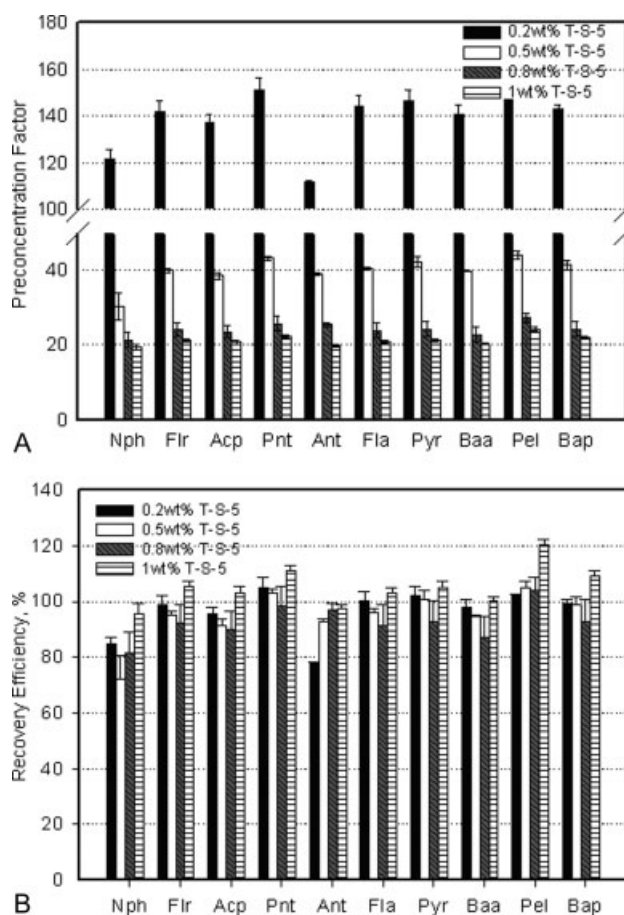
**Table 3. Viscosity of  $L_3$  Phase Separated from Selected Systems at 25°C**

Additive	Surfactant (wt %)							
	Tergitol 15-S-5			Brij 30		LE-203		
	0.2	0.5	1	0.5	1	0.5	1	
5.6 wt % NaCl	38.5	30.9	27.2					
2.5 wt % Na <sub>2</sub> SO <sub>4</sub>		22.9	21.7					
<i>n</i> -Pentanol								
1.2 wt %						9.0	14.2	
1.7 wt %				17.4				
1.8 wt %					18.7			

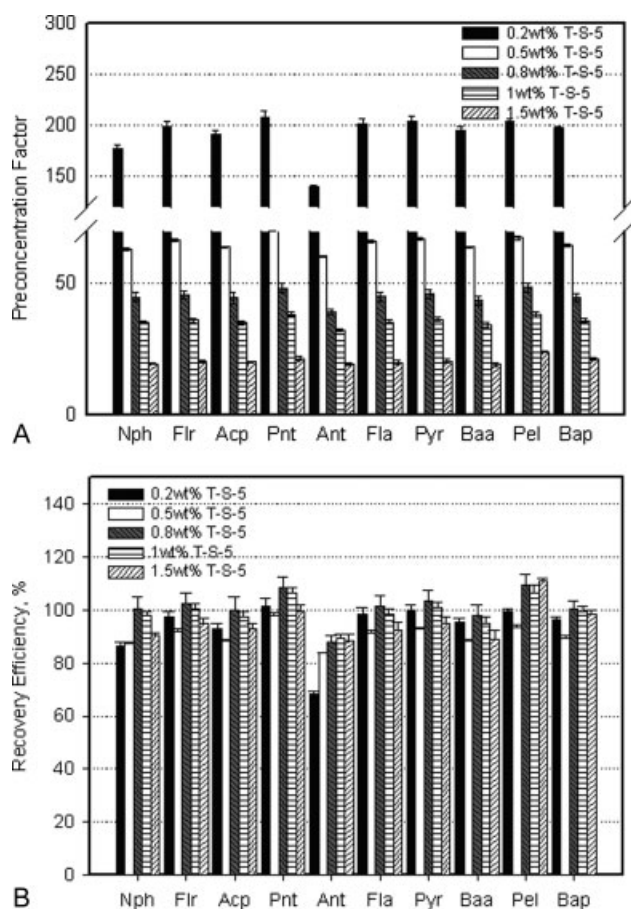
Unit of viscosity: mPa s.

