Water Solubility Enhancements of DDT and Trichlorobenzene by Some Surfactants Below and Above the Critical Micelle Concentration

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Water Solubility Enhancements of DDT and Trichlorobenzene by Some Surfactants Below and Above the Critical Micelle Concentration

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■ Water solubility enhancements of 1,1-bis(p-chlorophenyl)-2,2,2-trichloroethane (DDT) and 1,2,3-trichlorobenzene (TCB) by aqueous surfactants below and above their critical micelle concentrations (CMCs) have been studied at room temperature with the following surfactants: Triton X-100, Triton X-114, Triton X-405, Brij 35, sodium dodecyl sulfate, and cetyltrimethylammonium bromide. While the solubilities of DDT and TCB are greatly enhanced by all surfactants above the measured CMC, DDT also exhibits significant solubility enhancements below the CMC of the molecularly nonhomogeneous surfactants (the Triton series and Brij 35). The plot of the apparent DDT solubility against the concentration of Triton and Brij surfactants shows an uprising curve below the nominal CMC, which is attributed to the successive micellization of the heterogeneous monomer species. Above the CMC, the enhancement effect with the nonionic surfactants is closely proportional to the nonpolar chain content of the surfactant, whereas the effect with the ionic surfactants is less accountable in terms of their nonpolar chain contents. The solubilization power of a micelle relative to a bulk solvent is evaluated by a comparison of the observed micelle–water and solvent–water partition coefficients.

Introduction

The immense quantity of surfactants used in industrial and household applications gives rise to a concern over the direct and indirect effects of these compounds in the environment. While some surfactants (or their degradation products) could become potential contaminants in surface and ground water, their presence might also be expected to influence the behavior of other pollutants. One unique property of surfactants is their solubilization power for oils and other relatively water-insoluble compounds; this is attributed to the formation of pseudophase micelles through self-association of surfactant molecules as they reach critical micelle concentrations (CMCs). Although the solubilization effect of surfactants (generally as micelles) for nonpolar organic solutes is well-known in the literature (1–6), information regarding the effectiveness of the micellar phase relative to a bulk organic phase in solubilizing the solute is a subject of continuing interest (7).

In earlier studies, the solubilization power of a surfactant above its nominal CMC for a given solute is expressed in terms of the molar solubilization ratio (i.e., moles of solute per mole of the surfactant) (1, 7, 8), rather than the partition coefficient between the micellar phase and water. Since the partition effect of organic pollutants in aquatic systems is conveniently characterized in terms of some reference partition coefficients, e.g., octanol–water partition constants, it is of interest to compare the experimental micelle–water partition coefficients with these reference values. In so doing, one can more readily evaluate the effect of various types of surfactants on the apparent water solubility (or concentration) of an organic pollutant based on the surfactant concentration in water; it also enables one to compare the solvency of the more structured mi-

croscopic micellar phase with a bulk solvent phase in order to gain some insight into the factors influencing the solvency of a micellar phase.

The effect of surfactants below the CMC on solute solubility has hitherto received little attention. While available data in the literature (9–11) show essentially no enhancement of organic solute solubility at surfactant concentrations below the CMC, the solutes employed in previous studies are relatively too water soluble to be sensitive to dilute surfactants and further studies are warranted on very sparingly soluble solutes. Recent studies on solute solubility enhancement by dissolved organic matter (12–14) have shown that the apparent water solubility of some extremely water-insoluble organic solutes (e.g., DDT) can be significantly enhanced by low concentrations of some fractionated humic and fulvic acids, including those having relatively low molecular weights (< 1000 daltons) and high polar group contents. These enhancement effects were attributed to a partition-like interaction of solutes with the microscopic organic environment of dissolved organic macromolecules (13, 14). Since many surfactants have molecular weights and nonpolar group contents comparable to those of humic and fulvic acids, it is of potential interest to examine the solubility enhancement effect of highly water-insoluble compounds by selected surfactants at concentrations below their CMCs.

In this study, we investigated the water solubility enhancement of p,p'-DDT and 1,2,3-trichlorobenzene by a variety of commonly used surfactants, covering a wide range of surfactant concentrations both below and above their nominal CMC values. A conceptual model describing the partition equilibria of the solute (solubilizate) between surfactants (as monomers and micelles) and water is presented. The test solutes were chosen because of their extreme differences in water solubility and in sensitivity to dissolved organic matter (13, 14). The comparison of the partition effect of the solutes with various types of surfactants (below and above CMC) and with ordinary (bulk) organic solvents serves to elucidate the influence of surfactant structure and aggregation on the partition efficiency.
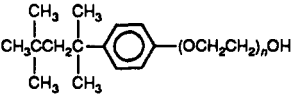
Theoretical Considerations

