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Micelles: Self-organized surfactant assemblies

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Surfactants can self-organize under specific environmental conditions in solution to form 'micelles'. The micelles are of two types, 'normal micelles' (called micelles), which are formed by surfactant association in water or polar solvents, and 'reverse micelles', which are formed in nonpolar media. The surfactants and micellar solutions have versatile uses in the fields of chemistry, biochemistry, pharmacy, medicine and industry to augment and control solubilization, stabilization, dispersion, cleaning, rates of chemical reactions, enhanced oil recovery, etc. In this review, fundamentals of formation of micelles, their physico-chemical properties and probable uses are presented for an overall grasp of the topic of contemporary interest.

AMPHIPHILIES are chemical compounds having dual affinity for water and oil. They have distinct nonpolar (liophilic or hydrophobic) and polar (hydrophilic or liophobic) sections in their molecules. Soaps, detergents, long chain alcohols (amines, aldehydes, etc.) and lipids constitute the class of amphiphiles. They are surface active, can reduce surface tension of the medium or interfacial tension between two immiscible liquids (e.g. oil and water), can assist solubilization, cleaning, dispersion, emulsification, etc. The amphiphiles comprising soaps and detergents show a special property in solution manifesting characteristic self-organization or association called 'micelle' formation[1,2]. Under appropriate conditions, amphiphiles (mostly of lipid types) may also form 'liquid crystals' in solution. The amphiphiles that form micelles and can be potentially used for surface chemical works are termed SURFace ACTive AgeNTS or SURFACTANTS. Soaps and detergents come under this heading. Soaps are prepared by the hydrolysis (saponification) of naturally occurring fats and oils, and detergents are synthetically prepared. Big industries are busy with the production of soaps and detergents all over the world. The innumerable possibilities of such products through chemical modification and synthesis and great many uses of amphiphiles in pharmaceutical, chemical, biochemical (including biomedical) and industrial fields have added tremendous scope of research and study in this area of surface and colloid science and technology. The investigations on micelles comprise a significant share in this area, a comprehensive accounting of which is of contemporary interest. In the following sections, the overall state of the art of basic aspects of surfactants and micelles including their potential uses are presented.

Types of micelle-forming amphiphiles or surfactants

The micelle-forming amphiphiles or surfactants essentially fall in two categories, 'ionic' and 'nonionic'. They

basically contain nonpolar polymethylene chain (called the tail) and an ionic or polar group (called the head). The nonpolar tail may have substitution and they may contain phenyl rings; the polar or the ionic head group may have distinctive variations. Table 1 gives examples of several typical micelle-forming amphiphiles whose solution properties have been extensively studied and have potential for future investigative inclusions.

The examples given in Table 1 are only a few of the vast number of surfactants possible directly from natural sources and through synthesis[3]. It is imperative that numerous possibilities of formation, by way of synthesis, exist.

Requirements for micelle formation

Molecular factor

As stated above, all amphiphile molecules have a distinct hydrophobic (HP) tail and a hydrophylic (HF) head (Figure 1).

Table 1. Examples of typical ionic and nonionic micelle forming amphiphiles[a]

Ionics	Nonionics
Sodium palmitate	Polyethylene glycol tertoctyl phenyl ether (Triton × 100)
Sodium oleate	Sorbitan monolaurate (Span 20)
Sodium decyl sulphate (NaDes)	Sorbitan monopalmitate (Span 40)
Sodium dodecyl sulphate (SDS)	Sorbitan monostearate (Span 60)
Sodium dodecyl sulphonate	Sorbitan monooleate (Span 80)
Sodium dodecyl benzene sulphonate (SDBS)	Polyoxyethylene (4) laurylether (Brij 30)
Sodium cholate (NaC)	Polyoxyethylene (23) laurylether (Brij 35)
Sodium deoxycholate (NaDC)	Polyoxyethylene (9) palmitylether (Brij 56)
Sodium chenodeoxycholate (NaDC)	Polyoxyethylene (9) stearylether (Brij 76)
Sodium taurochenodeoxy cholate (NaTCDC)	Polyoxyethylene (20) sorbitan monolaurate (Tween 20)
Sodium bis ethyl hexyl sulfo-succinate (AOT)	Polyoxyethylene (20) sorbitan monopalmitate (Tween 40)
Dodecyltrimethyl ammonium bromide (DTAB)	Polyoxyethylene (20) sorbitan monostearate (Tween 60)
Tetradecyltrimethyl ammonium bromide (TTAB)	Polyoxyethylene (20) sorbitan monooleate (Tween 80)
Hexadecyl (or cetyl) trimethyl ammonium bromide (CTAB)	Octylmethyl sulphoxide
Hexadecyl (or cetyl) pyri-dinium chloride (CPC)	Tetradecyl *N* betaine

[a]For ionics, abbreviations are given in parenthesis. They are commercial identities for nonionics. The numbers in parentheses correspond to the number of polyoxyethylene groups.

Depending on the molecular structure and type, a balance between hydrophilicity and hydrophobicity exists in the molecule. This is called hydrophilic–liphophilic–balance or HLB, which is important in categorizing surfactants as emulsifiers, detergents, wetting agents, solubilizing agents, micelle-forming types, etc[4]. It is imperative that surfactants having greater hydrophobicity are more surface active and vice-versa. In solution, mutual likings (interaction) between surfactant molecules, solvent (water) molecules, and surfactant and solvent molecules decide the ultimate state. When self-interactions of both surfactants and solvent molecules cannot be compensated by their mutual interactions, the surfactant molecules tend to associate in a regular pattern forming 'association colloids' or 'micelles'[5]. Instead of crowding at the interface, the amphiphiles hide their tails in the micellar interior creating similar (oily) environment, with their hydrophylic heads remaining out in the aqueous medium. It has been observed that micelle-forming amphiphiles in a homologous series need to have eight or more methylene (CH_2) groups in the chain, lower number cannot conveniently augment nonpolar association of the tails to overweigh the head group repulsion and hydrophilicity culminating to micelle formation (Figure 2).

