

Aggregation Behavior of 12-(1-Pyrenyl)dodecanoic Acid in Homogeneous and Micellar Solutions

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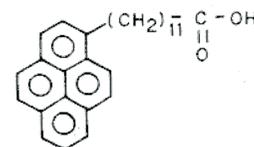
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The steady-state fluorescence emission from 12-(1-pyrenyl)dodecanoic acid (PyDDA) in aqueous, organic, and micellar solutions has been studied as a function of pH and concentration of PyDDA and selected surfactants. The pH-dependent aggregation of PyDDA in aqueous solution shows strong aggregation of the acid molecules through H-bonding and hydrophobic interaction of alkyl chains under suitable conditions, manifested as blue shifts in the excimer emission. Emission studies in dodecanoate solution responded to the premicellar aggregation phenomenon. Possible implications of this study to solid-liquid interfacial probing are discussed.

Introduction

Fatty acids and their derivatives have been the focus on many recent studies mainly due to their film-forming ability which has potential applications for biosensor and electronic devices.^{1,2} The physicochemical properties and structure of the film have to be controlled to optimize the quality of cast films.³ The above acids form mono- and multilayers at the aqueous solution-air interface and have been studied with their surface pressure-area (π -A) isotherms.⁴ A new dimension was added to the π -A information by coupling the fluorescence emission studies (steady-state and time-resolved) on films, using pyrene-labeled acids, with the available information on the condensed nature of these films.⁵

Fatty acids have also found application as flotation collectors for the enrichment of a variety of minerals.^{6,7} Unravelling of the adsorption mechanism of these acids on minerals, a prime concern in the effective control of the flotation efficiency, may be achieved by combining the classical adsorption data with spectroscopic information on the same system.⁸⁻¹⁴ Fluorescence spectroscopic studies with labeled fluorogen-bearing compounds in



12-(1-PYRENYL) DODECANOIC ACID [PyDDA]

Figure 1. Structure of 12-(1-pyrenyl)dodecanoate acid (PyDDA).

solution assisted by emission information from a Langmuir-Blodgett (L-B) film can be a starting point for correlating the properties of adsorbed layers with information on emission from the solid-liquid interface. This is particularly so since the complex mechanistic factors of flotation depend to a great extent on the solid-liquid and liquid-air interfaces.⁷

12-(1-pyrenyl)dodecanoic acid (PyDDA), for which the structure is represented in Figure 1, has been studied by many workers as a model L-B film compound.^{1,2} Aggregation of fatty acid molecules through H-bonding and other interactive forces was reflected in the monomer-excimer forming efficiencies of the pyrene moiety. In addition to L-B films and films on the water surface, these labeled acids have been studied also as vacuum-deposited thin films^{15,16} with pulsed and continuous light to explore their excimer-forming ability under time-resolved and steady-state conditions. The results indicated the importance of the ground state association of pyrene and the resultant variation in the excimer species formed. A brief description of the emission properties of pyrene-substituted dodecanoic acid at three pH values has been given by Itaya et al.^{16b} The present study aims toward exploring the emission behavior of PyDDA in micelles as well as in aqueous and organic media by steady-state fluorescence measurements. Such information is deemed to be essential for using this molecule as a probe for studying adsorbed surfactants at the solid-liquid interface. In the present work, the nature of emission of PyDDA has been studied in aqueous solution at different pH values and in cyclohexane, as well as in dodecanoate and sodium dodecyl sulfate (SDS) micelles.

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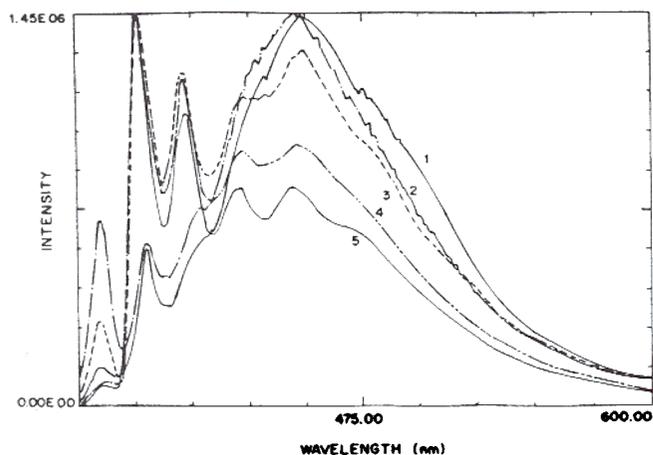


Figure 2. Fluorescence spectra of PyDDA in aqueous solution at different pH values; [PyDDA] = 3.3×10^{-6} M; λ_{ex} = 320 nm; pH Values: (1) 2.45; (2) 3.74, (3) 7.31, (4) 8.89, and (5) 10.50.