Tergitol 15-S-5 solutions. Additionally, extraction performance of the  $L_3$  phase resulted from these three surfactants with different additives was studied and compared under a constraint that phase transition temperatures from  $L_3$  phase to coexisting  $W + L_3$  phases of these systems were approximately the same. The results are presented later in Figure 7.

As aforementioned, one of the advantages in using the  $W + L_3$  coexisting phases, other than the  $W + L_1$  coexisting phases, to extract trace amount of hydrophobic solutes is reflected in the fluidic nature of  $L_3$  phase, which eases the sample handling in the preconcentration procedures, especially in sample analysis by HPLC, in comparison with other mesophases and concentrated  $L_1$  micelles used in the CPE process. Table 3 summarizes the viscosity of  $L_3$  phases resulted from selected systems. In general, the viscosity decreases with increasing surfactant concentration at the same level of additive introduced, which implies that under these circumstances packing of surfactant molecules is more loosen. Consequently, viscosity of surfactant-rich phase becomes smaller with an increasing surfactant concentration. Even though, viscosity of the  $L_3$  phase harvested from 0.2 wt % Tergitol 15-S-5 solution added with 5.6 wt % NaCl, which yields quite a high preconcentration factor near 200, is still as low as 38.5 mPa s only.



**Figure 4. Effect of Tergitol 15-S-5 concentration in the presence of 2.9 wt % NaCl on preconcentration factor and recovery efficiency of PAHs: (A) preconcentration factor; (B) recovery efficiency.**



**Figure 5. Effect of Tergitol 15-S-5 concentration in the presence of 5.6 wt % NaCl on preconcentration factor and recovery efficiency of PAHs: (A) preconcentration factor; (B) recovery efficiency.**

Figures 4 and 5 show effects of Tergitol 15-S-5 concentrations in presence of 2.9 and 5.6 wt % NaCl on the performance of the  $L_3$ -phase extraction processes. Preconcentration factors as high as 140 and 200 are obtained in the cases of using 0.2 wt % Tergitol 15-S-5 added with 2.9 and 5.6 wt % NaCl, respectively. The preconcentration factor decreases with an increase in surfactant concentration initially present in the bulk solution. For example, preconcentration factor

drops from 140 to 40 and 20, when the initial surfactant concentration increases from 0.2 to 0.5 wt % and 1 wt % in the presence of 2.9 wt % NaCl.

The main reason could be ascribed to the unsaturated nature of hydrophobic extracts solubilized in rapidly rising volume of the  $L_3$  phase (Table 4), when more surfactant is initially introduced. That is, more surfactant initially present tends to increase the phase volume of the  $L_3$  phase. Since the extracts are very hydrophobic and reside only in the surfactant-rich phase, the preconcentration factor, ideally equal to the ratio of the total volume of the original bulk phase to the surfactant-rich phase volume, will decrease, accordingly. In other words the extent of extraction, i.e. preconcentration factor, is mainly governed by the phase volume ratio after phase separation, not the saturated solubility of extracts in the  $L_3$  extractant phase.<sup>12</sup>