Physical factors

It is imperative that micelle formation becomes easier for surfactants having greater hydrophobicity (or increased chain length) in a homologous series. The other factors that can influence or control the phenomenon are solvent polarity and type, temperature, presence of additives (salts, etc.) and pressure[5].

The polarity of the medium favours surfactant association. Nonpolar medium offers environment similar to the surfactant tail so that their tendency of self-association is reduced. In a good nonpolar medium, viz. cyclohexane, carbon tetrachloride, hydrocarbons (heptane, octane, decane, etc.), formation of normal micelle as figured above may be totally absent; instead a reverse orientation of the surfactants with tails out and head groups in the

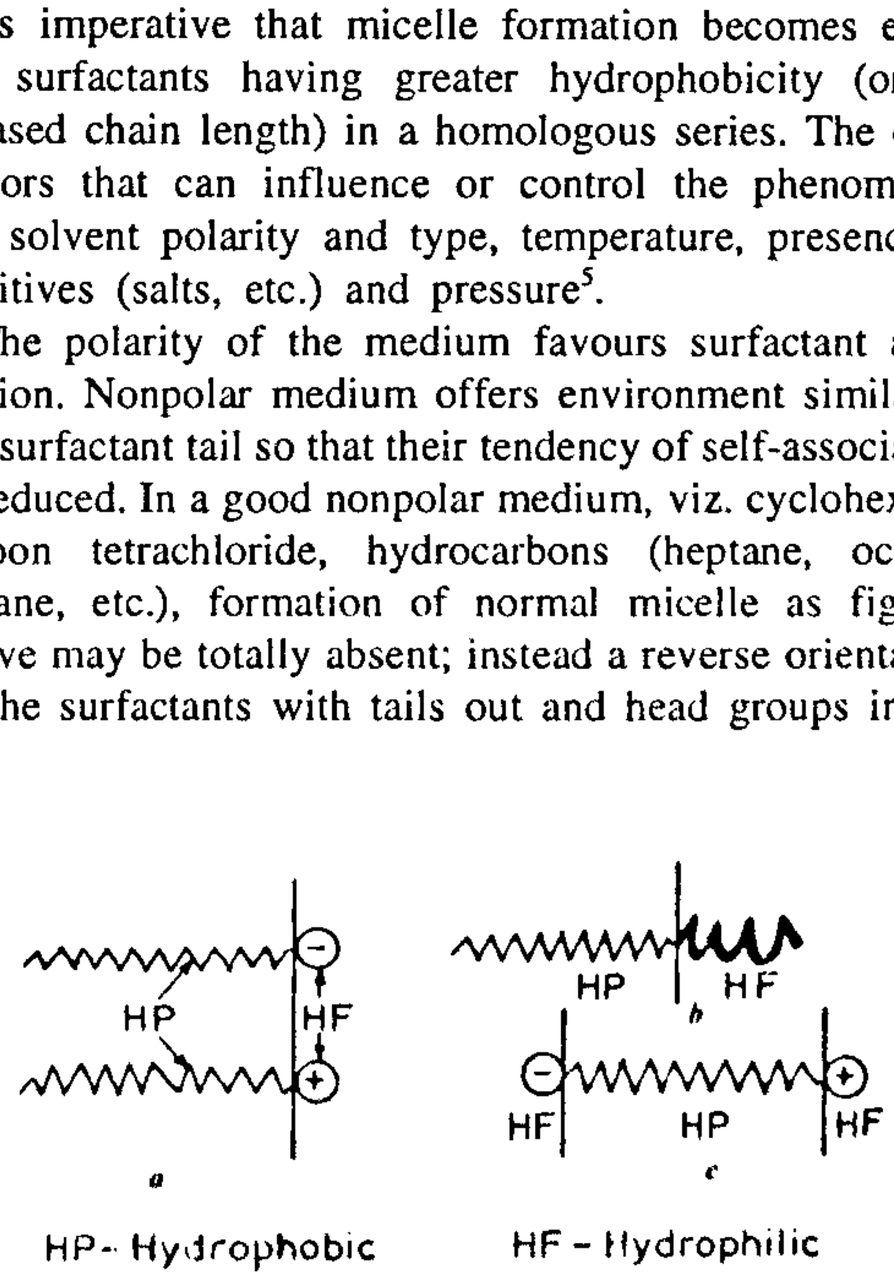

Figure 1 *a–c*. Perspective representations of surfactants. *a*, ionic; *b*, nonionic; *c*, zwitterionic.

micellar interior may occur; such entities are called 'reverse micelles'. A trace amount of water helps easier and stable formation of reverse micelles. This will be briefly discussed in a subsequent section.

The effect of temperature on micelle formation is essentially guided by the way temperature affects the solubility and other behaviours of surfactants in solution. Normally, surfactant solubility in water does not radically increase with temperature. Desolvation and changed solvent structure play a significant role in this respect. In general, micelle formation is favoured with increase of temperature in the lower range of temperature, at higher temperature range, the formation is disfavoured. The desolvated head groups may end up with greater electrostatic repulsion to resist micelle formation. The situation becomes complex by the changed polarity of the medium at higher temperature. Thus an overall comprehension[5–7] of the effect of temperature on the phenomenon of micellization may not be straightforward. At higher temperature, desolvation of the polar head groups of nonionic surfactants leads to phase separation, the solution becomes cloudy. The temperature at which the phenomenon starts is called the 'cloud point'[5–8]. The temperature stability of nonionic surfactants is often judged by their cloud points.

