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Separation Science and Technology

Publication details, including instructions for authors and subscription information:

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Online publication date: 10 September 2000

To cite this Article Kimchuwanit, Warophat, Osuwan, Somchai, Scamehorn, John F., Harwell, Jeffrey H. and Haller, Kenneth J.(2000) 'Use of a Micellar-Rich Coacervate Phase to Extract Trichloroethylene from Water', *Separation Science and Technology*, 35: 13, 1991 – 2002

To link to this Article: DOI: 10.1081/SS-100102085

URL: <http://dx.doi.org/10.1081/SS-100102085>

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ABSTRACT

At temperatures above the “cloud point,” aqueous nonionic surfactant micellar solutions can separate into two phases: a micellar-rich coacervate phase and a dilute phase. Because the coacervate phase is a concentrated micellar solution, organic solute tends to concentrate in the coacervate as a result of solubilization. In this study up to 91% of trichloroethylene (TCE) was extracted into the coacervate phase in one stage. The TCE concentration in the coacervate can be over two orders of magnitude greater than that in the dilute phase. Increasing temperature, surfactant concentration, and added NaCl concentration all improve the fraction of TCE extracted.

INTRODUCTION

Surfactant-based separation processes can be effective in the removal of dissolved organics from water (1), e.g., polluted wastewater or groundwater. These techniques have the advantage of having modest energy requirements

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and using environmentally friendly surfactants as the separating agent. When an aqueous solution containing a nonionic surfactant is heated above the temperature called "cloud point," the solution can separate into two phases (2, 3). The cloud point is strictly defined at a particular surfactant concentration (e.g., 1 wt%), but because the phase boundary between one-phase and two-phase regions is fairly independent of concentration, the cloud point is generally quite close to the lower consolute solution temperature (4). One phase is concentrated in surfactant micelles and is called the "coacervate" (2, 5). The other phase is dilute in surfactant micelles, but at a concentration slightly above the critical micelle concentration (CMC) (2, 6, 7). Because the coacervate phase is a concentrated micellar solution, any organic solute in the water will tend to solubilize in the micelles and concentrate in that coacervate phase. This aqueous phase/aqueous phase extraction process effectiveness has been demonstrated for the solute *tert*-butylphenol in previous work (8). However, *tert*-butylphenol as a solute makes surfactant regeneration difficult.

One economic constraint common to many surfactant-based separation processes is the need to recover the surfactant for reuse following the operation (9). For example, ionic surfactants can be precipitated (9). However, nonionic surfactants do not precipitate. If the solute contained in the coacervate is volatile enough, it can be removed by vacuum, steam, or gas stripping (10–12), leaving the solute-free surfactant solution for reuse. Although regeneration of the surfactant solution was not studied here, the potential for stripping the coacervate is one reason that trichloroethylene (TCE), a volatile toxic pollutant commonly encountered in wastewater or groundwater, was chosen for study. Vacuum stripping of TCE from concentrated surfactant solutions (although not coacervate) has been studied in a pilot scale vacuum stripper (11).

In this study, the effect of temperature, total surfactant concentration, TCE concentration, and salt concentration on the concentration of surfactant and TCE in the coacervate and the dilute phase were measured under equilibrium conditions.

BACKGROUND

The basis of the phase separation (or cloud point) extraction technique, initially reported by Watanabe (13), stems from the well-known phase phenomenon exhibited by some micellar surfactant solutions. There are several situations in which a surfactant solution can be in equilibrium with a separate, predominantly aqueous phase (14). The phase separation of zwitterionic micelle solutions and concentrated ionic (anionic or cationic) solutions have been reported (14–15). The best known example of this technique is the separation of a nonionic micellar phase above the cloud point temperature of polyoxyethylene surfactant solutions (16). The specific applications of such sys-

tems and their phase behavior for the extractive preconcentration, separation, or purification of metal chelates, biomaterials, and organic compounds have been thoroughly reviewed (17) with some relevant subsequent articles (18–19).

