2. Aggregation and adsorption at interfaces

Surfactants, literally, are active at a surface and that includes any of the liquid/liquid, liquid/gas or liquid/solid systems, so that the subject is quite broad. In this chapter particular emphasis is placed on adsorption and aggregation phenomena in aqueous systems. For a more thorough account of the theoretical background of surfactancy, the reader is referred to specific textbooks and monographs keyed throughout this chapter.

2.1 ADSORPTION OF SURFACTANTS AT INTERFACES

2.1.1 Surface tension and surface activity

Due to the different environment of molecules located at an interface compared to those from either bulk phase, an interface is associated with a surface free energy. At the air-water surface for example, water molecules are subjected to unequal short-range attraction forces and, thus, undergo a net inward pull to the bulk phase. Minimisation of the contact area with the gas phase is therefore a spontaneous process, explaining why drops and bubbles are round. The surface free energy per unit area, defined as the *surface tension* (γ_0), is then the minimum amount of work (W_{min}) required to create new unit area of that interface (ΔA), so $W_{min} = \gamma_0 \times \Delta A$. Another, but less intuitive, definition of surface tension is given as the force acting normal to the liquid-gas interface per unit length of the resulting thin film on the surface.

A surface-active agent is therefore a substance that at low concentrations adsorbs thereby changing the amount of work required to expand that interface. In particular surfactants can significantly reduce interfacial tension due to their dual chemical nature as introduced in Chapter 1. Considering the air-water boundary, the force driving adsorption is unfavourable hydrophobic interactions within the bulk phase. There, water molecules interact with one another through hydrogen bonding, so the presence of hydrocarbon groups in dissolved amphiphilic molecules causes distortion of this solvent structure apparently increasing the free energy of the system. This is known as the hydrophobic effect [1]. Less work is required to bring a surfactant molecule to the surface than a water molecule, so that migration of the surfactant to the surface is a spontaneous process. At the gasliquid interface, the result is the creation of new unit area of surface and the formation of an oriented surfactant monolayer with the hydrophobic tails pointing out of, and the head group inside, the water phase. The balance against the tendency of the surface to contract under normal surface tension forces causes an increase in the surface (or expanding) pressure π , and therefore a decrease in surface tension γ of the solution. The surface pressure is defined as $\pi = \gamma_0 - \gamma$, where γ_0 is the surface tension of a clean air-water surface.

Depending on the surfactant molecular structure, adsorption takes place over various concentration ranges and rates, but typically, above a well-defined concentration – the critical micelle concentration (CMC) – micellisation or aggregation takes place. At the CMC, the interface is at (near) maximum coverage and to minimise further free energy, molecules begin to aggregate in the bulk phase. Above the CMC, the system then consists of an adsorbed monomolecular layer, free monomers and micellised surfactant in the bulk, with all these three states in equilibrium. The structure and formation of micelles will be briefly described in Section 2.3. Below the CMC, adsorption is a dynamic equilibrium with surfactant molecules perpetually arriving at, and leaving, the surface. Nevertheless, a time-averaged value for the surface concentration can

be defined and quantified either directly or indirectly using thermodynamic equations (see Section 2.1.2).

Dynamic surface tension – as opposed to the equilibrium quantity – is an important property of surfactant systems as it governs many important industrial and biological applications [2-5]. Examples are printing and coating processes where an equilibrium surface tension is never attained, and a new area of interface is continuously formed. In any surfactant solution, the equilibrium surface tension is not achieved instantaneously and surfactant molecules must first diffuse from the bulk to the surface, then adsorb, whilst also achieving the correct orientation. Therefore, a freshly formed interface of a surfactant solution has a surface tension very close to that of the solvent, and this dynamic surface tension will then decay over a certain period of time to the equilibrium value. This relaxation can range from milliseconds to days depending on the surfactant type and concentration. In order to control this dynamic behaviour, it is necessary to understand the main processes governing transport of surfactant molecules from the bulk to the interface. This area of research therefore attracts much attention and recent developments can be found in references [6-8]. However, in the present chapter equilibrium surface tension will always be considered.

2.1.2 Surface excess and thermodynamics of adsorption

Following on the formation of an oriented surfactant monolayer, a fundamental associated physical quantity is the *surface excess*. This is defined as the concentration of surfactant molecules in a surface plane, relative to that at a similar plane in the bulk. A common thermodynamic treatment of the variation of surface tension with composition has been derived by Gibbs [9].

An important approximation associated with this Gibbs adsorption equation is the "exact" location of the interface. Consider a surfactant aqueous phase α in equilibrium with vapour β . The interface is a region of indeterminate

thickness τ across which the properties of the system vary from values specific to phase α to those characteristic of β . Since properties within this real interface cannot be well defined, a convenient assumption is to consider a mathematical plane, with zero thickness, so that the properties of α and β apply right up to that dividing plane positioned at some specific value X. Figure 2.1 illustrates this idealised system. **Figure 2.1** In the Gibbs approach to defining the surface excess concentration Γ , the Gibbs dividing surface is defined as the plane in which the solvent excess concentration becomes zero (the shaded area is equal on each side of the plane) as in (*a*). The surface excess of component *i* will then be the difference in the concentrations of that component on either side of that plane (the shaded area) (*b*)



Distance to interface

In the definition of the Gibbs dividing surface XX' is arbitrarily chosen so that the surface excess adsorption of the solvent is zero. Then the surface excess concentration of component *i* is given by

$$\Gamma_i^{\sigma} = \frac{n_i^{\sigma}}{A} \tag{2.1.1}$$

where A is the interfacial area. The term n_i^{σ} is the amount of component *i* in the surface phase σ over and above that which would have been in the phase σ if the bulk phases α and β had extended to the surface XX', without any change of composition. Γ_i^{σ} may be positive or negative, and its magnitude clearly depends on the location of XX'.