The surfactants have characteristic temperature-dependent phase behaviours, a knowledge of which in solutions may be profitable for physical–chemical understanding of their solution behaviours. This is shown in Figure 3. In this diagram, there are three distinct zones A, B and C depending on concentration and temperature. In zone A, only surfactant monomers occur in solution. In zone B, monomers remain in equilibrium with micelles, whereas in zone C, monomer and precipitate (or crystals), i.e. a separate phase, exists in solution. This phase map is helpful in the preparation of a solution of a surfactant according to the need of its solution composition. At the point P all the three phases co-exist and by the phase rule, it is an invariant point. The corresponding temperature is called Krafft temperature (T_K). To avoid or minimize the existence of precipitate, i.e. for the preparation of micellar solution at higher concentration (and only monomer solution at lower concentration), the working temperature should be above Krafft temperature (T_K) (refs 5, 9). The determination of T_K for surfactants is thus important.

The effect of pressure[7] on self-organization of surfactants has been studied. Pressure initially retards the association and after a threshold value (100–200 MPa), the process is favoured. This is supposed to be a consequence of water structure destruction, by the applied thrust to assist wider distribution of the surfactant molecules in solution to oppose their tendency of association. The release of surfactant monomers from the micelles in the lower range of pressure and their association at higher pressure together with the changed dielectric constant of the solution by the application of pressure also play their specific roles in surfactant organization. This has been supported by the measurement of aggregation number which shows a minimum for ionic surfactants and a rapid initial decrease for nonionic surfactants with respect to pressure.

Additives may have significant effects on surfactant self-organization[10]. A salting-out effect of salts influencing the surfactant activity to assist easier aggregation may arise. The study of the influence of salt is important for in most occasions in chemical studies amphiphiles are handled in electrolyte environments. Non electrolytes may both increase and decrease micellization tendency of surfactants[11,12]. The matter is complex because additives can influence solvent structure (fluidity) and polarity and can undergo direct interaction with the surfactants. In this regard urea and guanidine hydrochloride are conspicuous, they greatly hinder micellization and can break down water structure. The hydrophobic association and water structure destruction have a mutual correlation, a quantitative understanding of the phenomenon is still a matter of further research.

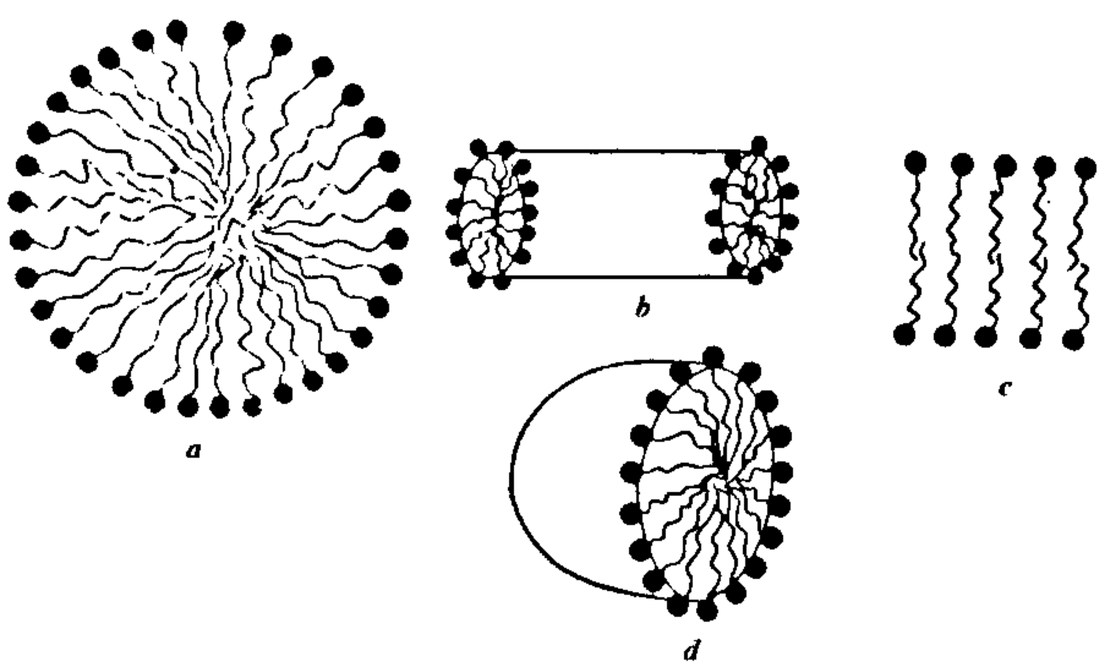

Figure 2 *a–d*. Schematic representation of geometrical forms of micelles. ***a***, spherical; ***b***, cylindrical; ***c***, lamellar; ***d***, oblate (bisected).