The cloud point temperature is the lowest temperature at which the nonionic surfactant solutions, above the CMC, become cloudy upon heating (18). Above the cloud point, the nonionic surfactant solution separates into two isotropic phases. The phases appear to consist of a micelle-poor phase and a concentrated micellar phase, or coacervate phase. The concentration of surfactant in the dilute phase is above its CMC at that temperature (2, 6, 7). The higher the degree of polymerization of the headgroup in the polyoxyethylene surfactant, the higher the cloud point (4).

The microstructure of the micelles in the coacervate probably consists of the surfactant hydrocarbon chains intertwining, removing themselves from the aqueous environment, and the hydrophilic groups covering the surface of the hydrophobic region. Kato et al. (20) studied the microstructure of micelles in concentrated nonionic surfactant solution by measuring the surfactant self-diffusion coefficient. They proposed that the microstructure is entangled micelles in a wormlike network at low temperatures and gradually changes to a multiconnected or cross-linked network when the temperature increases.

Several authors have shown that the addition of simple electrolytes can alter the cloud point if the electrolyte concentration is greater than 0.1 M, but there is no significant effect at electrolyte concentrations less than 0.01 M (21). Most simple anions such as sulfate, chloride, and carbonate typically depress the cloud point of nonionic surfactants because of their salting-out effect, with the effect of a given salt depending upon the hydrated radii of the ions (3, 22–27). On the other hand, some ions such as nitrate and thiocyanate raise the cloud point as a result of a salting-in effect (22, 24–27). The addition of nonpolar organic compounds that can be solubilized in the core of the micelle normally raises the cloud point, whereas polar organic compounds that can be solubilized closer to the hydrophilic head groups of the surfactants can depress the cloud point (28). The cloud point of aqueous nonionic surfactant solutions above the CMC increases dramatically with the addition of ionic surfactants (2, 29–33). The cloud point of a solution of mixed nonionic surfactants is intermediate between that of the two pure surfactants involved (28). Thus, the desired cloud point temperature for an application can be obtained by appropriate selection of the surfactants.

EXPERIMENTAL

Materials

Octylphenoxy poly(ethyleneoxy) ethanol with an average of 7 M of ethylene oxide per M of octylphenol, OP(EO)₇, from Rhodia Co., Ltd (Thailand)

(Igepal CA-620) was the surfactant used in this study. Reagent grade trichloroethylene (TCE) and reagent grade NaCl were from Farmitalia Carlo Erba. All chemicals were used as received. The water was deionized and distilled.

Methods

Several identical 100 mL separatory funnels containing a total volume of 100 mL of water, OP(EO)₇, TCE, and possibly NaCl were placed in an isothermal water bath until the volume of the coacervate phase did not change, generally about 2 d. After phase separation had occurred, the coacervate phase volume was measured. The OP(EO)₇ and TCE concentrations were measured in both the coacervate and dilute phases. Duplicate determinations were conducted to assure reliability of the measured concentrations.

The OP(EO)₇ concentrations were measured using a Perkin-Elmer model Lambda 16 UV/VIS spectrometer at 224 nm. TCE concentrations were analyzed using a Hewlett-Packard model HP5890 series II gas chromatograph equipped with a flame ionization detector. Static headspace sampling was used as the sample injection technique because of the high volatility of trichloroethylene. External standard quantitative calibrations were performed for the analysis of TCE concentration. The following conditions used for determination of TCE concentration: column: Shimadzu CBP-1; carrier: helium; oven: 80°C isothermal; injector: split 1 : 100, 150°C; detector: FID, 250°C.