Experimental Section

PyDDA was purchased from Molecular Probes and used as received. Lauric acid (dodecanoic acid) was from Alfa chemicals and sodium dodecyl sulfate (SDS) from Bio-Rad (electrophoresis grade). The pH of the solutions was adjusted from 1 M solutions of sodium hydroxide and hydrochloric acid (Fisher certified). Methanol and cyclohexanol were of HPLC grade (Aldrich). All the aqueous solutions were made in triple-distilled water. Lauric acid was dissolved in sodium hydroxide at a pH of ≈ 12 . Stock solutions of PyDDA were prepared in methanol (≈ 1 mM). The aqueous solutions of PyDDA were prepared initially at alkaline pH and acidified to obtain a lower pH. To ensure that PyDDA is not precipitated in homogeneous solution, excimer efficiency was monitored by changing the pH for several cycles, and constant values were observed at each pH. PyDDA is known to have an aqueous solubility of $> 3.3 \times 10^{-6}$ M, the concentration used in the present study.^{16c}

The fluorescence emission measurements were performed with a SPEX FLUOROLOG spectrofluorometer at an excitation wavelength of 320 nm. The emission spectra were corrected by means of a built-in program; the excitation spectra were not corrected.

Results and Discussion

Homogeneous Solutions. Figure 2 shows the fluorescence emission spectra of PyDDA at various pH values

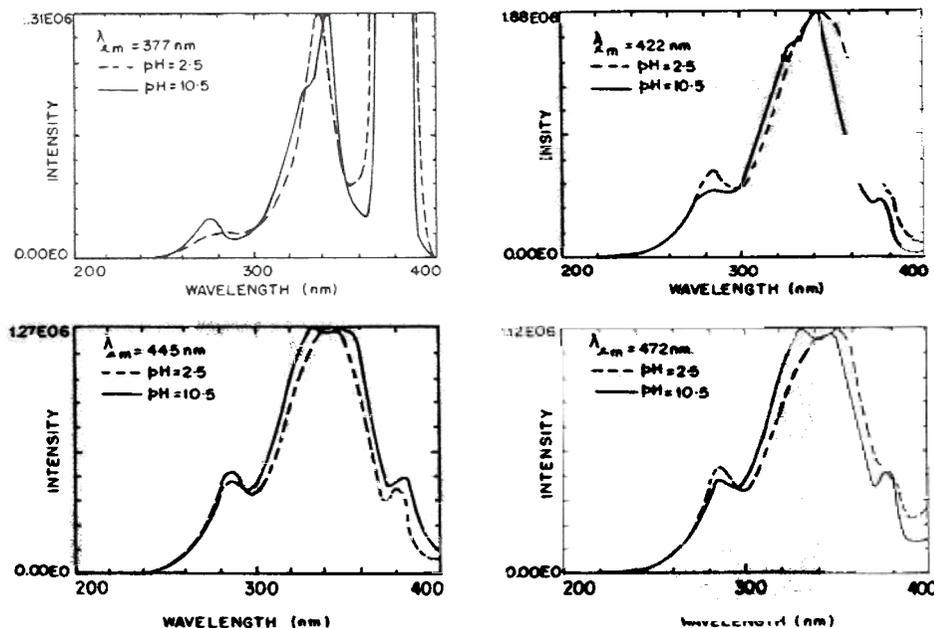


Figure 3. Excitation spectra of PyDDA in aqueous solution at two different pH values (2.5 and 10.5) at emission wavelengths of 377, 422, 445, and 472 nm.

ranging from 2.4 to 10.5. The broad excimer peak with a maximum at 445 nm appearing at low pH diminishes in intensity as the pH is increased; a peak at 425 nm is well-resolved at higher pH. Also, the monomer peaks appearing between 375 and 400 nm are red-shifted at higher pH values. A peak at ≈ 360 nm is due to Raman scattering from the solvent. In addition, the spectrum at pH 10.5 exhibits a shoulder at ≈ 472 nm. To throw light on the origin of these peaks, excitation spectra of the above samples were recorded at emission wavelengths of 377, 422, 445, and 472 nm at two extreme pH values of 2.5 and 10.5, and they are shown in Figure 3. The excitation spectra at all emission wavelengths under these conditions are seen to be different at the two pH values.

