

Interaction between 2-(1-Naphthyl)acetic Acid and Micelles of Nonionic Surfactants in Aqueous Solution

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The interaction of 2-(1-naphthyl)acetic acid (NAA) with nonionic octylphenoxypoly(ethoxy)ethanol (Triton X) and linear primary alcohol (C_{9-11}) poly(ethoxy)ethanol (Neodol 91) surfactants was followed in an aqueous system by UV and fluorescence spectroscopy. There was a distinct shift of the UV absorption maximum to a longer wavelength at surfactant concentrations above the critical micelle concentration (cmc), indicating an intermolecular interaction between NAA and surfactant micelles. Both surfactant concentration and system pH had significant effects. NAA-surfactant interaction occurred only at surfactant concentrations above the cmc where micelles were present and the interaction was favored when the NAA molecule was in the nondissociated form (pH 3.2, $pK_a = 4.2$). Equilibrium constants (K) for the NAA-micelle complex of the Triton X surfactants against buffer solution ranged from 80 to 1161, and $\log K$ was inversely related to the log of the number of oxyethylene units in the poly(oxyethylene) chain.

INTRODUCTION

Surfactants are amphipathic molecules that alter the energy relationships at interfaces (Rosen, 1989). They are frequently used in formulation and spray application of foliar-applied agrochemicals to improve performance of the active ingredient in crop production. However, occasionally surfactants may be without effect or reduce the response (Temple and Hilton, 1963). The bases for these effects are not well understood, and thus there is a need to develop a better understanding of surfactant action.

In studies on sorption of 2-(1-naphthyl)acetic acid (NAA) by isolated leaf and fruit cuticular membranes, surfactants dramatically depressed NAA sorption at concentrations above the critical micelle concentration (cmc) (Shafer and Bukovac, 1988). Such sorption systems simulate spray solutions and aqueous spray droplets applied to plant surfaces. In these systems, complex interactions may occur between the active ingredient and the surfactant as well as simultaneous interactions between both the active ingredient and the surfactant with the plant surface.

A first attempt to describe the interaction of spray droplets with plant surfaces requires an understanding of the surfactant/active ingredient system. The objective of this study was to characterize the interaction between NAA molecules and selected nonionic surfactant molecules in a simulated aqueous spray solution system.

EXPERIMENTAL PROCEDURES

Chemicals. NAA was purchased from Calbiochem Co. (San Diego, CA) and pyrene from Aldrich Chemical Co. (Milwaukee, WI); their chemical purities were 98+ and 97+ %, respectively. No further purification was attempted.

A series of octylphenol (OP)-type surfactants, α -[4-(1,1,3,3-tetramethylbutyl)phenyl]- ω -hydroxypoly(oxy-1,2-ethanediyl), prepared by condensing OP with ethylene oxide (EO), were selected. Trade names (registered trademarks, Rohm and Haas Co., Philadelphia, PA) for these nonionic surfactants are Triton X-45 (OP + 5 EO), Triton X-114 (OP + 7.5 EO), Triton X-100 (OP

+ 9.5 EO), Triton X-165 (OP + 16 EO), and Triton X-405 (OP + 40 EO) (Triton X also abbreviated TX). In addition, a series of nonionic linear primary alcohol (C_{9-11}) poly(ethoxy)ethanol surfactants (Neodol 91 with 6, 10, and 20 EO units, Shell Oil Co., Houston, TX) were used. All surfactants were mixtures of oligomers, where the listed EO number represents an average value of the oxyethylene units and the mole ratio distribution follows a Poisson distribution (*Triton Surface-Active Agents*, 1982). Pertinent physical/chemical characteristics are listed in Table I.

These surfactants were selected because they represent important groups being used in pesticide formulation and in spray application of agrochemicals. NAA was selected because it is an important plant growth regulator representative of the weak organic acid auxins.

Spectroscopic Procedures. The interaction between NAA and nonionic surfactants was studied in aqueous solution by UV (Benesi and Hildebrand, 1949; Tuong et al., 1977) and fluorescence (Ziemiecki et al., 1980) approaches proven useful in defining intermolecular interactions of acidic organic dyes with surfactants. All studies were conducted in a temperature-controlled environment at 23 °C.

