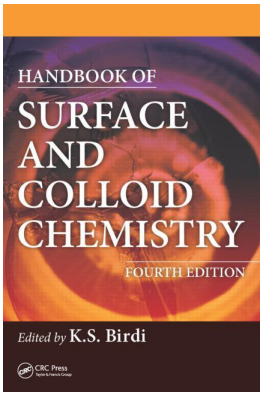

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Solvation in Heterogeneous Media

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7 Solvation in Heterogeneous Media

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CONTENTS

7.1 INTRODUCTION

Solute–solvent interactions play a key role in determining the observed kinetic, equilibrium, and spectroscopic properties of a solute in different media. Since most chemical and biological processes take place in solution, a detailed understanding of molecular interactions involving the solute and its immediate environment is required. It has long been known that physicochemical properties of a molecule (solute) depend considerably on the nature of the interacting molecules in its immediate environment. A solute molecule may be thought as a source of field that induces structural changes in a solvent. Three distinct regions may be distinguished around a solute molecule, namely, a *primary region* with completely oriented solvent molecules, a *secondary region* containing partially oriented solvent molecules, and a *bulk region* where the solvent molecules are not under the influence of the solute and normal distribution of solvent (as in pure solvent) prevails. The primary and the secondary regions where the influence of the solute is felt are commonly referred to as the *cybotactic region* [1]. The net molecular interaction taking place in this region is often referred to as *solvation interaction*. In dilute solutions, the nature of these interactions is mainly solute–solvent and solvent–solvent.

Both theoretical [2,3] and experimental [4] efforts have been made to understand such solvation interactions. Central to the study of this problem of interaction of a solute and its local environment is the question of how the free energy of a solute changes due to the presence of surrounding interacting molecules of the medium. An approach to the problem at a molecular level is fraught with

the inherent difficulty that only little information is available about the arrangement of molecules in the cybotactic region. The vast literature of solvent effect on the kinetic, equilibrium, and spectroscopic properties of a solute indicate that one needs to consider only a few modes of solute–solvent interaction [5,6]. One of them is a *nonspecific long-range interaction* due to the collective influence of solvent as a dielectric medium. This involves electrostatic interactions arising due to Coulomb and polarization forces. The continuum dielectric theory provides an isomorphic model for describing nonspecific interaction [5]. It has been found that this mode of interaction is determined by the relative permittivity (ε) and the refractive index (*n*) or any function thereof. Another is the *specific interaction* involving hydrogen bond donation (HBD) and the acceptance ability of solvents. Since specific solvation interactions are considered to be chemical in nature, the use of a continuum model for describing such interaction is severely limited [7]. Chemists have tried to understand the environmental effect by introducing the concept of *solvent polarity*, which is supposed to represent the overall solvation ability of the solvent and includes both nonspecific and specific modes of interaction [4,8]. For this, a *model process* [1] (e.g., a chemical equilibrium or kinetic process or spectral transition) is chosen, and changes in one of its parameters are recorded when the solvent is changed. Of the various polarity scales, the Z [1,9] and $E_T(30)$ [10] have passed the test of time and are most widely used. In view of the complexity of solute–solvent interaction, the representation of polarity by a single parameter (e.g., Z or $E_T(30)$) is not accurate and one has to use a multiparameter approach [11,12]. In this approach, it is assumed that the change of a physicochemical parameter of a solute (S) due to solvation, $\Delta(S, i)$, can be represented as

$$\Delta(S,i) = P_0(S) + \Sigma a_\alpha(S) P_\alpha(i) \tag{7.1}$$

where

i indicates a solvent

P_0 and a_α terms depend on the solute (S)

P_α's are the solvent properties pertinent to the α mode of interaction of the solute with a solvent

Equation 7.1 is known as the *linear solvation energy relationship* (*LSER*) [4,5,11] and has been found to be of great significance in the theory of solvent effect. Although the single or the multiparameter approach discussed earlier has been applied widely and successfully for describing solvation in pure solvents, their use in the case of heterogeneous media formed by the self-assembly of molecules is rather limited. For example, enhanced solubility of organic molecules in the micellar phase compared to the bulk aqueous medium points to the existence of significant interaction of the molecules with the micellar environment [13]. Successful attempts, however, have been made to find out the descriptors of specific and nonspecific modes of interaction of a solute with the heterogeneous medium [14–18]. Knowledge of the parameters describing specific and nonspecific solvation may be helpful to understand the solubilization of organic molecules like drugs in such media. The objective of this chapter is to discuss the possibility of applying the preceding parametric approach to the case of heterogeneous media and explore the present status of the field. The outline of the chapter is as follows. A brief discussion of the process of self-organization and commonly used microheterogeneous media will be done in Section 7.1. This will be followed by the common procedures for the description of solvation in a homogeneous medium in Section 7.2. The description of solvation in a heterogeneous medium in terms of suitable parameters will be discussed finally in Section 7.3.

7.2 SELF-ORGANIZED ASSEMBLES

Self-assembly is a type of process in which a disordered system of preexisting components forms an organized structure or pattern as a consequence of specific, local interactions among the components themselves, without any external intervention. Self-assembly is either static or dynamic

in nature. In static self-assembly, the ordered state is formed as a system approaches equilibrium, reducing its free energy. However in dynamic self-assembly, patterns of preexisting components organized by specific local interactions are commonly described as *self-organized assembles*. Self-assembly can be defined as the spontaneous and reversible organization of component molecular units (building blocks) into ordered structures by *noncovalent interactions*. An important aspect of *self-assembly* is the key role of weak molecular interactions (e.g., van der Waals, $\pi \rightarrow \pi$, hydrogen bonds) with respect to more *traditional* covalent, ionic, or metallic bonds. These weak molecular interactions play an important role especially in biological systems. Examples of *self-organization* in materials science include the formation of molecular crystals, colloids, lipid bilayers, phase-separated polymers, and self-assembled monolayers [19]. A characteristic common to nearly all self-assembled systems is their thermodynamic stability. For self-organization to take place without the intervention of external forces, the process must lead to a lower Gibbs free energy; thus self-assembled structures are thermodynamically more stable than the single, unassembled components. A direct consequence is the general tendency of self-assembled structures to be relatively free of defects. The existence of weak molecular interactions and the condition of thermodynamic stability endows these systems with a special property, namely, the sensitivity to perturbations exerted by the external environment, namely, change of salt concentration, temperature, pH of the medium, and pressure. The weak nature of interactions is responsible for the flexibility of the architecture and allows for rearrangements of the structure in the direction determined by thermodynamics. This gives rise to an important property, namely, reversibility to such type of assemblies. The specific molecular arrangements in self-assembled systems are crucial for a specific property (*functionality*) of the system. Different possible organized assembles are reported in the literature, namely, normal and reverse micelle formed by surfactants, cyclodextrins in aqueous and nonaqueous medium, and vesicles [20–28]. Systems like normal aqueous micelle and vesicles have been dealt with in the following section.

