



CHAPTER V

EFFECT OF NONIONIC SURFACTANT MOLECULAR STRUCTURE ON CLOUD POINT EXTRACTION OF PHENOL FROM WASTEWATER*

5.1 Abstract

Above a temperature known as the cloud point, aqueous solutions of nonionic ethoxylated surfactants separate into two phases: a coacervate phase concentrated in surfactant and a dilute phase with low surfactant concentration. The coacervate phase contains surfactant aggregates which are micelles or micelle-like and will solubilize any organic solutes originally present in the water, resulting in a liquid-liquid extraction known as a cloud point extraction (CPE). Removal of pollutants from water is an important potential application of CPE and we use phenol as a model organic pollutant in this work. In this study, we investigate the effect of surfactant structure on important equilibrium CPE parameters like cloud point, fractional coacervate volume, and phenol and surfactant partition ratios for alcohol ethoxylates (AEs), a major class of nonionic surfactants. Pure, homogeneous surfactants with linear hydrophobes are studied as well as commercial heterogeneous AEs with both linear and branched hydrophobes. The effects of degree of polymerization in the polyethoxylate group (EO number) as well as hydrophobe size (alkyl carbon number) are systematically investigated as well as the effect of hydrophobe branching. The solubilization equilibrium constant is shown to increase linearly with EO number and is unaffected by alkyl carbon number or hydrophobe branching from which we deduce that the phenol is solubilized with the benzene ring at the surface of the micelle core and the hydroxyl group having attractive interactions with the polyethoxylate chains in the palisade layer of the micelle. The effects of surfactant structural features on net intermicellar attractive forces, micellar excluded volume, and solubilization capacity are discussed. A model is developed

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which can predict the phenol partition ratio at a given temperature for any AE surfactant dependent on only one simple measured parameter: fractional coacervate volume. This universal model is somewhat unique to phenolics or short chain alcohols because of their solubilization loci in the micelle and mechanism of solubilization. Guidelines for surfactant selection for CPE of phenol or similar solutes are outlined.

Keywords: cloud point, extraction, nonionic surfactant, phenol, molecular structure

5.2 Introduction

Cloud point extraction (CPE) is a separation process that is of interest in the field of wastewater treatment (including contaminated groundwater remediation) where it has been shown to be an effective technique to remove dissolved organic contaminants from wastewater [1-12]. Polyethoxylated nonionic surfactants are utilized as the separating agent in the process. When the nonionic surfactant solution is at a concentration at least 3 to 20 times its CMC (depending on the system) and is at a temperature higher than its cloud point, phase separation will occur. Two micellar solutions are formed [2,3,5-14]. One is a concentrated surfactant micellar solution, known as a micellar rich phase or coacervate phase. The other is lean in surfactant micelles known as a dilute phase. The phenomenon takes place since increasing temperature induces the dehydration of surfactant poly(ethylene oxide) head groups, causing agglomeration of the micelles into a coacervate phase [15]. Organic solutes or contaminants tend to solubilize into surfactant micelles and concentrate in the coacervate phase. In a continuous multistage extractor, the number of stages can be increased until the dilute phase contains a low enough concentration of the pollutant to be emitted to the environment. A number of factors affect the cloud point [14,16-20], including the addition of polar organic solutes, such as fatty acids, aliphatic alcohols, and phenol, which generally lower the cloud point [17]. Some electrolytes can reduce the cloud point due to a salting-out effect [18]. In addition, lowering the number of ethylene oxide groups (EO number) or lengthening

the alkyl chain (alkyl carbon number) of the hydrophobic moiety of the nonionic surfactant lowers the cloud point [14,16,19,20].

Nonionic surfactants with a wide variety of structures are produced commercially. Various types and structures of nonionic surfactants had been selected for the study of CPE as reported in the literature [5-13], but there are few that have looked in detail at the effect of the surfactant structure itself on CPE. In this work, homologous series of alcohol ethoxylate (AE) nonionic surfactants with varied alkyl carbon number and EO number were studied systematically for CPE performance with phenol as the model aromatic pollutant being removed from wastewater. Alkylphenol ethoxylates have been widely used in the study of CPE in the past. However, environmental and health problems with alkylphenol ethoxylates have recently emerged with their persistence, bioaccumulation, and estrogenic effects [9,10]. Therefore, we have chosen the more environmentally benign AEs for study here.

This work presents the fraction of solute extracted, the coacervate fractional volume, and the concentrations of the solute and surfactant present in both phases after the separation in order to clearly understand the mechanism of surfactant structure effects on CPE. The CPE technique was successfully scaled-up to continuously remove aromatic contaminants from wastewater in a multi-stage rotating disc contactor by our research group [21-23]. Equilibrium batch data from the current study can be used to design the number of extraction stages or transfer units required to achieve a specified removal in either a batch or a continuous industrial separation.

5.3 Experimental

5.3.1 Materials

The structures of the nonionic surfactants used in this study, the trade names, the acronyms use here to refer to them, and their CMC values were given in Table 5.1. The homologous series of the polydisperse commercial alcohol ethoxylate $(R-OCH_2CH_2)_xOH$ nonionic surfactants with varied average alkyl carbon number (n) and average EO number (x), trade name Surfonic: TDA-5, TDA-6, TDA-8, TDA-

9, TDA-11, DDA-8, L12-8; and Neodol: 91-5, 91-6, 91-8) were contributed by Huntsman (USA) and Shell (USA), respectively. These surfactants are 100% active pure liquid and polydisperse in both degree of polymerization and in length of the alkyl chain. For the SURFONIC L series, the number following the “L” indicates the alcohol blend carbon number range. Ethoxylates in the L12 series are based on a blend of C10 to C12 primary linear alcohols. But since L12 is a blend of 10 to 12 carbons, we refer to the hydrophobe as an average of 11 carbons. DDA series are based on branched isododecyl (average C12) alcohol and TDA series are based on isotridecyl alcohol (average C13). The Neodol 91 series are based on a blend of C9 to C11 primary linear alcohol derivatives with at least 20% of 2-alkyl branching, so we consider the hydrophobe as 10 carbons. For all the commercial alcohol ethoxylates, the number following the hyphen indicates the average moles of ethylene oxide per mole of alcohol, e.g. Surfonic L12-8, DDA-8, TDA-8, Neodol 91-8 surfactants are 8-mole ethoxylates (average EO 8) of the specified alcohol or alcohol blend. Since the alcohol precursor is based on the modified oxo process, the Neodol surfactants are given the acronym MO here. The other commercial surfactants are referred to based on their hydrophobe structure (TDA, DDA, or L). The acronym was followed by the average EO number for TDA and DDA with a fixed hydrophobe (e.g., TDA 11) or by the alkyl carbon number, followed by the average EO number for L and MO where the hydrophobe size can vary (e.g. L 11-8). The homogeneous, Monodisperse polyoxyethylene nonionic surfactants (99% purity of alkyl carbon number and EO number), BD-6SY, BL-6SY, BM-6SY, BC-6SY, BL-5SY, BL-7SY, BL-8SY; (given the acronym here of C10EO6, C12EO6, C14EO6, C16EO6, C12EO5, C12EO7, C12EO8, respectively) were purchased from Nikko Chemicals (Tokyo, Japan). Reagent grade phenol (99.8% pure) and NaCl (99.9%) were purchased from Carlo Erba Inc. (Italy) and AJAX chemical company (Auburn, Australia), respectively. All chemicals were used as received. Distilled and deionized water was used throughout this study.