Figure 4 depicts the variation in the ratio of the excimer (445 and 425 nm) and monomer (377 nm) intensities (I_E/I_M) of PyDDA as a function of pH. The I_E/I_M values decreased markedly from pH 4, with very little change at high and low pH values.

Figure 5 shows the fluorescence emission spectra of PyDDA in cyclohexane along with that in water at natural pH. The spectrum in water corresponds to the one given earlier at low pH values. The spectrum in cyclohexane exhibits the characteristic fluorescence features of a covalently labeled pyrene moiety in a hydrophobic environment under conditions when the excimer is not formed.⁸ The emission spectrum of PyDDA in cyclohexane remained the same irrespective of its concentration up to 15 μ M (not shown in the figure).

Pyrene emission from PyDDA displayed strong dependence on the pH of the solution at a given concentration. At very low concentrations, 10^{-6} M, a negligible amount of excimer is formed. The pH-dependent excimer formation points to the possibility of different types of interaction between dodecanoic acid molecules in solution resulting in different types of excimers. The hydrophobic association between the alkyl chains has been recognized as an important factor in determining the overall interaction between these acid molecules.^{17,18} These effects added to the electrostatic requirements arising from the charge on the carboxylate group and the associative H-bonding between them lead to various structural responsibilities as represented in Figure 6.

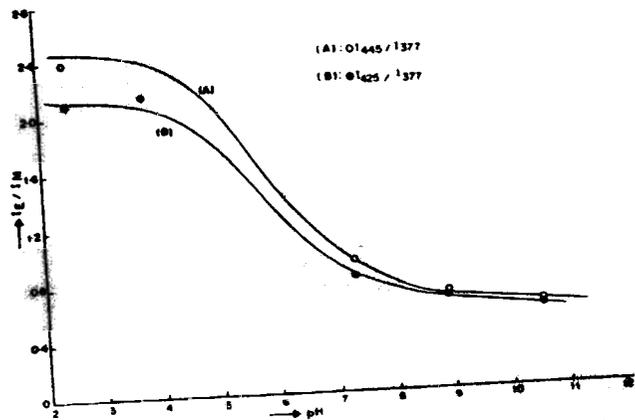


Figure 4. Ratio of intensities of excimer (445 and 425 nm) and monomer (377 nm) emission of PyDDA as a function of pH: (A) I_{445}/I_{377} ; (B) I_{425}/I_{377} .

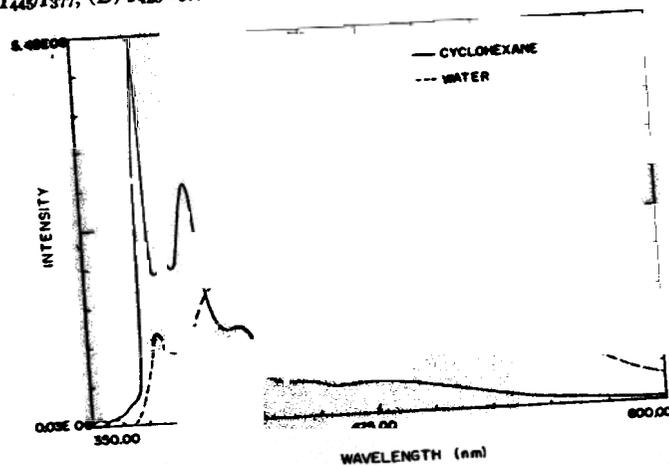


Figure 5. Fluorescence spectra of PyDDA in water (---) and in cyclohexane (-); [PyDDA] = 3.3×10^{-6} M; $\lambda_{ex} = 320$ nm.

At low pH, the acid molecules interact strongly through H-bonding and the alkyl chains interpenetrate, resulting in strong overlap of pyrene groups. At high pH, the ionized acid groups will tend to keep themselves apart such that the overlap of pyrene groups becomes less effective. In an organic medium, the association of carboxylic acid groups may occur as shown in Figure 6D much in the same way as benzoic acid dimerizes in benzene with the result that no effective overlap of pyrene groups takes place. Hence, in cyclohexane, practically no excimer is formed even at higher concentrations of PyDDA. At intermediate pH values, acid-soap may be formed between ionized and un-ionized acid molecules, but such dimeric species, as represented in Figure 6C, will have more or less the same type of structure as in Figure 6A.