7.2.1 Aqueous Normal Micelles and Vesicles Formed by Surfactants

The term *aqueous* or *normal micelle* is reserved for the organized assemblies formed in water by the aggregation of amphiphilic molecules, commonly known as *surfactants*. Surfactants are characterized by a polar head group and a nonpolar tail. They are of four types, namely, cationic, anionic, nonionic, or zwitterionic depending on the nature of the hydrophilic head group that is bound to the hydrophobic tail. A surfactant, when present at low concentrations in water, adsorbs onto interfaces significantly, thereby changing the interfacial free energy. When surfactant molecules are dissolved in water at concentrations above a critical value, known as the critical micelle concentration (*cmc*), they form aggregates called micelles [29]. The value of *cmc*, however, depends on several factors like surfactant structure, solvent, temperature, and addition of additives. As the concentration of surfactant is increased above the *cmc*, the addition of more monomer molecules results in the formation of more micelle, so that the concentration of the monomer remains practically constant (approximately equal to *cmc*) and the concentration of micelle increases. At surfactant concentration slightly above the *cmc*, the micelles are supposed to be spherical. Shape changes, however, are known to occur as the concentration of surfactant increases. Micelle is not a permanent entity but a dynamic structure that exists in thermodynamic equilibrium with its monomer. In water, the hydrophilic *heads* of surfactant molecules are always in contact with the solvent, regardless of whether the surfactants exist as monomers or as part of a normal micelle. However, the hydrophobic (lipophilic) *tails* of surfactant molecules have less contact with water when they are part of a micelle; this being the basis for the energetic drive for micelle formation, micelles composed of ionic surfactants have an electrostatic attraction to the ions that surround them (*counterions*) in solution. Although the closest counterions partially mask a charged micelle (by up to 90%), the residual of micelle charge affects the structure of the surrounding solvent at appreciable distances from the micelle influencing

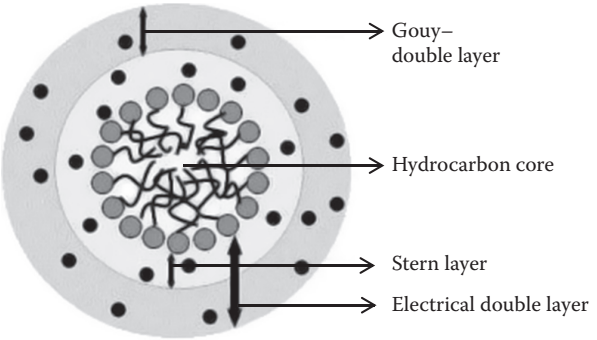

FIGURE 7.1 A model representing the cross section of a spherical ionic micelle.

many properties of the mixture. Adding salts to a colloid containing micelles can decrease the strength of electrostatic interactions and lead to the formation of larger ionic micelles [30]. From the thermodynamic point, the formation of micelles can be understood in terms of a balance between entropy and enthalpy.

Among different possible micellar shapes, the most prevalent is the spherical one as proposed by McBain [31] and supported by Hartley [32]; ellipsoidal and cylindrical shapes are also possible [33–38]. A simplified model for ionic micelles as given by Hartley [32] is useful for understanding features. The cross section of such a micelle is shown schematically in Figure 7.1. The core of a normal micelle is liquid-like, consisting of the hydrocarbon chains of the surfactants. A peripheral shell outside the core contains polar/ionic head groups. This shell, for ionic surfactants, usually has a width up to a few angstroms and is called *Stern layer*; it consists of surfactant head groups, bound counterions, and water molecules. Most of the counterions are dissociated from the micelle and are located in the *Gouy–Chapman double layer*, which is outside the Stern layer and whose width is up to several hundred angstroms [39–41]. The surface potential generated by the net charges of the Stern layer is usually in the range of 50–100 mV, and this acts as an electrostatic barrier to the passage of charged ions to and across the micellar surface. The presence of ionic groups at the micellar interface causes nearby water molecules to solvate the micelles through ion–dipole interaction. For nonionic micelles the shell outside the core is termed as the *Palisade layer* and consists of the polar head groups and hydrogen-bonded water molecules. Recent solvation dynamics studies using time domain optical spectroscopy indicate that the water molecules confined within a small volume of Stern layer/Palisade layer of the micellar interface are fundamentally different from water molecules at the bulk [42,43]. Micelles have particular significance because of their ability to increase the solubility of sparingly soluble substances in water. The spatial position of a solubilized substance in a micelle depends on its polarity. Nonpolar molecules will be solubilized in the micellar core, and substances with intermediate polarity will be distributed along the surfactant molecules in certain intermediate positions.

Apart from the formation of micellar aggregates in aqueous medium, certain naturally occurring or synthetic phospholipids as well as completely synthetic surfactants can form organized assembles. The assemblies formed from phospholipids are typically termed liposomes, and those formed from synthetic surfactants are designated as vesicles [44]. Depending on the method of preparation, the nature of surfactants, and the experimental conditions (pH, ionic strength, concentrations), different vesicular structures can exist. These range from small (8200–500 Å diameter) or large (0.1–10 μ diameter) single-walled bilayer structure to relatively larger (1000–8000 Å diameter) onion-like multicomponent structure. Unlike micelles, vesicles once formed do not break down upon dilution. Moreover, the hydrocarbon part of the vesicle is more ordered [44].

7.3 SOLVENT POLARITY AND SOLVATOCHROMIC PROBES FOR PURE SOLVENTS

Central to the problem of solvation is the question of how the free energy of the solute changes due to interaction with surrounding solvent molecules. But a straightforward solution of the problem is fraught with difficulties since only a little is known about the arrangement of the molecules in the *cybotactic region*. Chemists have introduced empirically the concept of solvent polarity that reflects the complex interplay of all types of solute–solvent interactions in the cybotactic region. Numerous attempts have been made to describe solvent polarity in terms of overall solute–solvent interaction, and several empirical descriptors of polarity have been proposed [1,4,8]. For this, a solvent-sensitive *reference process* or *model process* is introduced [1]. The process may involve a reaction in equilibrium, or a kinetic or a spectroscopic process. A study of free energy change for the process through suitable parameters (e.g., log K in the case of an equilibrium process or log k in the case of a kinetic process, E_T representing the transition energy for a spectroscopic process) in different solvents is supposed to provide an empirical measure of the solvation capability of a particular solvent for the given reference process. It should be emphasized that the polarity defined in this way refers to *microenvironment* around a solute molecule, and often the term *micropolarity* is used to indicate its difference from bulk polarity parameters. Several reference processes have been utilized to give various scales of solvent polarity; the first in this series is the *Y*-scale of Grunwald and Winstein [45] that used the solvolysis of *t*-butyl chloride as the model process. UV–visible spectroscopy provides a suitable model process for studying solvation. One may consider a spectroscopic transition in a solution to be represented by the following equation:

$$M_1\left(\text{Solv}\right) \pm h\nu \rightarrow M_2\left(\text{Solv}\right) \tag{7.2}$$

