# Surfactants: Fundamentals and Applications in the Petroleum Industry

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Glossary and Indexes

# Surfactants and Their Solutions: Basic Principles

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*This chapter provides an introduction to the occurrence, properties and importance of surfactants as they relate to the petroleum industry. With an emphasis on the definition of important terms, the importance of surfactants, their micellization and adsorption behaviours, and their interfacial properties are demonstrated. It is shown how surfactants may be applied to alter interfacial properties, promote oil displacement, and stabilize or destabilize dispersions such as foams, emulsions, and suspensions. Understanding and controlling the properties of surfactant-containing solutions and dispersions has considerable practical importance since fluids that must be made to behave in a certain fashion to assist one stage of an oil production process, may require considerable modification in order to assist in another stage.*

## Introduction

Surfactants are widely used and find a very large number of applications because of their remarkable ability to influence the properties of surfaces and interfaces, as will be discussed below. Some important applications of surfactants in the petroleum industry are shown in Table 1. Surfactants may be applied or encountered at all stages in the petroleum recovery and processing industry, from oilwell drilling, reservoir injection, oilwell production, and surface plant processes, to pipeline and seagoing transportation of petroleum emulsions. This chapter is intended to provide an introduction to the basic principles involved in the occurrence and uses of surfactants in the petroleum industry. Subsequent chapters in this book will go into specific areas in greater detail.

**Table 1.    Some Examples of Surfactant Applications in the Petroleum Industry**

*Gas/Liquid Systems*
  Producing oilwell and well-head foams
  Oil flotation process froth
  Distillation and fractionation tower foams
  Fuel oil and jet fuel tank (truck) foams
  Foam drilling fluid
  Foam fracturing fluid
  Foam acidizing fluid
  Blocking and diverting foams
  Gas-mobility control foams

*Liquid/Liquid Systems*
  Emulsion drilling fluids
  Enhanced oil recovery *in situ* emulsions
  Oil sand flotation process slurry
  Oil sand flotation process froths
  Well-head emulsions
  Heavy oil pipeline emulsions
  Fuel oil emulsions
  Asphalt emulsion
  Oil spill emulsions
  Tanker bilge emulsions

*Liquid/Solid Systems*
  Reservoir wettability modifiers
  Reservoir fines stabilizers
  Tank/vessel sludge dispersants
  Drilling mud dispersants

All the petroleum industry's surfactant applications or problems have in common the same basic principles of colloid and interface science. The widespread importance of surfactants in general, and scientific interest in their nature and properties, have precipitated a wealth of published literature on the subject. Good starting points for further basic information are classic books like Rosen's *Surfactants and Interfacial Phenomena* [1] and Myers' *Surfactant Science and Technology* [2], and the many other books on surfactants [3–19]. Most good colloid chemistry texts contain introductory chapters on surfactants. Good starting points are references [20–23], while for much more detailed treatment of advances in specific surfactant-related areas the reader is referred to some of the chapters available in specialist books [24–29]. With regard to the occurrence of related colloidal systems in the petroleum industry, three recent books

describe the principles and occurrences of emulsions, foams, and suspensions in the petroleum industry [*30–32*].

## *Definition and Classification of Surfactants*[4]

Some compounds, like short-chain fatty acids, are amphiphilic or amphipathic, i.e., they have one part that has an affinity for nonpolar media and one part that has an affinity for polar media. These molecules form oriented monolayers at interfaces and show surface activity (i.e., they lower the surface or interfacial tension of the medium in which they are dissolved). In some usage surfactants are defined as molecules capable of associating to form micelles. These compounds are termed surfactants, amphiphiles, surface-active agents, tensides, or, in the very old literature, paraffin-chain salts. The term surfactant is now probably the most commonly used and will be employed in this book. This word has a somewhat unusual origin, it was first created and registered as a trademark by the General Aniline and Film Corp. for their surface-active products.[5] The company later (ca. 1950) released the term to the public domain for others to use [*33*]. Soaps (fatty acid salts containing at least eight carbon atoms) are surfactants. Detergents are surfactants, or surfactant mixtures, whose solutions have cleaning properties. That is, detergents alter interfacial properties so as to promote removal of a phase from solid surfaces.

The unusual properties of aqueous surfactant solutions can be ascribed to the presence of a hydrophilic head group and a hydrophobic chain (or tail) in the molecule. The polar or ionic head group usually interacts strongly with an aqueous environment, in which case it is solvated via dipole–dipole or ion–dipole interactions. In fact, it is the nature of the polar head group which is used to divide surfactants into different categories, as illustrated in Table 2. In-depth discussions of surfactant structure and chemistry can be found in references [*1, 2, 8, 34, 35*].

## *The Hydrophobic Effect and Micelle Formation*

In aqueous solution dilute concentrations of surfactant act much as normal electrolytes, but at higher concentrations very different behaviour results. This behaviour is explained in terms of the formation of organized aggregates of large numbers of molecules called micelles, in which the

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[4] A glossary of frequently encountered terms in the science and engineering of surfactants is given in the final chapter of this book.

[5] For an example of one of GAF Corp's. early ads promoting their trademarked surfactants, see *Business Week*, March 11, 1950, pp. 42–43.