5.3.2 Cloud Point Determination

To measure the cloud point of the surfactants, the solution containing surfactant, solute, and electrolyte was transferred to a test tube with a thermometer and then the test tube was placed in an isothermal water bath. The solution was

Table 5.1 Trade name, acronym, molecular structures, and CMC of alcohol ethoxylate nonionic surfactants studied

Surfactant trade name	Company	Acronym	Molecular structure	CMC (mM) @ 25 °C
<i>Monodisperse nonionic surfactants (homogeneous surfactants)</i>				
BL-5SY	Nikko	C12EO5	linear C 12, EO 5	0.065 [*]
BL-6SY	Nikko	C12EO6	linear C 12, EO 6	0.067 [*]
BL-7SY	Nikko	C12EO7	linear C 12, EO 7	0.069 [*]
BL-8SY	Nikko	C12EO8	linear C 12, EO 8	0.071 [*]
BD-6SY	Nikko	C10EO6	linear C 10, EO 6	0.900 ⁺
BM-6SY	Nikko	C14EO6	linear C 14, EO 6	0.010 ⁺
BC-6SY	Nikko	C16EO6	linear C 16, EO 6	0.002 ⁺
<i>Polydisperse nonionic surfactants (commercial surfactants)</i>				
Surfonic TDA-5	Huntsman	TDA 5	branched isotridecyl C 13, EO 5	0.081 ⁻
Surfonic TDA-6	Huntsman	TDA 6	branched isotridecyl C 13, EO 6	0.094 ⁻
Surfonic TDA-8	Huntsman	TDA 8	branched isotridecyl C 13, EO 8	0.120 [*]
Surfonic TDA-9	Huntsman	TDA 9	branched isotridecyl C 13, EO 9	0.133 [*]
Surfonic TDA-11	Huntsman	TDA 11	branched isotridecyl C 13, EO 11	0.159 ⁻
Surfonic DDA-8	Huntsman	DDA 8	branched isododecyl C 12, EO 8	0.245 [*]
Surfonic L12-8	Huntsman	L 11-8	linear C10-C12, EO 8	0.149 [*]
Neodol 91-5	Shell	MO 10-5	20% branched C9-11, EO 5	0.655 ⁻
Neodol 91-6	Shell	MO 10-6	20% branched C9-11, EO 6	0.684 [*]
Neodol 91-8	Shell	MO 10-8	20% branched C9-11, EO 8	0.742 [*]

^{*} from suppliers [24-26]

⁺ from Rosen, 1989 [14]

⁻ from extrapolation of suppliers' CMC data

gradually heated until turbidity was observed, then the temperature was gradually dropped until the solution became clear. Turbidity indicates formation of a second liquid phase whose droplets scatter light, so if heating/cooling rates are low enough, the cloud point indicates a thermodynamic phase boundary. In our experiments, the cloud point obtained upon heating was the same as that measured upon cooling, the lack of hysteresis indicating that the equilibrium value is being obtained.

5.3.3 Procedures

The aqueous solution of phenol (a model solute) and surfactant was prepared at initial concentrations of 100 ppm and 70 mM, respectively, with 0.8 M NaCl for all systems. The solution was transferred into several test tubes and left in an isothermal water bath at 80 °C until the system reached equilibrium. The equilibrium time in the system was identified when there was no change in either phase height or concentration of surfactant in the dilute phase. In order to speed up the phase separation, the centrifugation can be employed if required [3]. After the phase separation reached equilibrium, the concentrations of surfactant and phenol in each phase were analyzed. The coacervate fractional volume was also measured. To prevent a disturbance of the equilibrium of the system from the temperature change during the sampling of both phases, a glass-made water bath was special designed and utilized in this work in order to let the phase separation be clearly seen, and so the samples could be sampled without removing the test tubes from the bath. Experiments were replicated enough times to ensure reproducibility with a precision of less than $\pm 5\%$ in phase volume and each concentration.

The phenol concentration was measured by using a CE 2000 series UV-spectrophotometer (Cecil Instrument Limited, Cambridge, UK) at 270 nm. The surfactant concentration was obtained from a Total Organic Carbon analyzer (TOC 5000A, Shimadzu) after subtracting the phenol contribution to that measurement. The external standard quantitative calibrations were obtained for the analysis of surfactant and phenol in both phases. Material balances were performed for both phenol and surfactant and closure within 5% indicated insignificant leakage from the system.

5.4 Theory

In aqueous surfactant solution, the ability of micelles to solubilize solutes is usually described by a solubilization equilibrium constant (K_m), which is defined by

$$K_m = X_m / C_u = [O]_{mic} / (C_u ([surfactant]_{mic} + [O]_{mic})) \quad (1)$$

where X_m is the mole fraction of solute in micelles, C_u is the concentration of unsolubilized organic solute, $[O]_{mic}$ is the solute concentration solubilized in surfactant micelles and $[surfactant]_{mic}$ is the surfactant concentration in micellar form. Eq. (1) describes the solubilization of the solute into the micelles in the dilute phase [27].

In CPE, in order to determine the tendency of the organic solute to solubilize into the surfactant aggregates in the coacervate phase, a coacervate solubilization equilibrium constant (K_c) can be defined in analogy to K_m [27].

$$K_c = X_c / C_u = [O]_{agg,c} / (C_u ([surfactant]_{agg,c} + [O]_{agg,c})) \quad (2)$$

where X_c is the mole fraction of solute in the coacervate aggregate, C_u is the concentration of unsolubilized organic solute in the coacervate phase, $[O]_{agg,c}$ is the solute concentration associated with surfactant aggregate in the coacervate phase, and $[surfactant]_{agg,c}$ is the surfactant concentration in the aggregate in the coacervate phase. The value of C_u is assumed to be equal in the dilute phase and the coacervate phase and so is the same in Eq. (1) and Eq. (2). This assumes that the solute is dilute enough to obey Henry's law and that the Henry's law constant is the same in both dilute and coacervate phases since both are aqueous solutions [27].

From material balances:

$$[O]_{agg,c} = [O]_c - C_u \quad (3)$$

$$[surfactant]_{agg,c} = [surfactant]_c - CMC \quad (4)$$

where $[O]_c$ and $[surfactant]_c$ are the total solute and surfactant concentration in the coacervate phase, respectively. The CMC is assumed to be equal to the monomeric surfactant concentration in the coacervate phase. Then,

$$K_c = ([O]_c - C_u) / (C_u ([O]_c - C_u + [surfactant]_c - CMC)) \quad (5)$$

By analogy, when considering the dilute phase,

$$K_m = ([O]_{dil} - C_u) / (C_u ([O]_{dil} - C_u + [\text{surfactant}]_{dil} - CMC)) \quad (6)$$

where $[O]_{dil}$ and $[\text{surfactant}]_{dil}$ are the total solute and surfactant concentration in the dilute phase. In a previous paper, our group has used dialysis experiments to prove that K_m in the dilute phase is very close to K_c [27], so we will make that assumption here. With $K_m = K_c$, all variables except K_c and C_u in Eq. (5) and Eq. (6) are measured in this work, so these two equations can be solved for K_c and C_u .