Now consider the internal energy U of the total system consisting of the bulk phases α and β

$$U = U^{\alpha} + U^{\beta} + U^{\sigma}$$

$$U^{\alpha} = TS^{\alpha} - PV^{\alpha} + \sum_{i} \mu_{i} n_{i}^{\alpha}$$

$$U^{\beta} = TS^{\beta} - PV^{\beta} + \sum_{i} \mu_{i} n_{i}^{\beta}$$
(2.1.2)

The corresponding expression for the thermodynamic energy of the interfacial region $\boldsymbol{\sigma}$ is

$$U^{\sigma} = TS^{\sigma} + \gamma A + \sum_{i} \mu_{i} n_{i}^{\sigma}$$
 (2.1.3)

For any infinitesimal change in T, S, A, μ , *n*, differentiation of Eq. 2.1.3 gives

$$dU^{\sigma} = TdS^{\sigma} + S^{\sigma}dT + \gamma dA + Ad\gamma + \sum_{i} \mu_{i} dn_{i}^{\sigma} + \sum_{i} n_{i}^{\sigma} d\mu_{i}$$
(2.1.4)

For a small, isobaric, isothermal, reversible change the differential total internal energy in any bulk phase is

$$dU = TdS - PdV + \sum_{i} \mu_{i} dn_{i}$$
(2.1.5)

similarly for the differential internal energy in the interfacial region

$$dU^{\sigma} = TdS^{\sigma} + \gamma dA + \sum_{i} \mu_{i} dn_{i}^{\sigma}$$
(2.1.6)

subtracting Eq. 2.1.6 from 2.1.4 leads to

$$S^{\sigma}dT + Ad\gamma + \sum_{i} n_{i}^{\sigma}d\mu_{i} = 0$$
(2.1.7)

Then at constant temperature, with the surface excess of component *i*, Γ_i^{σ} , as defined in Eq. 2.1.1, the general form of the Gibbs equation is

$$d\gamma = -\sum_{i} \Gamma_{i}^{\sigma} d\mu_{i}$$
 (2.1.8)

For a simple system consisting of a solvent and a solute, denoted by the subscripts 1 and 2 respectively, then Eq. 2.1.8 reduces to

$$d\gamma = -\Gamma_1^{\sigma} d\mu_1 - \Gamma_2^{\sigma} d\mu_2$$
(2.1.9)

Considering the choice of the Gibbs dividing surface position, i.e., so that $\Gamma_1^{\sigma} = 0$, then Eq. 2.1.9 simplifies to

$$d\gamma = -\Gamma_2^{\sigma} d\mu_2 \tag{2.1.10}$$

where Γ_2^{σ} is the solute surface excess concentration.

The chemical potential is given by

 $\mu_i = \mu_i^{o} + RT \ln a_i$ so at constant temperature $d\mu_i = cste + RTd \ln a_i$ (2.1.11)

where μ_i° is the standard chemical potential of component *i*.

Therefore applying to Eq. 2.1.10 gives the common form of the Gibbs equation for non-dissociating materials (e.g., non-ionic surfactants)

$$d\gamma = -\Gamma_2^{\sigma} R T d \ln a_2 \qquad (2.1.12)$$

 $\Gamma_2^{\sigma} = -\frac{1}{RT} \frac{d\gamma}{d\ln a_2}$ (2.1.13)

For dissociating solutes, such as ionic surfactants of the form R^-M^+ and assuming ideal behaviour below the CMC, Eq. 2.1.12 becomes

$$d\gamma = -\Gamma_R^{\sigma} d\mu_R - \Gamma_M^{\sigma} d\mu_M \qquad (2.1.14)$$

If no electrolyte is added, electroneutrality of the interface requires that $\Gamma_R^{\sigma} = \Gamma_M^{\sigma}$. Using the mean ionic activities so that $a_2 = (a_R a_M)^{1/2}$ and substituting in Eq. 2.1.14 gives the Gibbs equation for 1:1 dissociating compounds

$$\Gamma_2^{\sigma} = -\frac{1}{2RT} \frac{d\gamma}{d\ln a_2}$$
(2.1.15)

If swamping electrolyte is introduced (i.e., sufficient salt to make electrostatic effects unimportant) and the same gegenion M^+ as the surfactant is present, then the activity of M^+ is constant and the pre-factor becomes unity, so that Equation 2.1.13 is appropriate.

For materials that are strongly adsorbed at an interface such as surfactants, a dramatic reduction in interfacial (surface) tension is observed with small changes in bulk phase concentration. The practical applicability of this relationship is that the relative adsorption of a material at an interface, its surface activity, can be determined from measurement of the interfacial tension as a function of solute concentration. Note that in Eq. 2.1.13 and 2.1.15, for dilute surfactant systems, the concentration can be substituted for activity without loss of generality.

or

Figure 2.2 shows a typical decay of surface tension of water on increase in surfactant concentration, and how the Gibbs equation (Eq. 2.1.13 or 2.1.15) is used to quantify adsorption at the surface. At low concentrations a gradual decay in surface tension is observed (from the surface tension of pure water i.e., 72.5 mN m⁻¹ at 25 °C) corresponding to an increase in the surface excess of component 2 (region A to B). Then at concentrations close to the CMC, the adsorption tends to a limiting value so the surface tension curve may appear to be essentially linear (region B to C). However, in practice, for most surfactants in the pre-CMC region the γ -In c is curved so that the local tangent $-d\gamma/dln$ c is proportional to Γ_2^{σ} via Eq. 2.1.13 or 2.1.15. For single-chain, pure surfactants typical values for Γ_2^{σ} at the CMC are in the range 2 – 4 x 10⁻⁶ mol m⁻², with the associated limiting molecular areas being from 0.4 – 0.6 nm². **Figure 2.2** Determination of the interfacial adsorption isotherm from surface tension measurement and the Gibbs adsorption equation.



The value for the Gibbs pre-factor in the case of ionic surfactants has been a matter of discussion (e.g., refs. 10-13). Of particular concern is the question whether, in the case of ionics, complete dissociation occurs giving rise to a pre-factor of 2, or a depletion layer in the sub-surface could be present so that a somewhat lower pre-factor could be expected. Recent detailed experiments combining tensiometry and neutron reflectivity, which enables direct measurement of the surface excess (as detailed in Chapter 4), have confirmed the use of a pre-factor of 2 in the case of ionics [14].

Although the Gibbs equation is the most commonly used mathematical relation for adsorption at liquid-liquid and liquid-gas interfaces, other adsorption isotherms have been proposed such as the Langmuir [15], the Szyszkowski [16] and the Frumkin [17] equations. The Gibbs equation itself has been simplified by Guggenheim and Adam with the choice of a different dividing plane and where the interfacial region is considered as a separate bulk phase (of finite volume) [18].

2.1.3 Efficiency and effectiveness of surfactant adsorption

The performance of a surfactant in lowering the surface tension of a solution can be discussed in terms of (1) the concentration required to produce a given surface tension reduction and (2) the maximum reduction in surface tension that can be obtained regardless of the concentration. These are referred to as the surfactant *efficiency* and *effectiveness* respectively.