TABLE 1
Coacervate Extraction Data for

[TCE] (ppm)	[OP(EO) ₇] (M)	[NaCl] (M)	Temperature (°C)	Fractional coacervate volume	[Surfactant] (mM)	
					Dilute phase (D)	Coacervate phase (C)
50	0.01	0.1	30	0.0242	0.6667	384.2
50	0.03	0.1	30	0.0930	1.2202	314.7
50	0.05	0.1	30	0.1563	1.3608	313.4
50	0.05	0	30	0.1953	3.4335	238.7
50	0.05	0.05	30	0.1633	1.9748	294.3
50	0.05	0.1	35	0.0987	0.6417	506.1
50	0.05	0.1	40	0.0930	0.5722	520.0
50	0.05	0.1	45	0.0777	0.5916	636.2
50	0.05	0.1	50	0.0648	0.6048	741.2
100	0.05	0.1	30	0.1555	1.2469	316.4
200	0.05	0.1	30	0.1406	1.1744	347.4

RESULTS AND DISCUSSION

The results of this study are given in Table 1. The ratio of the surfactant or solute concentration in the coacervate phase to that in the dilute phase is defined as a partition ratio.

Cloud Point and CMC

The measured cloud point for OP(EO)₇ is 22°C with no added TCE and 16°C with 1.0 M (1.31×10^5 ppm) added TCE. At the highest TCE concentration used (200 ppm), the cloud point is essentially the same as that of pure OP(EO)₇ and is at least 8°C below the lowest temperature used here.

The CMC of OP(EO)₇ at 25°C is 0.184 mM. The temperature dependence of the CMC is small (34) (about a maximum of 30% difference over the temperature range used here), compared to the differences between the dilute phase surfactant concentration and the CMC. At the very low solubilizate concentrations and low loading of solute into the coacervate aggregate (solute/surfactant in coacervate), the effect of the presence of solute on the CMC is expected to be negligible. Thus, the CMC of OP(EO)₇ under the conditions used here is expected to be slightly less than 0.184 mM. As shown in Table 1, the dilute phase surfactant concentration of all systems investigated is at least three times the CMC.

Trichloroethylene/OP(EO)₇ System

[TCE] (ppm)		Fraction of surfactant in coacervate	Fraction of TCE in coacervate	$\frac{[\text{Surfactant}]_C}{[\text{Surfactant}]_D}$	$\frac{[\text{TCE}]_C}{[\text{TCE}]_D}$
Dilute phase (D)	Coacervate phase (C)				
16.73	1478	0.9347	0.6868	576.3	88.3
8.96	459	0.9635	0.8400	257.9	51.2
5.88	285	0.9771	0.8998	230.3	48.5
6.67	226	0.9440	0.8916	69.5	33.9
6.32	272	0.9668	0.8936	149.0	43.0
7.17	420	0.9886	0.8651	788.7	58.6
6.63	477	0.9894	0.8806	908.8	71.9
6.55	562	0.9891	0.8785	1075.4	85.8
6.30	663	0.9884	0.8795	1225.7	105.2
10.49	580	0.9790	0.9106	253.7	55.3
28.15	1204	0.9798	0.8750	295.8	42.8