5.5 Results and Discussion

Extraction performance is quantified here by the fractional coacervate volume (defined as the coacervate phase volume divided by total volume), phenol partition ratio or surfactant partition ratio (defined as the phenol or surfactant concentration in the coacervate phase divided by that in the dilute phase), and the fractional phenol extraction (defined as the weight of phenol which resides in the coacervate phase after equilibration divided by the original weight of phenol in the system all multiplied by 100 to yield a percentage). A low fractional coacervate volume means that a smaller coacervate stream must be treated to recover to surfactant by reuse (e.g., by vacuum stripping [28,29]) or disposal. This combined with a high phenol partition ratio, indicates the ability of the technique to preconcentrate the solute in analytical chemistry applications and the final dilute phase phenol concentration (e.g., if it is acceptable for discharge to the environment). The fractional phenol extraction can be calculated from these more basic parameters and is often a required criterion of performance. In this work, all concentrations are in M or mM units except for the phenol, which is in ppm since that is the convention for pollutants being removed from water in environmental science. We will refer to the average number of carbons in the hydrophobe as the alkyl carbon number and to the average degree of polymerization of the polyethoxylate as the EO number throughout this paper.

5.5.1 Effect of Surfactant Structure on Cloud Point

The cloud point (c.p.) of 70 mM nonionic surfactant solutions as a function of EO number and alkyl carbon number with 100 ppm of phenol and 0.8 M

NaCl given in Tables 5.2 and 5.3 are illustrated as in Figs. 5.1(a) and 5.1(b), respectively. The cloud point of the nonionic surfactant solution increases with EO number, and decreases with alkyl carbon number consistent with this well known effect [14,16]. With decreasing EO number or increasing alkyl carbon number, intermicellar attractive forces increase and cloud point decreases since cloud point is the temperature at which micelles agglomerate or coagulate into a micellar rich phase. From Fig. 5.1, the commercial surfactants DDA 8, TDA 8, TDA 6 and MO 10-6 show a substantially lower cloud point than the linear C12EO_x surfactant with the same alkyl carbon number and the same EO number in the hydrophile. This may be due to branching in the hydrophobe, but the heterogeneity of the commercial surfactants may also have an effect as compound purity has been attributed as a cause of such deviation in other work [19,20]. We tentatively attribute the cloud point depression of the DDA, TDA, and MO surfactants in Fig. 5.1 to hydrophobe branching.

5.5.2 Qualitative Effects of Surfactant Structure on CPE Efficiency and K_c

The fractional coacervate volume, the phenol and surfactant partition ratios, the concentrations of phenol and surfactant in the dilute phase and coacervate phase, and the fractional phenol extraction for the CPE of all surfactants studied are shown in Tables 5.2 and 5.3. Also shown in Tables 5.2 and 5.3 are the calculated values of K_c and C_u from Eqs. (5) and (6) as well as the fraction of phenol in the dilute phase which is unsolubilized ($C_u / [O]_{dil}$). The equilibrium condition was as follow: initial surfactant concentration = 70 mM, initial phenol concentration = 100 ppm, NaCl concentration = 0.8 M and operating temperature = 80 °C. Fig. 5.2 shows fractional coacervate volume and Fig. 5.3 shows the surfactant concentration in the coacervate phase as a function of EO number for the C12EO_x, TDA, and MO 10 series. An increase in the number of EO moieties present in a series of surfactants results in an increase in the fractional coacervate volume while the surfactant concentration in the coacervate phase decreases substantially. Since almost all (97-99%) of the surfactant is presented in the coacervate, this latter effect is required from a material balance. Fig. 5.4 shows the effect of alkyl carbon number on fractional coacervate volume and surfactant concentration in the coacervate phase for the C_nEO6 series. Increasing alkyl carbon number and increasing EO number cause

Table 5.2 CPE parameters for homogeneous surfactants: initial surfactant concentration = 70 mM, initial phenol concentration = 100 ppm, NaCl concentration = 0.8 M and temperature = 80 °C

Surfactant	Number of C and EO	Cloud point (°C)	Fractional coacervate volume	Dilute phase		Coacervate phase		Partition ratio		Fractional phenol extraction (%)	C _u (ppm)	Fraction of phenol in dilute phase which is unsolubilized (%)	K _c (L/mol)	Phenol partition ratio from Eq. (8)
				[Phenol] (ppm)	[Surfactant] (mM)	[Phenol] (ppm)	[Surfactant] (mM)	Phenol	Surfactant					
C12EO5	12, 5	25	0.032	43.3	1.16	1823.6	2112.2	42.1	1820.9	58.2	42.4	97.9	19.7	45.4
C12EO6	12, 6	41.5	0.050	40.7	1.51	1218.2	1354.5	29.9	897.0	61.2	39.4	96.9	21.9	32.1
C12EO7	12, 7	53.5	0.064	39.7	1.69	985.3	1064.2	24.8	629.7	62.9	38.3	96.4	23.0	27.4
C12EO8	12, 8	64	0.082	38.1	1.85	785.1	835.4	20.6	451.6	64.8	36.5	95.7	24.9	23.2
C10EO6	10, 6	50	0.042	41.5	1.75	1430.8	1558.0	34.5	888.8	60.2	40.7	98.2	21.7	38.2
C14EO6	14, 6	35.5	0.156	42.5	1.69	411.1	446.2	9.7	264.0	57.5	41.1	96.7	20.0	10.3
C16EO6	16, 6	30	0.214	40.0	1.65	319.3	335.6	8.0	203.4	63.0	38.6	96.6	21.5	7.5

*For all nonionic surfactant solutions reported in this paper, the micellar coacervate phase appeared as the top phase since the density of AE coacervate phase was lower than the aqueous dilute phase.

Table 5.3 CPE parameters for commercial surfactants: initial surfactant concentration = 70 mM, initial phenol concentration = 100 ppm, NaCl concentration = 0.8 M and temperature = 80 °C

Surfactant	Number of C and EO	Cloud point (°C)	Fractional coacervate volume	Dilute phase		Coacervate phase		Partition ratio		Fractional phenol extraction (%)	C _u (ppm)	Fraction of phenol in dilute phase which is unsolubilized (%)	K _c (L/mol)	Phenol partition ratio from Eq. (8)
				[Phenol] (ppm)	[Surfactant] (mM)	[Phenol] (ppm)	[Surfactant] (mM)	Phenol	Surfactant					
TDA 5	13, 5	24.2	0.037	43.6	0.75	1841.4	2017.3	42.2	2689.5	61.9	43.0	98.6	20.5	39.3
TDA 6	13, 6	26.5	0.042	40.1	1.19	1686.0	1789.6	42.0	1503.9	64.8	39.1	97.5	23.3	38.2
TDA 8	13, 8	30	0.057	38.2	1.44	1313.9	1291.5	34.4	897.3	67.5	36.9	96.6	26.5	33.3
TDA 9	13, 9	40.5	0.067	36.5	1.60	1176.0	1104.6	32.7	690.4	69.1	35.0	95.8	29.2	30.6
TDA 11	13, 11	55.5	0.081	34.1	2.13	980.1	925.2	28.8	430.1	71.6	32.1	94.1	31.6	29.0
DDA 8	12, 8	38	0.059	38.2	1.85	1305.0	1298.9	34.2	703.8	68.2	37.2	97.3	26.0	32.2
L11-8	10-12, 8	63	0.066	38.5	1.79	1135.4	1142.5	29.5	639.7	67.6	36.9	95.5	25.8	28.8
MO 10-5	9-11, 5	25	0.037	43.9	1.07	1829.1	2027.2	41.6	1888.7	61.5	43.5	99.2	20.0	39.3
MO 10-6	9-11, 6	41	0.043	42.9	1.18	1598.3	1687.5	37.3	1430.1	62.6	42.4	98.9	21.5	37.3
MO 10-8	9-11, 8	65.5	0.068	38.1	1.38	1101.0	1103.2	28.9	799.4	67.5	37.5	98.4	25.5	27.9

*For all nonionic surfactant solutions reported in this paper, the micellar coacervate phase appeared as the top phase since the density of AE coacervate phase was lower than the aqueous dilute phase.