According to the conventional phase-separation model for surfactants in aqueous solution (15), surfactants are assumed to exist in monomeric state below the CMC. Above the CMC, the concentration of monomers remains constant at CMC while the excess surfactant leads to the formation of pseudophase micelles. A general expression for the solubility enhancement of a solute by surfactants can be written in terms of the concentrations for monomers and micelles and the corresponding solute partition coefficients, giving

$$S_w^*/S_w = 1 + X_{mn}K_{mn} + X_{mc}K_{mc} \qquad (1)$$

where S_w^* is the apparent solute solubility at the total stoichiometric surfactant concentration of X, S_w is the intrinsic solubility in "pure water", X_{mn} is the concentra-

Table I. Structures and Properties of Selected Commercial Surfactants

surfactant	structure	MW	CMC, mg/L
Triton series:			
Triton X-100 (TX100)	$\bar{n} = 9.5$	628	130
Triton X-114 (TX114)	$\bar{n} = 7.5$	536	110
Triton X-405 (TX405)	$\bar{n} = 40$	1966	620
Brij 35 (BJ35)	$C_{12}H_{25}(OCH_2CH_2)_{23}OH$	1200	74
sodium dodecyl sulfate (SDS)	$C_{12}H_{25}OSO_3^-Na^+$	288	2100
cetyltrimethylammonium bromide (CTAB)	$C_{16}H_{33}N(CH_3)_3^+Br^-$	364	361

tion of the surfactant as monomers, and X_{mc} is the concentration of the surfactant in micellar form. The K_{mn} term is the partition constant of the solute between monomers and water and the K_{mc} term is the corresponding partition constant of the solute between micelles and water.

The separation of the concentration terms (i.e., X_{mn} and X_{mc}) accounts for differences in the partition efficiency of the solute with monomers and micelles. By eq 1, one would expect a plot of the apparent solute solubility (S_w^*) versus the total concentration of surfactant to be bilinear, giving a straight line with slope of K_{mn} from $X = O$ to X = CMC, followed by another straight line with slope of K_{mc} at $X \geq$ CMC. Because of the markedly greater organic environment of micelles relative to monomers, the increase in slope of the plot on exceeding the CMC should be very sharp, as has been noted previously (10, 11). The two distinct slopes define the values of K_{mn} and K_{mc} for a given solute-surfactant system.

The solvency of a micellar phase compared to that of a bulk organic solvent of a given molecular composition can be readily determined by comparing the calculated K_{mc} value against that of the solute between a selected solvent phase and water. Since the micelle is regarded as a pseudophase of microscopic size (15), the degree of solubility reduction of a solute in a micellar phase (relative to that in a compositionally similar bulk solvent) is an indication of how close the micelle approaches bulk solvent in its solvency.

Experimental Section

Surfactants were obtained either directly from the manufacturer or through a distributor and were used without further purification. Triton X-100 (TX100), Triton X-114 (TX114), and Triton X-405 (TX405) were obtained from Rohm and Haas; TX100 and TX114 were greater than 98% pure, while the TX405 was supplied as a 70% pure material in aqueous solution. Brij 35 (BJ35), manufactured by ICI Americas, Inc., was obtained from Aldrich Chemical Co., Inc., with a purity of 97+%. All Triton and Brij surfactants are molecularly nonhomogeneous because of variable ethylene oxide (EO) chain lengths in the monomers of each of these surfactants. Cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) were obtained from Aldrich with purities (active ingredients) of 95% and 98%, respectively; the results presented have been corrected for purity. Poly(ethylene glycol), with an average molecular weight of 1000 daltons, was supplied by Aldrich and used as received. p,p'-DDT (DDT) and 1,2,3-trichlorobenzene (TCB) were obtained from Aldrich. n-Hexane, used for standards preparation and sample extraction, was supplied as a high-purity UV-grade solvent by American Burdick and Jackson. Deionized water used for preparing solutions was obtained from a Sybron/Barnstead Nanopure II water treatment system.

Surface tensions of surfactant solutions were determined with a Model 20 surface tensiometer, manufactured by Fisher Scientific. This instrument operates on the duNouy principle, in which a platinum–iridium ring is suspended from a torsion balance, and the force (in dynes per centimeter) necessary to pull the ring free from the surface film is measured. The critical micelle concentration (CMC) was determined by measuring the surface tension of surfactant solutions over a wide concentration range and noting the inflection in the plot of surface tension versus log surfactant concentration; the plotted surface tension value was taken when stable readings were obtained for a given concentration of surfactant, as indicated by at least two consecutive measurements having nearly the same value.

Procedures for sample equilibration and solubility determination were essentially the same as described earlier by Chiou et al. (13). A series of concentrations was prepared for each surfactant at levels above and below the CMC; concentrations above the CMC were extended to approximately 3 times the CMC for a given surfactant. Solutions were placed in 25-mL Corex centrifuge tubes with Teflon cap liners, and either DDT or TCB was added to each tube in an amount slightly more than required to saturate the solution. Triplicate samples were prepared for each surfactant concentration; these samples were then equilibrated on a reciprocating shaker for ~48 h at 25 ± 1 °C. The samples were subsequently centrifuged at 5000 RPM (2987g) for 1 h to separate the undissolved solute. Solute particles adhering to the glass walls were carefully removed with a cotton swab, and the meniscus was subsequently aspirated to remove any particles suspended on the surface. This centrifugation/cleaning procedure was repeated twice more. A 2-mL aliquot of the supernatant was then carefully withdrawn with a volumetric pipet and extracted in n-hexane; dilutions were done in hexane as needed to bring the solute into a detectable concentration range. Analysis of DDT was carried out by gas chromatography using a cross-linked methyl silicone (0.88-μm film thickness) megabore capillary column (30 m × 0.53 mm) and a (^{63}Ni) electron capture detector. Analysis of TCB was done with a cross-linked 5% phenyl methyl silicone megabore capillary column (0.88-μm film thickness, 30 m × 0.53 mm) and a flame ionization detector.