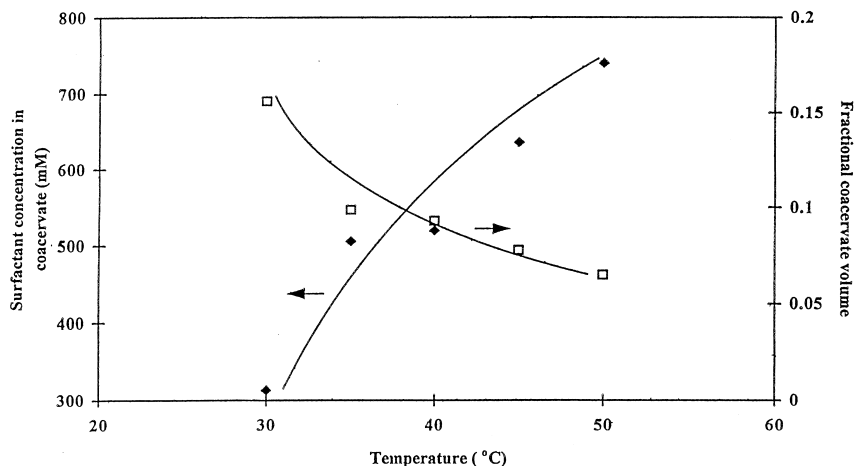


FIG. 1 Surfactant concentration in coacervate phase and fractional coacervate volume as a function of temperature (System: 50 ppm TCE, 0.05 M surfactant, and 0.1 M NaCl).

Effect of Temperature

The coacervate extraction of 4-*tert*-butylphenol was studied in previous work (7). It was concluded that increasing the temperature of a system above the cloud point results in increasing dissimilarity between the coacervate phase and the dilute phase, causing a decrease in the coacervate phase volume. The concentration of the surfactant, and the 4-*tert*-butylphenol, in the coacervate phase also increased. Nearly all of the surfactants (99%) and 4-*tert*-butylphenol (97%) end up in the coacervate phase after phase separation. In the current study, the same qualitative result was observed. As shown in Table 1 and Figs. 1 and 2, up to 98% of OP(EO)₇ and 91% of TCE is removed in the coacervate phase, whereas the concentration of TCE in the coacervate phase is as high as 105 times the concentration in the dilute phase. As the temperature increases, the separation improves; the fractional volume of the coacervate decreases, whereas the concentration of both TCE and surfactant in the coacervate phase increases, and these concentrations in the dilute phase are not much affected.

Effect of Added Electrolyte

When NaCl is present in aqueous nonionic surfactant solutions, it causes the depression of the cloud point because chloride ions are water structure makers (salting-out effect). As seen in Table 1 and Figs. 3 and 4, the surfactant concentration and the concentration of TCE in the coacervate phase and TCE partition ratio increase and the coacervate volume decreases as the NaCl

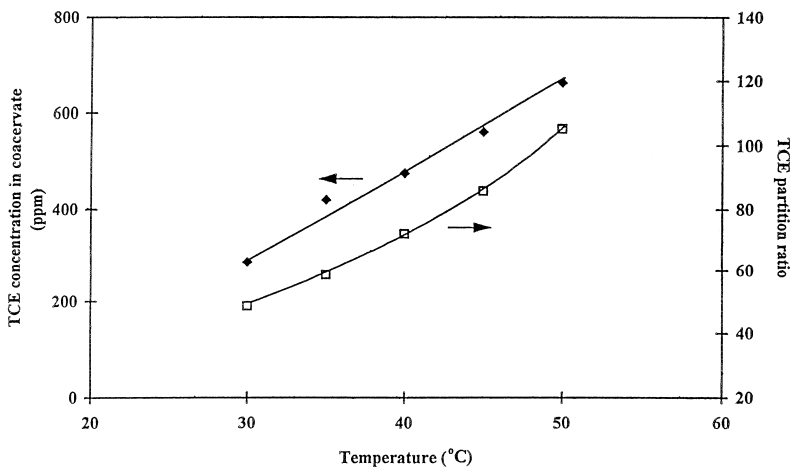


FIG. 2 Trichloroethylene concentration in coacervate phase and partition ratio as a function of temperature (System: 50 ppm TCE, 0.05 M surfactant, and 0.1 M NaCl).

concentration increases. Even though the dilute phase of most samples is clear, for the 0.05 M of OP(EO)₇ with no NaCl system, the dilute phase remains cloudy. Because the isothermal solution is further above the cloud point as the NaCl concentration increases, these results are consistent with the improved separation efficiency with increasing temperature as already dis-