<div align="center">

**Table 2.  Surfactant Classifications**

</div>

| Class | Examples | Structures |
|---|---|---|
| Anionic | Na stearate | $CH_3(CH_2)_{16}COO^-Na^+$ |
| | Na dodecyl sulfate | $CH_3(CH_2)_{11}SO_4^-Na^+$ |
| | Na dodecyl benzene sulfonate | $CH_3(CH_2)_{11}C_6H_4SO_3^-Na^+$ |
| Cationic | Laurylamine hydrochloride | $CH_3(CH_2)_{11}NH_3^+Cl^-$ |
| | Trimethyl dodecylammonium chloride | $C_{12}H_{25}N^+(CH_3)_3Cl^-$ |
| | Cetyl trimethylammonium bromide | $CH_3(CH_2)_{15}N^+(CH_3)_3Br^-$ |
| Nonionic | Polyoxyethylene alcohol | $C_nH_{2n+1}(OCH_2CH_2)_mOH$ |
| | Alkylphenol ethoxylate | $C_9H_{19}-C_6H_4-(OCH_2CH_2)_nOH$ |
| | Polysorbate 80 | $HO(C_2H_4O)_w$ $(OC_2H_4)_xOH$ |
| | $w + x + y + z = 20,$ | |
| | $R = (C_{17}H_{33})COO$ | $CH(OC_2H_4)_yOH$ |
| | | $\|$ |
| | | $CH_2(OC_2H_4)_zR$ |
| | Propylene oxide-modified | $(CH_3)_3SiO((CH_3)_2SiO)_x(CH_3SiO)_ySi(CH_3)_3$ |
| | polymethylsiloxane | |
| | EO = ethyleneoxy | $\|$ |
| | PO = propyleneoxy | $CH_2CH_2CH_2O(EO)_m(PO)_nH$ |
| Zwitterionic | Dodecyl betaine | $C_{12}H_{25}N^+(CH_3)_2CH_2COO^-$ |
| | Lauramidopropyl betaine | $C_{11}H_{23}CONH(CH_2)_3N^+(CH_3)_2CH_2COO^-$ |
| | Cocoamido-2-hydroxy-propyl sulfobetaine | $C_nH_{2n+1}CONH(CH_2)_3N^+(CH_3)_2CH_2CH(OH)CH_2SO_3^-$ |

lipophilic parts of the surfactants associate in the interior of the aggregate leaving hydrophilic parts to face the aqueous medium. An illustration presented by Hiemenz and Rajagopalan [22] is given in Figure 1. The formation of micelles in aqueous solution is generally viewed as a compromise between the tendency for alkyl chains to avoid energetically unfavourable contacts with water, and the desire for the polar parts to maintain contact with the aqueous environment.

   A thermodynamic description of the process of micelle formation will include a description of both electrostatic and hydrophobic contributions to the overall Gibbs energy of the system. Hydrocarbons (e.g., dodecane) and water are not miscible; the limited solubility of hydrophobic species in water can be attributed to the hydrophobic effect. The hydrophobic Gibbs energy (or the transfer Gibbs energy) can be defined as the difference between the standard chemical potential of the hydrocarbon solute in water and a hydrocarbon solvent at infinite dilution [36–40]

$$\Delta G_t^\circ = \mu_{HC}^\circ - \mu_{aq}^\circ \tag{1}$$

where $\mu_{HC}^\circ$ and $\mu_{aq}^\circ$ are the chemical potentials of the hydrocarbon dissolved in the hydrocarbon solvent and water, respectively, and $\Delta G_t^\circ$ is



(a)

Tail

Head    Water

(b)        (c)
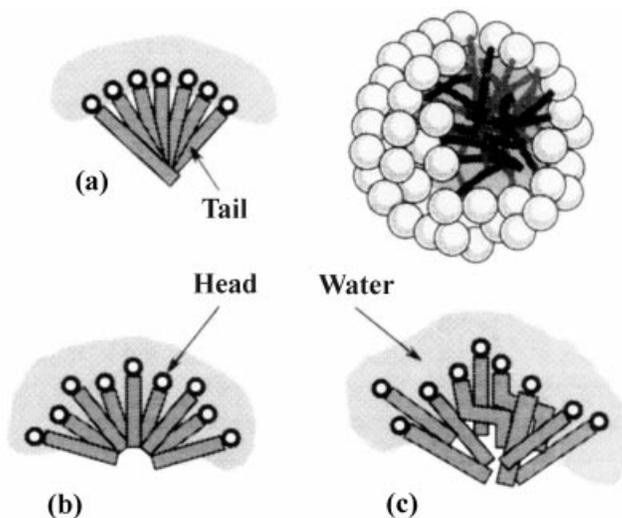
Figure 1.   Schematic representation of the structure of an aqueous micelle showing several possibilities: (a) overlapping tails in the centre, (b) water penetrating to the centre, and (c) chains protruding and bending. (From Hiemenz and Rajagopalan [22]. Copyright 1997 Marcel Dekker Inc., New York.)