A pure water blank was run (in triplicate) with each sample set as a check on analytical accuracy and to assure adequate equilibration. The solubility enhancement of DDT was measured in solutions of poly(ethylene glycol) that ranged from 0 to 200 mg/L as a test of the effect of ethoxy chains in the nonionic surfactants.

Results and Discussion

Table I shows the structures, molecular weights, and critical micelle concentrations (CMCs) of the selected
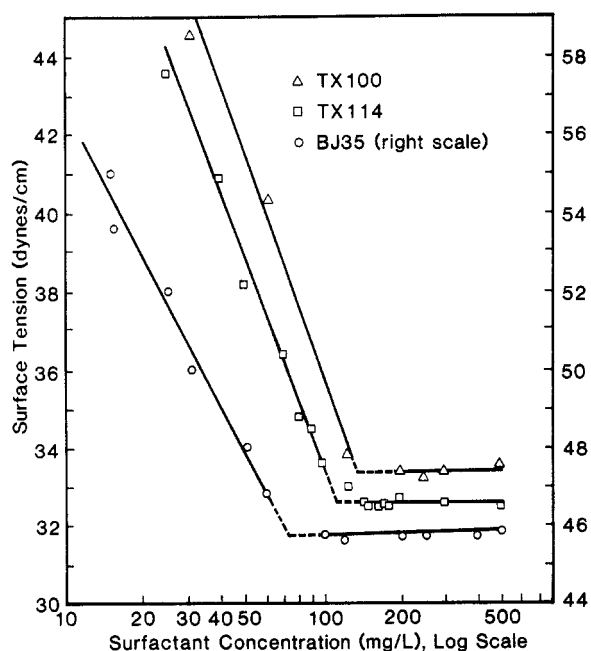
Figure 1. Plot of the surface tension versus the logarithm of surfactant concentration for TX100, TX114, and BJ35.
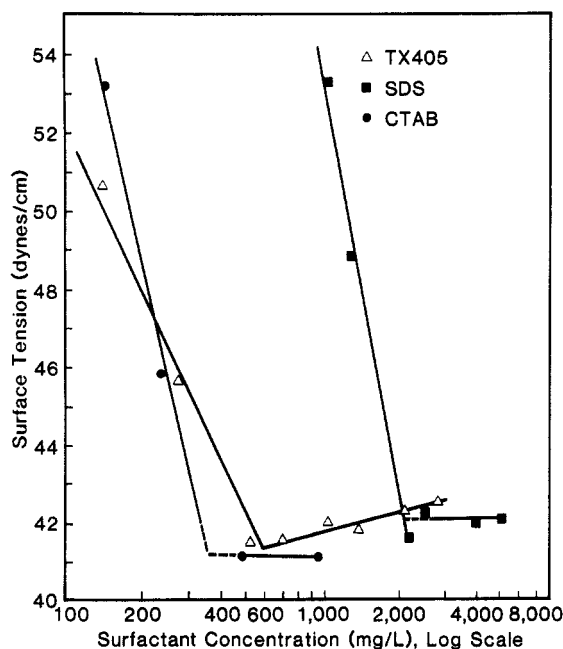

Figure 2. Plot of the surface tension versus the logarithm of surfactant concentration for TX405, SDS, and CTAB.

Figure 3. Plot of the surface tension versus the surfactant concentration for TX114, BJ35, and SDS. The indicated CMC values are taken from Figures 1 and 2.

Figure 4. Plot of the apparent DDT water solubility versus the aqueous concentration of TX100, TX114, and BJ35.

nonionic, anionic, and cationic surfactants used in this study. For the Triton series, the average EO chain length with each surfactant is denoted by the $\bar{n}$ value; the EO number of 23 for BJ35 is the average value.

