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APPENDIX

Use of a Surfactant Coacervate Phase to Extract Chlorinated Aliphatic Compounds from Water: Extraction of Chlorinated Ethanes and Quantitative Comparison to Solubilization in Micelles

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Abstract

At temperatures above the cloud point, aqueous solutions of nonionic surfactants separate into a coacervate phase and a dilute phase. The distribution of di-, tri-, and tetra- chloroethanes between these phases was shown to increasingly favor the coacervate phase as the hydrophobicity (degree of chlorination) of the solute increases. The solute solubilization equilibrium constant was shown to be very similar for solubilization into coacervate surfactant aggregates compared to micellar solubilization per aggregated surfactant molecule for octylphenol polyethoxylate surfactants and to increase with increasing temperature and increasing solute hydrophobicity. As temperature increases above the cloud point, the partition ratio increases primarily because the concentration of surfactant in the coacervate increases, secondly because the solubilization equilibrium constant in the coacervate surfactant aggregate increases, and thirdly because the concentration of micellized surfactant (and solubilization therein) in the dilute phase decreases.

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This work is dedicated to the memory of Sherril D. Christian who died on March 17, 2000

Introduction

As the temperature of an aqueous solution of nonionic surfactant is increased, a temperature may be reached where the solution turns cloudy; this temperature is referred to as the cloud point. Above the cloud point, the solution may separate into a micellar concentrated or coacervate phase, and a dilute phase.[1-4] The concentration of surfactant in the dilute phase can be very low but is generally above the critical micelle concentration (CMC). When an organic solute is originally present in an aqueous solution and nonionic surfactant is added to the water, at temperatures above the cloud point, the organic solute will tend to partition into the coacervate phase. This liquid/coacervate extraction (sometimes referred to as cloud point extraction) is a specific example of aqueous biphasic extractions.[5] This technique shows great potential for removing toxic solutes from polluted water. In a previous related study[6], the removal of trichloroethylene from water was investigated in detail. The present study focuses on chlorinated hydrocarbons, a major class of pollutants, and quantifies the effect of the degree of chlorination of the solute.

The vast majority of surfactant is present in the coacervate phase in some kind of aggregated form of the concentrated micellar solution. For example, Yoesting and Scamehorn[6] showed that the nonideality of mixed aggregate formation between anionic and nonionic surfactants is very similar in coacervate and in micelles. In this study, incorporation of the organic solute into the coacervate surfactant aggregates is quantitatively compared to solubilization into micelles composed of a surfactant of similar structure.

Experimental Section

Materials. Octylphenoxypoly(ethyleneoxy)ethanol with an average of 7 moles [OP(EO)$_7$: trade name Igepal CA-620], and 9 moles [OP(EO)$_9$: trade name Igepal CA-630] of ethylene oxide per mole of octylphenol from Rhodia were the nonionic surfactants used as received in this study. Reagent grade 1,2-dichloroethane and 1,1,1,2-tetrachloroethane from Fluka Chemika-Biochemika, and 1,1,1-trichloroethane, from J.T. Baker Inc. were used as received. The water was deionized and distilled.

Methods. In order to measure the distribution of solutes between dilute and coacervate phases, several identical 100-mL separatory funnels containing aqueous solutions with 50 mM $OP(EO)_7$ and an 1.0 mM of organic solute were placed in an isothermal water bath until equilibrium was reached, generally after about 2 days. After phase separation had occurred, the fractional volume of each phase was measured. The $OP(EO)_7$ and organic solute concentrations were measured[7] by using CE 2000 series UV spectrometer at 224 nm. and gas chromatography with a flame ionization detector, respectively, in both the coacervate and dilute phases.

In order to measure the micellar solubilization equilibrium constant, ordinary 5-mL equilibrium dialysis cells and transparent regenerated cellulose membranes (6000 Dalton molecular weight cutoff) were obtained from Fisher Scientific and used without modification in a technique called semi-equilibrium dialysis[8-10] which can be used to measure solubilization of an organic solute into micelles. When these experiments were performed, aqueous solution of 50 mM $OP(EO)_9$ plus 1.0 mM of organic solute was loaded in one compartment of the cell, and pure water was added to the other side. The cells were kept in a desiccator that was submerged in a thermostated bath until "semi-equilibrium" was reached, approximately 24 hours. The surfactant and solute concentrations were measured in both the retentate and permeate sides as described above.