the Gibbs energy for the process of transferring the hydrocarbon solute from the hydrocarbon solvent to water. In a homologous series of hydrocarbons (e.g., the $n$-alcohols or the $n$-alkanes), the value of $\Delta G_t^\circ$ generally increases in a regular fashion

$$\Delta G_t^\circ = (a - bn_c)RT \qquad (2)$$

where $a$ and $b$ are constants for a particular hydrocarbon series and $n_c$ is the number of carbon atoms in the chain. The transfer Gibbs energy, $\Delta G_t^\circ$, can be divided into entropic and enthalpic contributions

$$\Delta G_t^\circ = \Delta H_t^\circ - T\,\Delta S_t^\circ \qquad (3)$$

where $\Delta H_t^\circ$ and $\Delta S_t^\circ$ are the enthalpy and entropy of transfer, respectively. A significant characteristic of the hydrophobic effect is that the entropy term is dominant, i.e., the transfer of the hydrocarbon solute from the hydrocarbon solvent to water is accompanied by an increase in the Gibbs transfer energy ($\Delta G > 0$) [41]. The decrease in entropy is thought to be the result of the breakdown of the normal hydrogen-bonded structure of water accompanied by the formation of differently structured water, often termed icebergs, around the hydrocarbon chain. The presence of the hydrophobic species promotes an ordering of water molecules in the vicinity of the hydrocarbon chain. To minimize the large entropy effect, the "icebergs" tend to cluster [38], in order to reduce the number of water molecules involved; the "clustering" is enthalpically favoured (i.e., $\Delta H < 0$), but entropically unfavourable. The overall process has the tendency to bring the hydrocarbon molecules together, which is known as the hydrophobic interaction. Molecular interactions, arising from the tendency for the water molecules to regain their normal tetrahedral structure, and the attractive dispersion forces between hydrocarbon chains, act cooperatively to remove the hydrocarbon chain from the water "icebergs", leading to an association of hydrophobic chains.

Due to the presence of the hydrophobic effect, surfactant molecules adsorb at interfaces, even at low surfactant concentrations. As there will be a balance between adsorption and desorption (due to thermal motions), the interfacial condition requires some time to establish. The surface activity of surfactants should therefore be considered a dynamic phenomenon. This can be determined by measuring surface or interfacial tensions versus time for a freshly formed surface, as will be discussed further below.

At a specific, higher, surfactant concentration, known as the critical micelle concentration (cmc), molecular aggregates termed micelles are formed. The cmc is a property of the surfactant and several other factors, since micellization is opposed by thermal and electrostatic forces. A low cmc is favoured by increasing the molecular mass of the lipophilic part of the molecule, lowering the temperature (usually), and adding electrolyte.

Surfactant molar masses range from a few hundreds up to several thousands.

The most commonly held view of a surfactant micelle is not much different than that published by Hartley in 1936 [*41, 42*] (see Figure 1). At surfactant concentrations slightly above the cmc value, surfactants tend to associate into spherical micelles, of about 50–100 monomers, with a radius similar to that of the length of an extended hydrocarbon chain. The micellar interior, being composed essentially of hydrocarbon chains, has properties closely related to the liquid hydrocarbon.

## *Critical Micelle Concentration*

It is well known that the physico-chemical properties of surfactants vary markedly above and below a specific surfactant concentration, the cmc value [*2–9, 13, 14, 17, 35–47*]. Below the cmc value, the physico-chemical properties of ionic surfactants like sodium dodecylsulfate, SDS, (e.g., conductivities, electromotive force measurements) resemble those of a strong electrolyte. Above the cmc value, these properties change dramatically, indicating a highly cooperative association process is taking place. In fact, a large number of experimental observations can be summed up in a single statement: almost all physico-chemical properties versus concentration plots for a given surfactant–solvent system will show an abrupt change in slope in a narrow concentration range (the cmc value). This is illustrated by Preston's [*48*] classic graph, shown in Figure 2.

In terms of micellar models, the cmc value has a precise definition in the pseudo-phase separation model, in which the micelles are treated as a separate phase. The cmc value is defined, in terms of the pseudo-phase model, as the concentration of maximum solubility of the monomer in that particular solvent. The pseudo-phase model has a number of shortcomings; however, the concept of the cmc value, as it is described in terms of this model, is very useful when discussing the association of surfactants into micelles. It is for this reason that the cmc value is, perhaps, the most frequently measured and discussed micellar parameter [*39*].

Cmc values are important in virtually all of the petroleum industry surfactant applications. For example, a number of improved or enhanced oil recovery processes involve the use of surfactants including micellar, alkali/surfactant/polymer (A/S/P) and gas (hydrocarbon, $N_2$, $CO_2$ or steam) flooding. In these processes, surfactant must usually be present at a concentration higher than the cmc because the greatest effect of the surfactant, whether in interfacial tension lowering [*30*] or in promoting foam stability [*31*], is achieved when a significant concentration of micelles is present. The cmc is also of interest because at concentrations
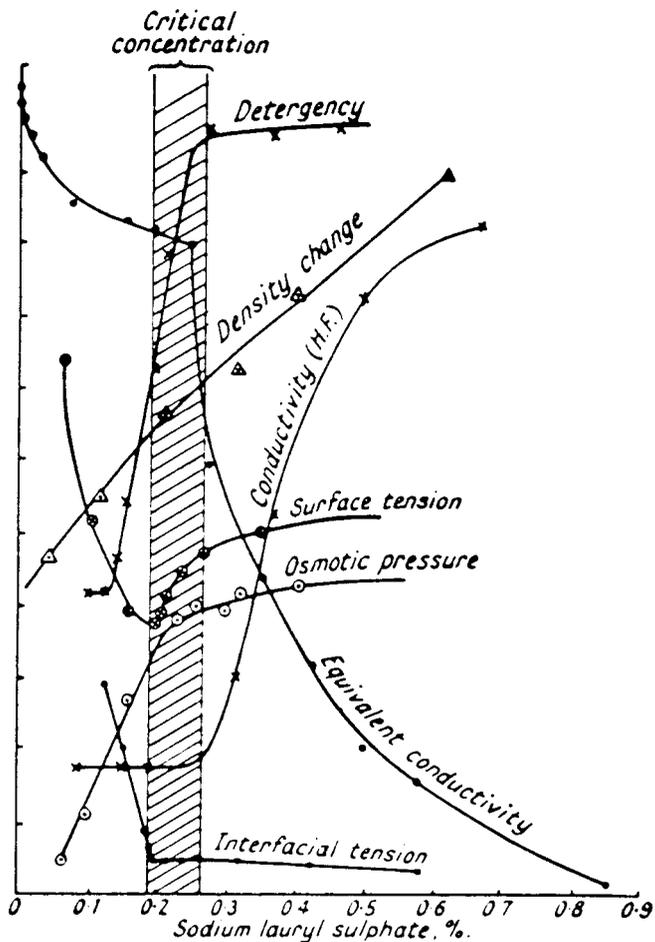
*Figure 2.   Illustration of the dramatic changes in physical properties that occur beyond the critical micelle concentration. (From Preston [48]. Copyright 1948 American Chemical Society, Washington.)*