A good measure of the *surfactant adsorption efficiency* is the concentration of surfactant required to produce a 20 mN m⁻¹ reduction in surface tension. At this value the surfactant concentration is close to the minimum concentration needed to produce maximum adsorption at the interface. This is confirmed by the Frumkin adsorption equation (2.1.16), which

relates the reduction in surface tension (or surface pressure π) and surface excess concentration.

$$\gamma_0 - \gamma = \pi = -2.303 \text{RT} \, \Gamma_{\text{m}} \log \left(1 - \frac{\Gamma_1}{\Gamma_{\text{m}}} \right)$$
 (2.1.16)

The maximum surface excess generally lies in the range $1 - 4.4 \times 10^{-10}$ mol cm⁻² [19]: solving Eq. 2.1.16 indicates that when the surface tension has been reduced by 20 mN m⁻¹, at 25°C, the surface is 84 – 99.9% saturated. The negative logarithm of such concentration, pC₂₀, is then a useful quantity since it can be related to the free energy change ΔG° involved in the transfer of a surfactant molecule from the interior of the bulk liquid phase to the interface. The surfactant adsorption efficiency thus relates to the structural groups in the molecule via the standard free energy change of the individual groups (i.e., free energies of transfer of methylene, terminal methyl, and head groups). In particular, for a given homologous series of straight-chain surfactants in water, CH₃(CH₂)_{*n*}-M, where M is the hydrophilic head group and *n* is the number of methylene units in the chain, and when the systems are at $\pi = 20$ mN m⁻¹, the standard free energy of adsorption is

$$\Delta G^{\circ} = n \Delta G^{\circ}(-CH_2-) + \Delta G^{\circ}(M) + \Delta G^{\circ}(CH_3-)$$
(2.1.17)

Then the adsorption efficiency is directly related to the length of the hydrophobic chain (the hydrophilic group remains the same), viz.

$$-\log(C)_{20} = pC_{20} = n \left[\frac{-\Delta G^{\circ}(-CH_2 -)}{2.303 RT} \right] + \text{constant}$$
 (2.1.18)

 $\Delta G^{\circ}(M)$ is considered as a constant and it is assumed that Γ_m does not differ significantly with increasing chain length, and that activity coefficients are unity. The efficiency factor pC₂₀ therefore increases linearly with the number of carbon atoms in the hydrophobic chain. This is also described by Traube's rule [20] (Eq. 2.1.19).

$$\log C_{\rm s} = B - n \log K_{\rm T} \tag{2.1.19}$$

 C_s is the surfactant concentration, B is a constant, *n* is the chain length within a homologous series and K_T is Traube's constant. For hydrocarbon straight chain surfactants K_T is usually around 3 [21] or by analogy to Eq. 2.1.18 is given by

$$\frac{C_n}{C_{n+1}} = K_T = \exp\left[\frac{-\Delta G^{\circ}(-CH_2 -)}{2RT}\right]$$
(2.1.20)

For compounds having a phenyl group in the hydrophobic chain it is equivalent to about three and one-half normal $-CH_2$ - groups.

The larger pC_{20} the more efficiently the surfactant is adsorbed at the interface and the more efficiently it reduces surface tension. The other main factors that contribute to an increase in surfactant efficiency are summarised below:

- A straight alkyl chain as the hydrophobic group, rather than a branched alkyl chain containing the same number of carbon atoms.
- A single hydrophilic group situated at the end of the hydrophobic group, rather than one (or more) at a central position.
- A non-ionic or zwitterionic hydrophilic group, rather than an ionic one.

 For ionic surfactants, a reduction in the effective charge by (a) use of a more tightly bound (less hydrated) counterion and (b) increase in ionic strength of the aqueous phase.

The choice of 20 mN m⁻¹ as a standard value of surface tension lowering for the definition of adsorption efficiency is convenient but somewhat arbitrary, and is not valid for systems where surfactants differ significantly in maximum surface excess or when the surface pressure is less than 20 mN m⁻¹. Pitt *et al.* [22] circumvented this problem by defining $\Delta\gamma$ as half the surface pressure at the CMC.

The performance of a surfactant can also be discussed in terms of *effectiveness of adsorption*. This is usually defined as the maximum lowering of surface tension γ_{min} regardless of concentration, or as the surface excess concentration at surface saturation Γ_m since it represents the maximum adsorption. γ_{min} , and Γ_m , are controlled mainly by the critical micelle concentration, and for certain ionics by the solubility limit or Krafft temperature T_k , which will be described briefly in Section 2.2.1. The effectiveness of adsorption is an important factor in determining such properties as foaming, wetting, and emulsification, since Γ_m through the Gibbs adsorption equation gives a measure of the interfacial packing.

The efficiency and effectiveness of surfactants do not necessarily run parallel, and it is commonly observed – as shown by Rosen's extensive data listing [19] – that materials producing significant lowering of the surface tension at low concentrations (i.e., they are more efficient) have smaller Γ_m (i.e., they are less effective). In determining surfactant efficiency the role of the molecular structure is primarily thermodynamic, while its role in effectiveness is directly related to the relative size of the hydrophilic and hydrophobic portions of the adsorbing molecule. The area occupied by each molecule is determined either by the hydrophobic chain cross-sectional area, or the area required for closest

packing of head groups, whichever is greater. Therefore, surfactant films can be tightly or loosely packed resulting in very different interfacial properties. For instance, straight chains and large head groups (relative to the tail cross section) favour close, effective packing, while branched, bulky, or multiple hydrophobic chains give rise to steric hindrance at the interface. On the other hand, within a series of single straight chain surfactants, increasing the hydrocarbon chain length from C8 to C20 will have little effect on adsorption effectiveness. [19]

2.2 SURFACTANT SOLUBILITY

In aqueous solution, when all available interfaces are saturated, the overall energy reduction may continue through other mechanisms. Depending on the system composition, a surfactant molecule can play different roles in terms of aggregation (formation of micelles, liquid crystal phases, bilayers or vesicles, etc). The physical manifestation of one such mechanism is crystallisation or precipitation of surfactant from solution – that is, bulk-phase separation. While most common surfactants have a substantial solubility in water, this can change significantly with variations in hydrophobic tail length, head group nature, counterion valence, solution environment, and most importantly, temperature.