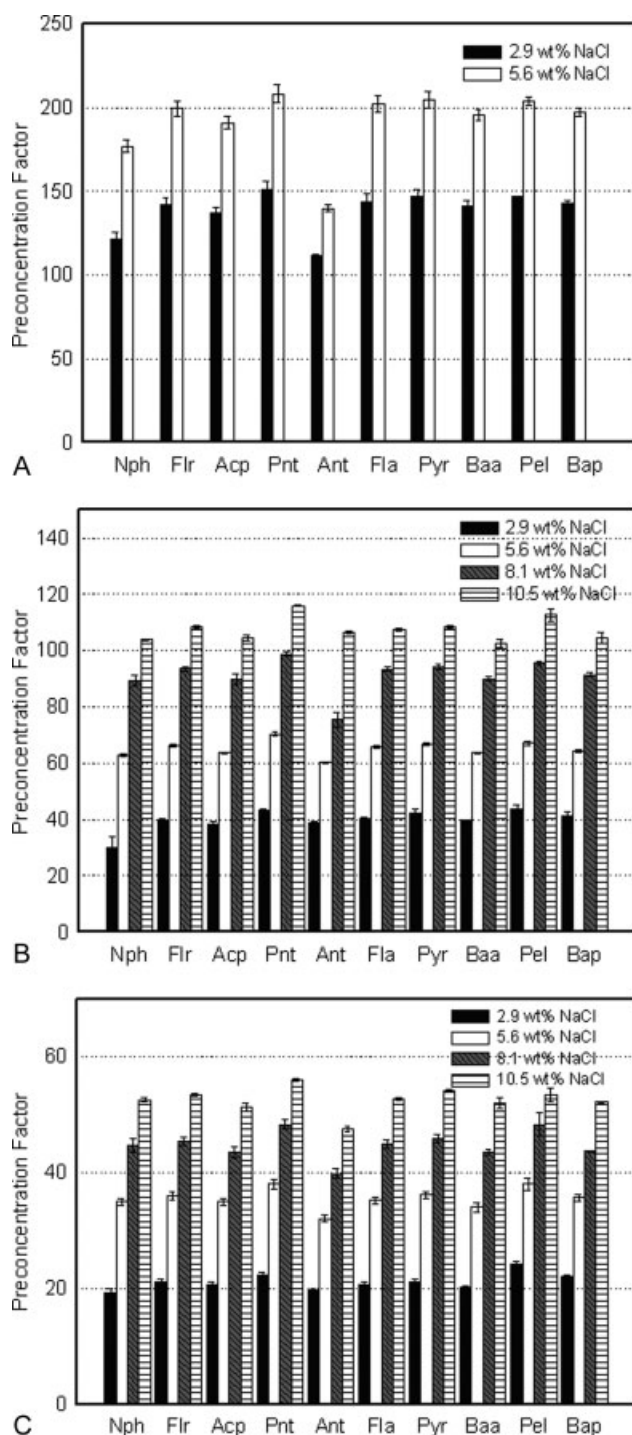
The obtained recovery efficiencies of PAHs are satisfactory, as majority of them are close to 100%. The expected high recovery efficiencies of these hydrophobic PAHs could be attributable to the fact that the  $L_3$  phase provides even better hydrophobic affinity than the concentrated  $L_1$  phase. In some cases, it slightly exceeds 100% and falls only around 80%. The uncertainties of the recovery efficiency indicated with error bars are estimated at around 5%. This is not uncommon in the microanalysis, since initial spiked concentrations of PAHs employed in this work are only 600 and 60 ppb and procedural errors, such as handling and evaporation, are not avoidable.<sup>26</sup>

Similarly, effects of NaCl concentrations added to Tergitol 15-S-5 solutions on the performance of  $L_3$ -phase extraction processes are shown in Figure 6. Preconcentration factors of PAHs generally grow with increasing concentration of NaCl present in solutions initially with constant surfactant concentrations. For instance, in 0.5 wt % Tergitol 15-S-5 solutions, preconcentration factors of PAHs rise from 40 to 65 and 105, when the initial concentration of added NaCl increase from 2.9 to 5.6 wt % and 10.5 wt %, respectively. The NaCl is known to impose salting-out effect on surfactants, in which sodium and chloride ions resulted from dissociation of NaCl in surfactant solutions are small enough to have stronger hydration power to compete with the oxygen atoms in the ethylene oxides of surfactant molecules on the free water molecules<sup>13,16,21</sup> As a result, surfactant-rich phase is dehydrated, so that its phase-volume diminishes and hydrophobic extracts are, therefore, more preconcentrated in the surfactant-rich phase. However, the limit in reducing the phase-vol-

**Table 4. Saturation Solubilities of PAHs in Selected  $L_3$  Phases at 25°C**

PAHs	Abbrev.	In Water* (mg/L)	1 wt % Tergitol 15-S-5 + 2.9 wt % NaCl (mg/L)	1 wt % Tergitol 15-S-5 + 1.5 wt % Na <sub>3</sub> PO <sub>4</sub> (mg/L)	1 wt % Brij 30 + 1.8 wt % <i>n</i> -pentanol (mg/L)
Naphthalene	Nph	31.70	$1.50 \times 10^5$	$9.34 \times 10^4$	$1.29 \times 10^5$
Acenaphthene	Acp	3.93	$1.14 \times 10^5$	$6.21 \times 10^4$	$1.03 \times 10^5$
Fluorene	Flr	1.98	$4.27 \times 10^4$	$4.35 \times 10^4$	$3.89 \times 10^4$
Phenanthrene	Pnt	1.29	$2.56 \times 10^4$	$1.81 \times 10^4$	$2.94 \times 10^4$
Fluoranthene	Fla	0.26	$5.32 \times 10^4$	$3.07 \times 10^4$	$3.37 \times 10^4$
Pyrene	Pyr	0.135	$5.00 \times 10^4$	$4.27 \times 10^4$	$3.72 \times 10^4$
Anthracene	Ant	0.073	$1.06 \times 10^4$	$6.77 \times 10^3$	$9.28 \times 10^3$
Benz[a]anthracene	Baa	0.014	$6.61 \times 10^3$	$6.56 \times 10^3$	$8.59 \times 10^3$
Perylene	Pel	$4.00 \times 10^{-4}$	$3.73 \times 10^3$	$2.17 \times 10^3$	$3.38 \times 10^3$