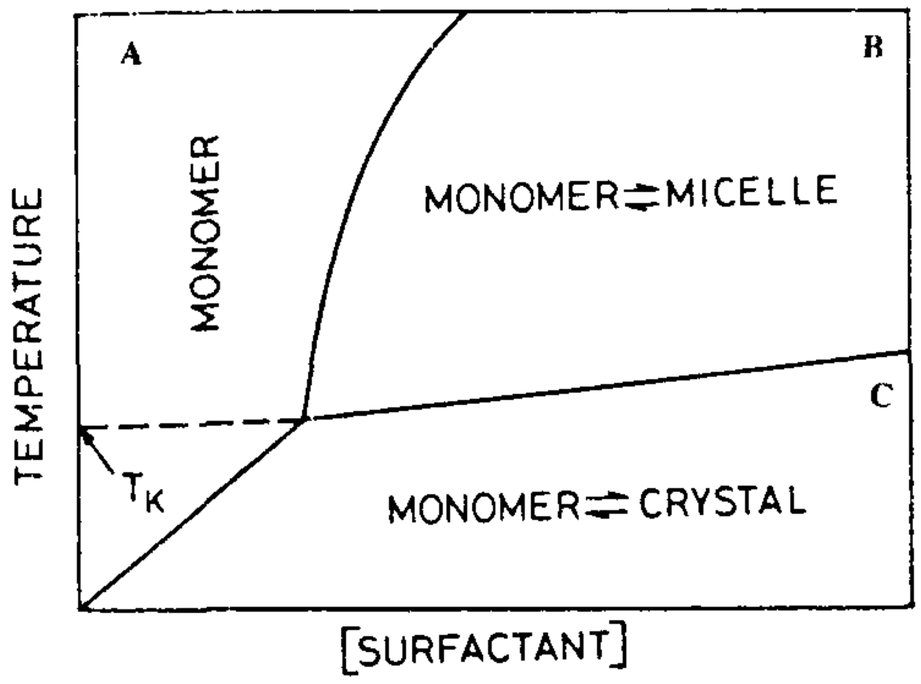

Figure 3. Temperature–[surfactant] profile showing different states in solution and the Krafft temperature, T_K.

Determination of micellar point

The phase map in Figure 3 indicates that under fixed environmental conditions, a threshold concentration is required for the formation of micelle. This threshold or critical concentration is called 'critical micelle concentration' or CMC. Its evaluation (determination) is an important physicochemical exercise for self-assembling surfactant solution.

A good number of methods can be used for the determination of CMC, viz. tensiometry, conductometry, viscometry, light scattering, fluorimetry, calorimetry, spectrophotometry, magnetic resonance, etc. The most frequently used methods are tensiometry, conductometry and fluorometry, the conductance method is applicable only to ionic surfactants. The physical properties of surfactant solutions measured by different methods at different concentrations demonstrate a distinct feature as shown in Figure 4. The properties show brakes in the plots which are considered as the CMC points for the surfactants under investigation. It is to be noted that the CMC values determined by different methods fall in a narrow range, the CMC is moderately method-dependent. The significant increase in the scattered radiation above CMC in the light scattering method[13] gives a direct proof of the formation of bigger species by self-association for the scattering phenomenon depends on the size of the scattering units. This and supports by other methods (e.g. self-diffusion by NMR)[14] have established the correctness of the concept of micelles first proposed by McBain[15] of USA (the first Director of the National Chemical Laboratory in independent India) which was severely but wrongly criticized by scientists in a Royal Society meeting in London.

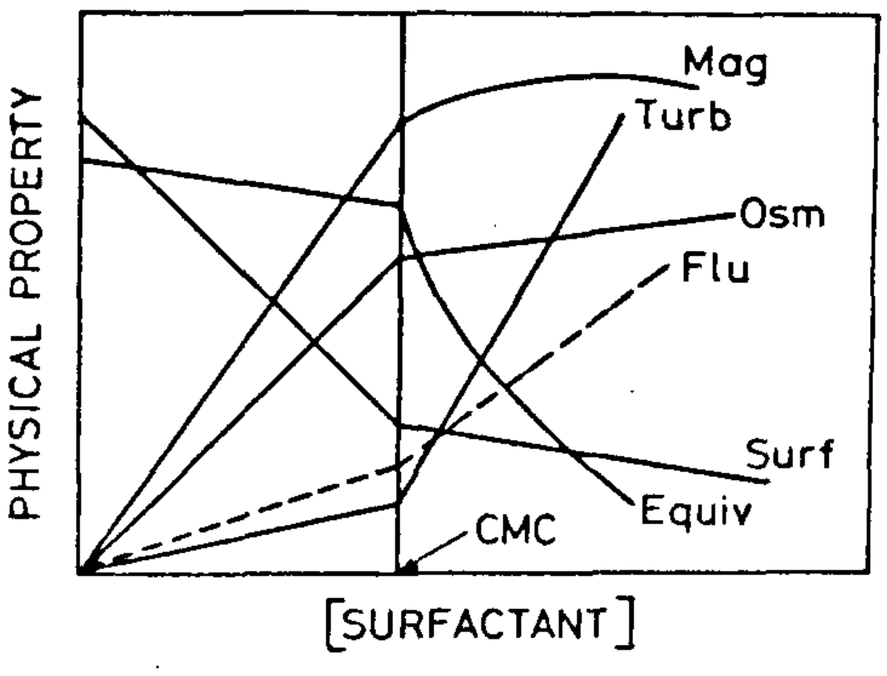

Figure 4. Evaluation of critical micelle concentration by different physical methods. Mag, magnetic resonance; Turb, turbidity; Osm, osmometry; Surf, surface tension; Equiv, equivalent conductance; Flu, fluorescence.

Micellar properties and features

Micelles are surfactant aggregates having regular structures and shapes. From dimension and other considerations they are colloids; their sizes normally cover the range of 1–10 nm. The ionic micelle forms an electrical double layer[16] surrounding it in the interfacial region (Figure 5). By virtue of surface charge and zetal potential, it exhibits electrophoresis under an applied electric field.

The micelles may assume different shapes, the spherical shape is most prevalent; ellipsoidal and cylindrical shapes are also not uncommon[3,5,16] (Figure 2). The shapes may undergo transition, thus spherical micelles of sodium-dodecylsulphate change to cylindrical configuration in salt environment[17]. In presence of salicylates, cetyl-trimethyl ammonium bromide, cetylpyridinium chloride, etc. can form long 'worm-like' micelles[18]. Such transition greatly influences (increases) the viscosity of the micellar solution, micellar mass increases significantly.