where M_1 and M_2 are the two different electronic states of a molecule and the positive and negative sign refer to absorption and emission, respectively. The effect of solvation is reflected in the spectroscopic behavior of the solute–solvent system. Interaction of different electronic states with the surrounding solvent molecules is also different, and this phenomenon leads to significant changes in the photophysical properties of the molecule. The observed spectral and photophysical parameters are thus characteristic of the molecule in its environment rather than the isolated one. Thus, a study of a spectral parameter is supposed to provide information regarding solvation interaction. It may be mentioned that while the initial state in a spectroscopic transition is an equilibrium state, the final state is a nonequilibrium Franck–Condon state. A differential solvation interaction between the two electronic states is responsible for the solvent sensitivity of a spectral parameter. In an absorption process, the observed parameter represents the differential solvation interaction of the solute molecule in the S_0 and S_1 state with an environment that is in equilibrium with the S_0 state. On the other hand, the observed emission parameter describes the microenvironment that is in equilibrium with the S_1 state. Moreover, the differential interaction will be large when the electronic transition induces a substantial change in the electronic distribution in the molecule. Thus, the optical response of molecules showing a charge transfer (CT) has been found to depend significantly on solvation interaction. As such, these molecules act as *micropolarity reporters* probing the local environment in a solution. Thus, a study of the parameters associated with the preceding process (e.g., band maximum and bandwidth in the case of absorption; band maximum, bandwidth, quantum yield, lifetime, and anisotropy in the case of fluorescence) provides information regarding solvation interaction. Spectroscopic parameters representing solvent polarity have thus been derived from the solvent-sensitive property of standard solutes (*reporters*/*probes*) absorbing light in the spectral region corresponding to UV–visible, IR, ESR, and NMR spectra. Most commonly, the parameters are wavelength (frequency) maximum

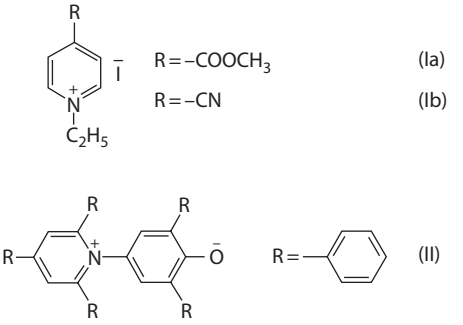

FIGURE 7.2 Some polarity probes (absorption probes).

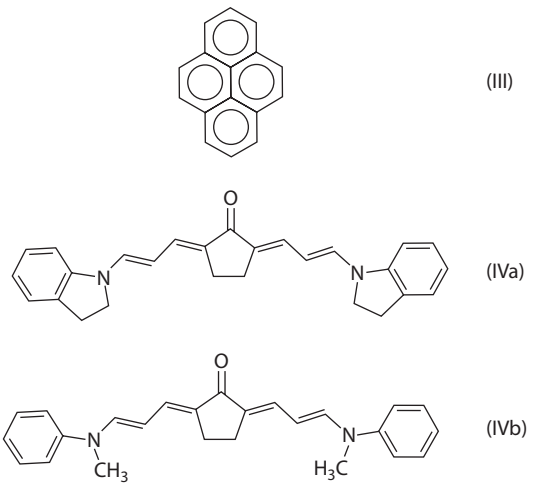

FIGURE 7.3 Some polarity probes (fluorescence probes).

of absorption/fluorescence band, intensity of band, etc. Sometimes the ratio of intensity of various spectroscopic bands has been used (e.g., I_1/I_3 ratio for pyrene emission). In general, several modes of solute–solvent interactions have been identified, namely, nonspecific (dipolarity and polarizability) and specific (acidity, basicity) modes. If one carefully selects an appropriate, sufficiently solvent-sensitive reference process, one may assume that this process would reflect faithfully all possible solute–solvent interactions. It should, therefore, give an empirical measure of the solvation capability of a particular solvent for the given reference process. Several compounds having solvent-sensitive absorption/emission bands have been utilized as *micropolarity reporters*. Probes may be classified as absorption probes or fluorescence probes depending on whether absorption or fluorescence spectral characteristics are utilized. A list of some important reporter molecules (probes) is given in Figures 7.2 and 7.3. Two main approaches for the description of micropolarity have been discussed here.

7.3.1 Single Parameter Approach

7.3.1.1 *Z*-Scale

In this scale, established by Kosower [9], 1-ethyl-4-carbomethoxypyridinium iodide (Figure 7.2, Ia) was chosen as the indicator solute. The position of the band shifts to blue as the solvating ability of

the solvent increases. The *Z*-value was defined as the maximum transition energy in kilo calories per mole corresponding to the longest wavelength CT band of this solute. Thus we have

$$Z\left(\text{kcal mol}^{-1}\right) = \frac{28{,}590}{\lambda_{\max}\left(\text{nm}\right)} \tag{7.3}$$

1-Ethyl-4-cyanopyridinium iodide (Figure 7.2, Ib) has also been used to establish a parallel scale [46].

7.3.1.2 E_T(30)-Scale

The indicator solute used by Kosower for the *Z*-scale is not quite soluble in certain nonpolar solvents. To overcome this difficulty, Dimroth and Reichardt suggested the use of pyridinium-*N*-phenol betaines as the indicator solute [10]. The E_T(30) value of a solvent is the maximum transition energy in kilo calories per mole of the longest wavelength band in that solvent of the solute shown in Figure 7.2, II. The E_T(30) value is obtained from λ_{max} values using an equation similar to Equation 7.3. The E_T(30) values of various neat solvents have been listed in Table 7.1. Owing to the large displacement of the solvatochromic absorption band, the E_T(30) values provide an

TABLE 7.1
List of Values of the Parameters E_T(30), α, β, π*

Sl. No.	Solvent	E_T(30)[a] (k cal mol^{-1})	α[b]	β[b]	π*[b]
1	Water	63.1	1.17	0.47	1.09
2	Methanol	56.3	0.93	0.66	0.60
3	Ethanol	51.9	0.83	0.75	0.60
4	1-Propanol	50.7	0.78	0.80	0.52
5	2-Propanol	48.6	0.76	0.84	0.48
6	1-Butanol	50.2	0.79	0.82	0.47
7	1-Hexanol	48.8	—	—	—
8	1-Octanol	48.5	—	—	—
9	Cyclohexanol	46.9	—	—	—
10	Acetone	42.2	0.08	0.48	0.71
11	2-Pentanone	41.1	—	0.50	—
12	3-Pentanone	39.3	—	0.45	0.72
13	Acetonitrile	46.0	0.19	0.40	0.75
14	Butyronitrile	42.5	0.00	0.44	0.71
15	Chloroform	39.1	0.44	0.00	0.58
16	Dichloromethane	41.1	0.30	0.00	0.82
17	Formamide	55.8	0.71	0.70	0.97
18	Dimethylformamide	43.8	0.00	0.69	0.88
19	Dimethylsulfoxide	45.1	0.00	0.76	1.00
20	Dioxane	36.0	0.00	0.37	0.55
21	Tetrahydrofuran	37.4	0.00	0.55	0.58
22	Ethylacetate	38.1	0.00	0.45	0.55
23	Benzene	34.5	0.00	0.10	0.59
24	Toluene	33.9	0.00	0.11	0.54
25	Hexane	31.0	0.00	0.00	−0.08
26	Cyclohexane	31.2	0.00	0.00	0.00
27	Heptane	31.1	0.00	0.00	−0.08