The CMC values were obtained through a conventional plot of the surface tension versus the logarithm of the surfactant concentration, as shown in Figures 1 and 2. By this plot, the concentration at which a pronounced break of the slope occurs is called the "critical micelle concentration". It should be noted, however, that the CMC of a surfactant varies to some extent, depending on the solution property measured and the evaluation method applied (4, 5). While the CMC value is generally better defined for molecularly homogeneous surfactants, the concept of CMC becomes relatively diffused for nonhomogeneous surfactants. As shown in Figure 3, when the surface tension is plotted against the concentration rather
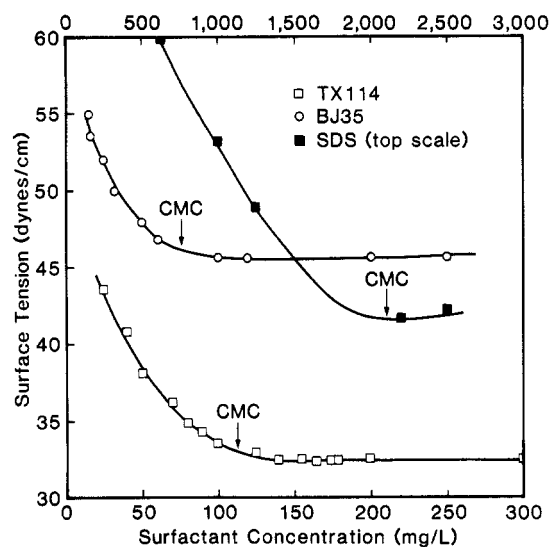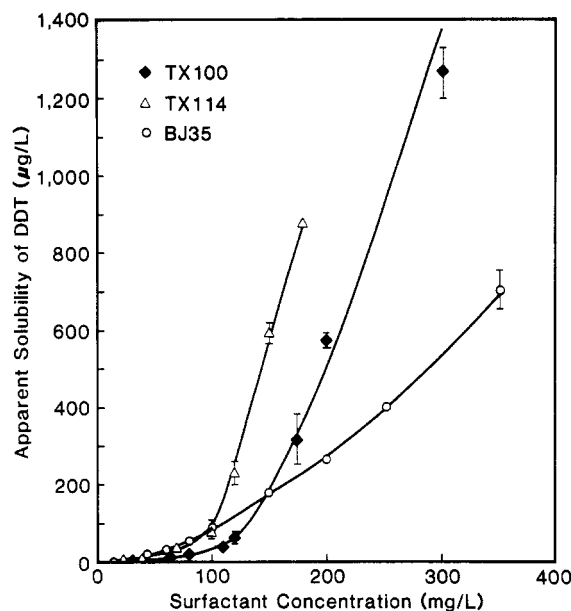
than log concentration, the previous sharp break of the slope with TX114 and BJ35 disappears, whereas the break with SDS remains relatively distinguishable. The lack of well-defined CMCs for nonhomogeneous surfactants (such as the Triton and Brij series) is speculated to result from the successive micellization of the heterogeneous monomers at different stoichiometric concentrations of the surfactant, which results in a breadth of the monomer–micelle transition zone. More discussion of this effect will be given later. In general, a direct confirmation of the successive micellization process by conventional methods is difficult because the surfactant concentration is generally quite dilute below the nominal CMC and because the conventional methods for CMC determination (e.g., by density, surface tension, and conductivity measurements) are not sensitive to aggregate formation.

The enhancement of the water solubility of DDT by TX100, TX114, and BJ35 at surfactant concentrations extending from far below CMC to far above CMC is shown in Figure 4. Results with TX405, SDS, and CTAB are shown in Figure 5. The enhancement data of TCB with
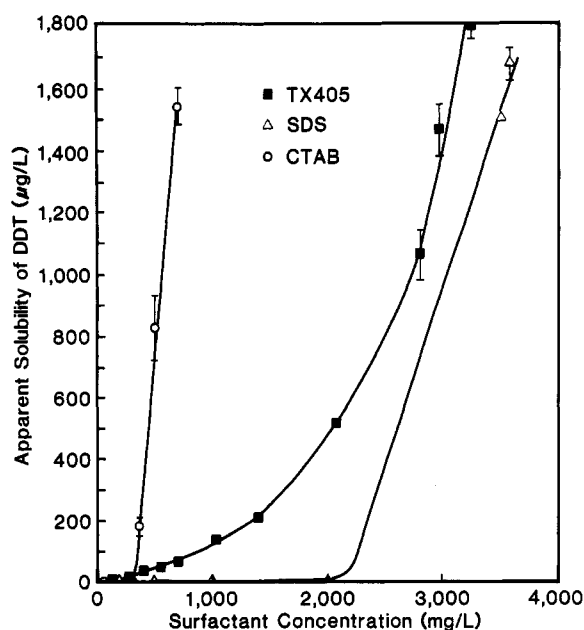
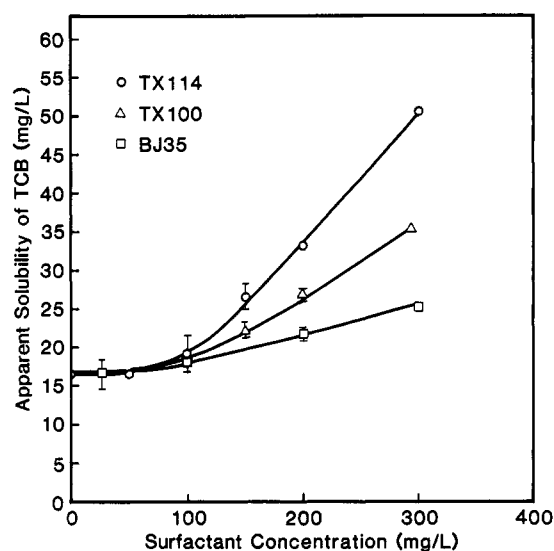**Figure 5.** Plot of the apparent DDT water solubility versus the aqueous concentration of TX405, SDS, and CTAB.