above this value the adsorption of surfactant onto reservoir rock surfaces increases very little. That is, the cmc represents the solution concentration of surfactant from which nearly maximum adsorption occurs.

**Cmc Measurements.**   The general way of obtaining the cmc value of a surfactant micelle is to plot some physico-chemical property of

**Table 3.   Some Common Cmc Methods**

UV/Vis, IR spectroscopy
Fluorescence spectroscopy
Nuclear magnetic resonance spectroscopy
Electrode potential/conductivity
Voltametry
Scattering techniques
Calorimetry
Surface tension
Foaming

interest versus the surfactant concentration and observe the break in the plot. Table 3 lists the most common cmc methods. Many of these methods have been reviewed by Shinoda [11] and Mukerjee and Mysels [49]. It should be noted that different experimental techniques may give slightly different values for the cmc of a surfactant. However, Mukerjee and Mysels [49], in their vast compilation of cmc values, have noted that the majority of values for a single surfactant (e.g., sodium dodecyl sulfate, or SDS, in the absence of additives) are in good agreement and the outlying values are easily accounted for.

For petroleum industry processes, one tends to have a special interest in the cmc's of practical surfactants that may be anionic, cationic, nonionic or amphoteric. The media are typically high salinity, high hardness electrolyte solutions, and in addition, the cmc values of interest span the full range from ambient laboratory conditions to oil and gas reservoir conditions of temperature and pressure. Irrespective of aiming for process development and optimization under realistic (reservoir) conditions of temperature and pressure, it remains common to determine cmc's experimentally at ambient laboratory conditions and assume that the same hold even at elevated temperatures and pressures. This can be an extremely dangerous assumption.

The nature and limits of applicability of specific methods for determining critical micelle concentrations vary widely. Most methods have been developed for a relatively small set of pure surfactants involving very dilute electrolyte solutions and only ambient temperature and pressure. The determination of cmc at elevated temperature and pressure is experimentally much more difficult than for ambient conditions and comparatively little work has been done in this area. Most high temperature cmc studies have been by conductivity measurements and have therefore been limited to ionic surfactants. For example, cmc's at up to 166 °C have been reported by Evans and Wightman [50]. Some work has been reported using calorimetry, up to 200 °C by Noll [51], and using $^{19}$F

NMR, up to 180 °C by Shinoda et al. [52]. Some work has been reported involving cmc determination by calorimetry (measuring heats of dilution or specific heats). Archer et al. [53] used flow calorimetry to determine the cmc's of several sulfonate surfactants at up to 178 °C. Noll [51] determined cmc's for dodecyltrimethylammonium bromide and commercial surfactants in the temperature range 25–200 °C using flow calorimetry. Surface tension is the classical method for determining cmc's but many surface tension methods are not suitable for use with aqueous solutions at elevated temperatures. Exceptions include the pendant, sessile, and captive drop methods which can be conducted with high-pressure cells [54, 55].

For any of the techniques applied it appears (Archer et al. [53]) that the uncertainties in the experimental cmc determinations increase with increasing temperature because at the same time the surfactant aggregation number decreases and the aggregation distribution increases. That is, the concentration range over which micellization occurs broadens with increasing temperature. Almost all of the elevated temperature cmc studies have involved carefully purified surfactants (not commercial surfactants or their formulations) in pure water or very dilute electrolyte solutions. Conducting cmc determinations at elevated pressure, as well as temperature, is even more difficult and only a few studies have been reported, mostly employing conductivity methods (La Mesa et al. [56]; Sugihara and Mukerjee [57]; Brun et al. [58]; Kaneshina et al. [59]; Hamann [60]) which, again, are unsuitable for nonionic or zwitterionic surfactants and for use where the background electrolyte concentrations are significant.

In the case where one needs to be able to determine cmc's for nonionic or zwitterionic surfactants, in electrolyte solutions that may be very concentrated, and at temperatures and pressures up to those that may be encountered in improved oil recovery operations in petroleum reservoirs, most of the established methods are not practical. One successful approach to this problem has been to use elevated temperature and pressure surface tension measurements involving the captive drop technique [8] although this method is quite time-consuming. Another approach is to use dynamic foam stability measurements. Foaming effectiveness and the ease of foam formation are related to surface tension lowering and to micelle formation, the latter of which promotes foam stability through surface elasticity and other mechanisms [61]. Accordingly, static or dynamic foam height methods generally show that foam height increases with surfactant concentration and then becomes relatively constant at concentrations greater than the cmc (Rosen and Solash [62]; Goette [63]). Using a modified Ross-Miles static foam height apparatus, Kashiwagi [64] determined the cmc of SDS at 40 °C to be 7.08 mM which compared well with values attained

by conductivity (7.2 mM) and surface tension (7.2 mM). Rosen and Solash [62] also found that foam production was related to cmc using the Ross-Miles method at 60 °C when they assessed SDS, potassium tetradecyl sulfonate, potassium hexadecyl sulfonate, and sodium hexadecyl sulfate.