The emission spectrum of PyDDA in water at high pH exhibits a shoulder at ~ 472 nm, the characteristic dynamic excimer of pyrene.¹⁹ This suggests that the interaction of high pH species occurs by more than one mechanism, leading to the formation of excimers of different types. The fluorescence excitation spectra at different wavelengths for the two extreme pH cases (Figure 3) also indicate this possibility; these spectra at all emission wavelengths are dissimilar under the two

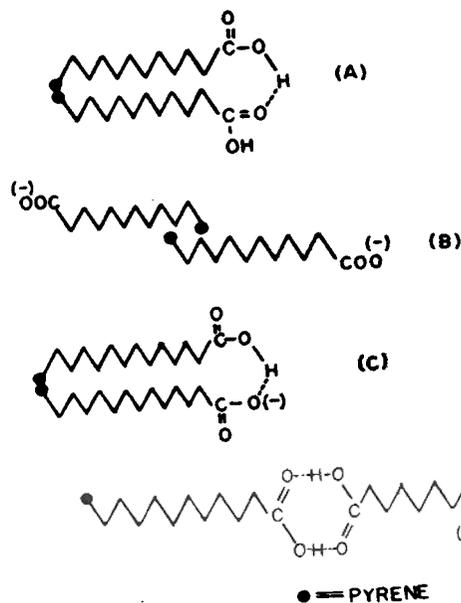


Figure 6. Association of PyDDA in (A) low-pH aqueous solution: H-bonding between un-ionized carboxylic acid groups and strong interaction between the hydrocarbon chains bring the pyrene groups closer. (B) High-pH aqueous solution: Due to the repulsive force between the carboxylate groups, the chains do not associate as strongly as in A. (C) Acid-soap complex formation between the neutral acid and conjugate base via H-bonding in aqueous solution. (D) Organic solvents: the dimeric association of two acid molecules (as benzoic acid in benzene) keeps the pyrene groups away from each other.

different pH conditions. The fluorescence spectra of ω -(1-pyrenyl)alkanoic acids as vacuum-deposited and L-B films at high surface pressures are also known to exhibit the 445 nm excimer band.¹⁵ The changes in the intensity at 377 nm as reflected in the I_E/I_M ratio (Figure 4) show a gradual variation with respect to pH, indicating a transition in the excimer forming structures with pH. The same trend is also observed in the ratio of intensity at 425 and 377 nm.

The shifts in the maximum of pyrene excimer emission are reported to be strongly dependent on the degree of overlap between the two pyrene groups involved in the excimer formation. Similar dependence is reported in the excimer emission maximum of crystalline pyrene with temperature,²⁰ where the pyrene-pyrene distance change with temperature. The pH-dependent variation in the excimer peak of PyDDA may also be attributed to change in the proximity of the two pyrene groups responsible for the excimer formation.² It is possible that the excimer at low pH may be formed from ground-state pyrene aggregates since the strong H-bonding and hydrophobic interaction between the acid molecules may favor such aggregate formation. That the monomer intensity at low pH almost vanishes as observed with thin films (vacuum deposited¹⁶ or L-B²) also suggests the possibility of ground-state aggregation at low pH.

The spectrum of PyDDA in cyclohexane shows characteristic emission features of pyrene moiety in a predominantly nonpolar environment, even though linear relations may not exist between the vibronic band intensities and solvent polarity. In this regard, it may be mentioned that Thomas et al. on the basis of their electron-transfer reaction studies with pyrene-labeled decanoic acid in micelles, has suggested a methanol-like environment for pyrene ra-

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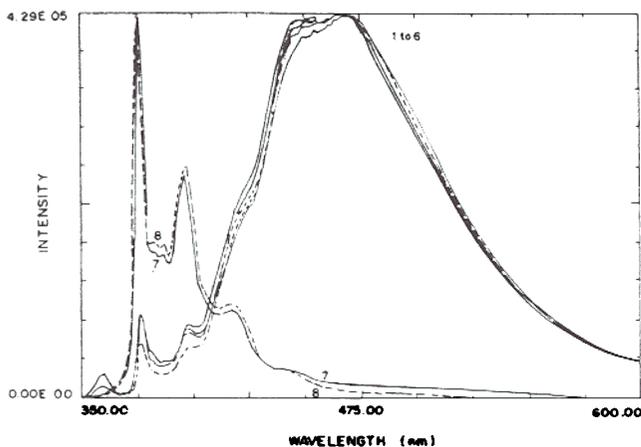


