

Study of Nano Sized Surfactant Aggregates and their Applications in the Bio-Physical Engineered Assemblies

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Abstract

This manuscript mainly deals with some models and concepts that are used to characterize the aggregational behavior of surfactant molecules. Thermodynamic and molecular approaches are also outlined in some detail in this paper. Micellar colloids are distinguished from other colloids by their association-dissociation equilibrium in solution between monomers, counter-ions and micelles. Surfactant solutions are unique solvent systems because the surfactant molecules form micelles in aqueous and non-aqueous solvents by self-assembly under the hydrophobic interaction with solvent molecules. According to classical thermodynamics, the standard Gibb's energy of formation of micelles at fixed temperature and pressure can be related to the critical micelle concentration (CMC). This relation is different for two models which are widely used to describe micelle formation, namely the Phase Separation and the Mass Action Models. The concept of molecular packing parameter is widely used to explain, rationalize and even predict molecular self-assembly in surfactant solutions. A particular value of the molecular packing parameter can be translated via simple geometrical relations into specific shape and size of the equilibrium aggregate. Surfactant solutions have attracted much attention from academia and industry because they play an important role in different industrial areas, e.g. chemical and oil industry, pharmaceutical and bio-industries, paper, emulsions, food and film industries.

Keywords

Self assembly, CMC, Surfactant, Phase separation, Pharmaceuticals etc.

I. INTRODUCTION

Surfactants are amphiphilic molecules containing both hydrophilic and hydrophobic parts. Because of the presence of hydrophilic and hydrophobic parts (Fig.1) they are compatible with water and oil both. At low concentrations, the solution

of ionic surfactant shows similar properties to those of simple electrolytes except that the surface tension which decreases rapidly with surfactant concentration. But at higher concentrations, unusual changes are recorded and suggest a changeover from a solution containing unimers to a situation where the surfactant occurs more and more in a self-assembled state. But this self-assembly does not occur at all concentrations. The concentration at which surfactant starts to form these self-assembled structures is known as "critical micelle concentration" abbreviated as CMC.

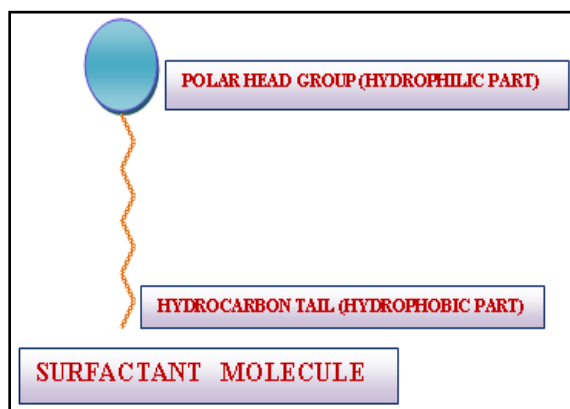


Fig. 1. Surfactant molecule

The CMC is the most important characteristic of a surfactant and can be measured by techniques like "surface tension" and "solubilization". Self-assembly gives various molecular architectures, depending upon the type of surfactant and the solution conditions. The first formed aggregates are generally approximately spherical in shape. The aggregates may also be globular or rod like or have the structure of spherical bilayers. The aggregates in which the interior is occupied by hydrophobic part is known as "micelle", while the closed aggregate with hydrophilic interior is known as "reverse micelle". As mentioned before, the

hydrophobic part is compatible with oil so there is a driving force for expelling them from the aqueous environment. It can be achieved either by macroscopic phase separation or by hiding the non-polar groups in some other way. When a polar group is attached to a hydrocarbon an opposing force is created, which counteracts phase separation. [1-5]

II. CRITICAL MICELLE CONCENTRATION

A. Phase separation model

Micelle formation is generally discussed in terms of phase separation model. CMC is the saturation condition of surfactant in the unimeric state. Surfactant addition above the CMC consequently only effects the micelle concentration, but not the unimer concentration. In many physicochemical investigations, it has been observed a number average over the different states that a surfactant molecule

can occupy. The phase separation model is particularly simple for interpretation of experimental observations. Below the CMC there are only unimers and the average of a quantity Q is simply

$$\langle Q \rangle = Q_{aq}$$

For a concentration above the CMC,

Since $C_{mic} = C_{tot} - CMC$ and $C_{aq} = CMC$

$$\langle Q \rangle = p_{mic} Q_{mic} + p_{aq} Q_{aq} = \frac{(1 - CMC/C_{tot})Q_{mix} + (CMC/C_{tot})Q_{aqu}}$$

For concentration, above CMC, $\langle Q \rangle$ approaches Q_{mic} .