Morrison et al. [65] describe a dynamic foam height method for the estimation of cmc's that is suitable for use at high temperatures and pressures. This method is much more rapid than the surface tension method, and is applicable to a wide range of surfactant classes, including both ionic and amphoteric (zwitterionic) surfactants. The method is suitable for the estimation of cmc's, for determining the minimum cmc as a function of temperature, for identifying the temperature at which the minimum cmc occurs, and for determining how cmc's vary with significant temperature and pressure changes. The method has been used to determine the temperature variation of cmc's for a number of commercial foaming surfactants in aqueous solutions, for the derivation of thermodynamic parameters, and to establish useful correlations [55].

**Cmc Values.**   Some typical cmc values for low electrolyte concentrations at room temperature are:

| | |
|---|---|
| Anionics | $10^{-3}$–$10^{-2}$ M |
| Amphoterics | $10^{-3}$–$10^{-1}$ M |
| Cationics | $10^{-3}$–$10^{-1}$ M |
| Nonionics | $10^{-5}$–$10^{-4}$ M |

Cmc values show little variation with regard to the nature of the charged head group. The main influence appears to come from the charge of the hydrophilic head group. For example, the cmc of dodecyltrimethylammonium chloride (DTAC) is 20 mM, while for a 12 carbon nonionic surfactant, hexaethylene glycol mono-*n*-dodecyl ether ($C_{12}E_6$), the cmc is about 0.09 mM [39, 41, 49]; the cmc for SDS is about 8 mM, while that for disodium 1,2-dodecyldisulfate (1,2-SDDS) is 40 mM [66]. In addition to the relative insensitivity of the cmc value of the surfactant to the nature of the charged head group, cmc's show little dependence on the nature of the counter-ion. It is mainly the valence number of the counter-ion that affects the cmc. As an example, the cmc value for $Cu(DS)_2$ is about 1.2 mM, while the cmc for SDS is about 8 mM [49, 67].

Cmc values often exhibit a weak dependence on both temperature [68–70] and pressure [59, 71], although, as shown in Figure 3, some surfactant cmc's have been observed to increase markedly with temperature above 100 °C [55, 65]. The effects of added substances on the cmc are complicated and interesting, and depend greatly on whether the additive is solubilized in the micelle, or in the intermicellar solution. The addition of electrolytes to ionic surfactant solutions results in a well
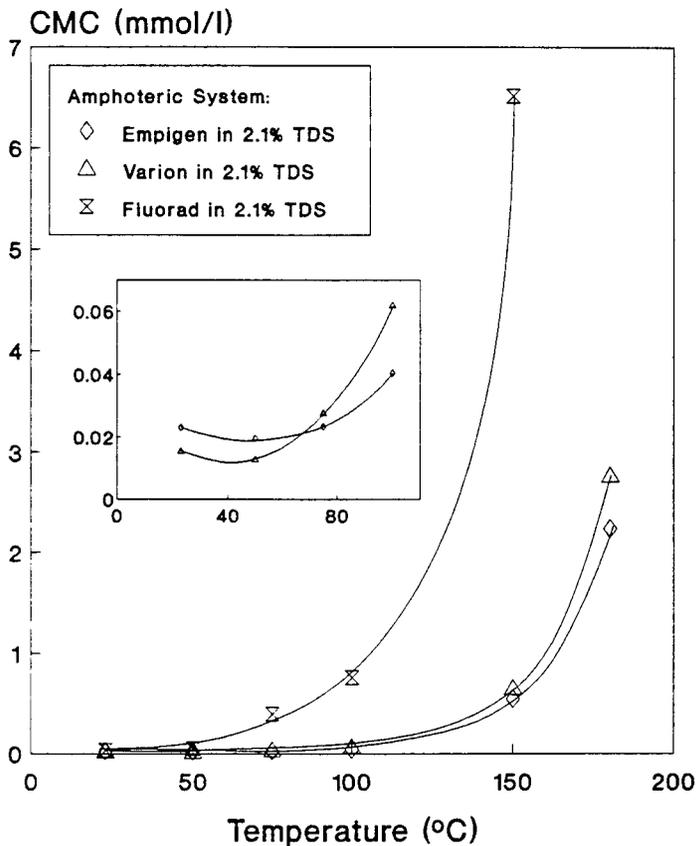
*Figure 3.    Temperature variation of the critical micelle concentrations of three amphoteric surfactants in 2.1% total dissolved solids brine solutions. (From Stasiuk and Schramm [55]. Copyright 1996 Academic Press, New York.)*

established linear dependence of log (cmc) on the concentration of added salt [72–76]. For nonionic micelles, electrolyte addition has little effect on cmc values. When non-electrolytes are added to the micellar solution, the effects are dependent on the nature of the additive. For polar additives (e.g., *n*-alcohols), the cmc decreases with increasing concentration of alcohol, while the addition of urea to micellar solutions tends to increase the cmc, and may even inhibit micelle formation [77, 78]. Nonpolar additives tend to have little effect on the cmc [79].