UV Measurements. UV and first-derivative UV absorption spectra were obtained with a Gilford Model 2600 spectrophotometer. The UV spectrum of a fixed concentration of NAA (100 μ M) in citrate buffer (20 mM, pH 3.2) was measured at a series of concentrations (0.1-1% w/v) of the linear alcohol surfactant Neodol 91 (C_{9-11} + 6 EO).

The effect of pH on interaction of NAA with a linear alcohol surfactant (C_{9-11} + 6 EO) was followed by changes in the first-derivative UV spectra of NAA (100 μ M) solutions at 294 nm in the presence of surfactant (0-0.25% w/v) at pH 3.2 (20 mM citrate buffer) and 6.5 (50 mM phosphate buffer). In this system, NAA was predominantly in the nondissociated form at pH 3.2 and in the dissociated form at pH 6.5 ($pK_a = 4.2$; Dippy et al., 1954). The surfactant was present in the monomeric form below 0.025% and at higher concentrations as a mixture of monomers and micelles.

The effect of the EO chain length on NAA interaction with surfactants was established by following changes in the UV absorption spectra of NAA (100 μ M, pH 3.2) at a range of concentrations (from below to above the cmc) of octylphenol surfactants (Triton X) with 5, 7.5, 9.5, 16, and 40 EO units and linear alcohol (C_{9-11}) surfactants containing 6, 10, or 20 EO units.

Fluorometric Measurement. NAA-surfactant interaction was also established by following NAA quenching of the fluorescence from the molecular probe, pyrene, over a series of surfactant concentrations. Fluorescence intensities were determined for pyrene (1 μ M) at different concentrations of NAA and Triton

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Table I. Physical/Chemical Characteristics of the Surfactants Used

surfactant	oxyethylene content	cmc, % w/v	micelle aggregation no. ^a
Triton X-45	5	0.005	296
Triton X-114	7.5	0.009	189
Triton X-100	9.5	0.019	146
Triton X-165	16	0.110	82
Triton X-405	40	0.170	30
Neodol 91-6	6	0.025	242
Neodol 91-10	10	0.029	138
Neodol 91-20	20	0.039	64

^a Micelle aggregation numbers were calculated according to the procedure of Levitz and Van Damme (1986).

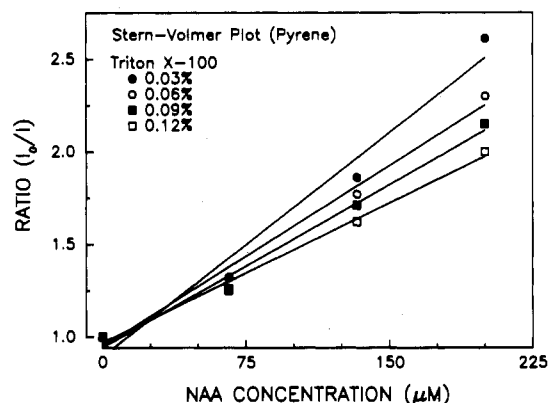


Figure 1. Stern-Volmer plots for NAA quenching of pyrene at various concentrations of NAA and Triton X-100 (OP + 9.5 EO). Excitation wavelength, 330 nm; emission wavelength, 400 nm; pyrene concentration, 1 μM.

X-100 (see Figure 1) in citrate buffer at pH 3.2. Similar studies were performed with TX-165 and TX-405 over a concentration range bridging the cmc (0.05–2.0%). Samples were subjected to an excitation wavelength of 330 nm, and fluorescence emission was measured at 400 nm with an Aminco Bowman spectrofluorometer. None of the samples were degassed. In all cases, the fluorescence of a control blank (surfactant/pyrene solution without NAA) was determined prior to measuring the fluorescence intensity of a quenched sample.

Calculation of Equilibrium Constants (*K*). The *K* values for our system were determined by three different methods. The first method (A), suggested by Tuong et al. (1977), is based on the relationship

$$\log \frac{[S_0] - \text{cmc}}{[NAA_0] - [NAA]} = -x \log [NAA] - \log \frac{xK}{n} \quad (1)$$

where $[S_0]$ is the surfactant molar concentration, cmc the critical micelle concentration, $[NAA_0]$ the total NAA molar concentration, $[NAA]$ the molar concentration of the free NAA, x the number of NAA molecules associated with each micelle, K the equilibrium constant, and n the number of surfactant molecules associated with a micelle (aggregation number). K can be expressed as

$$K = \frac{[\text{NAA-surfactant complex}]}{[\text{NAA}] [\text{surfactant}]}$$

Thus, both the equilibrium constant and the number of NAA molecules associated with each micelle can be calculated. This model assumes that the interaction occurs between NAA and surfactant micelles and that the association of NAA does not affect the aggregation number of the micelle.