[a] Refs. [8,10].
[b] Kamlet–Taft solvatochromic parameters, Refs. [45,67,70].

excellent and very sensitive characterization of the polarity of the solvents [4,8]. The compound can also act as polarity probe for the investigation of aqueous micellar solutions, microemulsions, and phospholipid bilayers as well as for investigation of interfacial properties of lipid membranes. The disadvantage of $E_T(30)$ probe is, however, that it has a low molar absorptivity and it is generally not fluorescent except under certain circumstances (dye embedded in polymer film or at a low temperature [47]). However, intense fluorescence is essential when probes are used in biological systems since they are mostly applied in highly diluted conditions. An important and widely used scale of solvent polarity has been proposed using a fluorescence probe *pyrene* (Figure 7.3, III). It has been known that the ratio of intensities of the first to third vibronic bands (I_1/I_3) of the $S_1 \rightarrow S_0$ emission of pyrene depends on the medium, and as such I_1/I_3 is often used as a measure of solvent polarity [48–54]. The ratio I_1/I_3 ranges from ~0.6 in hydrocarbon media to ~1.67 in water. A number of other fluorescence probes are known. Kessler and Wolfbeis introduced a group of ketocyanine dyes (Figure 7.3, IVa and IVb) that act as good solvent-sensitive fluorophores [55,56]. Depending on the solvent, these probes display a bright yellow to purple violet color and a strong green, yellow, and red fluorescence. Both the absorption and emission maxima are red shifted in going from nonpolar to polar solvent.

Polarity probes in general should exhibit the general features mentioned in the following text [56,57]:

(1) High spectral sensitivity to polarity changes (a spectral shift of both excitation and emission maxima is advantageous because of additional sensitivity and selectivity), (2) high fluorescence quantum yield, (3) long wavelength absorption and fluorescence so that they can be conveniently used in biological systems, and (4) photostability and thermal stability. Although a large number of polarity probes have been reported, none of them appreciably satisfies all the four criteria. It may be mentioned that the chemical structure of an ideal indicator compound should be such that all important nonspecific (dipolar, dispersion) and specific (HBD, hydrogen bond acceptance [HBA], and electron donor–acceptor) solute–solvent interactions are possible. Considering the wide variation in the chemical structure of the probe molecules used for characterization of solvent polarity, the establishment of a universal, generally valid solvent polarity scale seems unattainable.

7.3.2 Multiparameter Approach

The use of a single parameter (e.g., $E(A)$ or $E(F)$ or any other photophysical parameter) to describe solvent polarity is based on the assumption that it is necessary to take only one mechanism of solute–solvent interaction into account. The inadequacy of the dielectric model of solvent to represent the solvent effect on the various properties of solutes and proliferation of empirical polarity scales point to the existence of specific solute–solvent interaction. According to Equation 7.1 any solvent-dependent property (A) of a solute "S" in a solvent "i" can be represented as

$$A(S,i) = A(S) + B(S,i) \tag{7.4}$$

where $A(S)$ is a solvent-independent part. The term $B(S,i)$ is in general a complex function of both solvent and solute comprising several modes of solute–solvent interaction. Experimental data indicate that solvent effect on various kinetic, equilibrium, and spectroscopic parameters is essentially similar in their very nature. The similarity is considered to show that there are comparatively few mechanisms of physical interaction between solvent and solute [6,58–61]. In essence there are three types of interactions: (1) nonspecific long-range solvent–solute interaction, (2) specific short-range solute–solvent interaction, and (3) solvent–solvent interaction from the cavity effect. The most effective nonspecific interactions are considered to be determined by macroscopic physical parameters of the solvent, that is, the relative permittivity or dielectric constant (ε) and refractive index (n). The specific solvation is mainly determined by the acidity and basicity of the solvent, in terms of the Lewis concept, which are measures of the solvent hydrogen bond ability to donate (*HBD*) and to accept (*HBA*) a proton, respectively. Disruption and reorganization of solvent–solvent interaction

are measured by the work necessary to separate solvent molecules to create a suitable cavity, large enough to accommodate the solute.

It has been shown that under certain simplifying assumptions, the solute–solvent interaction term $B(S,i)$ may be factorized as [62]

$$B(S,i) = \sum a_\alpha(S) P_\alpha(i) \tag{7.5}$$

where suffix α represents various modes of interaction, the parameters $a_\alpha(S)$ and $P_\alpha(i)$ depending on the solute and solvent, respectively. This type of expression, often called *LSER*, has been found to be of great significance in the theory of solvent effect [11,62,63]. In general terms, *LSER* [8,64] is expressed by the following equation:

$$XYZ = XYZ_0 + \text{Cavity formation energy} + \sum \text{Solute} - \text{solvent interaction energy} \tag{7.6}$$

In the preceding equation, *XYZ* is a property linearly related to the free energy of the system. The term XYZ_0 denotes a constant and depends solely on the solute. Summation in the preceding equation extends over all the possible modes of solute–solvent interaction [65,66]. Two approaches in the use of the *LSER* equation may be distinguished, namely, the approach suggested by Koppel and Palm (*KP*) [58] and that by Abraham, Kamlet, and Taft (*AKT*) [11]. In the *KP* approach, functions of dielectric constant (ε) and refractive index (*n*) were used to describe the nonspecific interaction. Thus Onsager reaction field parameter $(\varepsilon - 1)/(2\varepsilon + 1)$ was used to describe the nonspecific dipolar interaction, while $(n^2 - 1)/(n^2 + 2)$ described the polarizability term. In the *AKT* approach, the dipolarity and polarizability were described by the experimentally determined parameter π* [62]. The specific interactions were described by the parameter "*E*" (electrophilic solvation ability) and "*B*" (nucleophilic solvation ability) in the *KP* procedure [58]. But *AKT* have preferred the use of *HBD* and *HBA* ability of solvent represented by the empirical parameter α and β, respectively [67]. The endothermic cavity formation term was taken in the *AKT* approach as equal to the solute molar volume times the Hildebrand cohesive energy density (δ_H^2) defined as the enthalpy of vaporization per unit volume [68]. The original *KP* approach did not take this factor into account although this term was introduced later by Makitra and Pirig [69]. Thus, the *KP* equation is

$$A = A_0 + yY + pP + eE + bB \tag{7.7a}$$

$$Y = \frac{2(\varepsilon - 1)}{(2\varepsilon + 1)}; \quad P = \frac{(n^2 - 1)}{(n^2 + 2)} \tag{7.7b}$$

while the *AKT* equation is

$$A = A_0 + \rho\pi^* + a\alpha + b\beta + m\delta_H^2 \tag{7.8a}$$

$$\delta_H^2 = \frac{(\Delta H - RT)}{V} \tag{7.8b}$$

where ΔH is the molar enthalpy of vaporization of the solvent whose molar volume is *V*. It has been found that the various empirical polarity parameters, for example, $E_T(30)$ and *Z*, depend linearly on α-, β-, and π*-values [47,70]. The Kamlet–Taft solvatochromic parameters π*, α, and β are usually determined by measuring the maximum transition energy of certain probes using the