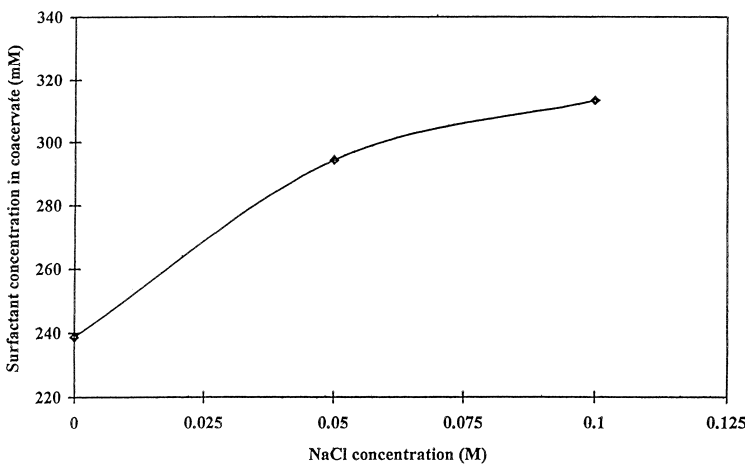


FIG. 3 Surfactant concentration in coacervate phase as a function of NaCl concentration (System: 50 ppm TCE, 0.05 M surfactant, and 30°C).

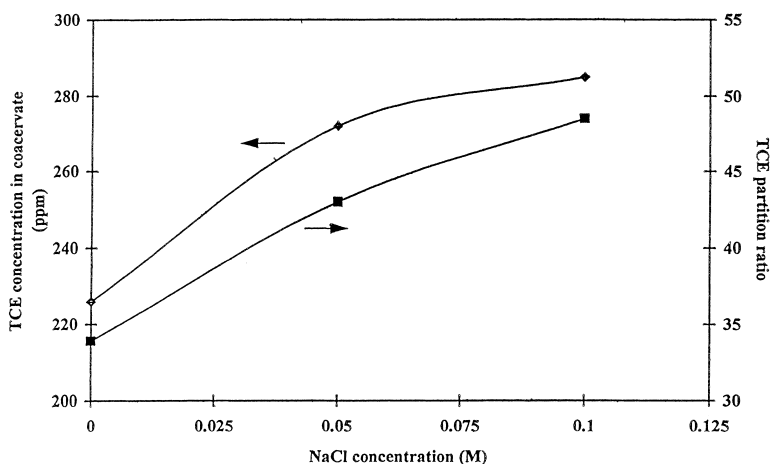


FIG. 4 Trichloroethylene concentration in coacervate phase and TCE partition ratio as a function of NaCl concentration (System: 50 ppm TCE, 0.05 M surfactant, and 30°C).

cussed. The concentration of surfactant in the dilute phase decreases substantially with increasing salinity, an effect not observed with increasing temperature. For at least some systems, as temperature increases above the cloud point a higher consolute solution temperature can be reached, above which the coacervate phase does not form, limiting the beneficial effect of increasing temperature. However, for the surfactants commonly of interest in this application, this higher consolute solution temperature is often above the boiling point of water and is not relevant. The difference between the system temperature and the cloud point can be increased by decreasing the degree of polymerization, increasing salinity, or increasing temperature.

Effect of Surfactant Concentration

As the initial concentration of surfactant increases at fixed temperature, the surfactant concentration in the coacervate phase remains nearly constant, so coacervate volume increases as required from material balances. Thus, there is more surfactant in micellar form present in the micelle-rich phase solution because of the volume increase, thereby increasing the solubilization capacity. Therefore, as shown in Fig. 5, the fraction of TCE in the coacervate phase increases when the initial surfactant concentration increases. However, as seen in Fig. 6, the partition ratio for both TCE and surfactant decreases. The dilute phase surfactant concentration increases substantially with increasing total surfactant concentration, resulting in a higher TCE solubilization in the micelles in the dilute phase and the reduced TCE partition ratio.