It is tempting to know the number of surfactant monomers that self-organize to form a micelle. The methods of light scattering and fluorescence quenching are conveniently used to estimate the aggregation number[19,20]. Normally, the aggregation number falls in the range of 20–200; the bile salt micelles can have lower aggregation number[21] of 4–10. The aggregation number varies with environmental variations. The transition from sphere to rod is associated with significant increase in the aggregation number[22].

The presence of ionic groups at the micellar interface causes ion–dipole interaction and water molecules associate to solvate the micelles. The nonionic micelles arrest water molecules at the pallisade layer by hydrogen bonding of water with the polyethylene oxide groups[23]. Water may remain trapped in this region. The interfacial properties of micelles are thus influenced by solvation. The solvation can be estimated by various methods, viz.

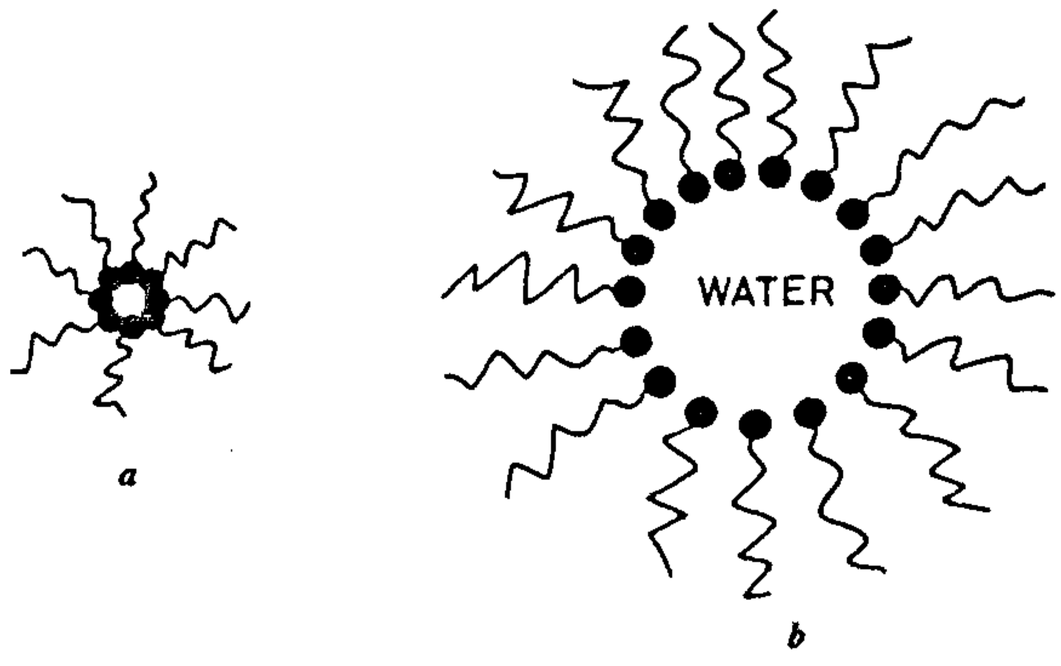

Figure 5 *a*, *b*. Schematic representation of reverse micelles. *a*, in absence of water; *b*, in presence of water.

light scattering, IR-spectra, viscosity, electrophoresis, ultrasonic, etc. According to Hartley[24], the interior of the micelle is oil-like, the aqueous medium remains outside the interfacial boundary. Menger[25] has proposed that water can penetrate inside the micelle up to a certain level, the idea gets support from fluorescence and NMR measurements.

An ionic micelle forms an electrical double layer surrounding its boundary where by virtue of increased charge density, counter-ions are attracted and occupy positions in the 'stern layer'. A fraction of the counter-ions is thus bound[26] in the region which may considerably reduce the surface charge density. Information about the counter-ion binding is necessary for the understanding of the electrical double layer as well as accurate calculation of thermodynamics of micellization to be discussed subsequently. The electrochemical methods, viz. conductance and potentiometric are employed for the estimation of counter-ion binding[27]. The extent of binding may be as high as 90%, quite a sizeable percentage of counter-ions may bind with the micelle greatly reducing the surface charge density and hence the double layer potential. The aggregation number and other properties, environmental variations can affect the counter-ion condensation of ionic micelles.

The polarity of the interior of micelles ought to be low like hydrocarbon oils. Fluorescence measurements[28] with suitable probes can estimate the magnitude of the polarity. A probe sitting at the interface should send the indication about the polarity of the interface. For information about the core, the probe should be well within the interior; an well oil soluble probe would serve the purpose. The physicochemical properties of micelles are presented in Table 2.

Table 2. Physicochemical properties of some typical surfactants

Surfactant[a]	CMC/m mol dm^{-3}	Aggregation number	% Counterion bound
SDeS[40]	41.0	30	40
SDS[25]	8.0	50	60
AOT[25]	3.0	15	10
NaC[20]	12.0	2	–
NaDC[20]	5.0	4	–
NaTC[20]	10.0	4	–
DTAB[30]	16.0	48	77
TTAB[30]	3.1	55	73
CTAB[30]	0.8	55	85
CPC[30]	0.83	–	58
Triton X-100[25]	0.03	134	–
Tween 20[25]	0.05	86	–
Tween 40[25]	0.023	92	–
Tween 60[25]	0.021	112	–
Tween 80[25]	0.01	124	–

[a] Superscripts refer to the temperature in °C. Abbreviations as in Table 1.