2.2.1 The Krafft temperature

As for most solutes in water, increasing temperature produces an increase in solubility. However, for ionic surfactants, which are initially insoluble, there is often a temperature at which the solubility suddenly increases very dramatically. This is known as the Krafft point or Krafft temperature, T_K , and is defined as the intersection of the solubility and the CMC curves, i.e., it is the temperature at which the solubility of the monomeric surfactant is equivalent to its CMC at the same temperature. This is illustrated in Figure 2.3. Below T_K , surfactant monomers only exist in equilibrium with the

hydrated crystalline phase, and above T_K , micelles are formed providing much greater surfactant solubility.

The Krafft point of ionic surfactants is found to vary with counterion [23], alkyl chain length and chain structure. Knowledge of the Krafft temperature is crucial in many applications since below T_K the surfactant will clearly not perform efficiently; hence typical characteristics such as maximum surface tension lowering and micelle formation cannot be achieved. The development of surfactants with a lower Krafft point but still being very efficient at lowering surface tension (i.e., long chain compounds) is usually achieved by introducing chain branching, multiple bonds in the alkyl chain or bulkier hydrophilic groups thereby reducing intermolecular interactions that would tend to promote crystallisation.

Figure 2.3 The Krafft temperature T_K is the point at which surfactant solubility equals the critical micelle concentration. Above T_K , surfactant molecules form a dispersed phase; below T_K , hydrated crystals are formed.



Temperature / °C

2.2.2 The Cloud point

For non-ionic surfactants, a common observation is that micellar solutions tend to become visibly turbid at a well-defined temperature. This is often referred to as the cloud point, above which the surfactant solution phase separates. Above the cloud point, the system consists of an almost micelle-free dilute solution at a concentration equal to its CMC at that temperature, and a surfactant-rich micellar phase. This separation is caused by a sharp increase in aggregation number and a decrease in intermicellar repulsions [24, 25] that produces a difference in density of the micelle-rich and micelle-poor phases. Since much larger particles are formed, the solution becomes visibly turbid with large micelles efficiently scattering light. As with Krafft temperatures, the cloud point depends on chemical structure. For polyoxyethylene (PEO) non-ionics, the cloud point increases with increasing EO content for a given hydrophobic group, and at constant EO content it may be lowered by decreasing the hydrophobe size, broadening the PEO chain-length distribution, and branching in the hydrophobic group [26].

2.3 MICELLISATION

In addition to forming oriented interfacial monolayers, surfactants can aggregate to form *micelles*, provided their concentration is sufficiently high. They are typically clusters of between 50–200 surfactant molecules, whose size and shape are governed by geometric and energetic considerations. Micelle formation occurs over a fairly sharply defined region called the *critical micelle concentration* (CMC). Above the CMC, additional surfactant forms the aggregates, whereas the concentration of the unassociated monomers remains almost constant. As a result, a rather abrupt change in concentration dependence at much the same point can be observed in common equilibrium or transport properties (Figure 2.4).

Figure 2.4 Schematic representation of the concentration dependence of some physical properties for solutions of a micelle-forming surfactant.



surfactant concentration

2.3.1 Thermodynamics of micellisation

Micelles are dynamic species, in that there is a constant, rapid interchange – typically on a microsecond timescale – of molecules between the aggregate and solution pseudo-phases. This constant formation-dissociation process relies on a subtle balance of interactions. These come from contacts between (1) hydrocarbon chain – water, (2) hydrocarbon – hydrocarbon chains, (3) head group – head group, and (4) from solvation of the head group. Therefore, the net free energy change upon micellisation, ΔG_m , can be written as

 $\Delta G_{m} = \Delta G(HC) + \Delta G(contact) + \Delta G(packing) + \Delta G(HG)(2.3.1)$

where

- ∆G(HC) is the free energy associated with transferring hydrocarbon chains out of water and into the oil-like interior of the micelle.
- ∆G(contact) is a surface free energy attributed to solvent-hydrocarbon contacts in the micelle.
- ∆G(packing) is a positive contribution associated with confining the hydrocarbon chain to the micelle core.
- ∆G(HG) is a positive contribution associated with head group interactions, including electrostatic as well as head group conformation effects.

Aggregation of surfactant molecules partly results from the tendency of the hydrophobic groups to minimise contacts with water by forming oily microdomains within the solvent. There, alkyl – alkyl interactions are maximised, while hydrophilic head groups remain surrounded by water. The traditional picture of micelle formation thermodynamics is based on the Gibbs-Helmholtz equation ($\Delta G_m = \Delta H_m - T\Delta S_m$). At room temperature the process is characterised by a small, positive enthalpy, ΔH_m , and a large, positive entropy of micellisation, ΔS_m . The latter is considered as the main contribution to the negative ΔG_m value, and so has led to the controversial idea that micellisation is an entropy-driven process. High positive values of ΔS_m are indeed surprising since aggregation, in terms of configurational entropy, should result in a negative contribution (i.e., formation of ordered aggregates from free surfactant monomers). In addition, large values of ΔH_m would have been expected since hydrocarbon groups have very little solubility in water, and consequently a high enthalpy of solution.

One mechanism that accounts for such conflicts is that when alkyl groups are surrounded by water, the H₂O molecules form clathrate cavities (i.e., stoichiometric crystalline solids in which water forms cages around solutes), thereby increasing either the strength or number of effective hydrogen bonds [27]. Therefore, the predominant effect of the hydrocarbon molecule is to increase the degree of structure in the immediately surrounding water. This is one of the main features of the *hydrophobic effect*, a subject that was explored in detail by Tanford [1] to account for the very slight solubility of hydrocarbons in water. During the formation of micelles, the reverse process occurs: as lyophobic residues aggregate, the highly structured water around each chain collapses back to ordinary bulk water thereby accounting for the apparent large overall gain in entropy, ΔS_m . This water-structure effect was also invoked by other researchers [28, 29].

Such an interpretation, however, has been strongly challenged by more recent studies of aqueous systems at high temperatures (up to 166°C) and micellisation in hydrazine solutions [30]. In these systems water loses most of its peculiar structural properties and the formation of structured water around lyophobic species is no longer possible.