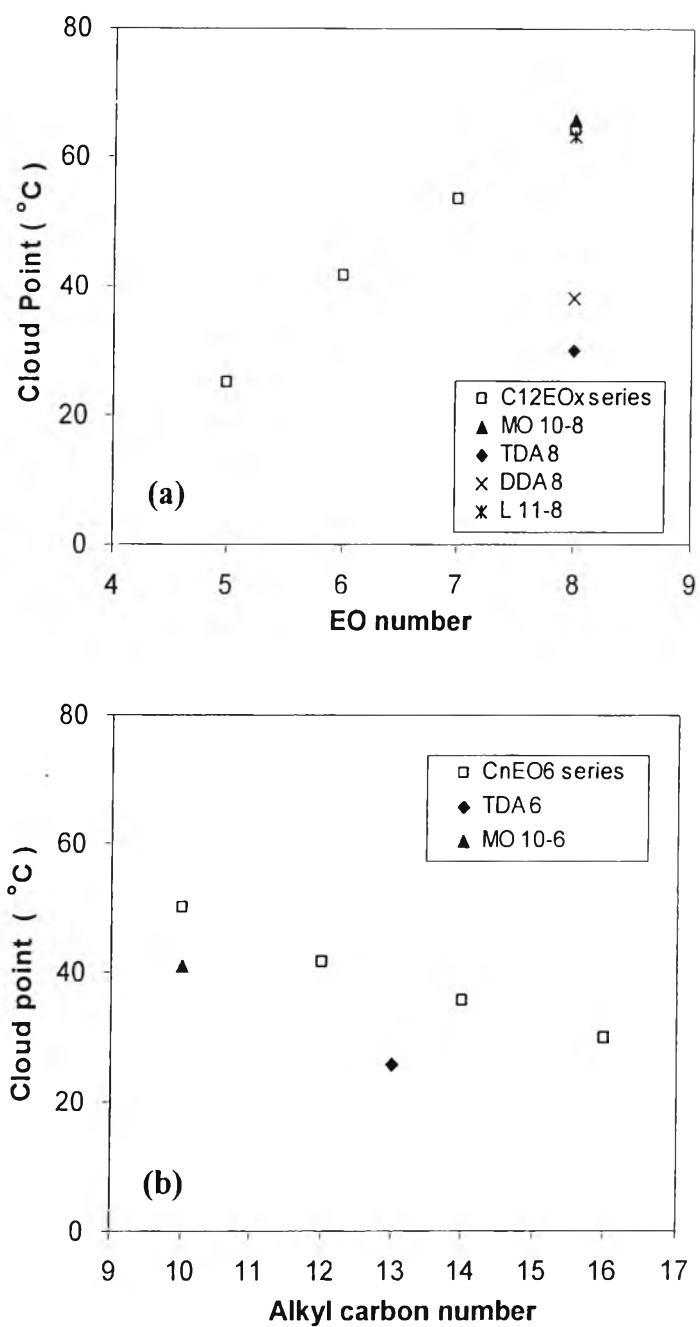


Figure 5.1 Effects of (a) EO number and (b) alkyl carbon number on cloud point (°C) of commercial (closed symbol) and homogeneous (open symbol) nonionic surfactants. (system: surfactant concentration 70 mM, phenol concentration 100 ppm, and NaCl concentration 0.8 M)

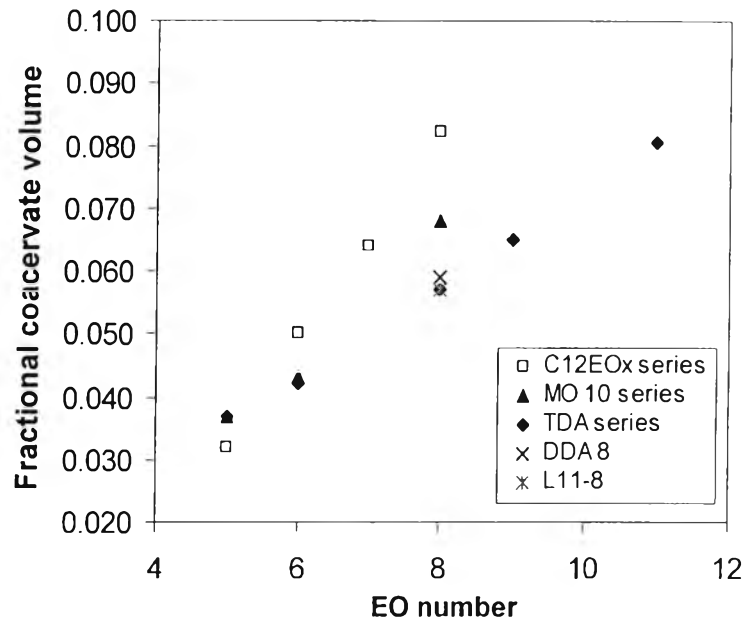


Figure 5.2 Fractional coacervate volume as function of EO number of various nonionic surfactants.

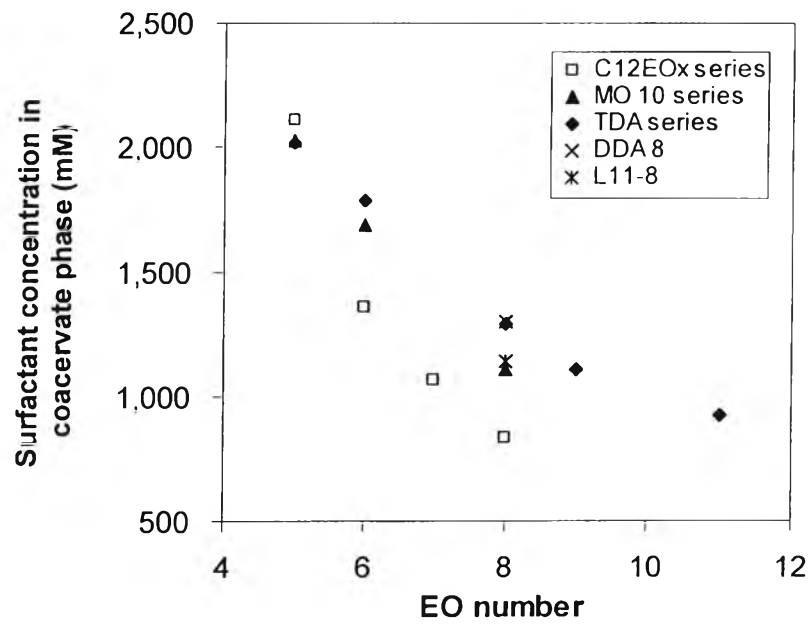


Figure 5.3 Surfactant concentration in the coacervate phase as function of EO number of various nonionic surfactants.

the fractional coacervate volume to increase, which is hypothesized to be due to higher micellar excluded volumes, resulting in a less concentrated coacervate. From Fig. 5.2, the branched commercial surfactants at $EO = 8$ have lower fractional coacervate volume, even when the average alkyl carbon number is higher compared to C12EO8, so we hypothesize that increasing hydrophobe branching reduces micellar excluded volume. This latter effect is not as clear as the alkyl carbon number or EO number effect as shown in Figs. 5.2 and 5.4. Heterogeneity might also be a cause as branching and heterogeneity are both present in commercial surfactants.