Energetics of micellization

All physicochemical processes are energetically controlled. The spontaneous formation of micelle is obviously guided by thermodynamic principle. The matter is treated under two formalisms[29–31]: (i) mass action principle, and (ii) 'pseudophase principle'. According to the first principle, above CMC, the concentrations of monomer and micelle are interdependent. Increase of monomer concentration increases micellar concentration and vice-versa in accordance with the following equilibrium

$$n\,(S^-\text{ or }S^+\text{ or }S) \overset{K_M}{\rightleftharpoons} (S_n^-\text{ or }S_n^+\text{ or }S_n), \qquad (1)$$

where S^- or S^+ or S = surfactant monomer; S_n^- or S_n^+ or S_n = micelle; n = aggregation number, and K_M = micellization constant with free energy of micellization $(\Delta G_M^o) = RT \ln K_M$. At CMC, by conceptual approximation, the free energy of micellization expressed per mole of monomer unit ($\Delta G_m^o = \Delta G_M^o/n$) is given by the relation,

$$\Delta G_m^o = RT \ln CMC. \qquad (2)$$

Considering counter-ion binding to ionic micelles, eqn (2) is modified to

$$\Delta G_m^o = (1+f)\,RT \ln CMC, \qquad (3)$$

where f = fraction of counter-ion bound to a micelle.

For nonionic surfactants, $f = 0$ and eqn (3) is reduced to eqn (2). It is seen that in case of ionic micelles, for accurate calculation of ΔG_m^o, determination of f is a must.

In the pseudophase model, the monomer concentration at and above CMC remains nonvariant; with increasing surfactant concentration above CMC micelles are only formed. This is like solubility of a sparingly soluble salt where above the solubility limit excess amount separates out as the insoluble phase. The micellar pseudophase on the other hand remains in solution. Based on the phase equilibrium,

$$\text{monomer} \rightleftharpoons \text{micelle} \qquad (4)$$

at a constant temperature, chemical potential of surfactant monomer in solution (μ_m) is equal to the chemical potential of the monomer in the pseudomicellar phase (μ_M) thus,

$$\mu_m = \mu_M . \qquad (5)$$

Explicitly,

$$\mu_m^o + RT \ln a_m = \mu_M^o + RT \ln a_M . \qquad (6)$$

Wherefrom we again get

$$\Delta G_m^o = \mathrm{RT} \ln \mathrm{CMC} \tag{7}$$

for nonionic micelle, and

$$\Delta G_m^o = (1+f)\,\mathrm{RT} \ln \mathrm{CMC} \tag{8}$$

for ionic micelle. The μ_m^o and μ_M^o are the standard chemical potentials of monomer and micelle respectively and a_m and a_M are their corresponding activities ($a_M = 1$, for pseudophase is taken to be pure phase). The two models thus lead to the same interpretation of results. It is to be noted that in the above thermodynamic treatments, at the critical micelle concentration, the equilibrium concentration of free monomer is considered equivalent to CMC.

Applying Gibbs–Helmholtz equation, the standard enthalpy of micellization (ΔH_m^o) at constant pressure, P for nonionic micelles is given by the relation

$$\Delta H_m^o = -\mathrm{RT}^2 \left(\frac{\partial \ln \mathrm{CMC}}{\partial T} \right)_P = R \left(\frac{\partial \ln \mathrm{CMC}}{\partial (1/T)} \right)_P . \tag{9}$$

The entropy of micellization (ΔS_m^o) follows from the Gibbs equation,

$$\Delta S_m^o = \left(\frac{\Delta H_m^o \, \Delta G_m^o}{T} \right). \tag{10}$$

The factor $(1+f)$ has to be included in the above relations for ionic micelles. The measurement of CMC at different temperatures is required for the evaluation of ΔH_m^o and ΔS_m^o. It is assumed that the aggregation number and counter-ion binding of the micelle are not affected by temperature variation at least in the range of measurements, which is not large in practice. Calorimetric measurements may offer direct determination[32,33] of both CMC (i.e. ΔG_m^o) and ΔH_m^o at a constant temperature from which ΔS_m^o readily follows.

The ΔS_m^o values are essentially positive, negative values are seldom obtained[16,34]. The micellization process therefore ends up with increase of entropy, an overall disorder state is envisaged. This is due to the release of solvent molecules attached with the nonpolar tails of surfactant monomers by hydrophobic hydration during self organization, the entropy gain by the process exceeds the loss by amphiphile association, solvation, etc., making the overall entropy change positive.

Mixed micelles

Mixed surfactants after a critical concentration should also micellize[5,35,36] yielding CMC. The tendency is guided by their attractive (synergistic) and repulsive (antagonistic) interactions. This is reflected in their CMC values compared to the CMC of their components. The occurrence of mixed surfactants and hence mixed micelles are common in industrial, pharmaceutical and biological fields; physicochemically, they work better than pure surfactants in solution. A schematic representation of mixed micelles is presented in Figure 6.

It is interesting to observe that although cationic and anionic surfactants may form insoluble ion-pairs at nearly equal molar proportions, they get solubilized if the proportion of one of them is appreciably larger than the other[37]. Thus mixed micelles of ionic–ionic, ionic–nonionic and nonionic–nonionic combinations are possible whose physicochemical studies are required for formulations, uses and basic understanding.

The CMC of ideal mixtures of surfactants is given by Client's[5,35] equation,

$$\frac{1}{(\mathrm{CMC})_{\mathrm{mix}}} = \sum_i \frac{\alpha_i}{(\mathrm{CMC})_i}, \tag{11}$$

where α_i and $(\mathrm{CMC})_i$ are the mole fraction and CMC of the ith component respectively.

In most occasions the equation is not found to be obeyed, it may take the form

$$\frac{1}{(\mathrm{CMC})_{\mathrm{mix}}} = \frac{\alpha_i}{f_i (\mathrm{CMC})_i}, \tag{12}$$

where the new term f_i is the activity coefficient of the ith species.

There are recent theories[38–40] to account for the mole fraction, activity coefficient, extent of interaction among the surfactants in the mixed micelles formed. The theories need improvement to account for all kinds of combinations, but the approaches are of considerable merit[41]. The propositions and equations are essentially on binary combinations, for higher combinations modifications are necessary. In mixed state, fundamental studies on binary systems are considerable, ternary combinations have been rarely investigated.