The mechanism of micelle formation from surfactant monomers, S, can be described by a series of step-wise equilibria:

 $S + S \xleftarrow{K_2} S_2 + S \xleftarrow{K_3} S_3 \dots \xleftarrow{K_n} S_n + S \xleftarrow{} \dots$ (2.3.2)

with equilibrium constants K_n for $n = 2 - \infty$, and where the various thermodynamic parameters (ΔG° , ΔH° , ΔS°) for the aggregation process can be expressed in terms of K_n . However, each K_n cannot be measured individually, so different approaches have been proposed to model the energetics of the process of self-association. Although not totally accurate, two simple models are generally encountered: the closed-association and the phase separation models. In the closed-association model, with the size range of spherical micelles around the CMC being very limited, it is assumed that only one of K_n value is dominant, and micelles and monomeric species are considered to be in chemical equilibrium.

$$nS \longleftrightarrow S_n$$
 (2.3.3)

n is the number of molecules of surfactant, S, associating to form the micelle (i.e., the aggregation number). In the phase separation model, the micelles are considered to form a new phase within the system at and above the critical micelle concentration, and

$$nS \longleftrightarrow mS + S_n$$
 (2.3.4)

where *m* is the number of free surfactant molecules in the solution and S_n the new phase. In both cases, equilibrium between monomeric surfactant and micelles is assumed with a corresponding equilibrium constant, K_m , given by

$$K_{m} = \frac{[\text{micelles}]}{[\text{monomers}]^{n}} = \frac{[S_{n}]}{[S]^{n}}$$
(2.3.5)

where brackets indicate molar concentrations and *n* is the number of monomers in the micelle, the aggregation number. Although micellisation is itself a source of non-ideality [31, 32], it is assumed in Eq. 2.3.5 that activities may be replaced by concentrations.

From Eq. 2.3.5, the standard free energy of micellisation per mole of micelles is given by

$$\Delta G_{m}^{\circ} = -RT \ln K_{m} = -RT \ln S_{n} + nRT \ln S \qquad (2.3.6)$$

while the standard free energy change per mole of surfactant is

$$\frac{\Delta G_{m}^{\circ}}{n} = -\frac{RT}{n} \ln S_{n} + RT \ln S$$
 (2.3.7)

Assuming n is large (\sim 100) the first term on the right side of Eq. 2.3.7 can be neglected, and an approximate expression for the free energy of micellisation per mole of a neutral surfactant becomes

$$\Delta G_{M,m}^{o} \approx RT \ln(CMC)$$
 (2.3.8)

In the case of ionic surfactants, the presence of the counterion and its degree of association with the monomer and micelle must be considered. The massaction equation becomes

$$nS^{x} + (n-p)C^{y} \leftrightarrow S^{a}_{n}$$
(2.3.9)

where C is the concentration of free counterions. The degree of dissociation of the surfactant molecules in the micelle, α , the micellar charge, is given by $\alpha = p/n$.

The ionic equivalent to Eq. 2.3.5 is then

$$K_{m} = \frac{[S_{n}]}{[S^{x}]^{n} \times [C^{y}]^{(n-p)}}$$
(2.3.10)

where p is the concentration of free counterions associated with, but not bound to the micelle. The standard free energy of micelle formation becomes

$$\Delta \mathbf{G}_{\mathbf{m}}^{\circ} = -\mathbf{RT}\left\{\ln[\mathbf{S}_{n}] - n\ln[\mathbf{S}^{x}] - (n-p)\ln[\mathbf{C}^{y}]\right\}$$
(2.3.11)

At the CMC $[S^{-}(^{+})] = [C^{+}(^{-})] = CMC$ for a fully ionised surfactant, and the standard free energy change per mole of surfactant can be obtained from the approximation:

$$\Delta G_{M,m}^{\circ} \approx \mathrm{RT}\left(2 - \frac{p}{n}\right) \ln(\mathrm{CMC})$$
 (2. 3.12)

When the ionic micelle is in a solution of high electrolyte content, the situation described by Eq. 2.3.12 reverts to the simple non-ionic case given by Eq. 2.3.8.

From the Gibbs function and second law of thermodynamics, ΔS° for non-ionic surfactants is given as

$$\Delta S^{\circ} = -\frac{d(\Delta G^{\circ})}{dT} = -RT \frac{d\ln(CMC)}{dT} - R\ln(CMC)$$
 (2.3.13)

From the Gibbs function and Eq. 2.3.8 and 2.3.13, the enthalpy of micellisation for non-ionic surfactants, ΔH° , is given by

$$\Delta H^{\circ} = \Delta G^{\circ} + T\Delta S^{\circ} = -RT^{2} \frac{dln(CMC)}{dT}$$
(2.3.14)

and similarly for ionics,

$$\Delta H^{\circ} = -RT^{2} \left(2 - \frac{p}{n}\right) \frac{d\ln(CMC)}{dT}$$
 (2.3.15)

Both the phase separation and closed association models have disadvantages. One difficulty is activity coefficients: assuming ideality can be erroneous considering the large effective micelle size and charge in comparison to dilute solutions of surfactant monomers. However, the model described above is useful enough to be applied to the systems presented in this study. Another disadvantage is the assumption of micellar monodispersity. To counteract this problem, the multiple equilibrium model was proposed, which is an extension of the closed association model. It allows a distribution function of aggregation numbers in micelles to be calculated. A full account of this model and its derivation can be found in references [33-35].

2.3.2 Factors affecting the CMC

Many factors are known to affect strongly the CMC. Of major effect is the structure of the surfactant, as will be described below. Also important, but to a lesser extent, are parameters such as counterion nature, presence of additives and change in temperature.

The hydrophobic group: the 'tail'

The length of the hydrocarbon chain is a major factor determining the CMC. For a homologous series of linear single-chain surfactants the CMC decreases logarithmically with carbon number. The relationship usually fits the Klevens equation [36]

$$\log_{10}(CMC) = A - Bn_c$$
 (2.3.16)

where *A* and *B* are constants for a particular homologous series and temperature, and n_c is the number of carbon atoms in the chain, C_nH_{2n+1} . The constant *A* varies with the nature and number of hydrophilic groups, while *B* is constant and approximately equal to $log_{10} 2$ ($B \approx 0.29 - 0.30$) for all paraffin chain salts having a single ionic head group (i.e., reducing the CMC to approximately one-half per each additional -CH₂- group).

Interestingly, for straight-chain dialkyl sulfosuccinates Eq. 2.3.16 is still valid [37] and $B \approx 0.62$, which essentially doubles the value for the single chain compounds. Alkyl chain branching and double bonds, aromatic groups or some

other polar character in the hydrophobic part produce noticeable changes in CMC. In hydrocarbon surfactants, chain branching gives a higher CMC than a comparable straight chain surfactant [19], and introduction of a benzene ring in the chain is equivalent to about 3.5 carbon atoms.