The second method (B), developed by Benesi and Hildebrand (1949), assumes formation of a 1:1 complex between NAA and the nonionic surfactant micelles. If this condition is satisfied, the K value can be determined using

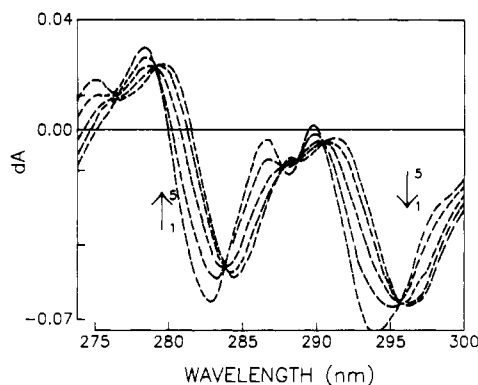


Figure 2. First-derivative UV absorption spectra of NAA at several concentrations of Neodol 91 (C₉₋₁₁ + 6 EO) surfactant. NAA concentration, 100 μM; surfactant concentrations (see arrows), 0 (1), 0.10 (2), 0.25 (3), 0.50 (4), and 1% (5) (w/v); pH 3.2.

$$\frac{[NAA_0]b}{d - d_0} = \frac{1}{\epsilon - \epsilon_0} + \frac{1}{K(\epsilon - \epsilon_0)[S_0]} \quad (2)$$

where $[NAA_0]$ and $[S_0]$ represent the total molar concentrations of NAA and surfactant, respectively, b is the optical path length of the solution, d and d_0 are the absorbances of NAA at the determined wavelength of the complex in the presence and absence of surfactant, respectively, and ϵ and ϵ_0 are the respective molar extinction coefficients of the NAA-micelle complex and NAA at the above wavelength.

The third method (C), proposed by Ziemiecki et al. (1980), is based on fluorescence quenching of pyrene. First, Stern-Volmer constants (S) are determined for each surfactant at several concentrations above and below the cmc using

$$I_0/I = 1 + S[Q] \quad (3)$$

where I_0 and I represent the relative fluorescence intensities in the absence and presence of quencher (NAA) at a total quencher concentration of $[Q]$ and S , the Stern-Volmer constant, is obtained from the slope (Figure 1). A linear relationship between the I_0/I ratio and NAA concentration is required to satisfy this model (Figure 1). Second, K is calculated using

$$\frac{1}{S} = \frac{1}{aK} + \frac{[M]}{a} \quad (4)$$

where the values of S , obtained with eq 3, are plotted against the molar micelle $[M]$ concentration.

For derivation of equations and discussion of theory, the reader is referred to Tuong et al. (1977) and Benesi and Hildebrand (1949) for the UV methods and Ziemiecki et al. (1980) for the fluorescence procedure.

RESULTS AND DISCUSSION

NAA-Surfactant Interaction. The UV absorption spectrum of NAA did not change in the presence of the linear alcohol surfactant at concentrations below the cmc (data not presented). At concentrations above the cmc, the absorption maxima was shifted to longer wavelengths and the wavelength of the absorption maximum increased with increasing surfactant concentration (Figure 2). The magnitude of this shift was small but distinct (from 280.5 nm for NAA in buffer only to 282.5 nm at high surfactant concentration). The first derivative of the absorption spectrum was used because it provides for more precise definition of the absorption maximum, the maximum being at the wavelength where the first derivative equals zero. In an earlier study (Shafer and Bukovac, 1989), and confirmed in this study, an isosbestic point was evident at about 281.5 nm. Similar results were obtained with the other surfactant systems studied (data not presented).