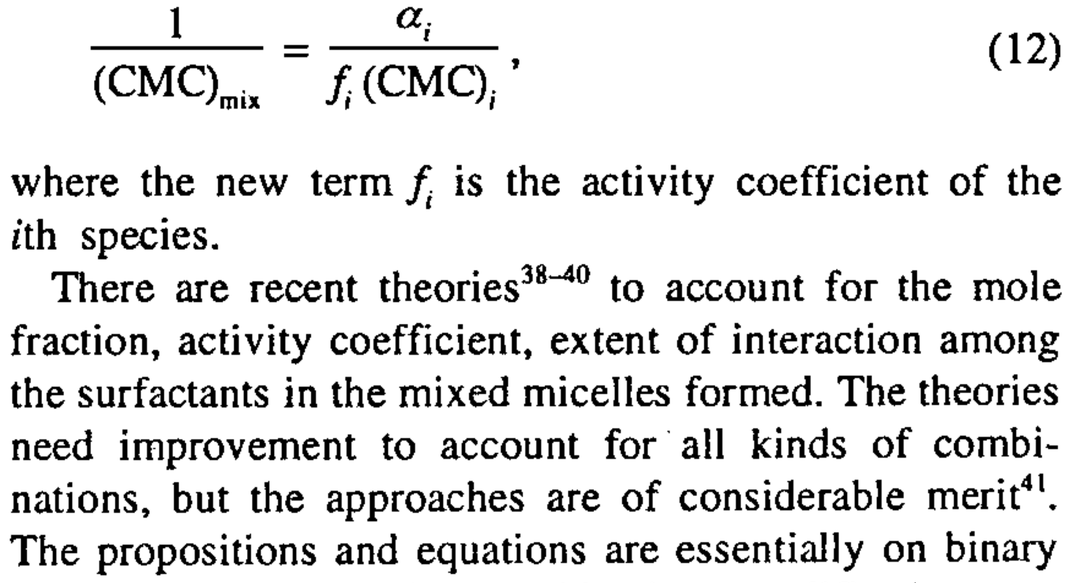

Figure 6. Schematic representation of ionic micelle showing counter-ion binding and the electrical double layer.

Reverse micelles

The micelles so far discussed are formed in aqueous medium. The surfactants may also self-assemble in non-polar solvents, viz. hydrocarbons, carbon tetrachloride, benzene, cyclohexane, chloroform, etc. They organize in a reverse manner, with their heads oriented towards the interior or core and the nonpolar tails towards the solvent. They are called 'reverse micelle'. In most occasions, the presence of water helps reverse micelles formation. Thus, there exists a tiny water core surrounded by the surfactant tails embedded in oil medium (Figure 7). Spectrophotometric, fluorimetric and calorimetric methods are used for the understanding of the beginning of their formation (i.e. CMC) and characterization[42–44].

Dimensionally reverse micelles are comparable with normal micelles; both are thermodynamically stable. Their aggregation number and thermodynamics of formation can be assessed following the same arguments as for normal micelles. The counter-ion binding to the ionic surfactant head in the water pool of reverse micelles is difficult to estimate.

The reverse micelles can consume water or polar solvent in the interior, the core increases in size and may exceed micellar dimension. Such stable dispersions are called water-in-oil (W/O) microemulsions[45]. In an analogous manner, normal micelles can accommodate oil to bulge in size forming oil-in-water (O/W) microemulsions. More addition of water and oil in the two categories of microdispersions ends up in the formation of bigger particle size yielding emulsions. Further discussion on this topic is beyond the scope of this article.

Uses of micelles

Micellar solutions are called 'compartmentalized liquids', the micelles serving as compartments which can help dissolution of polar and nonpolar compounds in normal and reverse micellar solutions respectively. This is an advantage which is not achieved otherwise. Solubilization and dispersion[46] are two important uses of micellar solution. During detergency, the micelles supply amphiphiles to act at the dirt–fabric interface for dislodging the dirt[5,16,34] which finally is dispersed in the aqueous medium by their incorporation in the micelle for easy removal by washing.

About 50% of underground oil is recovered by pumping, and water as well as steam flooding, the rest 50% remains trapped in the pores and cracks of underground rocks which is difficult to recover. It has been established through research that by flooding micellar and microemulsion solution in the underground rocks, the interfacial tension between oil and aqueous solution can be greatly reduced to decrease the Laplace pressure under the curved oil meniscus in the pores to help mobilize the oil for easy recovery[16,47]. By this tertiary recovery or 'enhanced recovery' process another 30% of the underground oil can be recovered. But because of high price of surfactants etc. the method may not be on the whole cost effective. Further research in this direction has potential prospect.

The micellar solutions can influence reaction kinetics, both enhancement and retardation of the reaction rate may occur[4,8,49]. Substrate binding and solubilization in the micelle are the main reasons for influencing the reaction kinetics. The activation barrier may be potentially affected. The reverse micelles may show significant influence on the reaction rates[50]. Thus quick formation of products and often formation of new products can be achieved. Micellar kinetics are thus also compared with enzyme kinetics. It has been found that enzyme activities may also be enhanced and reduced by trapping them inside the aqueous pool of reverse micelles; the enzyme may show increased stability in compartmentalized liquids[51–53]. The kinetics of substrate splitting etc. have been found to occur with altered efficiency; supra activities have also been reported. This has generated great impact of application of micellar medium-induced chemical and biochemical reaction processes.