The hydrophilic group

For surfactants with the same hydrocarbon chain, varying the hydrophile nature (i.e., from ionic to non-ionic) has an important effect on the CMC values. For instance, for a C12 hydrocarbon the CMC with an ionic head group lies in the range of 1×10^{-3} mol dm⁻³, while a C12 non-ionic material exhibits a CMC in the range of 1×10^{-4} mol dm⁻³. The exact nature of the ionic group, however, has no dramatic effect, since a major driving force for micelle formation is the entropy factor discussed above.

Counterion effects

In ionic surfactants micelle formation is related to the interactions of solvent with the ionic head group. Since electrostatic repulsions between ionic groups are greatest for complete ionisation, an increase in the degree of ion binding will decrease the CMC. For a given hydrophobic tail and anionic head group, the CMC decreases as $Li^+ > Na^+ > K^+ > Cs^+ > N(CH_3)_4^+ > N(CH_2CH_3)_4^+$ > $Ca^{2+} \approx Mg^{2+}$. For cationic series such as the dodecyltrimethylammonium halides, the CMC decreases in the order $F^- > Cl^- > Br^- > I$. In addition, varying counterion valency produces a significant effect. Changing from monovalent to di- or trivalent counterions produces a sharp decrease in the CMC.

Effect of added salt

The presence of an indifferent electrolyte causes a decrease in the CMC of most surfactants. The greatest effect is found for ionic materials. The principal effect of the salt is to partially screen the electrostatic repulsion between the head groups and so lower the CMC. For ionics, the effect of adding electrolyte can be empirically quantified viz.

$$\log_{10}(CMC) = -a \log_{10} C_{i} + b$$
 (2.3.17)

Non-ionic and zwitterionic surfactants display a much smaller effect and Eq. 2.3.17 does not apply.

Effect of temperature

The influence of temperature on micellisation is usually weak, reflecting subtle changes in bonding, heat capacity and volume that accompany the transition. This is, however, quite a complex effect. It was shown, for example, that the CMC of most ionic surfactants passes through a minimum as the temperature is varied from 0 to 70°C [38]. As already mentioned (Section 2.2), the major effects of temperature are the Krafft and cloud points.

2.3.3 Structure of micelles and molecular packing

Early studies [39,40] showed that, with ionic single alkyl chain compounds spherical micelles form. In particular, in 1936 Hartley [41] described such micelles as spherical aggregates whose alkyl groups form a hydrocarbon liquid-like core, and whose polar groups form a charged surface. Later, with the development of zwitterionic and non-ionic surfactants, micelles of very different shapes were encountered. The different geometries were found to depend mainly on the structure of the surfactant, as well as environmental conditions (e.g., concentration, temperature, pH, electrolyte content).

In the micellisation process, molecular geometry plays an important role and it is essential to understand how surfactants can pack. The main structures encountered are spherical micelles, vesicles, bilayers, or inverted micelles. As described previously, two opposing forces control the self-association process: hydrocarbon – water interactions that favour aggregation (i.e., pulling

surfactant molecules out of the aqueous environment), and head group interactions that work in the opposite sense. These two contributions can be considered as an attractive interfacial tension term due to hydrocarbon tails and a repulsion term depending on the nature of the hydrophilic group. More recently, this basic idea was reviewed and quantified by Mitchell and Ninham [42] and Israelachvili [43], resulting in the concept that aggregation of surfactants is controlled by a balanced molecular geometry. In brief, the geometric treatment separates the overall free energy of association to three critical geometric terms (Figure 2.5):

- the minimum interfacial area occupied by the head group, *a*₀;
- the volume of the hydrophobic tail(s), *v*,
- the maximum extended chain length of the tail in the micelle core, l_c .

Formation of a spherical micelle requires l_c to be equal to or less than the micelle core radius, R_{mic} . Then for such a shape, an aggregation number, N, can be expressed either as the ratio of micellar core volume, V_{mic} , and that for the tail, ν .

$$N = V_{\rm mic} / v = \left[(4/3)\pi R_{\rm mic}^3 \right] / v$$
 (2.3.18)

or as the ratio between the micellar area, A_{mic} , and the cross-sectional area, a_0 :

$$N = A_{\rm mic} / a_{\rm o} = \left[4\pi R_{\rm mic}^2 \right] / a_{\rm o}$$
 (2.3.19)

Equating Eq. 2.3.18 and 2.3.19

$$v/(a_0 R_{\rm mic}) = 1/3$$
 (2.3.20)

Since l_c cannot exceed R_{mic} for a spherical micelle

$$v/(a_0 l_c) \le 1/3$$
 (2.3.21)

More generally, this defines a critical packing parameter, P_c , as the ratio of volume to surface area:

$$P_{\rm c} = v/(a_{\rm o}l_{\rm c})$$
 (2.3.22)

The parameter v varies with the number of hydrophobic groups, chain unsaturation, chain branching and chain penetration by other compatible hydrophobic groups, while a_0 is mainly governed by electrostatic interactions and head group hydration. P_c is a useful quantity since it allows the prediction of aggregate shape and size. The predicted aggregation characteristics of surfactants cover a wide range of geometric possibilities, and the main types are presented in Table 2.1 and Figures 2.6 and 2.7.

Table 2.1 Expected aggregate characteristics in relation to surfactant critical packing parameter, $P_c = v/a_o/c$

P _c	General Surfactant type	Expected Aggregate Structure
< 0.33 Singl	e-chain surfactants with large ad groups	Spherical or ellipsoidal micelles
0.33 - 0.5 Singl	le-chain surfactants with small ad groups, or ionics in the presence	Large cylindrical or rod-shaped micelles
of	large amounts of electrolyte	Vesicles and flexible bilayers structures
0.5 - 1.0 Dout	ple-chain surfactants with large	
he	ad groups and flexible chains	Planar extended bilayers
1.0 Dout	ple-chain surfactants with small	
he	ad groups or rigid, immobile chains	Reversed or inverted micelles
>1.0 Dout	ple-chain surfactants with small	
he	ad groups, very large and bulky	
hy	drophobic groups	

Figure 2.5 The critical packing parameter P_c (or surfactant number) relates the head group area, the extended length and the volume of the hydrophobic part of a surfactant molecule into a dimensionless number $P_c = v/a_0/c$.