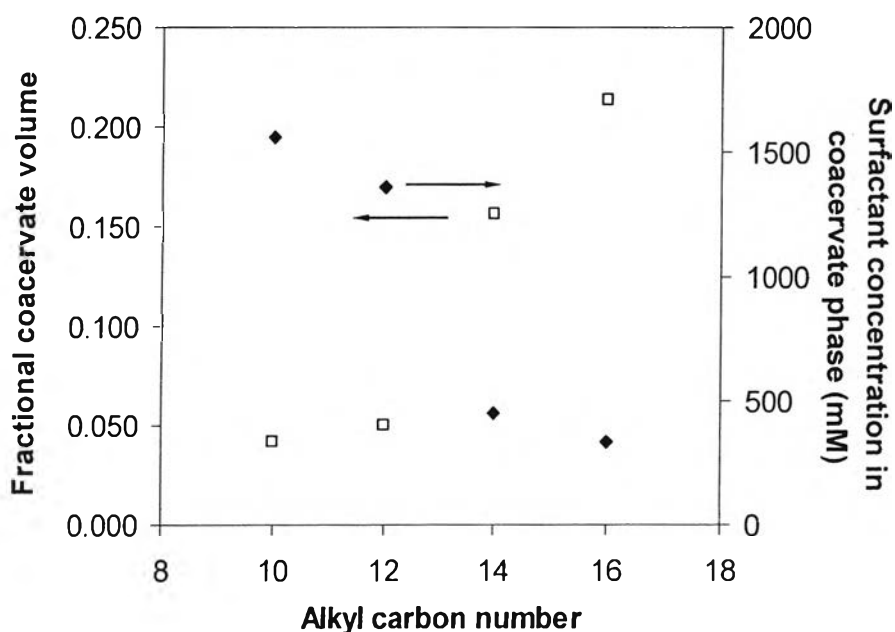


Figure 5.4 Fractional coacervate volume (open symbol) and surfactant concentration in the coacervate phase (closed symbol) as function of alkyl carbon number of homogeneous nonionic surfactants (C_nEO6 series).

Figs. 5.5 and 5.6 shows that the surfactant concentration in the dilute phase increases with increasing EO number, decreases with increased hydrophobe branching, and is not systematically affected by alkyl carbon number. Fig. 5.6 shows that the dilute phase phenol concentration does not vary systematically with alkyl carbon number. A rather surprising result in Fig. 5.7 is that the dilute phase phenol concentration depends only on EO number and not on alkyl carbon number or

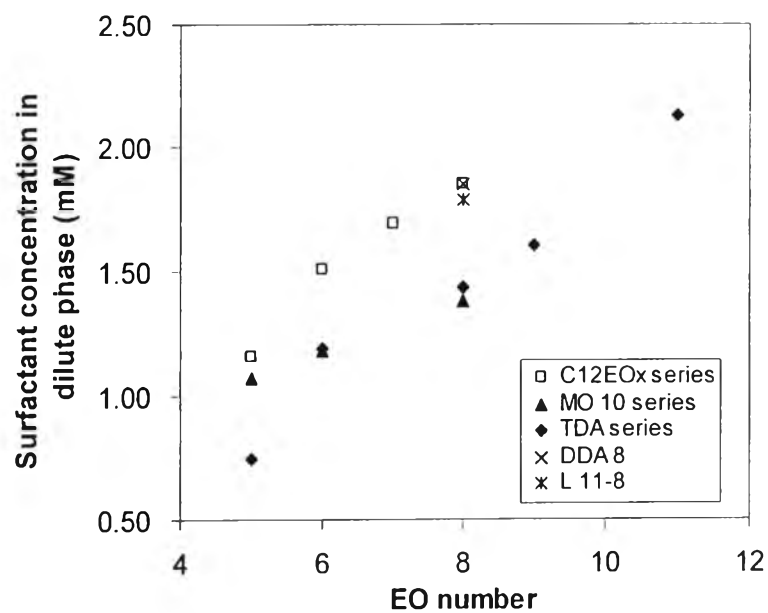


Figure 5.5 Surfactant concentration in the dilute phase as function of EO number of various nonionic surfactants.

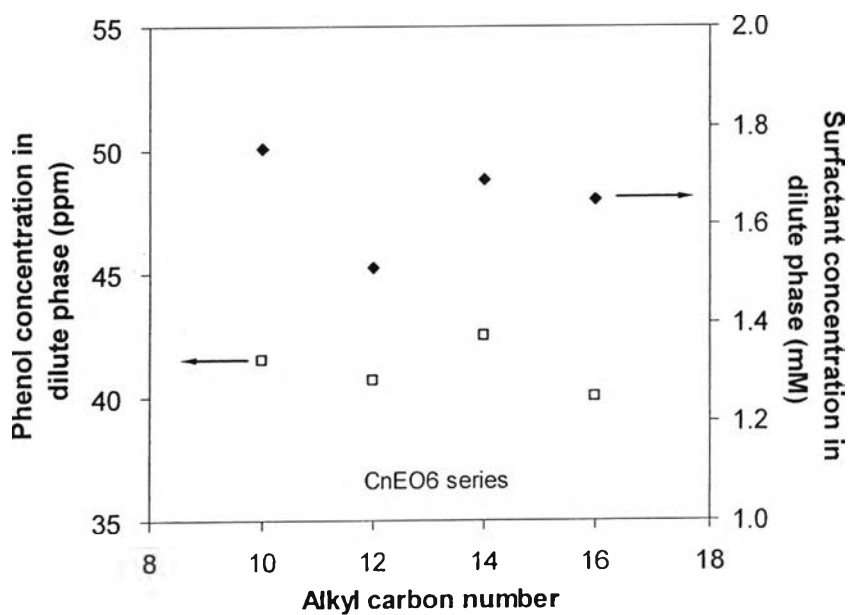


Figure 5.6 Phenol (open symbol) and surfactant (closed symbol) concentration in the dilute phase as function of alkyl carbon number of homogeneous nonionic surfactants (C_nEO₆ series).

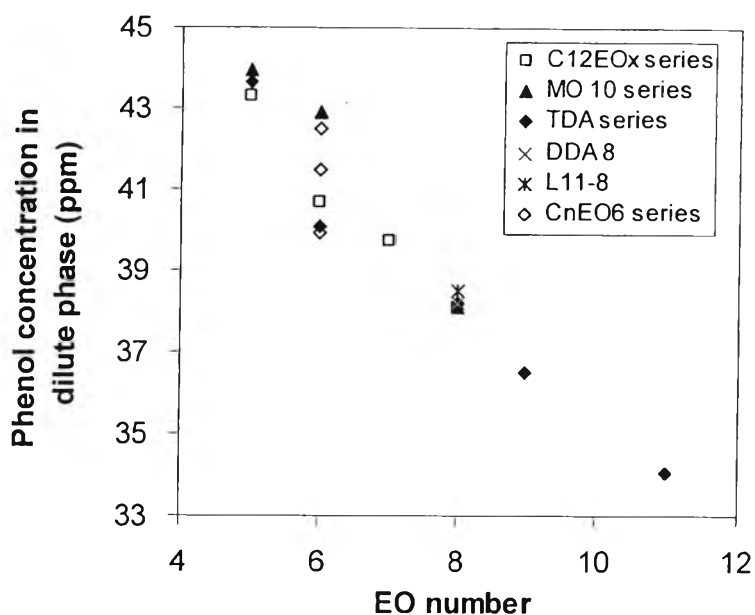


Figure 5.7 Phenol concentration in the dilute phase as function of EO number of various nonionic surfactants.

branching. The result is explained by Figs. 5.8 and 5.9 where K_c is independent of alkyl carbon number and hydrophobe branching, but increases linearly with EO number. Phenol solubilizes in the coacervate surfactant aggregates with the benzene ring in the palisade layer at the edge of the hydrophobic core with the phenol hydroxyl group sticking into the hydrophilic region of the micelle where the EO chains wrap around them. So, the more EO groups, the greater the dipole-dipole interaction with the -OH group in the phenol and the greater is K_c . Since the benzene ring only extends three to four carbon groups into the micelle or aggregate core, increasing the core diameter (increasing alkyl carbon number or decreasing branching) does not significantly increase solubilization. Kandori *et al.* [30] also concluded that the phenol solubilizes in the palisade layer in nonylphenol ethoxylate nonionic surfactant micelles.