The CMC values were obtained from the change in slope of surface tension vs. log (surfactant concentration) plot. Surface tension was measured by DuNouy ring tensiometry using a Cahn DCA-322 dynamic contact angle analyzer. The cloud points were visually determined as the temperature at which a 50 mM surfactant solution became turbid at a heating rate of $1^0C/minute$.

Theory

Solubilization in Micelles. In aqueous surfactant solution, solubilization, that is the ability to dissolve the organic solutes in micelles, is an important property of surfactants.[2,11] Solubilization studies in the laboratory have provided accurate vapor pressure results for volatile hydrocarbons in anionic and cationic micelles.[12-16] Numerous solubilization data have also been obtained for polar organic solutes by

using the semi-equilibrium dialysis (SED) method.[8-10,17-20] In SED experiments (Figure 1), ordinary equilibrium dialysis cells are used with membranes permeable to small molecules (such as the organic solute and surfactant monomers) but impermeable to the surfactant micelles. Initially, the retentate side of the cell contains the surfactant solution with the solute and the permeate side contains only water. The slow migration of surfactant through the membrane (over a period of 16-24 h) occurs simultaneously with the migration of the unsolubilized organic solute, which ordinarily diffuses rapidly enough to reach equilibrium with the solutions on both sides of the membrane. After equilibration, the solute concentration on the permeate side is almost equal to the unsolubilized solute concentration on the retentate side of the membrane.

The ability of micelles to solubilize solutes in the retentate is described by a solubilization equilibrium constant (K) defined by:

$$K_m = X_{m,ret} / C_u = [O]_{mic,ret} / (C_u ([Surfactant]_{mic,ret} + [O]_{mic,ret})) \tag{1}$$

where $X_{m,ret}$ is the mole fraction of solute in micelles in the retentate, C_u is the concentration of unsolubilized or monomeric organic solute, $[O]_{mic,ret}$ is the retentate concentration of organic solute associated with surfactant micelles and $[Surfactant]_{mic,ret}$ denotes retentate concentration of surfactant in micellar form. A small correction needs to be made to account for formation of a few micelles (with solubilization therein) in the permeate[8,10,17-20] and eq. 1 applies to the permeate as well:

$$K_m = X_{m,per} / C_u = [O]_{mic,per} / (C_u ([Surfactant]_{mic,per} + [O]_{mic,per})) \tag{2}$$

where $X_{m,per}$ is the mole fraction of solute in micelles in the permeate, C_u is the concentration of unsolubilized or monomeric organic solute, $[O]_{mic,per}$ is the permeate concentration of organic solute associated with surfactant micelles and $[Surfactant]_{mic,per}$ denotes permeate concentration of surfactant in micellar form.

It is assumed that C_u is the same in permeate and retentate (activity coefficient of unsolubilized solute is the same), as well as the value of K_m. The total concentration of organic solute and surfactant in the two compartments can be related to C_u and to the concentration of surfactant monomer (CMC) by material balances:

$$[O]_{ret} = C_u + [O]_{mic,ret} \tag{3}$$

$$[O]_{per} = C_u + [O]_{mic,per} \tag{4}$$

$$[Surfactant]_{ret} = CMC + [Surfactant]_{mic,ret} \tag{5}$$

$$[Surfactant]_{per} = CMC + [Surfactant]_{mic,per} \tag{6}$$

where $[O]_{ret}$ and $[O]_{per}$ refer to the total solute concentration in retentate and permeate, respectively; and $[Surfactant]_{ret}$ and $[Surfactant]_{per}$ refer to the total surfactant concentration in retentate and permeate, respectively.

While the monomeric surfactant concentration (equals critical micelle concentration or CMC) is mildly dependent on the presence of solubilizate,[2] at the low solute concentrations used here, the CMC is assumed to be that of the pure surfactant.