solvatochromic comparison method [71–73]. For the determination of π*, the commonly used probes are *4-nitroanisole*, *2-nitroanisole*, *4-ethyl-nitrobenzene*, and *N*,*N-diethyl-4-nitroaniline*. For these probes, the energy of maximum absorption depends only on the *dipolarity–polarizability* modes of interaction with solvent. For setting up the β scale, a spectroscopic or thermodynamic property of two indicator solutes of differing H-bonding ability (e.g., *4-nitroaniline* and *N*,*N-diethyl-4-nitroaniline*) in a series of solvents was compared. The value of enhanced solvatochromic displacement normalized with respect to a reference solvent hexamethylphosphoramide (HMPA) gave a dimensionless parameter. To eliminate the specific role of solute, the procedure was repeated for multiple indicators and the average of the dimensionless parameter gave β. A similar procedure using multiple linear regression analysis (MLRA) was adopted for setting up the α-scale. Here due to various complications, the requirements for the indicator solute were considered to be relatively stringent. Sixteen diverse properties involving 13 indicators were used to calculate the final α-values [62]. Table 7.1 lists the relevant polarity parameters of some pure solvent. In fact, the *LSER* equations with these parameters have been used in hundreds of studies involving the effect of solvent on kinetic spectroscopic and equilibrium properties of a solute. Catalan has introduced the parameters *SPP*, *SA*, and *SB* for representing the solvent *dipolarity–polarizability* (nonspecific mode), solvent acidity, and solvent basicity (the specific modes) of a solvent. These parameters are obtained from spectroscopic measurements and their success in accounting for medium effects on reactivity and a host of physiochemical properties is well documented and widely perceived [74–77].

7.4 SOLVATION IN MICROHETEROGENEOUS MEDIA

Micellar phases provide unique environments, and as such they are used in various areas of chemistry. They are used as media for enhancing the solubility of hydrophobic drug molecules [78,79] and as catalysts [80] and detergents [22]. They are also used to alter the selectivity of separation in liquid chromatography and micellar electrokinetic chromatography (MEKC) [81–84]. The utility of micelles in these and other applications depends largely on the interaction of micelle with organic molecules (solutes). As discussed earlier, it is customary to represent the totality of interaction of solute with its environment in terms of polarity parameters. Spectroscopic procedures have been used extensively to characterize the polarity of microheterogeneous media. The use of an effective relative permittivity to describe the polarity of the location of the solute has often been done. The $E_T(30)$ probe (Figure 7.2, II) has also been extensively used to measure the polarity of such media [84]. As discussed earlier, the use of a single parameter to describe solvation has often been criticized. It is desirable to characterize solvation in terms of several independent modes of solute–solvent interaction. According to this procedure, any property of a solute in a medium is described in terms of linear dependence through *LSER* on the solvent parameters representing the independent modes of solute–solvent interaction (Equations 7.7 and 7.8). Three independent modes, namely, dipolarity/polarizability, *HBD*, and *HBA*, represented conveniently by the three parameters π*, α, and β, respectively, have been recognized.

A problem arises in applying the preceding methodology to micellar solutions. A micellar medium is essentially microheterogeneous. The micellar pseudo-phase always remains in equilibrium with the aqueous phase containing surfactant monomers. The indicator molecules are distributed between the aqueous and micellar phases present in a micellar solution. Since the spectroscopic properties of an indicator depend on its immediate environment, the spectrum (absorption/fluorescence) of the indicator in the micellar phase will differ from that in the aqueous phase. The observed spectrum of an indicator in the solution is a concentration-weighted sum of the indicator's spectra in the aqueous and micellar phases, rendering the determination of the spectrum of the indicator in the micellar phase impossible. In order to obtain the value of a spectroscopic parameter (e.g., maximum energy of absorption/fluorescence, steady-state anisotropy, and lifetime) in the two phases, a knowledge of the distribution coefficient of the solute between the two phases is necessary. This introduces a complication in the data analysis, which is absent when using the Kamlet–Taft methodology to characterize bulk liquids [14].

7.4.1 Estimation of Micellar Phase Property Free from Aqueous Phase Contribution

Two procedures have been adopted to resolve the preceding problem. Vitha et al. have used a modified curve resolution method [14,15]. This method is based on singular value decomposition (SVD) of a matrix of spectra recorded at several concentrations of surfactant. The method assumes that only two components, namely, the indicator in the aqueous and micellar phase, contribute to the observed spectra. A knowledge of the molar volume of the surfactant and the aggregation number is also required. The curve resolution method gives three parameters: the distribution coefficient and the spectra of the indicator solute in the two phases. The value of the spectroscopic parameter of interest (e.g., the position of band maximum) was then determined from the spectrum in the micellar phase.

The method used by Fuguet et al. [16,17] and Shannigrahi and Bagchi [18] also assumed that the observed value of a spectroscopic parameter is a concentration-weighted sum of the values of the parameter in the two phases. The outline of their procedure is given in the following text. Micellization is essentially a dynamic process involving equilibrium between the surfactant molecules (S) in the aqueous phase and those in the micelles. For nonionic surfactants, the process can be represented by the following equation:

$$nS\ (\text{aqueous phase}) \rightleftharpoons Sn\ (\text{micellar phase}) \tag{7.9}$$

For ionic micelles, the cation or anion of the amphiphilic molecule remains in equilibrium between the two phases. An indicator solute distributes itself between the two phases. Any property (P) of the solute that has dependence on its local environment can be used to reveal the equilibrium process. Due to difference in polarity, the value of P is expected to be different in the two phases. The value of P for such systems will be determined by the time average location of the probe in the two phases [85]. The measured value of P in a micellar media can be assumed to be represented by a mole fraction average of the aqueous phase property (P_{aq}) and micellar phase property (P_m), as given by the following equation:

$$P = \frac{\left(n_{aq}P_{aq} + n_m P_m\right)}{\left(n_{aq} + n_m\right)} \tag{7.10}$$

where

n refers to the number of moles of the solute
subscripts m and aq denote the micellar phase and aqueous phase, respectively

The calculation of the value of P_m and P_{aq} requires knowledge of n_m and n_{aq}, which in turn are related to the *distribution coefficient* of the indicator solute between the two phases. It has been shown that the parameters are related as follows [17,18]:

$$P = \frac{\left[KvC_sP_m + \left(1 - vC_s\right)P_{aq}\right]}{\left[KvC_s + \left(1 - vC_s\right)\right]} \tag{7.11}$$

where

v is the molar volume of the surfactant
C_s is the concentration of the surfactant in the aggregated phase, as given by $C_s = C_T - cmc$, where C_T is the total surfactant concentration
K is the molar-based distribution coefficient of the indicator between the two phases