Figure 7. Emission spectra of PyDDA in SDS solution: [PyDDA] = 2.1×10^{-6} M; λ_{ex} = 320 nm; [SDS]: (1) 0.0, (2) 5×10^{-5} , (3) 1×10^{-4} , (4) 1.5×10^{-4} , (5) 5.0×10^{-4} , (6) 1.0×10^{-3} , (7) 1.3×10^{-2} , (8) 3.8×10^{-2} M.

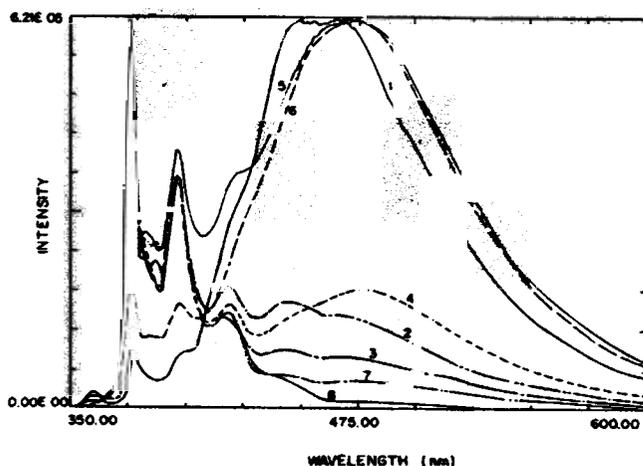


Figure 8. Influence of sodium dodecanoate on the emission spectra of PyDDA at alkaline pH; [PyDDA] = 2.1×10^{-6} M; λ_{ex} = 320 nm; [sodium dodecanoate]: (1) 0.0, (2) 1.0×10^{-3} , (3) 2.0×10^{-3} , (4) 4.0×10^{-3} , (5) 1.0×10^{-2} , (6) 1.6×10^{-2} , (7) 2.0×10^{-2} , (8) = 8.0×10^{-2} M.

than a hydrocarbon one. As discussed earlier, the existence of dimeric cyclic H-bonded structures in hydrocarbons makes the formation of an excimer difficult. Naturally, an increase in the concentration of PyDDA in this type of solvent cannot be expected to contribute toward excimer formation, since intermolecular excimer formation from such dimeric species will not be significant at concentration levels used here.

In Surfactant Solutions. Figure 7 shows the emission spectra of PyDDA in sodium dodecyl sulfate solutions at concentrations ranging from 5×10^{-5} to 3.8×10^{-2} M at a constant PyDDA concentration of 2.1×10^{-6} M. The spectrum above the CMC of SDS (8.3×10^{-3} M) is similar to the one obtained in the cyclohexane solution (Figure 5).

Figure 8 shows the emission spectra of PyDDA in dodecanoate solutions at alkaline pH. In the pre-micellar region, the spectrum changes from a typical alkaline aqueous spectrum (as in Figure 2) into one in a hydrocarbon environment (as in Figure 5) through an intermediate range where dynamic excimers with emission maximum of ~ 472 nm are formed. Figure 9 shows the variation of I_{445}/I_{377} and Figure 10 the variation of I_{396}/I_{377} for the two surfactants.

In dodecyl sulfate solution, the un-ionized form of PyDDA does not have any specific interaction with SDS below its cmc. But, in the postmicellar region, PyDDA

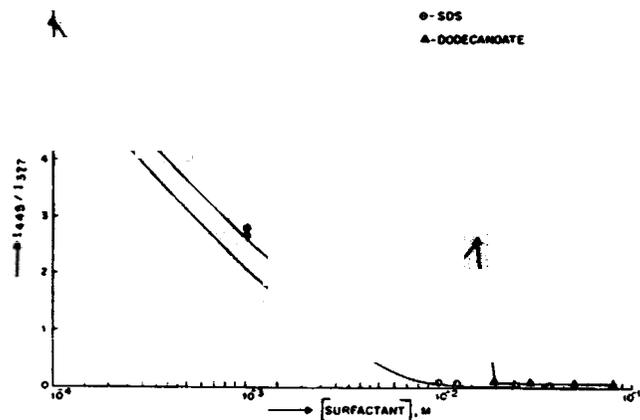


Figure 9. Variation in the ratio of intensities ($\pm 5\%$) of excimer (I_{445}) and monomer (I_{377}) with [SDS] and [dodecanoate].