Combining these equations yields:

$$K_m = ([O]_{ret} - C_u) / (C_u([Surfactant]_{ret} - CMC + [O]_{ret} - C_u)) \tag{7}$$

$$K_m = ([O]_{per} - C_u) / (C_u([Surfactant]_{per} - CMC + [O]_{per} - C_u)) \tag{8}$$

Simultaneous solution of eqs. 7 and 8 for K_m and C_u permits calculation of solubilization equilibrium constants directly from measurable parameters in SED experiments.

Extraction into Coacervate. Aqueous solutions of most nonionic surfactant micelles become turbid after heating to a temperature known as the cloud point. Above this temperature, the solution separates into two phases as shown in Figure 2: one, generally small in volume, composed of a concentrated micellar solution (referred to as the micellar-rich or coacervate phase) and the other, the bulk aqueous

solution (aqueous or dilute phase) in which the surfactant concentration is generally on the order of 2 to 20 times the CMC as shown in Figure 2.

The overall distribution coefficient or partition ratio (solute concentration ratio in coacervate to that in dilute phase) is normally reported in studies of coacervate extraction. This only requires straightforward measurement of total concentration in coacervate and dilute phases. In addition in this study, we wish to directly compare the tendency of the solute to "solubilize" into the surfactant aggregate in the coacervate to that tendency in micelles.

This comparison requires definition of a coacervate solubilization equilibrium constant (K_c) exactly analogous to K_m for micelles:

$$K_c = X_c / C_u \qquad (9)$$

where X_c is the mole fraction of solute in the coacervate aggregate and C_u is the concentration of unsolubilized solute. From the definition of X_c and correcting for surfactant and solute not in aggregated form:

$$K_c = ([O]_c - C_u) / C_u ([Surfactant]_c - CMC + [O]_c - C_u) \qquad (10)$$

where $[O]_c$ and $[Surfactant]_c$ are the total solute and surfactant concentrations in the coacervate phase.

In order to apply eq. 10, the value of C_u is assumed to be the same in dilute and coacervate phases (i.e., unassociated solute activity coefficients are assumed to be the same in the two phases when the system reaches equilibrium). The surfactant monomer concentration (CMC) is assumed to be the same in dilute and coacervate phases also, so surfactant concentration in aggregated form in the coacervate is equal to total coacervate surfactant concentration minus the CMC (this correction is very small so the validity of this approximation is of little concern). Since micelles are present in the dilute phase, the micellar solubilized solute concentration must be subtracted from the measured total solute concentration in the dilute phase to obtain C_u. The value of K_m obtained from SED experiments for OP(EO)$_9$ is assumed to be

the same as that for OP(EO)$_7$ in the dilute phase, both at the same temperature. Simultaneous solution of eqs. 1, 3, and 5 to describe micellization in the dilute phase and eq. 10 permits calculation of K_c from measurable parameters and K_m. For solutes and surfactants of the type used here, K_m can depend on solute concentration.[10,21]; this was not accounted for here since this would be a small correction at the very low solute mole fractions in micelles under these conditions.

Results and Discussion

Effect of Temperature on Coacervate Extraction. The CMC of OP(EO)$_7$ and OP(EO)$_9$ with no organic solutes at the various temperatures is shown in Table 1. The CMC decreases as the temperature and the number of EO groups increase. The cloud point of the 50 mM OP(EO)$_7$ system (same concentration as used in coacervate extraction experiments) is shown in Table 2 at several solute concentrations. The cloud point is only mildly dependent on the presence of the solute at the low solute concentrations used. The cloud point depression is greater as the degree of chlorination of the solute increases. Note that the CMC can be measured even above the cloud point since the clouding does not occur until a surfactant concentration at least several times the CMC is attained.