The preparation of ultrafine monodisperse particles of colloidal dimensions is of great need in heterogeneous catalysis, magnetic tape production, biomedical application, etc. These can be conveniently prepared in compartmentalized (reverse micellar) media; thus microfine particles (often called nanoparticles) of desired sizes can be obtained through necessary chemical reactions[54,55]. The oxides of iron, aluminium, chromium, nickel, etc.; sulphates of calcium, barium etc.; oxalates and phosphates of calcium, etc.; are examples of such materials which have prospects of preparation at the microfine monodisperse level by the above surface chemical method. The process of emulsion polymerization can be performed in reverse micelles for the preparation of polymers of controlled molecular weight and size. This is a significant advancement in the application of the micellar medium in technology.

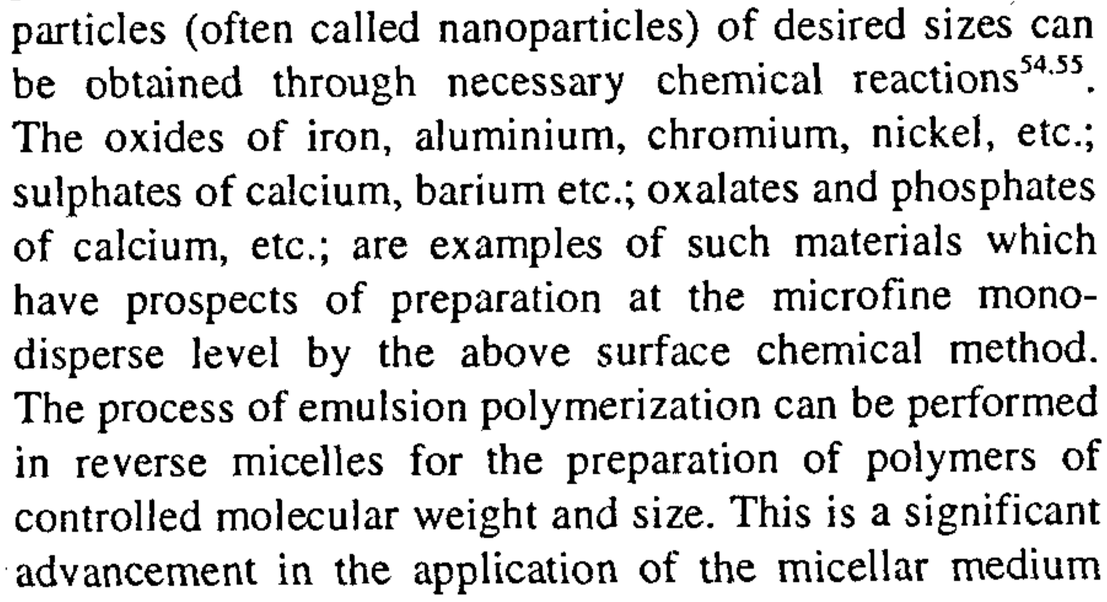

Figure 7 *a, b.* Schematic representation of mixed micelles. *a*, normal micelle; *b*, reverse micelle.

Photochemical reactions are influenced by micellar medium[15,56]; the interfacial region can affect the photochemical pathways changing the quantum yield. For example, in photo-decarbonylation of asymmetrical diaryl ketones of general formula ACOB in micellar medium, the yield of AB is very high compared to AA and BB which is much low without micelles[57]. The molecule ACOB in a micelle essentially forms AB; the probability of reaction between two such molecules in two different micelles to form AA and BB is obviously very low.

Micellar solutions have prospects in carrier-mediated transport. A material otherwise insoluble can be captured by the micelle in one solution and is transferred into another. This principle is often used in phase transfer catalysis using micelles as carriers. Separation of proteins and other polar compounds by the use of reverse micelles has been demonstrated[58,59].

In presence of salt, anionic micelles undergo sphere to rod transition, making the solution viscous or thick. They undergo shear thinning assisting easier application. This principle is used in the preparation of shampoo which would be otherwise too watery to apply on hair[15]. Control of viscosity of preparations with nonionic surfactants is done by varying the length of the hydrophilic polyoxyethylene head group for effective surface wetting and detergency.

Pollutants can be solubilized by the micelles; both organic and inorganic pollutants are amenable to such conditions. Using micelles of desired size, they can be retained by the membrane while the solution is ultrafiltered for their removal[60,61]. The surfactants can form chelate with metal ions aided by hydrophobic association, counter-ion binding can hold organic ions on them. They can be removed as well by ultrafiltration.

Micellar medium may be utilized for stereospecific reactions; one enantiomer may be favoured over another by virtue of strong orientational effects of polar amphiphilic reactants[62].

Despite citing above a good number of avenues for profitable utilization of micellar medium, their large scale uses have become only limited. This is because of low substrate solubility, temperature and salt instability and difficulties in the separation of products from the surfactants. It is hoped that these hurdles will be overcome through exhaustive basic research and planned trials employing newly developed surfactants; until then the field remains challengingly open to scientists and technologists. The versatility of micellar solution is the key factor for its continued study and appropriate documentation.

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Immunodiagnostic approaches to detect bovine tuberculosis

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Even though tuberculosis is an ancient disease, its early diagnosis is still a global problem. Conventional diagnostic tests along with some improved techniques and molecular biological approaches have been reviewed. The current status and the pitfalls of the diagnostic procedures are reported. An attempt has also been made to give some insight of the future prospect of the field of research.

A recent report of the World Health Organization shows that multidrug resistant tuberculosis, which often leads to death; has emerged as a new global challenge. The WHO, which has declared TB as a global emergency, has warned that the TB crisis will continue to grow unless immediate action is taken to stop its growth. The public health risk is more in agrarian countries like India, as bovine tuberculosis is a serious problem even now. The relationship between bovine tuberculosis and human tuberculosis has been reviewed earlier and it has been established that tuberculosis in cattle may be transmitted to man via milk, milk products, meat and directly in the cowbyre[1]. The resurgence of the devastating disease has led to renewed interest in the development of improved diagnostic tests for tuberculosis in animals and a review of control measures.