Figure 7. Plot of the apparent TCB water solubility versus the aqueous concentration of SDS and CTAB. The concentration for CTAB is given by the top scale.

Figure 6. Plot of the apparent TCB water solubility versus the aqueous concentration of TX114, TX100, and BJ35.

Figure 8. Plot of the apparent DDT water solubility versus the ratio of surfactant concentration (X) to critical micellar concentration (CMC) for TX100, TX114, TX405, BJ35, SDS, and CTAB.

TX100, TX114, and BJ35 are given in Figure 6, and the enhancement data of TCB with SDS and CTAB are given in Figure 7. Earlier studies (13, 14) give the solubility of DDT and TCB in pure water (S_w) as 5.5 μg/L and 18 mg/L, respectively, at 25 °C.

For DDT, large solubility enhancements and sharply rising slopes are recognized as surfactant concentrations exceed the (nominal) CMC values of TX100, TX114, SDS, and CTAB. The change in slope for BJ35 and TX405, the two (nonhomogeneous) nonionic surfactants with relatively long EO chains, is more gradual. The observed difference in solubility enhancement effect by surfactants above and below their CMCs is a result of the difference in the ability of micelles and monomers to concentrate DDT by partition interactions.

The impact of aqueous surfactants on the solubility of TCB is much smaller in magnitude over the whole range of surfactant concentrations. Below the CMC, the data are not precise enough to demonstrate any solubility enhancement. The smaller effect with TCB (relative to DDT) is attributed to its much greater water solubility,
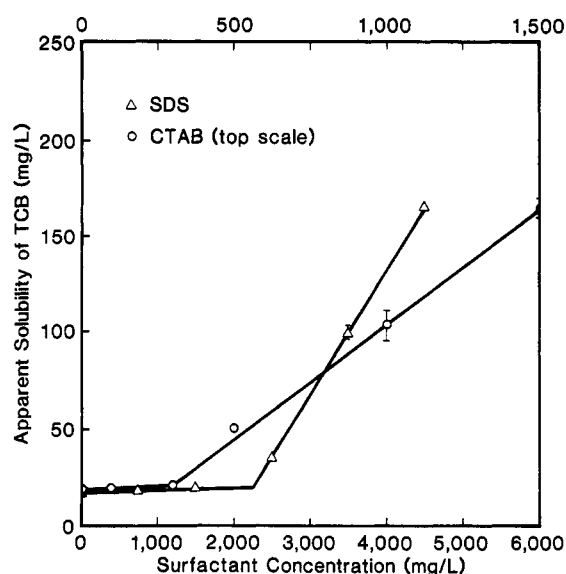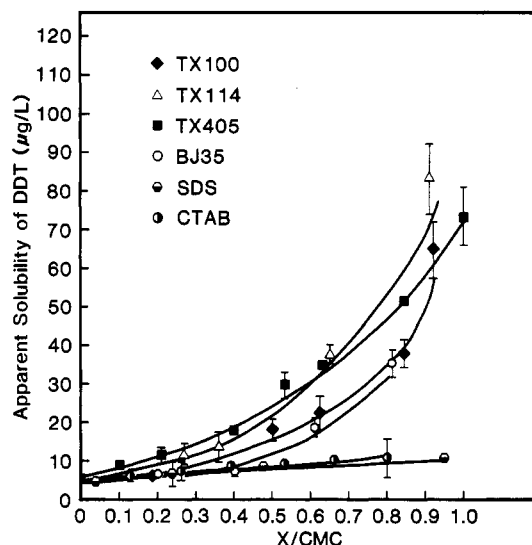
which in essence reduces its partition efficiency with the dilute organic fraction of the dissolved surfactant.

A close examination of the solubility enhancement data of DDT at surfactant concentrations below the CMC, as illustrated in Figure 8 with the concentration of each surfactant normalized to its CMC, reveals significant solubility enhancements with BJ35, TX100, TX114, and TX405. The data with molecularly homogeneous SDS and CTAB show relatively insignificant but linear enhancement below CMCs. This linear relationship is predicted by the conventional phase-separation model (eq 1). However, for the Triton and Brij surfactants, which are molecularly nonhomogeneous, the slope of the plot changes fairly smoothly, with an upward curvature below the nominal CMC that becomes increasingly steeper near and beyond the CMC. These characteristics are not predicted by the conventional theory for homogeneous surfactants; the nonlinear relation near the nominal CMC is strongly indicative of a continuous aggregate formation. This effect may be attributed to a sequential micellization of the heterogeneous monomers because of their unequal solubilities in water. As a result, the monomer–micelle tran-