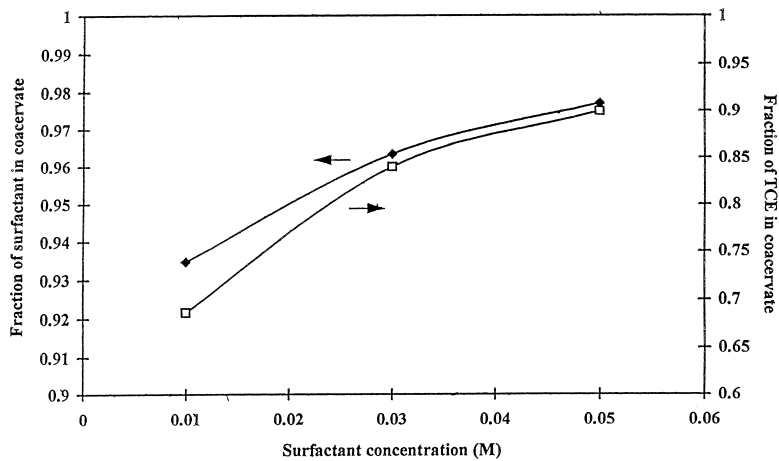


FIG. 5 Fraction of surfactant and TCE in coacervate phase as a function of surfactant concentration (System: 50 ppm TCE, 0.1 M NaCl, and 30°C).

Effect of TCE Concentration

As shown in Table 1 and Figs. 7 and 8, when the initial concentration of TCE increases, the fractional coacervate volume, TCE partition ratio, the fraction of TCE in the coacervate, and the fraction of surfactant in the coacervate are all relatively unaffected. Because the TCE : surfactant ratio in the systems studied was very low (<0.04 M ratio) under all conditions studied here, the lack of effect of initial TCE concentration is not unexpected.

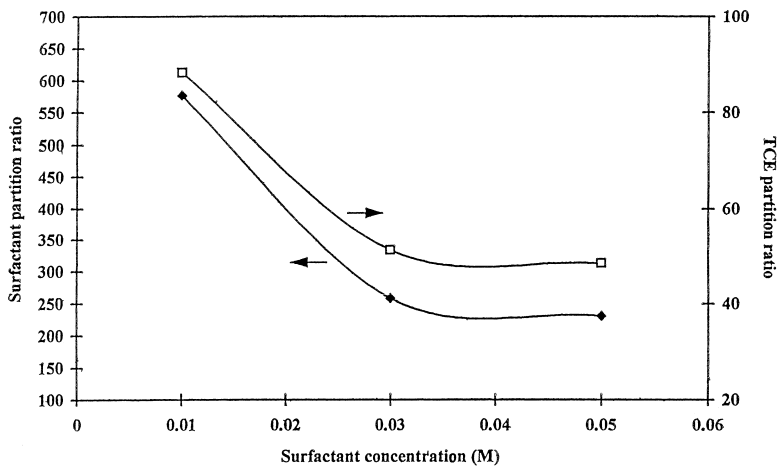


FIG. 6 Surfactant and TCE partition ratio as a function of surfactant concentration (System: 50 ppm TCE, 0.1 M NaCl, and 30°C).

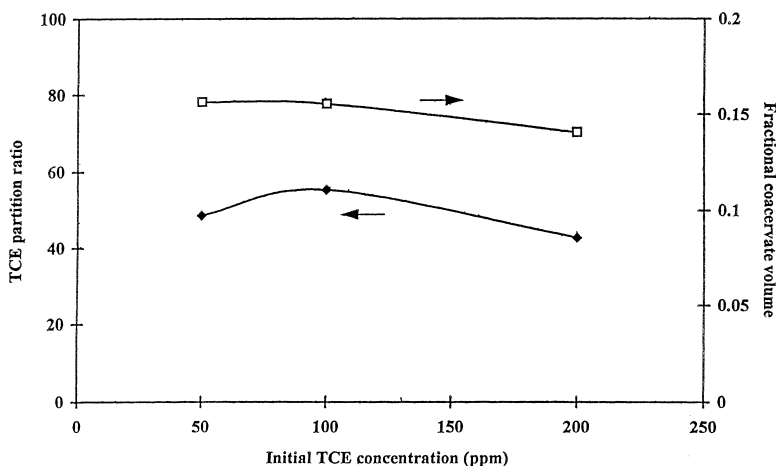


FIG. 7 TCE partition ratio and fractional coacervate volume as a function of initial concentration of TCE (System: 0.05 M surfactant, 0.1 M NaCl, and 30°C).