Table 3 shows the concentrations in coacervate and dilute phases, fractional distributions of components in phases, and partition ratio of solute and surfactant. Up to 99 % of OP(EO)$_7$, 79 % of 1,2-dichloroethane, 84 % of 1,1,1-trichloroethane, and 87 % of 1,1,1,2-tetrachloroethane are removed in the coacervate phase. As the temperature increases, the separation improves; the fractional volume of the coacervate decreases, partition ratio increases, and fraction of solute in coacervate increases. The reason is when the temperature of the system increases, the system is further from the lower consolute solution temperature (which is approximately the cloud point), resulting in increasing dissimilarity between the coacervate phase and dilute phase, causing a decrease in the coacervate phase volume. The concentration of the surfactant and the chloroethanes in the coacervate phase increases with increasing temperature while these concentrations in the dilute phase are not much affected.

Effect of Organic Solute Structure on Coacervate Extraction. The 1,1,1-trichloroethane and 1,1,1,2-tetrachloroethane both partition more effectively into the coacervate phase than 1,2-dichloroethane as seen in Table 3. The large increase in the distribution coefficient with an increase in solute hydrophobicity is probably mainly due to the decrease in the water solubility of the hydrocarbon compounds with increasing degree of chlorination.[22] However, the degree of chlorination of the solute affects the partition ratio of the surfactant also as seen in Table 3, complicating the interpretation of data. For example, in a cloud point (or coacervate) extraction of a series of chlorinated phenols, Frankewich and Hinze[4] observed an increase in the fraction of solute in the coacervate from mono- to di- to tri- chlorination, a decrease for the tetra-, and a large increase for the penta-.

Comparison of Solute Solubilization between Coacervate and Micelles. In order to compare solubilization in coacervate and micelles, a surfactant with a higher cloud point was used for micelle solubilization studies (7 vs. 9 ethylene oxides in hydrophilic group). The solubilization of the chlorinated hydrocarbons is predominately in the core of the micelle and changing the hydrophilic group length slightly is expected to have very little effect on K_m.[23] Table 4 shows the SED data and calculated value of K_m. Table 5 shows the comparison between K_m and K_c. The solute coacervate solubilization equilibrium constant is an average of 13 % higher than the micelle solubilization equilibrium constant, which indicates that they are nearly the same within experimental precision for the octylphenol polyethoxylate surfactants studied. This supports the view that the surfactant aggregates in the coacervate are micelle-like in structure. The coacervate has been proposed to contain wormlike micelles from measurements of the nonionic surfactant self-diffusion coefficient. An entangled wormlike micelles network is formed at low temperatures and gradually changes to a multiconnect cross-links network when temperature is increased.[24] Whatever the exact structure, the aggregate structure probably consists of the surfactant hydrocarbon chains intertwining, removing themselves from aqueous solution, and hydrophilic groups covering the surface of this hydrophobic region.[7]

If the correction due to micelles in the permeate (and solubilization therein) were ignored, the error in the value of K_m would be about 7 %. If the correction due

to micelles in the dilute phase (and solubilization therein) were ignored, the error in the value of K_c would be about 5 %. In other words, about 93 % of the solute in the permeate in SED experiments and about 95 % of the solute in the dilute phase in equilibrium with coacervate is unsolubilized, so ignoring the existence of micelles does not lead to gross errors. This is the first time this has been analyzed for the coacervate system, so it is important to have shown that the micelles in the dilute phase do not substantially reduce the efficiency of the separation, at least for volatile chlorinated alkanes.

Interpretation of Temperature Effects. It is interesting to note that the partition ratio increases much more rapidly with temperature than the value of K_c. For example, the ratio of partition ratios at 50 °C to 30 °C are 3.43, 2.66, and 2.65 for the di, tri, and tetrachloroethanes, respectively and equivalent ratios of K_c are 1.62, 1.21, and 1.22 for these same compounds. As temperature increases above the cloud point, the partition ratio increases primarily because the concentration of surfactant in the coacervate increases, secondly because the solubilization equilibrium constant in the coacervate surfactant aggregate increases, and thirdly because the concentration of micellized surfactant (and solubilization therein) in the dilute phase decreases. As an example calculation, of the increase in the partition ratio from 30 °C to 50 °C for the tetrachloroethane, 75 % is due to the increase in coacervate surfactant concentration, 16 % is due to the increase in the coacervate solubilization constant, and 9 % is due to the reduction in the concentration of surfactant in micelles in the dilute phase.