Table II. Partition Coefficients of Solutes in Monomeric Surfactant–Water (K_{mn}) and Micelle–Water (K_{mc}) Systems

surfactant	log K_{mn} p,p'-DDT	log K_{mc} p,p'-DDT	log K_{mc} 1,2,3-TCB
Triton X-100 (TX100)	4.26	6.15	3.82
Triton X-114 (TX114)	4.59	6.18	3.95
Triton X-405 (TX405)	3.92	5.56	ND[a]
Brij 35 (BJ35)	4.18	5.75	3.31
sodium dodecyl sulfate (SDS)	2.68	5.38	3.54
cetyltrimethylammonium bromide (CTAB)	3.54	5.88	3.80

[a] ND, not determined.

sition of a heterogeneous surfactant may be expected to be considerably less sharp than that of a homogeneous surfactant. This reasoning is in accord with the relatively smooth solubility enhancement curves with TX405 and BJ35 over the region of the nominal CMC (Figures 4 and 5), as these two surfactants supposedly have a higher degree of molecular heterogeneity than other Triton surfactants because of their larger average EO chain lengths. With these considerations, the data for Triton and Brij surfactants can be reconciled by the phase-separation model by taking account of the molecular heterogeneity. In these systems, calculations of the approximate partition coefficients of DDT with monomeric surfactants (K_{mn}) were made by taking the linear slopes of the plot in Figures 4 and 5 at high dilution ($X < 0.3$ CMC) of the surfactants. The calculated log K_{mn} values are given in Table II.

As stated earlier, conventional methods for CMC determinations are not sensitive to incipient formation of aggregates. In comparison, measurement of the solubility enhancement appears to be much more sensitive to surfactant aggregates. This can be partially rationalized by the fact that the change in surface tension (as related mainly to monomers) of a surfactant solution on exceeding the CMC is generally less than a factor of 3 (6), whereas the associated change in the apparent solubility of DDT (which is strongly a function of the concentration of micelles) can be more than 2 orders of magnitude. For this reason, determination of the solubility enhancement data of DDT or other extremely water-insoluble compounds may prove to be the most sensitive method to date on detecting the association transition of the surfactant in water.

The solubility enhancement of DDT below the CMC was restricted primarily to the nonionic surfactants. One of the major factors causing the difference in enhancement effect by nonionic and ionic surfactants is speculated to be the degree of hydration with the dissolved surfactant molecules. In the case of ionic surfactants such as SDS and CTAB, the hydration sphere with the ionic group may extend to a large portion of the adjacent nonpolar chain, thus reducing the molecular forces (i.e., the van der Waals forces) between DDT and the nonpolar group of the surfactant. For nonionic surfactants, the hydration effect with the nonionic polar group (such as the EO chain) should be less significant and thus less interfering with the molecular interaction of the nonpolar hydrocarbon group with DDT. The observed order of the DDT solubility enhancement by the nonionic surfactants below CMC is TX114 > TX100 > BJ35 > TX405, which is the same order as their ratios of nonpolar-to-polar group contents. Comparison of the data for nonionic and ionic surfactants is difficult because of the complication in hydration effect and possibly other structural constraints with ionic surfactants.

Whereas the ionic polar group of a surfactant is not expected to promote solute solubilization, the influence of the polar EO chain in BJ35 and the Triton series is not as clear. In this study, the impact of the EO chain in surfactants below the CMC was assessed by studying the apparent solubility of DDT in water containing up to 200 mg/L of poly(ethylene glycol) with a molecular weight of 1000 daltons. The observed data indicated no discernible solubility enhancement, which may be attributed to the failure of the EO chain to provide sizable nonpolar organic segments for attaining effective partition interations with the nonpolar solute (13).

We now consider the solubility enhancement data above the CMC. The distinct and sharp-rising slopes relating the apparent solubility of DDT and TCB to surfactant concentration far above the CMC allow the solute partition coefficient between the micellar phase and pure water (i.e., the K_{mc} value) to be accurately determined for each solute–surfactant pair, according to eq 1. The calculated K_{mc} values are shown in Table II. In comparison with K_{mn} values, the markedly greater K_{mc} values indicate that micelles are far more effective to solubilize DDT because of the wider extent of the organic environment in a pseudophase state. Based on the difference between K_{mc} and K_{mn}, micelles of the nonionic surfactant are ~40 times more effective than their monomers in solubilizing DDT. Larger differences are noted with the two ionic surfactants mainly because of their very small K_{mn} values.