Figure 2.6 Changes in the critical packing parameters (P_c) of surfactant molecules give rise to different aggregation structures.



2.4 LIQUID CRYSTALLINE MESOPHASES

Micellar solutions, although the subject of extensive studies and theoretical considerations, are only one of several possible aggregation states. A complete understanding of the aqueous behaviour of surfactants requires knowledge of the entire spectrum of self-assembly. The existence of liquid crystalline phases constitutes an equally important aspect and a detailed description can be found in the literature [e.g. 44, 45]. The common features of liquid crystalline phases are summarised below.

2.4.1 Definition

When the volume fraction of surfactant in a micellar solution is increased, typically above a threshold of about 40%, a series of regular geometries is commonly encountered. Interactions between micellar surfaces are repulsive (from electrostatic or hydration forces), so that as the number of aggregates increases and micelles get closer to one another, the only way to maximise separation is to change shape and size. This explains the sequence of surfactant phases observed in the concentrated regime. Such phases are known as mesophases or lyotropic (solvent-induced) liquid crystals.

As the term suggests, liquid crystals are characterised by having physical properties intermediate between crystalline and fluid structures: the degree of molecular ordering is between that of a liquid and a crystal and in terms of rheology the systems are neither simple viscous liquids nor crystalline elastic solids. Certain of these phases have at least one direction that is highly ordered so that liquid crystals exhibit optical birefringence.

Two general classes are encountered depending on whether one is considering surfactants or other types of material. These are *thermotropic* liquid crystals, in which the structure and properties are determined by temperature (such as employed in LCD cells). For *lyotropic* liquid crystals structure is

determined by specific interactions between solute and solvent: surfactant liquid crystals are normally lyotropic.

2.4.2 Structures

The main structures associated with two-component surfactant–water systems are: hexagonal (normal or inverted), lamellar, and several cubic phases. Table 2.2 summarises the notations commonly associated with these phases and their structures are shown in Figure 2.7.

- The *hexagonal phase* is composed of a close-packed array of long cylindrical micelles, arranged in a hexagonal pattern. The micelles may be "normal" (in water, H₁) in that the hydrophilic head groups are located on the outer surface of the cylinder, or "inverted" (H₂), with the hydrophilic group located internally. Since all the space between adjacent cylinders is filled with hydrophobic groups, the cylindrical micelles are more closely packed than those found in the H₁ phase. As a result, H₂ phases occupy a much smaller region of the phase diagram and are much less common.
- The *lamellar phase* (L_{α}) is built up of alternating water-surfactant bilayers. The hydrophobic chains possess a significant degree of randomness and mobility, and the surfactant bilayer can range from being stiff and planar to being very flexible and undulating. The level of disorder may vary smoothly or change abruptly, depending on the specific system, so that it is possible for a surfactant to pass through several distinct lamellar phases.
- The *cubic phase* may have a wide variety of structural variations and occurs in many different parts of the phase diagram. These are optically isotropic systems and so cannot be characterised by polarising light microscopy. Two main groups of cubic phases have been identified:

- The micellar cubic phases (I₁ and I₂) built up of regular packing of small micelles (or reversed micelles in the case of I₂). The micelles are short prolates arranged in a body-centred cubic close-packed array [46,47].
- ii. The bicontinuous cubic phases (V₁ and V₂) are thought to be rather extended, porous, connected structures in three dimensions. They are considered to be formed by either connected rod-like micelles, similar to branched micelles, or bilayer structures. Denoted V₁ and V₂, they can be normal or reverse structures and are positioned between H₁ and L_{α} and between L_{α} and H₂ respectively.

In addition to having different structures these common forms also show different viscosities, in the order

Cubic > Hexagonal > Lamellar

Cubic phases are generally the more viscous since they have no obvious shear plane and so layers of surfactant aggregates cannot slide easily relative to each other. Hexagonal phases typically contain 30-60% water by weight but are very viscous since cylindrical aggregates can move freely only along their length. Lamellar phases are generally less viscous than the hexagonal phases due to the ease with which each parallel layers can slide over each other during shear.

Table 2.2Most common lyotropic liquid crystalline and other phases foundin binary surfactant–water systems.

Phase structure	Symbol	Other names
Lamellar	L_{α}	Neat
Hexagonal	H_1	Middle
Reversed hexagonal	H ₂	
Cubic (normal micellar)	I ₁	Viscous isotropic
Cubic (reversed micellar)	I_2	
Cubic (normal bicontinuous)	\mathbf{V}_{1}	Viscous isotropic
Cubic (reversed bicontinuous)	V ₂	
Micellar	L_1	
Reversed micellar	L_2	

Figure 2.7 common surfactant liquid crystalline phases. See Table 2.2 for identification.



2.4.3 Phase diagrams

The sequence of mesophases can be identified simply by using a polarising microscope and the isothermal technique known as a phase cut. Briefly, starting from a small amount of surfactant, a concentration gradient is set up spanning the entire phase diagram, from pure water to pure surfactant. Since crystal hydrates and some of the liquid crystalline phases are birefringent, viewing in the microscope between crossed polars shows up the complete sequence of mesophases.

Transformations between different mesophases are controlled by a balance between molecular packing geometry and inter-aggregate forces. As a result, the system characteristics are highly dependent on the nature and amount of solvent present. Generally, the main types of mesophases tend to occur in the same order and in roughly the same position in the phase diagram. Figure 2.8 shows a classic binary phase diagram of a non-ionic surfactant $C_{16}EO_8$ -water. The sequence of phases is common to most non-ionic surfactants of the kind C_iE_j , although the positions of the phase boundaries, in terms of temperature and concentration limits, depend somewhat on the chemical identity of the surfactant.

Figure 2.8 Phase diagram for the non-ionic $C_{16}EO_8$ illustrating the various liquid crystalline phases. L₁ and L₂ are isotropic solutions. See Table 2.2 for details of the other phases. (After Mitchell *et al. J. Chem. Soc. Faraday Trans. I* **1983**, *79*, 975).



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Appendix 1 – Tensiometric methods

Tensiometry is a very accessible method but only provides indirect determination of the surface excess via surface tension measurements and application of the Gibbs equation (see Section 2.1.2. equations 2.1.13 and 2.1.15). Below, the main features of drop volume and du Noüy ring tensiometry techniques are described.