These data suggest that there was an intermolecular interaction between NAA and surfactant micelles but not

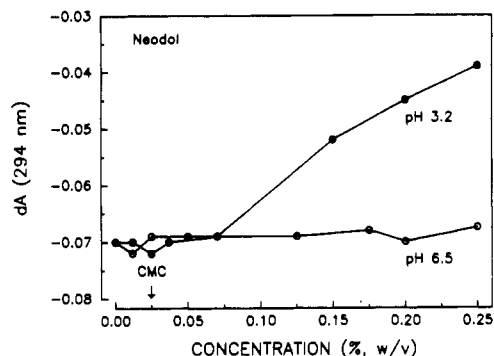


Figure 3. Effect of Neodol 91 ($C_{9-11} + 6$ EO) concentration and pH on the first-derivative UV absorption of NAA at 294 nm. NAA concentration, 100 μ M. Assay conditions: 20 mM citrate buffer (pH 3.2) and 50 mM phosphate buffer (pH 6.5).

with surfactant monomers. The shift in the absorption maximum indicates that NAA is present in two distinctly different environments, one as free NAA (nonassociated) in the aqueous bulk (intermicellar) and the other associated (complexed) with micelles. Further, the presence of an isosbestic point provides evidence that NAA exists in only these two molecular environments, as was also demonstrated for anthraquinoid acid dyes by Tuong et al. (1977).

The observed intermolecular interaction between NAA and nonionic surfactant micelles was pH dependent (Figure 3). When the NAA molecule was in the dissociated form (pH 6.5), no change was observed in the UV spectrum over a wide surfactant concentration range; however, a marked increase in UV absorption was observed with an increase in surfactant concentration when NAA was in the nondissociated form (pH 3.2). This suggests a high affinity between the nondissociated NAA molecules and surfactant micelles.

Since changes occurred in the NAA UV absorption spectra only when the NAA was in the nondissociated form and when micelles were present, and UV absorption increased linearly with an increase in micelle concentrations, i.e., as surfactant concentration was increased above the cmc (Figure 3), we conclude that the interaction in our system occurred between the nondissociated NAA molecules and the micelles and not with surfactant monomers. These findings are consistent with results on interaction of nonionic surfactants with molecules of very different chemistries from that of NAA, e.g., anthraquinoid and thiazine dyes (Tuong and Hayano, 1977; Bhowmik and Mukhopadhyay, 1988). Solution pH may have important practical implications in the performance of NAA and other pesticides of similar chemistry/polarity, because the degree of dissociation will influence the interaction with surfactant micelles, particularly since surfactants are frequently included in pesticide sprays at concentrations above the cmc.

Equilibrium constants for the NAA-surfactant (Triton X series) interaction calculated by the three different methods were in good agreement for the NAA/TX-100, NAA/TX-165, and NAA/TX-405 systems (Table II). The highest K values (461–510) were obtained with TX-100 and progressively lower values for TX-165 (264–328) and TX-405 (60–80). Using eq 1, the K values calculated for the TX-45 and TX-114 systems were 1161 and 743, respectively (method A, Table II). These values were considerably higher than those calculated for the TX-100, TX-165, and TX-405 systems (Table II). Equilibrium constants for the TX-114 and TX-45 systems were not calculated according to method B or C (eqs 2 and 4) because our data for these systems did not conform to a 1:1 NAA/

Table II. Equilibrium Constants (K) for the NAA/Triton X Surfactant Complexes^a

surfactant	UV absorption method		fluorometric method C
	A	B	
Triton X-45	1161	— ^b	— ^b
Triton X-114	743	— ^b	— ^b
Triton X-100	461	504	510
Triton X-165	264	328	296
Triton X-405	80	80	60

^a Assay conditions: pH 3.2, 23 °C. Methods A, B, and C represent models proposed by Tuong et al. (1977), Benesi and Hildebrand (1949), and Ziemiecki et al. (1980), respectively. ^b K value was not calculated because 1:1 NAA/micelle association was not satisfied.