Among all surfactants studied, the sequence of the observed K_{mc} values for DDT is TX114 ≥ TX100 > CTAB > BJ35 > TX405 > SDS; the sequence based on the K_{mc} values of TCB is TX114 > TX100 = CTAB > SDS > BJ35. If one assumes that the inner nonpolar core of the micelle is mainly responsible for solute solubilization and that the hydration of the outer polar zone of the micelle is localized, the K_{mc} value should then be approximately proportional to the nonpolar group content of the surfactant, provided that the micelle size is sufficiently large. This expectation is largely confirmed by the K_{mc} values with the Triton series and BJ35, which have comparable nonpolar groups but different EO chain lengths; it is not fulfilled when the ionic surfactants are included for comparison. As to the size of micelles, the reported monomer aggregation number is 71 for SDS, 40 for BJ35, 276 for $C_9H_{19}C_6H_4(OC_2H_4)_{10}OH$, 44 for $C_9H_{19}C_6H_4(OC_2H_4)_{30}OH$, and 20 for $C_9H_{19}C_6H_4(OC_2H_4)_{50}OH$ at room temperature (5). While the latter three nonionic surfactants show considerable differences in aggregation number, and similar differences may be inferred between TX100 and TX405, the observed difference in K_{mc} values between TX100 and TX405 appears to correlate better with the nonpolar group content rather than with the micellar size. Therefore, the difference in micellar size does not appear to be a major factor for the observed differences in K_{mc} of ionic and nonionic surfactants. More likely, the difference is related to the size and intensity of the nonpolar interior of the micelle and to the accessibility of this inner core to the organic solute (solubilizate). For micelles of ionic surfactants that are expected to be more strongly hydrated at the charged sites, such hydrations may obscure portions of the inner core and thus reduce the partition efficiency of the solute. This is consistent with the K_{mc} values of DDT and TCB with the two ionic surfactants in that when these values are normalized to their nonpolar group contents (59% and 62% by weight for SDS and CTAB, respectively), they are smaller than the corresponding values with the nonionic surfactants (whose nonpolar group contents are 35%, 30%, 9.6%, and 14% for TX114,

TX100, TX405, and BJ35, respectively).

To determine the solvency of a pseudophase micelle relative to that of a bulk organic phase, one may simply compare the observed K_{mc} value of a solute with its corresponding solvent–water partition coefficient. In view of the common use of the octanol–water partition coefficient (K_{ow}) in fate assessment and the partial resemblance of the octanol structure to nonionic surfactants, 1-octanol is a useful reference solvent for comparison. The experimental log K_{ow}s for DDT and TCB are 6.36 and 4.14 (16, 17), respectively. One should note, however, that the experimental K_{ow} value is based on the apparent solute concentration in octanol-saturated water rather than on the corrected concentration in pure water as is used in eq 1. The corrected K_{ow} for DDT is log K_{ow} = 6.73 (16). For TCB, which is markedly more soluble in water, this correction is relatively small, giving an estimated corrected value of ~4.20 based on extrapolation of available data (16). The observed K_{mc} values of DDT and TCB with all surfactants are lower than the corresponding K_{ow} values, the difference being related to the type of surfactant.

For TX114, which has the lowest polar group content among the four nonionic surfactants, the observed ratio of K_{ow} to K_{mc} is about 3.5 for DDT and 1.8 for TCB. Therefore, as far as TCB is concerned, the solvency of the micellar phase of TX114 appears to be comparable to that of bulk octanol; the small difference in K_{mc} and K_{ow} can be attributed more logically to the weight fraction of the elongated polar group in TX114 relative to the OH in octanol rather than to the smaller micellar size. The larger difference between K_{mc} and K_{ow} for DDT with TX114 may be a consequence of the much larger size and bulkier shape of DDT, which does not permit the whole molecule to be placed in close proximity to the nonpolar environment of the micelle. The increased downward deviation of the K_{mc} values of DDT and TCB with TX405 and BJ35 from the corresponding K_{ow} values is largely a result of the decreasing nonpolar group content with the surfactant. Indeed the normalized log K_{mc} values of DDT and TCB with respect to the nonpolar chain contents of nonionic surfactants, 6.63 ± 0.03 SD and 4.30 ± 0.15 SD, respectively, are relatively constant and comparable to the log K_{ow} values. It is apparent from these results that the polar EO chain comprising part of the micellar phase for the nonionic surfactants has a relatively small affinity for DDT and TCB (or similar nonpolar organic compounds).

Although the data with the ionic surfactants are less accountable in terms of their nonpolar versus polar group contents, it is nevertheless clear that the nonpolar interior of the micelle is mainly responsible for solute solubilization. This is evidenced by the observation that when the K_{mc} values for the micelles are normalized to their nonpolar contents, the resulting values for SDS and CTAB are still appreciably smaller than the K_{ow} values, while the normalized value is greater for CTAB than for SDS; this would not be true if the ionic polar groups should promote solute solubilization. In general, the present data are in agreement with the earlier observed order of the solubilizing power for organic solutes by the inner nonpolar core of the micelle as nonionic > cationic > anionic surfactants that have the same nonpolar chain length (1, 9, 18).

We now consider the potential impact of surfactants on the mobility of pollutants. It is apparent from this study that predictions of the effect of surfactants on solute solubility are complicated by the association transition of the surfactant. At low surfactant concentrations as generally found in natural waters, the effect should be largely insignificant for relatively water-soluble solutes but might become important for extremely insoluble solutes, especially with those heterogeneous surfactants that contain large fractions of low-CMC components. At concentrations far above the CMC, surfactants would have considerably greater impacts on water solubility of a wide range of organic pollutants. Although the surfactant concentration in environmental waters is generally low, certain circumstances such as run-off waters following the application of pesticide formulation products, streams and ponds receiving untreated waste waters, and leachates from waste disposal and landfill sites could potentially give high concentrations of surfactants in micellar form to facilitate the pollutant transport before the surfactants are diluted out during their movement.