Lubrizol, Nikko Chemical, Phillips Petroleum, Pilot Chemical, Procter and Gamble, Reckitt and Coleman, S.C. Johnson Wax, Schlumberger, Shell, Sun, Unilever, and Witco. Dr. Scamehorn holds the Asahi Glass Chair in chemical engineering at the University of Oklahoma. Surfactant was provided by Rhodia Co. Ltd. (Thailand).

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Table 1 CMC of Surfactants with No Organic Solutes.

Temperature (°C)	CMC (mM)	
	OP(EO)$_7$	OP(EO)$_9$
30	0.092	0.083
40	0.086	0.076
50	0.075	0.066

Table 2 Cloud Points of 50 mM OP(EO)$_7$ System.

Solute Concentration (mM)	0	1.0
1,2-dichloroethane	22 °C	19 °C
1,1,1-trichloroethane	22 °C	16 °C
1,1,1,2-tetrachloroethane	22 °C	15 °C

Table 3 Liquid-Coacervate Extraction Data : Initial $[OP(EO)_7]$ = 50 mM, Initial [solute] = 1.0 mM.

System	Temperature (°C)	Fractional coacervate volume	$[OP(EO)_7]$ (mM)		[Solute] (mM)		Fraction in Coacervate		Partition Ratio = [in coacervate]/ [in dilute phase]	
			Dilute	Coacervate	Dilute	Coacervate	$OP(EO)_7$	Solute	$OP(EO)_7$	Solute
$OP(EO)_7$ / dichloroethane	30	0.12	1.13	393	0.28	4.05	0.98	0.66	348	14.5
	40	0.08	1.05	560	0.29	7.47	0.98	0.69	533	25.8
	50	0.06	0.74	777	0.25	12.46	0.99	0.79	1050	49.8
$OP(EO)_7$ / trichloroethane	30	0.12	0.98	409	0.23	7.06	0.98	0.81	417	30.7
	40	0.08	0.72	603	0.18	8.81	0.99	0.81	838	48.9
	50	0.06	0.59	816	0.11	9.00	0.99	0.84	1383	81.8
$OP(EO)_7$ / tetra chloroethane	30	0.13	0.76	422	0.22	7.14	0.99	0.83	555	32.5
	40	0.08	0.52	633	0.17	9.26	0.99	0.83	1217	54.5
	50	0.07	0.49	846	0.15	12.90	0.99	0.87	1727	86.0

Table 4 Semiequilibrium Dialysis Data for Micellar Solubilization of 50 mM OP(EO)$_9$

and 1.0 mM Organic Solute Initial Retentate Concentrations.

Organic Solute	Temperature	Initial		Permeate		Retentate		Km
	($^\circ$C)	[OP(EO)$_9$]	[Solute]	[OP(EO)$_9$]	[Solute]	[OP(EO)$_9$]	[Solute]	(L/mol)
		(mM)	(mM)	(mM)	(mM)	(mM)	(mM)	
Dichloroethane	30	50	1.0	1.13	0.28	48.9	0.72	33.7
	40	50	1.0	1.05	0.25	49.0	0.75	43.0
	50	50	1.0	0.74	0.20	49.3	0.80	63.6
Trichloroethane	30	50	1.0	1.98	0.19	48.0	0.81	80.9
	40	50	1.0	0.72	0.17	49.3	0.83	83.1
	50	50	1.0	0.59	0.14	49.4	0.86	109.8
Tetrachloroethane	30	50	1.0	0.76	0.17	49.2	0.83	83.7
	40	50	1.0	0.52	0.16	49.5	0.84	89.1
	50	50	1.0	0.49	0.15	49.5	0.86	99.3