## The Krafft Point

The solubilities of micelle-forming surfactants show a strong increase above a certain temperature, termed the Krafft point $(T_k)$. This is explained by the fact that the single surfactant molecules have limited solubility whereas the micelles are very soluble. Referring to the illustration from Shinoda [11] in Figure 4, below the Krafft point the solubility of the surfactant is too low for micellization so solubility alone determines the surfactant monomer concentration. As temperature increases the solubility increases until at $T_k$ the cmc is reached. At this temperature a relatively large amount of surfactant can be dispersed in micelles and solubility increases greatly. Above the Krafft point maximum reduction in surface or interfacial tension occurs at the cmc because the cmc then determines the surfactant monomer concentration. Krafft points for a number of surfactants are listed in references [1, 80].

   Nonionic surfactants do not exhibit Krafft points. Instead, the solubility of nonionic surfactants decreases with increasing temperature, and these surfactants may begin to lose their surface active properties above a transition temperature referred to as the cloud point. This occurs because above the cloud point a surfactant rich phase of swollen micelles separates, and the transition is usually accompanied by a marked increase in dispersion turbidity.
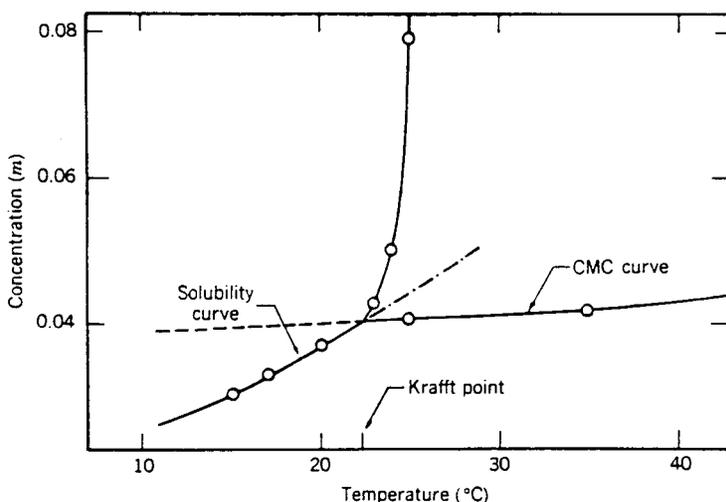


Figure 4.    Example of a "phase behaviour" diagram for a surfactant in aqueous solution, showing the cmc and Krafft points. (From Shinoda et al. [11]. Copyright 1963 Academic Press, New York.)

**Table 4.    Typical Methods of Surfactant Analysis**

| Surfactant Class | Method |
|---|---|
| *Anionic* | |
| alkyl sulfates and sulfonates | Two-phase or surfactant-electrode monitored titration |
| petroleum and lignin sulfonates | Column or gel permeation chromatography |
| phosphate esters | Potentiometric titration |
| sulfosuccinate esters | Gravimetric or titration methods |
| carboxylates | Potentiometric titration or two-phase titration |
| *Nonionic* | |
| alcohols | NMR or IR spectroscopy |
| ethoxylated acids | Gas chromatography |
| alkanolamides | Gas chromatography |
| ethoxylated amines | HPLC |
| amine oxides | Potentiometric titration |
| *Cationic* | |
| quaternary ammonium salts | Two-phase or surfactant-electrode monitored titration, or GC or HPLC |
| *Amphoteric* | |
| carboxybetaines | Low pH two-phase titration, gravimetric analysis, or potentiometric titration |
| sulfobetaines | HPLC |

## Analysis

Numerous methods have been developed for the quantitative determination of each class of surfactant. The analysis of commercial surfactants is greatly complicated by the fact that these products are mixtures. They are often comprised of a range of molar mass structures of a given structural class, may contain surface-active impurities, are sometimes intentionally formulated to contain several different surfactants, and are often supplied dissolved in mixed organic solvents or complex aqueous salt solutions. Each of these components has the potential to interfere with a given analytical method. Therefore surfactant assays may well have to be preceded by surfactant separation techniques. Both the separation and assay techniques can be highly specific to a given surfactant/solution system. This makes any substantial treatment beyond the scope of the present chapter. Good starting points can be found in the several books on surfactant analysis [81–86]. The characterization and analysis of surfactant demulsifiers is discussed in Chapter 2 of this book. Table 4 shows some typical kinds of analysis methods that are applied to the different surfactant classes.

There are a number of reviews available for surfactants in specific industries [87], and for specific surfactant classes. References [81–90] discuss methods for the determination of anionic surfactants, which are probably the most commonly encountered in the petroleum industry. Most of these latter methods are applicable only to the determination of sulfate- and sulfonate-functional surfactants. Probably the most common analysis method for anionic surfactants is Epton's two-phase titration method [91, 92] or one of its variations [93, 94]. Related, single-phase titrations can be performed and monitored by either surface tension [95] or surfactant-sensitive electrode [84, 85, 96–98] measurements. Gronsveld and Faber [99] discuss adaptation of the titration method to oleic phase samples.