Scale-up of Separation

To make the coacervate extraction or cloud-point extraction industrially viable, two technological challenges are clear. First, surfactant-recovery techniques need to be developed. Vacuum stripping of coacervate-containing volatile organics like TCE will be a direct follow-up to this work and was a

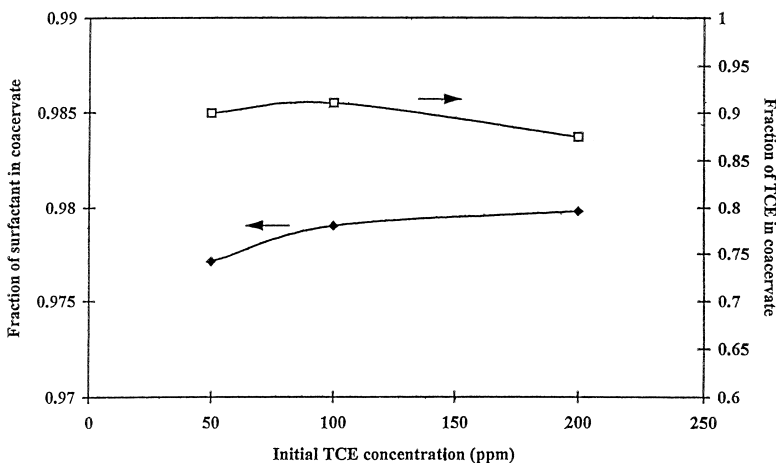


FIG. 8 Fraction of surfactant and TCE in coacervate phase as a function of initial concentration of TCE (System: 0.05 M surfactant, 0.1 M NaCl, and 30°C).

primary incentive to study a volatile solute, even though partition ratios are not nearly as high as for some low-volatility solutes. Secondly, the coacervate phase can be very viscous and have a density quite similar to that of the dilute phase, making phase separation after the extraction step sometimes slow. Thus, the physical behavior of the system in a multistage extractor may be troublesome. For example, whether the coacervate plugs the system and requires downstream treatment for phase separation (e.g., expensive centrifugation vs. gravity settling) are also focuses of future work.

ACKNOWLEDGMENTS

Financial support was provided by National Science Foundation Grant CBT 8814147, an Applied Research Grant from the Oklahoma Center for the Advancement of Science and Technology, the Center for Waste Reduction Technologies of the American Institute of Chemical Engineers, Agreement No. N12-N10, the TAPPI Foundation, the National Research Council of Thailand, Tuntex Petrochemical Co. Ltd. (Thailand), and U.S. Agency for International Development (University Development Linkages Project). In addition, support was received from the industrial sponsors of the Institute for Applied Surfactant Research including Akzo Nobel, Albemarle, Clorox, Colgate-Palmolive, Dial, Dow, DuPont, Halliburton, Huntsman, ICI, Kerr-McGee, Lubrizol, Nikko Chemical, Phillips Petroleum, Pilot Chemical, Procter and Gamble, Reckitt and Coleman, S. C. Johnson Wax, Schlumberger, Shell, and Unilever. Surfactant was provided by Rhodia Co. Ltd. (Thailand). Dr. Scamehorn holds the Asahi Glass Chair and Dr. Harwell holds the Conoco/DuPont Professorship in chemical engineering at the University of Oklahoma.

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Received by editor August 30, 1999

Revision received January 2000