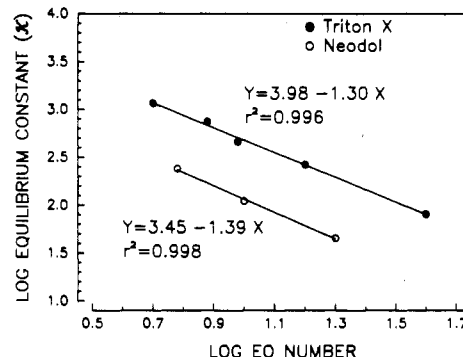


Figure 4. Relationship between the log of the equilibrium constant and log EO number in the poly(oxyethylene) chain for NAA and selected Triton and Neodol surfactants: Triton X-45 (5 EO), Triton X-114 (7.5 EO), Triton X-100 (9.5 EO), Triton X-165 (16 EO), Triton X-405 (40 EO), Neodol 91 (6 EO), Neodol 91 (10 EO), Neodol 91 (20 EO).

micelle relationship dictated by these models (Benesi and Hildebrand, 1949; Ziemiecki et al., 1980). Since our data fit the requirements of these models, we conclude that one NAA molecule is associated (complexed) with one micelle for systems TX-100, TX-165, and TX-405. However, using method A (eq 1), a model not requiring a 1:1 association, we calculated that 3 and 8 NAA molecules are associated with each micelle in the TX-114 and TX-45 systems, respectively. On the basis of a gel filtration study, association of NAA with micelles of TX-114 did not alter the micelle aggregation number (Heredia and Bukovac, 1990).

There was a highly significant negative linear correlation ($r^2 = 0.996$) between the log of the K values and the log of the number of EO units in the hydrophile chain (Figure 4). A curvilinear relationship was found between the K values and the hydrophile/lipophile balance (Figure 5), a function of the oxyethylene content (Griffin, 1954). Similar relationships were found for the Neodol surfactants (Figures 4 and 5).

The following explanation can be offered for the high affinity between the NAA molecules and the micelles of nonionic surfactants with short and thus more hydrophobic poly(oxyethylene) (POE) chains. Micelles made up of monomers of these surfactants exhibit two distinct environments, a relatively "dry" micelle core made up of the nonpolar octylphenol moieties and a relatively "wet" outer mantle of partially hydrated polar oxyethylene units (Tanford et al., 1977; Dressick et al., 1984). Further, the packing of the monomers during micelle formation, particularly of short-chain oxyethylene monomers, is accompanied by dehydration of the micellar polar mantle, leading to greater hydrophobicity (Turro and Kuo, 1985; Keh et al., 1989). Presumably the interactions between the nondissociated NAA molecule and the micelle in our study occur in the hydrated POE region (mantle) of the

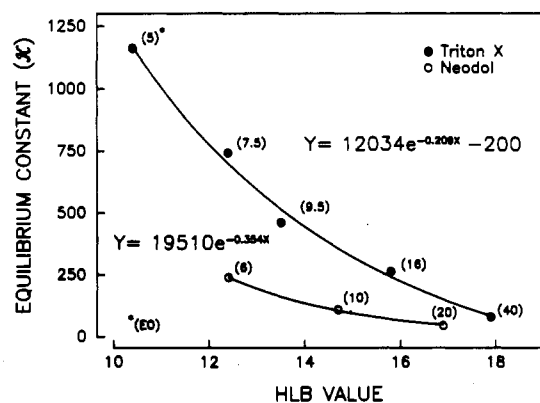


Figure 5. Relationship between the equilibrium constant and the hydrophile/lipophile balance (HLB) for NAA and selected Triton and Neodol surfactants: Triton X-45 (5 EO), Triton X-114 (7.5 EO), Triton X-100 (9.5 EO), Triton X-165 (16 EO), Triton X-405 (40 EO), Neodol 91 (6 EO), Neodol 91 (10 EO), Neodol 91 (20 EO).

micelle. This conclusion is supported by the fact that we have a high correlation between K and micelles that have identical core composition but differ in composition of the mantle (EO chain lengths). Further, we believe that the interaction involves competition between the micelle and water for complexing (solvation) of the NAA molecules. Our data suggest that for the NAA/TX-45 and NAA/TX-114 systems the association between the POE chain and the NAA molecule is favored over the hydration of the POE chain. In addition, with short POE chains, an interaction between the π molecular orbitals of the aromatic ring and the lone electron pairs on the ether oxygen of the POE chain may contribute to the stability of the complex.

Work underway is focusing on obtaining a better understanding of the mechanisms of association of the NAA molecule with surfactant micelles and the calculation of distribution coefficients for NAA between the aqueous and micellar phases.

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