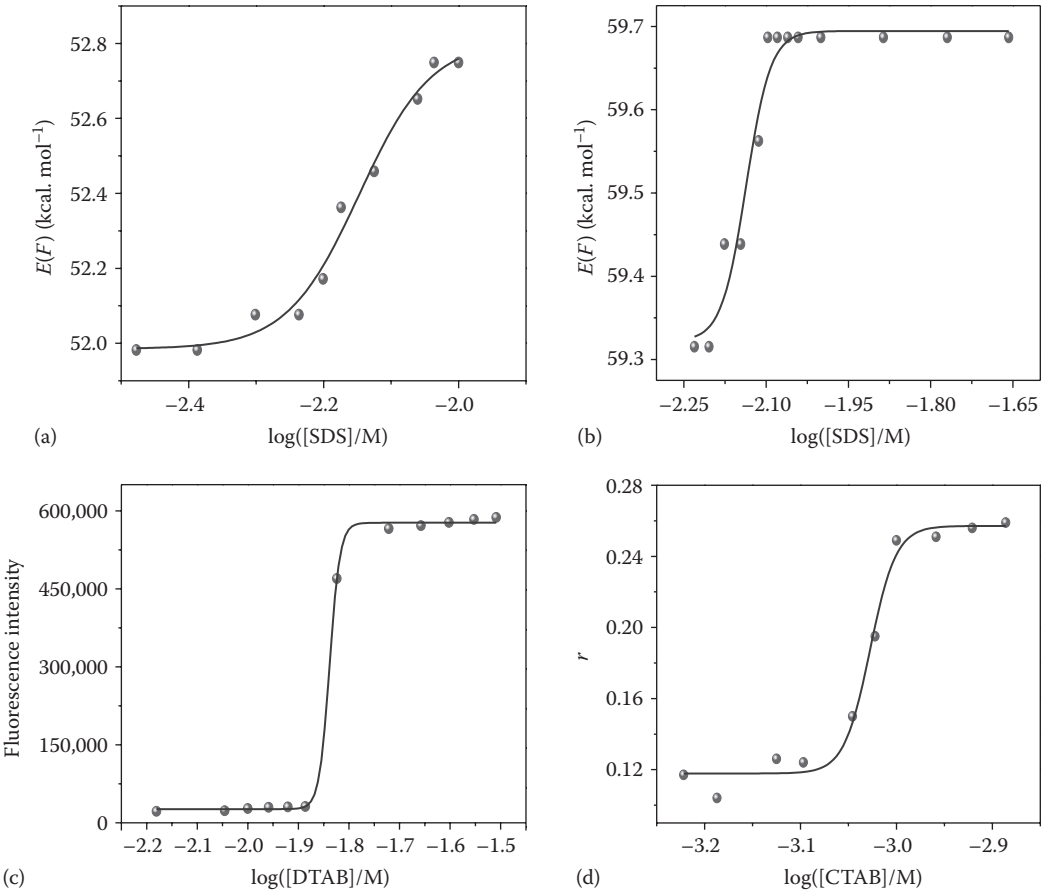

FIGURE 7.4 Plot of the parameters *energy of* (a) *maximum absorption*/ (b) *fluorescence*, (c) *fluorescence intensity* and (d) steady-state anisotropy (*r*) of (Va) in the aqueous solution of surfactants as a function of log C_T. C_T for the surfactants have been denoted by surfactant. (From Kedia, N. et al., *Spectrochim. Acta A*, 131, 398, 2014.)

The variation of these parameters as a function of log C_T can be studied. Figure 7.4 shows representative plots describing such variation. Values of these parameters change abruptly after a certain concentration. Data points can be fitted to Boltzmann sigmoid equation. It has been proposed that the value of *cmc* can be obtained from the inflexion point of the Boltzmann sigmoid curve obtained by plotting a solute property as a function of C_T [86,87]. Truly speaking, P is related to log C_s by Boltzmann equation as can be seen from Equation 7.11. Thus, the fitting of the experimental data point to the Boltzmann sigmoid plot involving the parameter P and log C_T is only approximate, and hence the assignment of concentration at the inflexion point as *cmc* is likely to be in error. Equation 7.11 can be used for the determination of the *cmc* value [88]. An iterative procedure can be adopted as follows. Equation 7.11 can be rearranged as

$$P = P_{aq} + (KP_m - P_{aq})v(C_T - cmc) + (1 - K)vP(C_T - cmc) \tag{7.12}$$

The value of concentration of surfactant at the inflexion point of P versus log C_T plot is taken as the guess value of *cmc*. The parameter P_{aq} is then determined by linear regression analysis using Equation 7.12. It follows from Equation 7.11 or 7.12 that $P = P_{aq}$ at $C_T = cmc$. Thus, the value of the concentration for which $P = P_a$ was found out from the P versus log C_T curve. This gives the output value of *cmc*. The preceding procedure can be repeated by using the output *cmc* value as the input

to get a new output *cmc*. The iteration can be continued until the input and output *cmc* values are within a specified range (e.g., within ±2%). Once *cmc* is determined, values of P_m, P_{aq}, and K can be found out by a linear regression analysis using Equation 7.12. The procedure also requires the value of molar volume of the surfactant. It is apparent from Equation 7.9 that values of parameters in micellar solution, as found out from the iterative procedure, are close to the value of the parameter at a concentration of surfactants much above the *cmc* value. But in view of the possibility of a change in the shape of the micelle, the use of too high a concentration is not advisable.

7.4.2 Determination of Polarity Parameters

The Kamlet–Taft version of *LSER* is expressed by the following equation:

$$A = A_0 + m\delta_H^2 + p\pi^* + a\alpha + b\beta \tag{7.8a}$$

In this equation, the cavity term is written as a product of the coefficient m (depending on the molar volume of the solute) and the Hildebrand solubility parameter, δ_H^2, of the solvent [68], and the solute–solvent interaction is written in terms of nonspecific (π^*) and specific (α and β) interaction parameters. Since entropy does not change during a spectroscopic transition [89], the transition energy can be regarded as related to a change in free energy. Again, during a spectroscopic transition, the volume of the solute remains constant and as a result the cavity term drops out [12]. Thus, one can write the maximum energy of transition (E) of the solute (S)–solvent (i) system as follows:

$$E(S,i) = E_0(S) + p(S)\pi^*(i) + a(S)\alpha(i) + b(S)\beta(i) \tag{7.13}$$

The Kamlet–Taft solvatochromic parameters π^*, α, and β for a micellar medium are usually determined by measuring the spectroscopic parameters of certain probes using known correlation equations. The correlation equations are, however, obtained from studies in pure solvents. It is assumed that the correlation equation obtained for pure solvents is also valid for micellar media. Both absorption [14–17] and fluorescence [18,90] probes have been used for estimating values of α, β, and π^* for the micellar media.