## Surfactants and Surface Tension

In two-phase dispersions, a thin intermediate region or boundary, known as the interface, lies between the two phases. The physical properties of the interface can be very important in all kinds of petroleum recovery and processing operations. Whether in a well, a reservoir or a surface processing operation, one tends to encounter large interfacial areas exposed to many kinds of chemical reactions. In addition, many petroleum industry processes involve colloidal dispersions, such as foams, emulsions, and suspensions, all of which contain large interfacial areas; the properties of these interfaces may also play a large role in determining the properties of the dispersions themselves. In fact, even a modest surface energy per unit area can become a considerable total surface energy. Suppose we wish to make a foam by dispersion of gas bubbles into water. For a constant gas volume fraction the total surface area produced increases as the bubble size produced decreases. Since there is a free energy associated with surface area, this increases as well with decreasing bubble size. The energy has to be added to the system to achieve the dispersion of small bubbles. If this amount of energy cannot be provided, say through mechanical energy input, then another alternative is to use surfactant chemistry to lower the interfacial free energy, or interfacial tension. The addition of a small quantity of a surfactant to the water, possibly a few tenths of a percent, would significantly lower the surface tension and significantly lower the amount of mechanical energy needed for foam formation. For examples of this simple calculation for foams and emulsions, see references [61] and [100] respectively.

The origin of surface tension may be visualized by considering the molecules in a liquid. The attractive van der Waals forces between molecules are felt equally by all molecules except those in the interfacial region. This imbalance pulls the latter molecules towards the interior of the liquid. The contracting force at the surface is known as the surface

tension. Since the surface has a tendency to contract spontaneously in order to minimize the surface area, bubbles of gas tend to adopt a spherical shape: this reduces the total surface free energy. For emulsions of two immiscible liquids a similar situation applies to the droplets of one of the liquids, except that it may not be so immediately obvious which liquid will form the droplets. There will still be an imbalance of intermolecular force resulting in an interfacial tension, and the interface will adopt a configuration that minimizes the interfacial free energy. Physically, surface tension may be thought of as the sum of the contracting forces acting parallel to the surface or interface. This point of view defines surface or interfacial tension ($\gamma$), as the contracting force per unit length around a surface. Another way to think about surface tension is that area expansion of a surface requires energy. Since the work required to expand a surface against contracting forces is equal to the increase in surface free energy accompanying this expansion, surface tension may also be expressed as energy per unit area.

There are many methods available for the measurement of surface and interfacial tensions. Details of these experimental techniques and their limitations are available in several good reviews [101–104]. Table 5 shows some of the methods that are used in petroleum recovery process research. A particular requirement of reservoir oil recovery process research is that measurements be made under actual reservoir conditions of temperature and pressure. The pendant and sessile drop methods are the most commonly used where high temperature/pressure conditions are required. Examples are discussed by McCaffery [105] and DePhilippis et al. [106]. These standard techniques can be difficult to apply to the measurement of extremely low interfacial tensions (<1 to 10 mN/m). For ultra-low tensions two approaches are being used. For moderate temperatures and low pressures the most common method is that of the spinning drop, especially for microemulsion research [107]. For elevated temperatures and pressures a captive drop method has been developed by Schramm et al. [108], which can measure tensions as low as 0.001 mN/m at up to 200 °C and 10,000 psi. In all surface and interfacial tension work it should be appreciated that when solutions, rather than pure liquids, are involved appreciable changes can occur with time at the surfaces and interfaces, so that techniques capable of dynamic measurements tend to be the most useful.

When surfactant molecules adsorb at an interface they provide an expanding force acting against the normal interfacial tension. Thus, surfactants tend to lower interfacial tension. This is illustrated by the general Gibbs adsorption equation for a binary, isothermal system containing excess electrolyte:

$$\Gamma_s = -(1/RT)(d\gamma/d \ln C_s) \tag{4}$$

**Table 5.  Surface and Interfacial Tension Methods used in Petroleum Research**

| Method | Static Values | Dynamic Values | Surface Tension | Interfacial Tension | Contact Angle | High $T$, $P$ Capability |
|---|---|---|---|---|---|---|
| Capillary rise | ✓ | ≈ | ✓ | ✗ | ✗, need $\theta = 0$ | ✗ |
| Wilhelmy plate | ✓ | ≈ | ✓ | ✗ | ✓, need to know $\gamma$ | ✗ |
| du Nouy ring | ✓ | ✗ | ✓ | ✗ | ✗, pure liquids only | ✗ |
| Drop weight | ✓ | ✗ | ✓ | ✓ | ✗, need $\theta = 0$ | ✓ |
| Drop volume | ✓ | ✗ | ✓ | ✓ | ✗, need $\theta = 0$ | ✓ |
| Pendant drop | ✓ | ✓ | ✓ | ✓ | ✗ | ✓ |
| Sessile drop | ✓ | ✓ | ✓ | ✓ | ✓ | ✓ |
| Oscillating jet | ✓ | ✓ | ✓ | ✗ | ✗ | ✗ |
| Spinning drop | ✓ | ≈ | ✓ | ✓ | ✗ | ✗ |
| Captive drop | ✓ | ✓ | ✓ | ✓ | ✗, forces $\theta = 0$ | ✓ |
| Maximum bubble pressure | ✓ | ≈ | ✓ | ✗ | ✗ | ✗ |
| Surface laser light scattering | ✓ | ✓ | ✓ | ≈ | ✗ | ✓ |
| Tilting plate | ✓ | ≈ | ✗ | ✗ | ✓ | ✗ |

where $\Gamma_s$ is the surface excess of surfactant (mol/cm$^2$), $C_s$ is the solution concentration of the surfactant (M), and $\gamma$ may be either surface or interfacial tension (mN/m). This equation can be applied to dilute surfactant solutions where the surface curvature is not great and where the adsorbed film can be considered to be a monolayer. The packing density of surfactant in a monolayer at the interface can be calculated as follows. According to equation 4, the surface excess in a tightly packed monolayer is related to the slope of the linear portion of a plot of surface tension versus the logarithm of solution concentration. From this, the area per adsorbed molecule ($a_S$) can be calculated from

$$a_S = 1/(N_A \Gamma_s) \tag{5}$$

where $N_A$ is Avogadro's number. Numerous examples are given by Rosen [1].