\*From Ref. 24.



**Figure 6. Effect of NaCl concentration in Tergitol 15-S-5 solutions on PAH preconcentration factors: (A) 0.2 wt % Tergitol 15-S-5; (B) 0.5 wt % Tergitol 15-S-5; (C) 1.0 wt % Tergitol 15-S-5.**

ume of surfactant-rich phase in order to increase the preconcentration factors by salting-out dehydration is not unbound. If the surfactant-rich phase is over-dehydrated, such as 1 wt % Brij 30 solution with addition of more than 2.8 wt %  $\text{Na}_2\text{SO}_4$ , solid-like surfactant phases or other mesophases are often resulted. This will undesirably bring about great diffi-

culty in sample handling and separation of concentrated extracts from the bulk solution.

In CPE techniques, their preconcentration performance is also affected greatly by the temperature difference between the cloud-point and the experimental temperature,<sup>16</sup> since temperature plays an important role in hydration extent of nonionic surfactants and the associated phase characteristics.<sup>13,21</sup> Analogously, it is surmised that a similar mechanism arising from temperature should be observed in the  $L_3$ -phase extraction process.<sup>1</sup> Hence, the performances of various  $L_3$ -based extraction processes from these three nonionic surfactants added with different additives but keeping approximately the same phase-transition temperature are compared (Figure 7). Namely, the temperature difference between the phase-transition temperature and the experimental temperature are intentionally fixed.

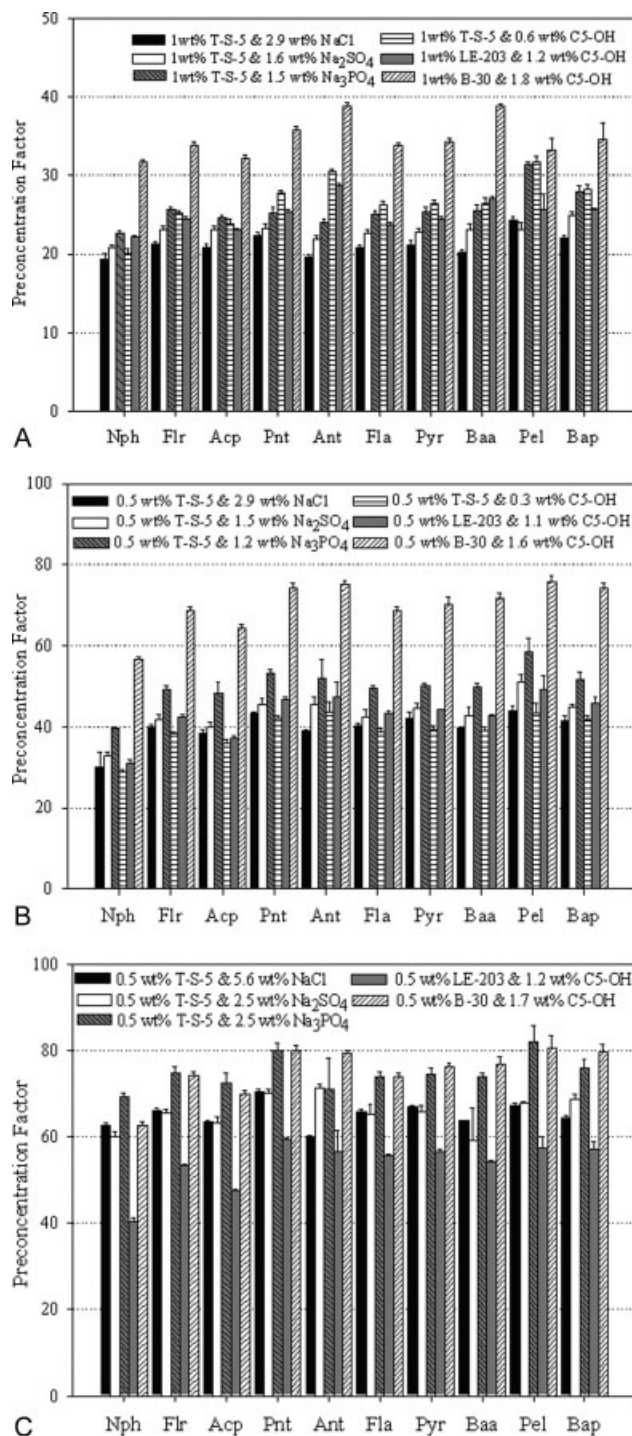
As mentioned previously, Table 3 indicates that these  $L_3$  phases are not very viscous and easily separated from coexisting water phases. Consequently, mass-transfer resistance of the extracted PAHs from the bulk phase to the  $L_3$  phases upon phase separation into the coexisting  $W + L_3$  phases should not be concerned.<sup>12</sup>