Table 5 Summary of Partitioning and Solubilization Parameters for the Solute

| System	Temperature (°C)	K_m (L/mol)	K_c (L/mol)	Partition Ratio of Solute	Fractional Coacervate Volume	$[OP(EO)_9]$ in Dilute Phase/CMC
OP(EO)$_n$ / Dichloroethane	30	33.7	44.5	14.5	0.12	12.3
	40	43.0	53.4	25.8	0.08	12.2
	50	63.6	72.2	49.8	0.06	9.9
OP(EO)$_n$ / Trichloroethane	30	80.9	94.1	30.7	0.12	10.7
	40	83.1	94.4	48.9	0.08	8.4
	50	109.8	114.2	81.8	0.06	7.9
OP(EO)$_n$ / tetra-chloroethane	30	83.7	92.0	32.5	0.13	8.3
	40	89.1	96.7	54.5	0.08	6.0
	50	99.3	111.9	86.0	0.07	6.5
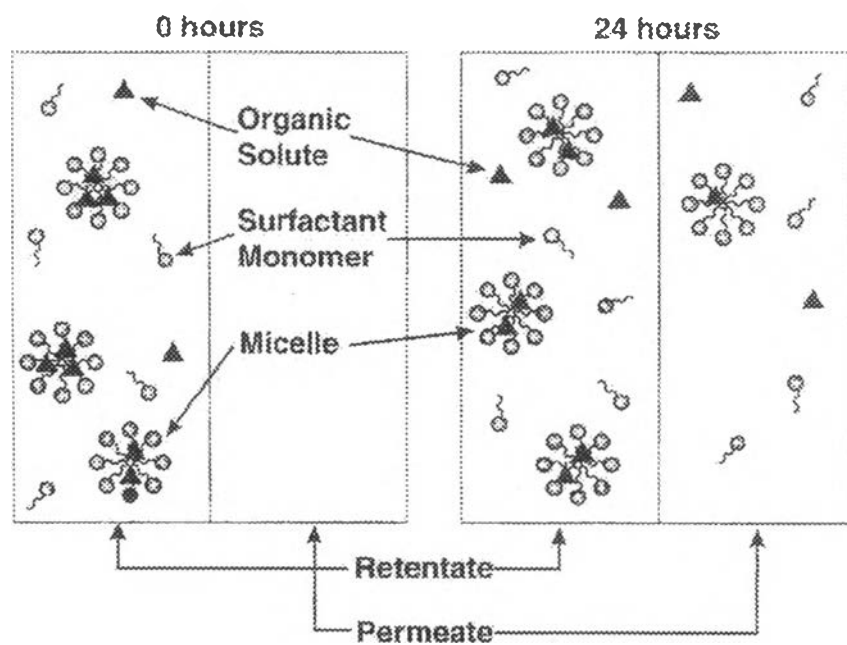
Figure 1 Schematic of semiequilibrium dialysis.
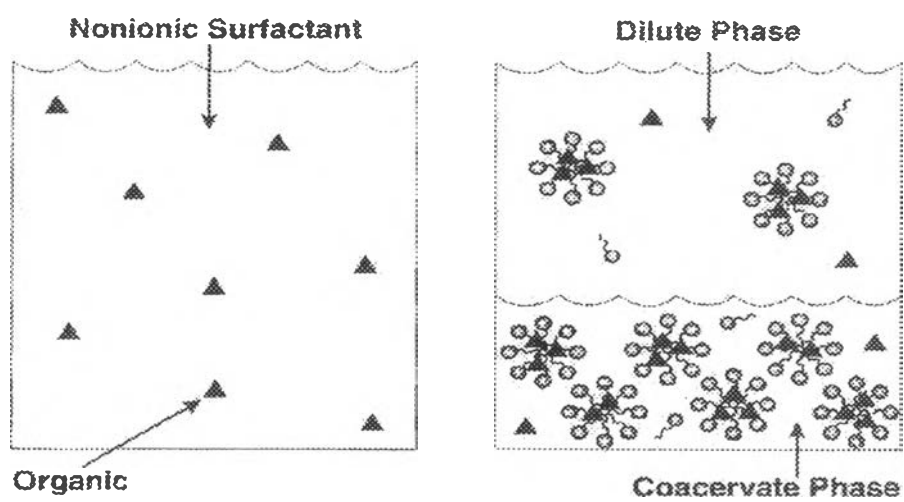
Figure 2 Schematic of liquid-coacervate extraction.

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