When surfactants concentrate in an adsorbed monolayer at a surface the interfacial film may take on any of a number of quite different properties which will be discussed in the next several sections. Suitably altered interfacial properties can provide a stabilizing influence in dispersions such as emulsions, foams, and suspensions.

## *Surface Elasticity*

As surfactant adsorbs at an interface the interfacial tension decreases (at least up to the cmc), a phenomenon termed the Gibbs effect. If a surfactant stabilized film undergoes a sudden expansion, the immediately expanded portion of the film must have a lower degree of surfactant adsorption than unexpanded portions because the surface area has increased. This causes an increased local surface tension which produces immediate contraction of the surface. The surface is coupled, by viscous forces, to the underlying liquid layers. Thus, the contraction of the surface induces liquid flow, in the near-surface region, from the low tension region to the high tension region. The transport of bulk liquid due to surface tension gradients is termed the Marangoni effect [27]. In foams, the Gibbs–Marangoni effect provides a resisting force to the thinning of liquid films.

The Gibbs–Marangoni effect only persists until the surfactant adsorption equilibrium is re-established in the surface, a process that may take place within seconds or over a period of hours. For bulk liquids and in thick films this can take place quite quickly, however, in thin films there may not be enough surfactant in the extended surface region to re-establish the equilibrium quickly, requiring diffusion from other parts of the film. The restoring processes are then the movement of surfactant along the interface from a region of low surface tension to one of high

surface tension, and the movement of surfactant from the thin film into the now depleted surface region. Thus the Gibbs–Marangoni effect provides a force to counteract film rupture in foams.

Many surfactant solutions show dynamic surface tension behaviour. That is, some time is required to establish the equilibrium surface tension. After the surface area of a solution is suddenly increased or decreased (locally), the adsorbed surfactant layer at the interface requires some time to restore its equilibrium surface concentration by diffusion of surfactant from, or to, the bulk liquid (see Figure 5, [*109*]). At the same time, since surface tension gradients are now in effect, Gibbs–Marangoni forces act in opposition to the initial disturbance. The dissipation of surface tension gradients, to achieve equilibrium, embodies the interface with a finite elasticity. This explains why some substances that lower surface tension do not stabilize foams [*21*]; they do not have the required rate of approach to equilibrium after a surface expansion or contraction. In other words, they do not have the requisite surface elasticity.

At equilibrium, the surface elasticity, or surface dilational elasticity, $E_G$, is defined [*21, 110*] by

$$E_G = \frac{d\gamma}{d\ln A} \tag{6}$$

where $\gamma$ is the surface tension and $A$ is the geometric area of the surface. This is related to the compressibility of the surface film, $K$, by $K = 1/E_G$. $E_G$ is a thermodynamic property, termed the Gibbs surface elasticity. This is the elasticity that is determined by isothermal equilibrium measurements, such as the spreading pressure–area method [*21*]. $E_G$ occurs in very thin films where the number of molecules is so low that the surfactant cannot restore the equilibrium surface concentration after deformation. An illustration is given in [*61*].

The elasticity determined from nonequilibrium dynamic measurements depends upon the stresses applied to a particular system, is generally larger in magnitude than $E_G$, and is termed the Marangoni surface elasticity, $E_M$ [*21, 111*]. For foams it is this dynamic property that is of most interest. Surface elasticity measures the resistance against creation of surface tension gradients and of the rate at which such gradients disappear once the system is again left to itself [*112*]. The Marangoni elasticity can be determined experimentally from dynamic surface tension measurements that involve known surface area changes, such as the maximum bubble pressure method [*113, 115*]. Although such measurements include some contribution from surface dilational viscosity [*112, 114*] the results are frequently simply referred to in terms of surface elasticities.

Numerous studies have examined the relation between $E_G$ or $E_M$ and foam stability [*111, 112, 115*]. From low bulk surfactant concentrations,

(a)                    (b)                    (c)

Original state of thin film

Local mechanism        Higher local
caused a thin section  surface tension developed

Low surfactant         Action of elasticity    Surfactant molecules
concentration gradient pulls back surfactant    diffuse from bulk
(no elasticity)        molecules into thinned section  solution to surface

                       Returning surfactant    Surfactant concentration
                       molecules drag back     gradient in surface
                       underlaying layers      removed
                       of liquid with them

Film thinned and       Surface film repaired   Film thinned and
easily ruptured        by surface transport    easily ruptured
                       mechanism

*Figure 5.    Illustration of the Gibbs–Marangoni effect in a thin liquid
film. Reaction of a liquid film to a surface disturbance. (a) Low surfactant
concentration yields only low differential tension in film. The thin film is
poorly stabilized. (b) Intermediate surfactant concentration yields a
strong Gibbs–Marangoni effect which restores the film to its original
thickness. The thin film is stabilized. (c) High surfactant concentration
(>cmc) yields a differential tension which relaxes too quickly due to
diffusion of surfactant. The thinner film is easily ruptured. (From Pugh
[109]. Copyright 1996 Elsevier, Amsterdam.)*