Figure 7 summarize the experimental outcomes from 1 and 0.5 wt % surfactant solutions with the transition temperatures from  $L_3$  phase to the  $W + L_3$  coexisting phases adjusted at around 15 and 11°C, respectively. Under the conditions of the same phase transition temperature,  $L_3$  phases separated from solutions with a higher surfactant concentration give a smaller preconcentration factor (Figures 7a,b). Similarly,  $L_3$  phases from solutions of the same surfactant concentration but with lower phase transition temperature yield a larger preconcentration factor (Figures 7b,c).

Interestingly, the largest preconcentration factor is found in the Brij 30 solution with addition of n-pentanol, compared to other surfactant-additive systems having the same surfactant concentration and the same  $W + L_3$  phase transition temperature. Furthermore, among three electrolytes added to Tergitol 15-S-5 solutions,  $\text{Na}_3\text{PO}_4$  brings in a larger preconcentration factor for the  $L_3$  phase extraction process, even though the phase transition temperature and the Tergitol 15-S-5 concentration used are practically kept constant. However, in terms of the obtained preconcentration factors for Tergitol 15-S-7 systems, n-pentanol may not work as effectively as sulfate and phosphate anions (Figures 7a,b). It is inferred that n-pentanol, as a co-surfactant, tends to stay with the surfactant aggregates, in contrast to the electrolytes that also go into the water phase. That is, the phase volume of the  $L_3$  phase may have been slightly swollen by the presence of the n-pentanol, which reduces the preconcentration factors of the  $L_3$  phase. Unfortunately, in the Brij 30 systems, the same electrolytes could not decrease the phase transition temperature effectively and stop short to ca. 40°C only, before the solid surfactant phase rather than the desired liquid  $L_3$  phase precipitates out.

Table 4 summarizes the apparent PAH solubilities in selected  $L_3$  phases garnered from 1 wt % surfactant solutions. The apparent solubilities of PAH species in the  $L_3$  phases are enhanced by a factor from 4000 (naphthalene) to  $3.7 \times 10^5$  (pyrene) and  $10^7$  (perylene), compared to their corresponding aqueous solubilities. Coincidentally, the magnitude of solubility enhancement factors of PAHs by the  $L_3$  phases generally follows a reverse trend of their aqueous solubility. Namely, a





**Figure 7. Effect of additives in surfactant solutions on preconcentration factors of PAHs.**

The surfactant-additive solutions possess close phase transition temperature. (A) Phase transition temperature  $\sim 15^{\circ}\text{C}$  and 1 wt % surfactant solutions; (B) phase transition temperature  $\sim 15^{\circ}\text{C}$  and 0.5 wt % surfactant solutions; (C) phase transition temperature  $\sim 11^{\circ}\text{C}$  and 0.5 wt % surfactant.

more hydrophobic PAH generally tends to have a larger factor.<sup>27</sup> Combining these experimental data and preconcentration data, PAH concentrations in the  $L_3$  sponge phases after

extraction are less than 1% of their apparent solubility limits. Explicitly, the  $L_3$  phases are still far yet to be saturated. This certainly implies more PAH compounds could be extracted into the  $L_3$  phases. With the very good solubilization capacities for the PAH compounds by the  $L_3$  phases, the  $L_3$ -phase extraction technique could be further applicable to mobilization and extraction of PAH contaminants sorbed on particulates and clays in the aquifer.