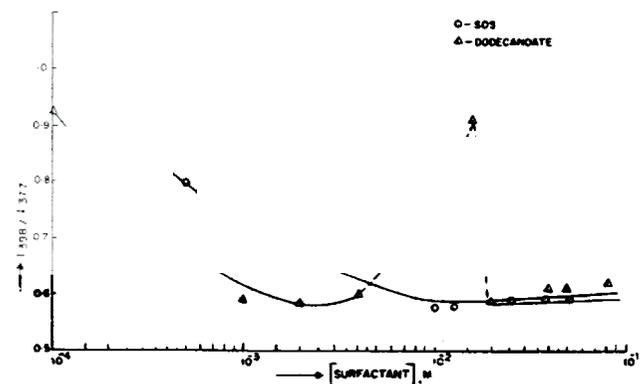


Figure 10. Dependence of the ratio of intensities ($\pm 5\%$) of excimer (I_{396}) and monomer (I_{377}) on [SDS] and [dodecanoate].

emits the characteristic spectrum of pyrene monomers in a hydrocarbon environment. This indicates that PyDDA is solubilized in SDS micelles, the interior of the micelles providing the highly hydrophobic environment. However, no excimer is formed as the molar ratio of PyDDA to SDS is very small; in other words, individual pyrene groups are screened by alkyl chain ends of the unlabeled molecules. The situation is quite different in the sodium dodecanoate case. Here, the dodecanoate being prepared from dodecanoic acid at alkaline pH, PyDDA in solution prefers to be in the ionized form. At its natural pH, PyDDA shows the characteristic blue shift (Figure 8, scan 1). In dodecanoate solutions at low concentrations (pH > 11), PyDDA shows a spectrum similar to that in alkaline solutions (Figure 8, scan 2). As the concentration of dodecanoate is increased, the excimer is red-shifted to yield the usual dynamic excimer, i.e. the two-center sandwich-type excimer.²⁰ These results indicate that PyDDA is in a flexible state in the above concentration range. This trend is especially maintained for concentrations immediately preceding the cmc of the surfactant. Such an observation suggests the importance of the existence of pre-micellar aggregates in surfactant solutions. Figures 9 and 10 show clear evidence for this phenomenon in the dodecanoate case. In the case of SDS, even if pre-micellar aggregates are formed, it is not registered by PyDDA as it may not be associated in these aggregates. This might be due to the possibility of stronger H-bonding between carboxylate groups of dodecanoate and of PyDDA, probably through a water molecule. The pre-micellar aggregate formation is highlighted in Figure 10 by broken lines. Similar type of bonding may not be favored between sulfate and carboxylate acid groups inhibiting the inclusion of PyDDA in SDS pre-micellar aggregates. The

possibility that premicellar aggregates may not be formed at all in the SDS case is not excluded here. The excimer peak at 445 nm is observed only when PyDDA is incorporated into the relatively small premicellar aggregates. In bigger micellar aggregates, the typical monomer spectrum is observed.

The parameter I_{398}/I_{377} as plotted in Figure 10 may not have much significance as an index of polarity. A similar ratio (I_{383}/I_{372}) for free pyrene has been widely used to figure out the microscopic polarity of its environment,⁸ but such a correlation was not found with pyrene-labeled compounds²¹ even though sporadic attempts to exploit this ratio may be found in recent literature.²²

As mentioned earlier, the interfacial phenomena involved in various processes like emulsification, detergency, and flotation may be understood by resorting to fluorescence emission studies with pyrene-labeled carboxylic

acids, carboxylic acid being a commonly used surfactant in many processes. PyDDA may find application as a fluorescent probe sensitive to colloidal surfactant aggregates (surfactant clusters existing as adsorbed layers on a solid). The results obtained in homogeneous and micellar solutions suggest the implications of the presence of small premicellar surfactant aggregates and of pH-dependent changes in the analysis of excimer emission of pyrene-labeled hydrolyzable surfactants. Furthermore, the present system may serve to yield new insights into the question of interfacial polarities from acid-dissociation constant values.²³

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