7.4.2.1 Method Using Absorption Probes

For the determination of π^*, the commonly used probes are *4-nitroanisole*, *2-nitroanisole*, *4-ethyl-nitrobenzene*, and *N,N-diethyl-4-nitroaniline*. For these probes, the energy of maximum absorption depends only on the *dipolarity–polarizability* modes of interaction of solvent. Expressing the wavenumbers of transition, σ, in kilokaisers (1 kK = 1000 cm^{-1}), the following relations are known [17]:

$$\text{For 4-nitroanisole,}\quad \pi^* = \frac{(34.12 - \sigma)}{2.343} \tag{7.14}$$

$$\text{For 2-nitroanisole,}\quad \pi^* = \frac{(32.56 - \sigma)}{2.428} \tag{7.15}$$

$$\text{For 2-ethyl-nitrobenzene,}\quad \pi^* = \frac{(37.67 - \sigma)}{2.259} \tag{7.16}$$

$$\text{For } N,N\text{-diethyl-4-nitroaniline,}\quad \pi^* = \frac{(27.52 - \sigma)}{3.182} \tag{7.17}$$

For determining β-values, the commonly used probes are 4-*nitrophenol* and 4-*nitroaniline*. The transition energy of these probes depends on both β and π*. For example, for 4-*nitroaniline* the wavenumber of transition is related to β as follows [17]:

$$\beta = \frac{(31.10 - 3.14\pi^* - \sigma)}{2.79} \tag{7.18}$$

Similarly the α-values are determined by using $E_T(30)$, $E_T(33)$, and $Fe(LL)_2(CN)_2$ as α and π*-probes (transition energy depends on α- and π*-values) [91–93]. The $E_T(33)$ probe is a bis chlorosubstituted derivative of $E_T(30)$ probe. It has the advantage over the $E_T(30)$ probe because of its water solubility.

Thus, relations (7.19) and (7.20) are valid for Dimroth–Reichardt $E_T(30)$ and $E_T(33)$–betaine, respectively:

$$\alpha = 0.197\sigma - 2.091 - 0.899[\pi^* - 0.211\delta] - 0.148\beta \tag{7.19}$$

$$\alpha = 0.203\sigma - 2.809 - 0.899[\pi^* - 0.211\delta] - 0.148\beta \tag{7.20}$$

In the preceding equations, δ is a correction factor to account for the polarizability of the medium [4,67]. Its value is zero for nonaromatic and nonchlorinated pure organic solvents. For the *Fe complex*, the transition energy (E) in kcal mol^{-1} is given by the following equation:

$$E = 39.71 + 3.31\pi^* + 4.50\alpha \tag{7.21}$$

The value of α can be obtained using a known value of π* determined by using other probes. This relies on the assumption that these α-probes reside in the same region in the micellar phase as do the π*-probes.

7.4.2.2 Method Using Fluorescence Probes

Dong and Winnik [54] have found that the I_1/I_3 ratio of pyrene fluorescence for homogeneous media is correlated with the π*-values of a series of protic solvents as

$$\left(\frac{I_1}{I_3}\right) = 1.304\pi^* + 0.46 \tag{7.22}$$

This equation can be used to estimate π* for heterogeneous media and the values agree well with those obtained by using other fluorescence probes [94]. The preceding empirical relation has often been used to calculate π* employing the micellar phase value of I_1/I_3 for mixed micelle of varying composition [90].

It is known that the position of the maximum fluorescence of ketocyanine dyes in a solution is highly solvent sensitive and the energy of maximum fluorescence, $E(F)$, is linearly dependent on the solvatochromic parameters, α and π*. The dyes are solubilized in the micelle–water interface [95]. It is believed that the polarity characteristics of the micelle–water interfacial region resemble those of aqueous alkanols [49]. The values of $E(F)$ of ketocyanine dyes have been determined in various pure *n*-alkanols and mixed binary aqueous alkanol systems for which the values of solvatochromic parameters (α and π*) are known [96]. An MLRA of $E(F)$ with the

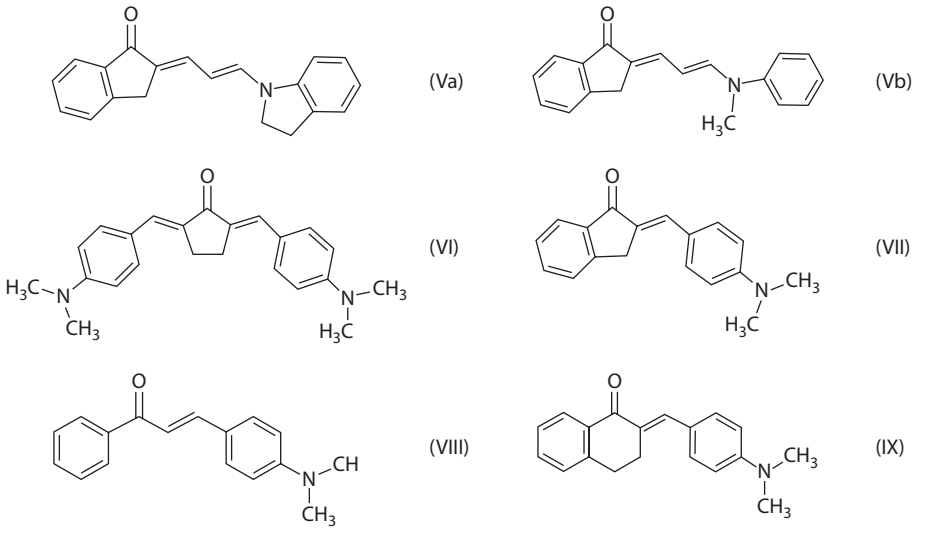

FIGURE 7.5 Fluorescence probes.

solvatochromic parameters has been performed. It has been found that the $E(F)$ of the ketocyanine dyes, (Va) and (Vb) (Figure 7.5), correlates well with the α- and π*-parameters for a series of pure alkanols and water–alkanol mixtures. Thus, Equations 7.23 and 7.24 are found to be obeyed for dyes (Va) and (Vb), respectively:

$$E(F)\ (\text{kcal mol}^{-1}) = 58.65 - 4.05\alpha - 1.71\pi^* \tag{7.23}$$

$$E(F)\ (\text{kcal mol}^{-1}) = 59.80 - 3.60\alpha - 0.60\pi^* \tag{7.24}$$

One can assume that these relationships are also valid for heterogeneous media. The value of α for the micellar phase can be obtained using Equations 7.22 and 7.23 from the known values of $E(F)$ and π* for the micellar phase.

The coefficients $p(s)$, $a(s)$, and $b(s)$ in Equation 7.13 depend on the solute and are related, respectively, to dipolarity/polarizability and the *HBA* and *HBD* ability of the solute [12]. Equation 7.13 can be used to treat the solvatochromic transition energy (E) for a *fixed solute* for a series of solvents whose π*-, α-, and β-values are known. MLRA of E with π*, α, and β will then provide the p, a, and b terms. This procedure is used to get the *LSER* equation for a particular solute [8]. Conversely, the equation can be used to analyze the transition energy of a series of solutes of known p, a, and b values in a fixed solvent (medium) to get the π*-, α-, and β-values of the medium. Ketocyanine dyes provide an interesting series of solutes, which are characterized by solvatochromic fluorescence [55]. The spectroscopic transition leading to the fluorescence in these molecules has been established as due to intramolecular charge transfer (ICT) involving the carbonyl oxygen and nitrogen atom of the amino group [55,97–99]. Shannigrahi et al. studied the solvatochromic fluorescence energy of the ketocyanine (Figure 7.3, IVa and IVb) and other structurally related dyes (Figure 7.5, Va, Vb, VI, VII, VIII) extensively in various pure solvents [97–99]. MLRA of maximum fluorescence energy in pure solvents has been done with solvent parameters π*, α, and β to get p, a, and b coefficients for the solutes. MLRA of the energy of maximum fluorescence, $E(F)$, of different solutes in the micellar phase has been sought with the known solute parameters p, a, and b to get the values of π*, α, and β for the micellar phase [18].