As mentioned previously, the purpose of adding salting-out agents to surfactant solutions is mainly to decrease the phase transition temperatures of surfactant solutions. That is, addition of these electrolytes is to salt out surfactant molecules or, equivalently, to increase their hydrophobicity, so that the existing phase temperatures of surfactant aggregates could be reduced appropriately.<sup>14–16,21</sup> In general, the extent of salting-out effect by an ion depends on both charge and hydrated radius of this ion.<sup>21</sup> In brief, those highly hydrated ions tend to salt it out more on hydrophobic organics in aqueous media. The salting-out effects for the common anions on the nonionic surfactant and neutral hydrophobic organics are generally in the order of  $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{F}^- > \text{Cl}^- > \text{Br}^- > \text{NO}_3^- > \text{I}^-$ .<sup>21</sup>

Nonetheless, these salting-out agents would not only interact with surfactant molecules, but also the organics solutes.<sup>28</sup> Schlautman et al.<sup>28</sup> have shown, in general, the extent of salting-out effect of electrolytes on hydrophobic organic solutes in aqueous media is linearly proportional to solute's surface area, which is positively correlated with the molecular weights of hydrophobic organic solutes.<sup>27</sup> Thus, with the same salting-out agent at the same concentration, perylene and naphthalene should have the most and the least influence of being salted-out. Consequently, the relative reduction in saturation solubility of perylene and naphthalene should be the most and the least prominent among all PAH species studied in this work. Alternatively, it is rational to infer that perylene and naphthalene possess the largest and the smallest solubility enhancement factors among all PAHs employed in this work, which coincidentally is consistent with our experimental observation (Table 4).

As aforementioned, several factors could have a profound effect on the success of extraction processes. In the CPE and  $L_3$  phase extraction processes, two important factors regulating their preconcentration factors and performance are the volume ratio of surfactant-rich phase to the coexisting water phase after phase separation, and the solubilization capacity of extracts in the surfactant-rich phase. In these surfactant-based extraction techniques, most of extracts will be favorably extracted to the surfactant-rich phase. If there is not any extract left over in the coexisting water phase, the preconcentration factor is ideally equal to the volume ratio of original bulk phase to the surfactant-rich phase.

In this work, since the PAH compounds are far yet to be saturated in the  $L_3$  phase, the former is dominant in determining the preconcentration performance. Additionally, temperature has been well known to play a vital role in the phase behaviors of surfactants. Especially, temperature effect is more obvious on those of nonionic surfactants.<sup>14–16</sup> It is not clear why the preconcentration factors differ observably among the systems having the same surfactant at the same concentration and the same phase-transition temperature.

Certainly, it warrants more investigations on the  $L_3$ -based extraction processes.

In summary, the preconcentration performance of these  $L_3$ -based extraction processes for hydrophobic extracts are promising. More importantly, these extraction processes do not use any organic solvents, but mainly the biodegradable surfactants, common additives, and the environmentally benign solvent, i.e., water. The obtained preconcentration factors are satisfactory and as high as ca. 200. Unlike the conventional liquid–liquid extraction technique, in which extract solubilities in the extractant phase play very crucial role in the extraction performance and the preconcentration factor,<sup>12</sup> the main factor determining the performance of such  $L_3$ -based extraction techniques is ascribed to the phase-volume ratio of the  $L_3$  phase to the coexisting water phase, since apparent solubilities of extracts in  $L_3$  phases haven usually been enhanced high enough.

## Conclusions

PAHs with two to five fused rings are successfully extracted and preconcentrated from aqueous solutions with the  $L_3$  sponge phase as an extractant. NaCl, Na<sub>2</sub>SO<sub>4</sub>, Na<sub>3</sub>PO<sub>4</sub>, *n*-butanol, *n*-pentanol, and *n*-hexanol studied in this work all show their capability as salting-out agents to dehydrate the surfactant-rich phase, i.e. the  $L_3$  sponge phase. They also facilitate the possible extraction process performed at lower temperatures, such as at ambient temperature (25°C). Moreover, the viscosity of the  $L_3$  sponge phase is as low as 10–40 mPa s. Specifically, the easy operational conditions of the  $L_3$  sponge phase is not compromised with additives, in contrast to that of the CPE processes. They still retain their fluidic nature. The conditions explored in this work show that it is possible at 25°C to get a relatively larger preconcentration factor, at least greater than ca. 200. In general, a greater preconcentration factor can be achieved by increasing the concentration of added salt and/or decreasing the surfactant concentration.

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