Since the surfactant concentration in the dilute phase increases with increasing EO number (Fig. 5.5) and K_c increases with increasing EO number (Fig. 5.9), it seems like solubilization into micelles in the dilute phase would increase with increasing EO number and the dilute phase phenol concentration increase rather than decrease (Fig. 5.7) with EO number. As seen in Tables 5.2 and 5.3, almost all of the phenol in the dilute phase is unsolubilized (94.1 to 99.2%) and the value of C_u decreases as EO number increases because of increased solubilization (K_c) into the

coacervate surfactant aggregates, reducing the unsolubilized phenol concentration in both coacervate and dilute phases. With increasing EO number, the fractional coacervate volume increases, the coacervate surfactant concentration decreases, and the dilute phase surfactant concentration increases. The latter two effects cause the surfactant partition ratio to decrease with increasing EO number as seen in Fig. 5.10. Since the dilute phase phenol concentration decreases with increasing EO number (Fig. 5.7), the partition ratio of phenol decreases less rapidly with increasing EO number (Fig. 5.11) than that of the surfactant partition ratio. Moreover, surfactant and phenol partition ratio decreases with increasing alkyl carbon number, because of a consistent increase in the fractional coacervate volume and a decrease in the coacervate surfactant concentration (Fig. 5.12). Frankewish and Hinze [7] studied various factors affecting CPE, including variation of surfactant alkyl chain length and ethylene oxide groups on CPE of phenol and 4-chlorophenol. They reported a decrease in the phenol distribution coefficient (or partition ratio) as surfactant alkyl chain length increased and as the number of ethylene oxide groups in the surfactant increased. Also, the phase volume ratio (of the coacervate phase) was found to increase as alkyl chain length increased, which explained an offset of the extraction performance of more hydrophobic surfactants in that work.

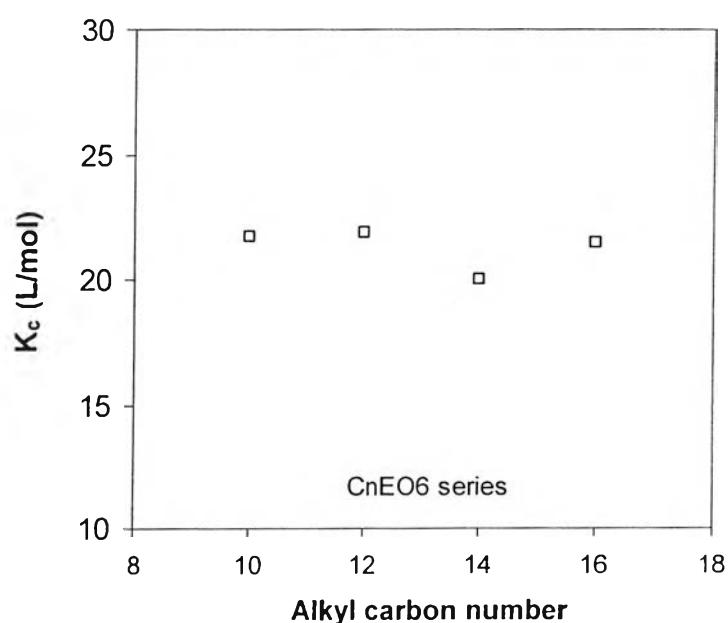


Figure 5.8 Coacervate solubilization equilibrium constant (K_c) as function of alkyl carbon number of homogeneous nonionic surfactants (CnEO6 series).

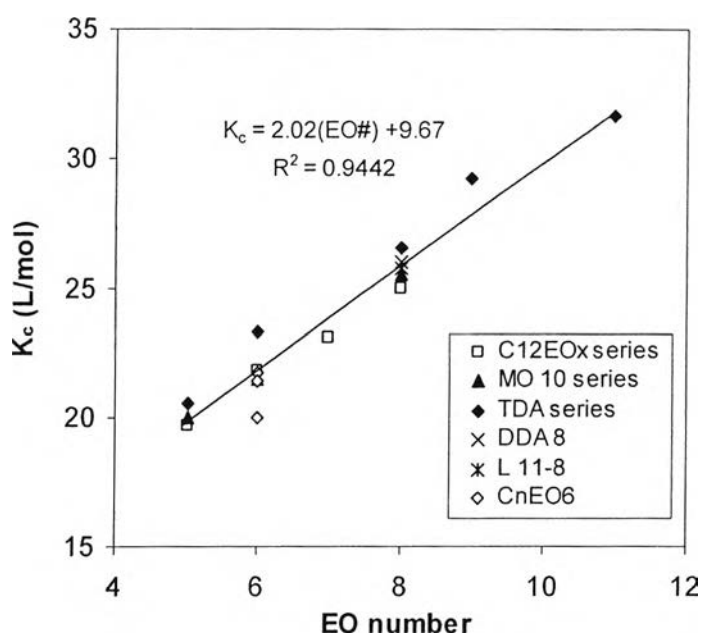


Figure 5.9 Coacervate solubilization equilibrium constant (K_c) as function of EO number of commercial (closed symbol) and homogeneous (open symbol) nonionic surfactants.

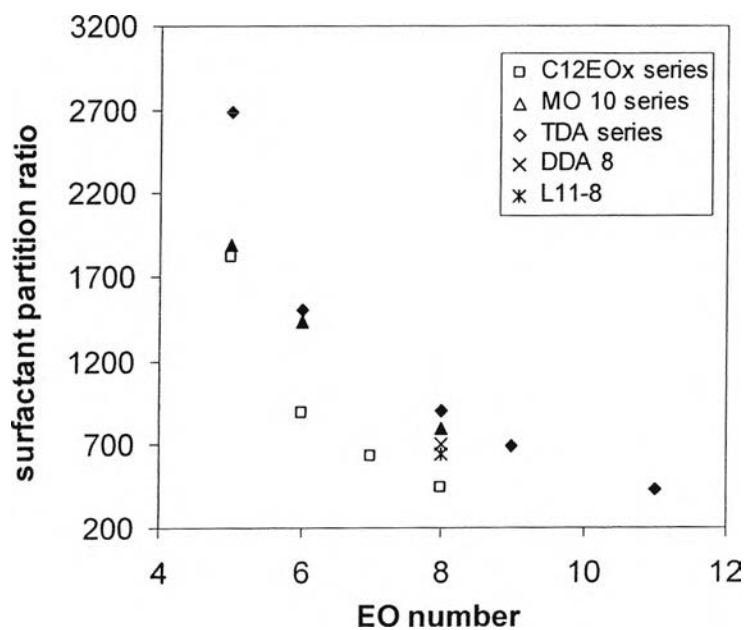


Figure 5.10 Surfactant partition ratios as function of EO number of various nonionic surfactants.