Most techniques for measuring equilibrium surface tension involve stretching the liquid-air interface at the moment of measurement. Equilibrium surface tension can be obtained by measuring a force, pressure or drop size. The ring and plate methods both measure a force, whereas the capillary height and maximum bubble pressure methods rely on pressure. The pendant drop, sessile drop, drop volume, drop weight and spinning drop methods all measure one or more dimensions of a drop.

A.1. DU NOÜY RING TENSIOMETRY

The ring method [A1-A4] involves a platinum-iridium ring, attached to a vertical wire, being immersed horizontally into the liquid, see figure A.1 below.



Figure A.1 Schematic of Du Noüy ring

The surface tension is calculated from the force required to pull the ring through the interface. Assuming the ring supports a cylinder of liquid, the surface tension is given by

$$\gamma_{\rm eq} = \frac{F}{4\pi R} \tag{A.1}$$

where R is the radius of the ring. At equilibrium the maximum force is given by

$$F = (\rho_1 - \rho_2)gV \tag{A.2}$$

where ρ_1 and ρ_2 are densities of the liquid phase and the liquid or gas phase above it, g is acceleration due to gravity (9.81 ms⁻²), and V is the volume of liquid raised by the ring. For a dilute aqueous solution-air interface, ρ_1 is assumed to be the density of water, and ρ_2 , the density of air, so by measuring the weight of the liquid raised above the surface, the surface tension can be calculated.

However, the main disadvantage of the ring method is that a correction factor is required. This is because the liquid column lifted by the ring is not quite a cylinder, and that the balance measures the weight of the water lifted. This correction factor has been determined by Harkins and Jordan [A1] and is incorporated as follows:

$$\gamma_{\rm eq} = \gamma_{\rm eq}^* \cdot f = \frac{F}{4\pi R} \cdot f \tag{A.3}$$

where *f* is the dimensionless Harkins and Jordan Factor and γ_{eq} the measured value in mN m⁻¹

The correction factor can be determined by the equation published by Zuidema and Waters, based on an interpolation of the Harkins and Jordan correction factor tables (see A4).

$$f = 0.725 + \sqrt{\frac{0.01452 \cdot \gamma_{eq}^{*}}{\frac{1}{4}U^{2}(\rho_{1} - \rho_{2})} + 0.04534 - \frac{1.679}{R/r}}$$
(A.4)

where R is the mean ring radius (typically 10 mm), r is the radius of the crosssection of the wire (typically 0.2 mm), U is the wetting length (typically 120 mm)

A final correction is applied to allow for the calibration, done with reference to the surface tension for water at 20°C. The final correction factor, after inserting the known dimensions of the ring and assuming (ρ_1 - ρ_2) = 1 for a water-air interface, is now

$$fk = 1.07 \left(0.725 + \sqrt{4.036 \times 10^{-4} \cdot \gamma_{eq}^{*} + 1.28 \times 10^{-2}} \right)$$
(A.5)

A.2 DROP VOLUME TENSIOMETRY - DVT

The principle behind DVT is the determination of the maximum size of a drop formed at the end of a well-defined capillary. A modern commercial rig (e.g. Lauda TVT1 drop volume tensiometer) is fully automated and sophisticated dosing regimes can be selected so that dynamic surface tension may be followed. A full description of this method is given elsewhere [A2, A3]. Briefly, as shown in figure A.2, the stepper motor lowers a barrier onto a syringe plunger and causes a drop to form at the capillary tip. As the stepper motor continues the drop will grow until the weight of the drop acting downward (mg) exceeds the tension force acting upward $(2\pi r_{cap}\gamma)$. The drop will then detach from the capillary and a light sensor detects this movement. Hence the maximum volume of the drop, V, is related to the surface tension, γ , via equation A.6 [A4]

$$\gamma = \frac{V\Delta\rho g}{2\pi r_{cap}} f$$
 (A.6)

where $\Delta \rho$ is the density difference between the two phases, g is the acceleration due to gravity, and r_{cap} is the capillary radius; f is a correction

factor accounting for the point of drop detachment being not at the capillary tip but at its own neck [A5].



Figure A.2 Schematic of a drop volume tensiometer

A.3 CALCULATION OF ACTIVITY COEFFICIENTS

When studying the surface tension-concentration behaviour of ionic surfactants, activity rather than concentration should be used. Whilst in very dilute solution, i.e., below 1×10^{-3} mol dm⁻³, activity coefficients can safely be regarded as unity, at higher concentrations, i.e., above 1×10^{-3} mol dm⁻³, this assumption is no longer valid. Coulombic interactions between ions increase result in departure from ideal behaviour and require the use of Debye-Hückel theory to consider the effect of ionic strength. This is explained in detail in standard texts [A6, A7] and only relevant equations are given here. At very low electrolyte concentrations, the mean activity coefficient γ_{\pm} can be calculated from the Debye-Hückel limiting law

$$\log \gamma_{\pm} = -A |z_{+}z_{-}| I^{1/2}$$
 (A.7)

where z is the charge on the ion, I is the ionic strength and A is a constant. The form of I and the constant A are given below

$$I = \frac{1}{2} \sum_{i} m_{i} z_{i}^{2}$$
 (A.8)

$$A = \frac{F^3}{4\pi N_a \ln 10} \left(\frac{\rho}{2(\varepsilon_o \varepsilon_r RT)^3}\right)^{1/2}$$
(A.9)

where m is the molality, z is the charge valency, and ρ is the solvent density. F, N_a, R, ϵ_0 and ϵ_r are all standard physical constants.

For 1:1 electrolytes equation (A.7) is valid for concentrations below approximately 0.01 mol dm⁻³. For other valence types, or higher concentrations, the Debye-Hückel extended law must be used

$$\log \gamma_{\pm} = -\frac{A|z_{+}z_{-}|I^{1/2}}{1 + BaI^{1/2}}$$
(A.10)

where *a* is the mean effective ionic diameter which typically ranges from 3-9 Å [A8] and B is a constant given by

$$\mathbf{B} = \left(\frac{2F^2\rho}{\varepsilon_0\varepsilon_r RT}\right)^{1/2}$$
(A.11)

Equation (A.10) extends the validity of Debye-Hückel theory for 1:1 electrolytes up to concentrations of 0.1 mol dm⁻³ [A7]. For aqueous solutions at 298 K, A = $0.509 \text{ mol}^{-1/2} \text{ kg}^{1/2}$ and B = $3.282 \times 10^9 \text{ m}^{-1} \text{ mol}^{-1/2} \text{ kg}^{1/2}$.

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