Finally, it is of interest to compare the solute partition coefficients with surfactants and the corresponding values with dissolved aquatic humic–fulvic acids from earlier studies (13, 14). The observed partition coefficients of DDT with aquatic humic–fulvic acids are significantly greater than with monomeric ionic surfactants and are comparable in magnitude with the monomeric nonionic surfactants as shown in Table II; they are however considerably lower (by orders of magnitude) than values with either ionic or nonionic micelles. This finding suggests that the aquatic humic–fulvic acids at normal environmental concentrations (<100 mg/L) exist mainly in an unassociated state, which is consistent with the observed linear dependence of the apparent solute solubility on the humic–fulvic acid concentration. While the molecular structures of aquatic humic–fulvic acids are not well-defined, the data indicate that these acids at low concentrations in water do not appear to form the kind of micellar environment that is established by ordinary surfactants.

Conclusions

This study shows that some commercial surfactants can produce significant water solubility enhancement even at concentrations below the CMC for otherwise extremely water-insoluble organic compounds, such as DDT. This effect is attributed to a partition-like interaction with the nonpolar content of the dilute surfactant, similar to the enhancement effect caused by dissolved humic materials (13, 14). The observed nonlinear relation between the apparent solubility of DDT and the surfactant concentration below the nominal CMC for Triton and Brij surfactants is speculated to result from the successive micellization of the heterogeneous monomers. The enhancement effect by the selected nonionic surfactants below their CMCs is comparable in magnitude to the effect with aquatic humic substances. For the nonionic surfactants studied, the calculated K_{mc} values are closely in proportion to the nonpolar group content of the surfactant and the normalized values are comparable with K_{ow} values. The inner nonpolar core of the micellar phase appears to have a high degree of solvency for TCB and DDT in spite of the microscopic size of the micelle. The solvency of an ionic surfactant is less accountable in terms of its molecular composition.

Triton X-405, 9002-93-1; Brij 35, 9002-92-0.

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Ozonation Byproducts. 2. Improvement of an Aqueous-Phase Derivatization Method for the Detection of Formaldehyde and Other Carbonyl Compounds Formed by the Ozonation of Drinking Water

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■ A method for the determination of low molecular weight aldehydes in water using aqueous-phase derivatization with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride has been improved by the use of high-resolution capillary GC. Detection limits with GC/ECD and GC/MS with selected ion monitoring are in the low microgram per liter (ppb) range. The method has been used to evaluate levels of aldehydes in three surface water treatment plants and one ground water treatment plant before and after ozonation. Aldehydes are increased as result of ozonation, with formaldehyde being the most prevalent. Higher yields are observed in the plant treating surface water with the highest TOC level, but very low yields are observed in a high TOC ground water. Spiking studies show that the raw ground water has a very high demand for formaldehyde, suggesting that the aldehydes may be converted into secondary byproducts.

Introduction

Public water utilities have been searching for alternatives to the use of chlorine in drinking water treatment since the discovery of potentially harmful chlorination byproducts such as trihalomethanes. Of the alternatives, ozone is becoming increasingly attractive, especially for pretreatment and for treatment (*1*). It has been shown that the use of ozone is effective for removal of taste and odor compounds, color, and dissolved iron and manganese. Ozone treatment has also been shown to decrease tri-

halomethane formation potential and improve flocculation. Recently, ozone in combination with hydrogen peroxide has been shown to be effective for the oxidation of organics such as trichloro- and tetrachloroethylene in contaminated ground water (*2*, *3*).

In spite of the use of ozone in drinking water treatment for over eight decades, there is not enough information available about the formation of ozone byproducts during drinking water treatment or the fate of these byproducts in distribution systems. Of special interest are byproducts that may be toxic to humans or other species that use or may be exposed to ozonated water. Ozone, like chlorine, reacts with the natural constituents present in water to produce a number of byproducts (*4–8*). Ozone byproducts are usually oxygenated compounds, polar in nature, and sometimes unstable. As a result, the analyses of ozonation byproducts using conventional analytical techniques has proven to be difficult. In this paper we have modified a method first used by Yamada and Somiya (*8*) for the analysis of C_1–C_3 carbonyl compounds in ozonated water and applied the modified method to the study of three full-scale water treatment plants and one pilot plant using ozonation.

Methods for the Analysis of Carbonyl Compounds in Water

In the first paper of this series (*9*) ozonation byproducts from a treatment plant were analyzed by the Closed Loop Stripping Analysis method. This method is exceptionally sensitive for neutral volatiles in the C_6–C_{15} range but fails to detect low molecular weight, polar compounds such as formaldehyde, glyoxal, etc. Techniques for direct aqueous derivatization, for example with 2,4-dinitrophenylhydrazine appear to be useful for the analyses of such compounds and have been widely used (*10–12*). Another

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