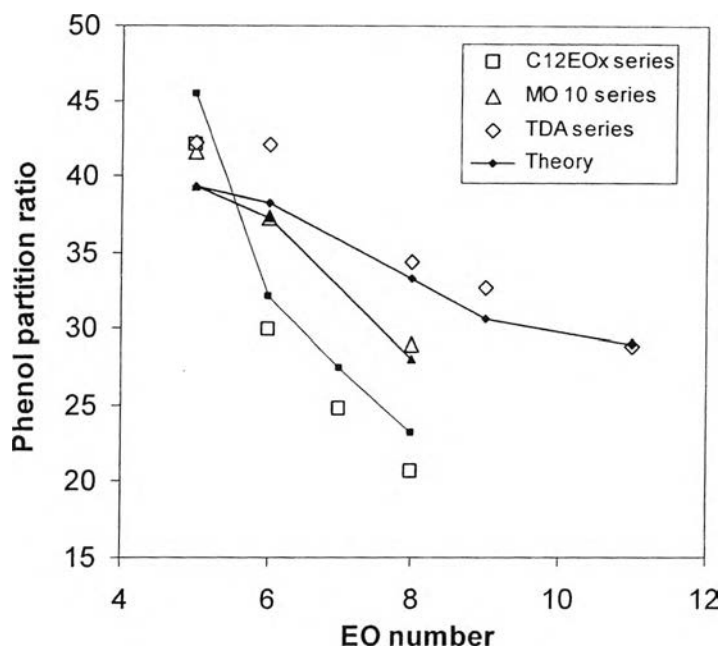


Figure 5.11 Experimental and theoretical phenol partition ratios as function of EO number of various nonionic surfactants.

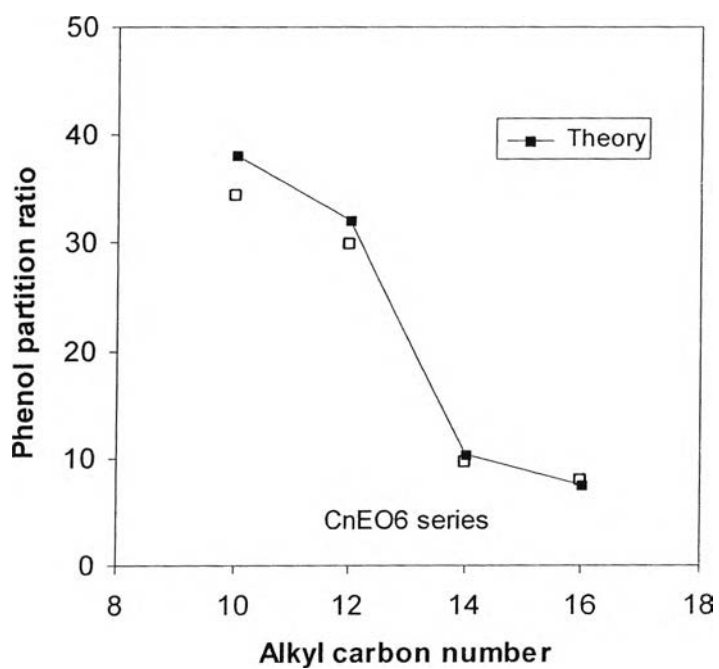


Figure 5.12 Experimental and theoretical phenol partition ratios as function of alkyl carbon number of homogeneous nonionic surfactants (CnEO6 series).

5.4.3 Modeling Surfactant Structure Effects on CPE Efficiency

Three basic intermolecular forces are hypothesized to control the important CPE efficiency parameters: net intermicellar attraction; micellar excluded volume; and tendency of the phenol to solubilize in micelles. Table 5.4 summarizes the qualitative effects of surfactant structure on these parameters.

The net intermicellar attraction is inversely related to the cloud point and so increases with decreasing EO number, increasing alkyl carbon number, and increasing hydrophobe branching as discussed with respect to Fig. 5.1. As intermicellar attraction increases, micelles can coagulate into a coacervate phase at a lower temperature or a lower cloud point. The micellar excluded volume determines the density of the coacervate phase when it forms as it indicates the volume occupied by each micelle and is proportional to fractional coacervate volume. The micellar excluded volume at constant temperature increases with increasing EO number, increasing alkyl carbon number, and decreasing hydrophobe branching. The tendency of a solute to solubilize in micelles increases with increasing K_c (shown to be similar to K_m for ethoxylated nonionic surfactant [27]) and increases with increasing EO number as shown in Fig. 5.9 and is not significantly affected by alkyl carbon number or hydrophobe branching. Over the range of EO numbers studied here, the best fit line to all the systems studied is:

$$K_c = 2.02 (\text{EO}\#) + 9.67 \quad (7)$$

where K_c is in (L/mol) and EO# is the average degree of polymerization of the polyethoxylate group.

The fractional coacervate volume is a crucial practical parameter in that it indicates the reduction in volume of a feed waste stream from which phenol is being extracted. It also is closely tied to the phenol partition ratio (PR_{phenol}), since a majority (57.5% to 71.6%) the phenol is in the coacervate phase, so the coacervate phenol concentration is approximately inversely proportional to fractional coacervate volume (FCV). Within a series with EO number alone varying, fractional coacervate volume varies linearly with EO number (Fig. 5.2). However, unlike K_c , there is no universal correlation observed for fractional coacervate volume as alkyl carbon

Table 5.4 Summary of effect of nonionic surfactant molecular structure on CPE parameters

Surfactant structure	Net micellar attraction	Micellar excluded volume	Tendency for phenol to solubilize, K_c	Cloud point	Fractional coacervate volume	Phenol partition ratio
Increase EO number	Decrease	Increase	Increase	Increase	Increase	Decrease
Increase C number	Increase	Increase	No change	Decrease	Increase	Decrease
Increase hydrophobe branching	Increase	Decrease	No change	Decrease	Decrease	Increase

number (Fig. 5.4) or hydrophobe branching (Fig. 5.2) varies. Therefore, we assume that fractional coacervate volume is measured for the system of interest.

We hypothesize that the value of phenol partition ratio is proportional to K_c and inversely proportional to fractional coacervate volume. These assumptions are reasonable for systems in which the solute is predominantly presented in the coacervate (here 57.5% to 71.6%) or alternatively, the dilute phase dominates the volume (here > 78.4%), and the dilute phase solute is predominantly unsolubilized (here > 94.0 %). While these approximations are not precise, our goal is to develop a very simple mathematical model to predict CPE efficiency and we are just demonstrating that there is justification for the assumptions made. We further hypothesize that the proportionality constant (A) is universally applied to all ethoxylated alcohols at the specified temperature, added electrolyte concentration, solute concentration, and surfactant concentration.

$$PR_{\text{phenol}} = A (K_c) / (\text{FCV}) \quad (8)$$

Where PR_{phenol} is the phenol partition ratio and FCV is the fractional coacervate volume.

Eq. (7) is used to calculate K_c used in Eq. (8). All systems studied yielded a value of A, which were averaged to obtain the universal A (value of universal A = 0.074 ± 0.005 mol/L). This value of A was then used to predict the PR_{phenol} as shown in Tables 5.2 and 5.3 and Figs. 5.11 and 5.12. Given that homogeneous and commercial branched and unbranched surfactants from 10 to 16

carbon numbers and 5 to 11 EO numbers are included, the prediction agrees with the data remarkably well with an average deviation of 6.1%. So, if EO number is known, and fractional coacervate volume measured, phenol partition ratio can be calculated for a given ethoxylated alcohol at 80 °C with 0.8 M NaCl. Other parameters such as fractional phenol extraction can be calculated from these basic parameters. We don't address prediction of surfactant partition ratio or surfactant concentration in the dilute phase here. Other than the cloud point, the fractional coacervate volume is the easiest parameter to measure in these systems as no concentrations of solute or surfactant needs to be measured. After equilibration in a graduated tube (tightly sealed to avoid evaporation), the phase volumes are visually noted.