For a particular micelle, (*m*), the energy of maximum transition for a particular solute, (*s*), is given by the following equation:

$$\left[E_m(s) - E_0(s)\right] = a(s)\alpha_m + b(s)\beta_m + p(s)\pi_m^* \tag{7.25}$$

The values of α_m, β_m, and $\neq_m^*$ that give the best correlation in the least-squares sense of $[E_m(s) - E_0(s)]$ with $a(s)$, $b(s)$, and $p(s)$ for the seven solutes were then determined. Alternatively, one has for the micellar and aqueous phase:

$$\left[E_m(s) - E_{aq}(s)\right] = a(s)\left[\alpha_m - \alpha_{aq}\right] + b(s)\left[\beta_m - \beta_{aq}\right] + p(s)\left[\pi_m^* - \pi_{aq}^*\right] \tag{7.26}$$

A correlation analysis involving $[E_m(s) - E_{aq}(s)]$ in place of $[E_m(s) - E_0(s)]$ provides $\Delta\alpha = [\alpha_m - \alpha_{aq}]$, $\Delta\beta = [\beta_m - \beta_{aq}]$, and $\Delta\pi^* = [\pi_m^* - \pi_{aq}^*]$, that is, the change of the parameters as one goes from an aqueous phase to a micellar phase.

7.4.3 Polarity of the Micellar Phase

Values of the solvatochromic parameters for micellar phases formed by cationic, anionic, and neutral surfactants, as obtained by different workers, have been listed in Table 7.2.

Most of the indicator solutes used in the literature are polar and they probe the polar region of a micelle. It has been found that the π*-, α-, and β-values for the aqueous phase, as determined from the value of the parameter in the aqueous phase (P_{aq} in Equation 7.12), are almost equal to the values in pure water. Thus, the addition of surfactant molecules at concentrations below *cmc* does not have any significant influence on the solvation properties of water. On the contrary, values of the solvatochromic parameters in the micellar phase differ significantly from those in the aqueous phase. It appears that a micellar phase is characterized by a high polarity. This is rationalizable in view of the fact that the probes reside in the polar part of the micelle and report the values accordingly.

It appears that the *HBD* strength of the micellar region is, in general, less than that of the aqueous phase. The change from the aqueous phase follows the order CTAB > SDS = TX100. Note that the anionic micelle formed by SDS has better *HBD* strength than the other micelles. Thus, the values of α for the micellar phase of SDS and DTAB as reported by Vitha et al. are 0.873 and 0.700,

TABLE 7.2
Solvatochromic Parameters for Various Micellar Phases

Micellar Phase	α	β	π*
SDS	1.14[a], 1.10[b], 0.873[c], 1.18[f], 1.2[g]	0.70[a], 0.42[b], 0.401[d]	0.52[a,f], 1.14[b], 1.06[d], 0.58[g]
CTAB	0.87[a], 0.62[c], 0.94[g]	0.53[a], 0.47[b]	0.68[a], 0.96[c], 0.69[g]
DTAB	0.700[e], 1.03[g]	0.486[e]	1.02[a], 0.70[g]
TX100	1.06[a], 0.92[f]	0.71[a]	0.56[a], 0.72[f]
Water	1.17	0.47	1.09

[a] Ref. [18].
[b] Ref. [17].
[c] Ref. [16].
[d] Ref. [14].
[e] Ref. [15].
[f] Ref. [90].
[g] Ref. [88].

respectively [14,15]. Similarly, Fuguet et al. reported $\alpha = 0.82$ and 0.62 for SDS and CTAB, respectively [16,17]. The values of β indicate that ionic micelles have relatively more *HBA* basic than the aqueous phase. The neutral TX100 micelle on the other hand has *HBA* ability comparable to that of the aqueous phase. π^*-values for the micellar phase of the surfactant are less than that of the aqueous phase for all the micelles. The micellar phase consists of a hydrocarbon core and a polar region. The polar head groups, the bound counterions (in the case of ionic micelles), and water molecules bound to the head groups mainly constitute the polar region. The polarity monitored by the dye molecules used in the present study corresponds to this region of the micelles. The solvation properties in the micellar phase arise partly due to the presence of bound water molecules and counterions. The head group in an SDS micelle ($-O-SO_3^-$) can bind more water molecules than a head group in CTAB ($-N(CH_3)_3^+$). In the former case, the negative charge is distributed over the oxygen atoms, while in the case of ($-N(CH_3)_3^+$), the intervening methyl groups restrict the water molecules from coming closer to the head group. Moreover, the counterion (Na^+) in the case of SDS can bind more water molecules by solvation than the corresponding counterion (Br^-) in CTAB. The greater *HBD* ability of the anionic SDS micelle relative to the cationic CTAB micelle can be rationalized due to the presence of a larger number of bound water molecules in the Stern layer of the micelle. On the other hand, the TX100 monomer surfactant molecule possesses some *HBD* strength due to the presence of –OH groups. Thus, a higher value of *R* is expected for TX100 micelles. The higher *HBA* ability of SDS relative to CTAB micelles can also be rationalized in terms of the presence of water molecules as explained earlier. Moreover, in the case of SDS, the presence of ($-O-SO_3^-$) head groups adds to the *HBA* basicity of the micelle formed. The head group of the neutral TX100 surfactant contains a phenyl group followed by a polyoxyethylene chain terminating in a hydroxyl group. Thus, the polar region is expected to resemble an alcohol environment. Also, the determined solvatochromic parameters are close to that of ethanol ($\alpha = 0.86$, $\beta = 0.75$, $\pi^* = 0.54$), which closely resembles the chain end of the surfactant.

7.5 CONCLUDING REMARKS

The difficulty with the use of absorption probes is that a higher probe concentration, as required for some of the probes for the determination of maximum absorption, can lead to a change in micellar structure. The use of fluorescent probes is thus better. Moreover, the use of different indicator solutes for determining different parameters rests on the assumption that all indicator molecules probe the same region of the micelle. It is instructive to determine the parameters using different absorption/fluorescence probes and to examine whether convergent results are obtained. A recent study by Kedia et al. indicates that convergent values of a parameter are obtained when different probes are used. Moreover, for the same probe the use of different spectroscopic properties gives almost the same result. For example, ketocyanine dyes have solvent-sensitive absorption and fluorescence bands. The analysis of maximum energy of absorption or fluorescence gives similar values of a solvatochromic parameter [88]. It has been observed that the probe distributes itself in two different regions of a catanionic vesicle formed by DTAB and SDS, and the solvatochromic parameters (α and π^*) of the regions have been estimated. It is important to mention that a spectroscopic procedure involving indicator solutes can provide only the solvatochromic parameters (α, β, and π^*). No information can be obtained regarding the δ_H^2 parameter. To determine this parameter, one has to study a thermodynamic property. Maitra et al. [100] have determined the δ_H^2 value of SDS micellar phase from solubility studies using a ketocyanine dye (Figure 7.5, Vb).

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