In general, the greater the difference between the operating temperature and the cloud point, the better the separation (lower fractional coacervate volume, higher partition ratios) when varying temperature or EO number within a series. In our previous papers, this was demonstrated by altering operating temperature at constant cloud point [11,12,22,27] or altering the cloud point by changing the solute type or concentration [11,12,21,23,27]. In this work, our initial inclination was to correlate CPE performance to cloud points at a given operating temperature since cloud points are generally available from suppliers or are trivial to measure. However, referring to Table 5.4, increasing alkyl carbon number causes cloud points to decrease while fractional coacervate volume increases (in contrast to the effect of EO number or hydrophobe branching), so the net intermicellar attraction and the micellar excluded volume follow the same trend, both increasing with alkyl carbon number. Therefore, as a warning to other researchers, using the cloud point as the correlating parameter for CPE efficiency makes inclusion of variable hydrophobe size difficult or impossible.

5.5.4 Generalizing Predictions of CPE Efficiency

The remarkable universal applicability of the model (Eqs. (7) and (8)) used here for phenol at 80 °C and 0.8 M NaCl for any ethoxylated alcohol raises the question of its usefulness for other solutes or surfactant classes. Phenol has a short hydrophobic portion (benzene ring) and a highly polar hydroxyl group. The small hydrophobic group anchored to the micelle surface by the hydroxyl group is the

reason K_c only depends on EO number and not on surfactant hydrophobe length or branching. A solute with a polar group, but a longer hydrophobic group, like *n*-decanol, would locate in the hydrophobic region much deeper in the micellar core [14,31] and the value of K_c would depend on the surfactant hydrophobe structure. A very hydrophobic solute like toluene or trichloroethylene would solubilize throughout the micellar core [14,31,32] and K_c would depend on the surfactant hydrophobe, but not much on EO number in general. Also, the success of the model depended on the high water solubility of phenol along with a modest K_c , resulting in the vast majority of phenol in the dilute phase being unsolubilized, so the solute concentration in the dilute phase only varies slightly with solute structure (hence, the assumption that phenol partition ratio is proportional to K_c). We have shown [27] that most of the solute in the dilute phase can be solubilized in micelles for highly hydrophobic, nonpolar molecules like tetrachloroethane. As in this work, the reason for trends in the surfactant concentration (micelle concentration) in the dilute phase is not obvious, so this kind of model would not be useful for these systems.

In summary, phenol was a fortuitous solute to choose since a combination of high water solubility, small hydrophobic group, and a polar portion which interacts strongly with surfactant EO groups made prediction of phenol partition ratio less complex than for other solutes. But, short chain phenolics, chlorinated phenolics, etc. do constitute important classes of pollutants so the model presented here can be of widespread importance, even it is not appropriate for extension to all solutes.

5.5.5 Practical Application of CPE for Phenol Removal

The fraction of phenol extracted was 57.5% to 71.6% from Tables 5.2 and 5.3. This relative insensitivity and relatively modest removal in one stage may be surprising since the fractional coacervate volume varied from 0.032 to 0.214. The reason is the relatively high unsolubilized phenol concentration (modest K_c) causing a relatively high dilute phase phenol concentration. On the other hand, the coacervate can be quite concentrated in phenol compared to the feed (concentration ratio from 3.2 to 18.4). Due to a higher K_c , increasing EO number tends to slightly increase fractional phenol extraction while commercial branched surfactants are slightly better than linear AEs. When there is a higher volume fraction of coacervate, this is

compensated by the coacervate being more dilute in phenol causing the fractional phenol extracted to not change much.

Given the relative insensitivity of fractional phenol extraction and dilute phase phenol concentration, the practical parameter which can be greatly dependent on surfactant structure is fractional coacervate volume (roughly inversely proportional to phenol and surfactant concentration in the coacervate phase). The lower the fractional coacervate volume, the less volume of coacervate needs to be treated to recover surfactant/ remove solute, reducing cost. For example, we have demonstrated that vacuum stripping can effectively regenerate coacervate containing volatile solutes like toluene [28,29]. In a different application, CPE can preconcentrate solutes for analysis in analytical chemistry [13] and minimum coacervate volume/maximum preconcentration is desired. It must be noted that the fraction of phenol in the coacervate phase is only ca. 60% in this work, so CPE may not be as attractive for phenol analysis as for more hydrophobic solutes. The primary structural ways to increase coacervate concentration are to decrease EO number and decrease alkyl carbon number of the surfactant. The surfactants with the smallest coacervate volume in Tables 5.2 and 5.3 all had EO number = 5. As alkyl carbon number decreases, the cloud point increases, so one must be careful to not exceed the operating temperature. Therefore, we conclude from this structure/property relationship study that low EO number is desirable with a carbon number not very sensitive (C 9-13 covers most commercial samples) and branching gives slight advantages. These conclusions do not necessarily apply to other solute classes.

The relatively modest reduction in phenol concentration from feed to dilute phase (ca. 60%) is not a substantial problem in water clean-up since the CPE process can be staged and any degree of separation attained. For example, at 40 °C with octylphenol ethoxylate surfactant, we have shown that a height of transfer unit for phenol removal in a rotating disc liquid-liquid extraction is 35.4 cm [23], meaning that every 35.4 cm of column height is equivalent to a one stage batch separation. The height of the column can be chosen to achieve the desired separation.

The systems studied here were at equilibrium. Since CPE in an industrial or large-scale remediation application is a dynamic process, other considerations are important in surfactant selection. The two phases must separate

from each other in a reasonable time in settlers in a continuous extraction column or a large-scale batch unit. In this study, we have qualitatively observed vast differences in settling rates with different surfactants, some taking weeks to yield a clear phase separation with no obvious relationship to surfactant structure.

The cloud point must be below the operating temperature. At lower operating temperatures, many surfactant structures could not be considered for this reason. In this study, we chose a high operating temperature of 80 °C so we could study a wide range of surfactants with cloud points below 80 °C, compared with 30-50 °C typically used in our previous studies [11,12,21-23,27]. This cloud point constraint was also the reason we chose such a high salinity (0.8 M NaCl), since this depressed the cloud points of high EO number or low alkyl chain number surfactants and permitted study of a wider range of surfactant structures. In this study, the coacervate phase was less dense than the dilute phase, so the coacervate was the top phase. However, we have observed the opposite for AE surfactants under some conditions not used in this study (e.g., at low NaCl concentration of high EO number surfactants). In a number of previous studies our group has published for alkylphenol ethoxylate surfactants [11,12,21-23,27], the coacervate was always denser than the dilute phase including continuous steady-state operation of a rotating disc extractor [21-23]. Obviously, the design of such a flow device would need to be different when the densities of extract and raffinate phases are inverted. For example, an inefficiency of our continuous extraction column is due to entrainment of coacervate droplets in the overhead dilute phase, yet entrainment of dilute phase into the coacervate bottoms is not significant [21-23]. When the phase densities are inverted, column dynamics are unknown and would need to be studied.

5.6 Conclusions

The only surfactant structural property which the solubilization equilibrium constant depends on is EO number for homogeneous and commercial AEs. Phenol partition ratio depends on EO number and fractional coacervate volume at a specified temperature and added electrolyte concentration. The fractional phenol extraction does not depend greatly on surfactant structure. For practical CPE of water

containing phenol, an AE surfactant with low EO number (e.g. 5) and a normal commercial range of alkyl carbon numbers (9-13) is recommended for use.

5.7 Acknowledgements

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