Micelles are formed in a step wise process, so the elementary step is the equilibrium between a unimer and a micellar aggregate:



The basic concept behind the driving force of the micelle formation is the elimination of the contact between the alkyl chains and the water. Micelle, in a wide concentration range above the CMC viewed as microscopic liquid hydrocarbon droplets covered with the polar head groups, which are in interaction with water. The larger spherical micelle is more efficient, since the volume-to-area ratio increases. Decreasing the micelle size always leads to an increased hydrocarbon-water contact. It appears that the radius of the micelle core constituted of the alkyl chain is close to the extended length of the alkyl chain i.e. in the range of 1.5 to 3 nm. When a micelle radius equals the length of

an extended surfactant, molecule it does not mean that the surfactant molecules are extended. Only the surfactant molecule needs to be extended to fulfill the requirements mentioned. As such, the majority of the surfactant molecules are in the disordered state with many gauche conformations. Micelle may for many purposes be considered as a microscopic droplet of oil. This explains the large solubilization capacity towards a broad range of non-polar and weakly polar substances.

The number of surfactant molecules present in the micelle is known as “aggregation number”, it becomes a better approximation the higher the aggregation number, the greater the number of surfactant molecules in the micelle. Aggregation number is a related and equally important characteristic of a micelle, which is best determined in fluorescence quenching experiments. [6-12]

B. Mass action model

In fact, by analyzing experimental observations around the CMC using the “mass-action model” some information on the micelle aggregation numbers can be obtained. Based on the mass action law model and the general relation between the free energy change and the equilibrium constant

$$\Delta G^\circ = -RT \ln K$$

The approximate relation for the micelle formation:

$$\Delta G^\circ = -RT \ln CMC$$

Here ΔG° represents the free energy difference between a unimer in the micelle and some suitably chosen reference state. This is a convenient starting point for thermodynamic considerations.

As mentioned earlier, in polar solvents, aggregation results from the insolubility of the non-polar parts in water. The packing of the hydrocarbon chains result from the drive to minimize contact with water. Aggregation is opposed by the hydrophilic interaction, giving a repulsion between a polar head group on the micelle surface, the head groups will arrange themselves to minimize the unfavorable repulsions. The self-assembly of an amphiphile depends on the strength of an opposing force. It must be strong enough to compete with one alternative, which is macroscopic phase separation, but must also be limited in magnitude, since otherwise the unimeric state will be the most stable one. Examples of the head groups giving amphiphiles that are too weak are hydroxyl, aldehyde, ketone and amine groups. For a long chain

alcohol, macroscopic phase separation results rather than micelle formation.

For ionic surfactants, the counterion dissociation plays a great role. Because of the counterions, macroscopic phase separation becomes entropically very unfavorable and there is a very strong tendency to form small micelle. Co-solutes may affect amphiphile self-assembly in many different ways one of them being that they can stabilize the micelle by reducing the polar interactions.

For ionic surfactants:

- 1) neutralize the charges by adding an oppositely charged surfactant
- 2) screen the repulsions between head groups
- 3) rather even out the uneven counterion distribution by adding electrolyte
- 4) dilute the charges by introducing a non-ionic amphiphile, like a long chain alcohol

In all cases marked reduction of CMC and an increase in micelle size observed. [13-18]

III. INTERMOLECULAR INTERACTIONS

It is not sufficient to only consider the interaction between surfactant molecules because of the trivial fact that micelles don't form in the gas phase. The solvent plays a crucial role for the micellar aggregation and water in this respect is almost unique. Micelle can't form in a solvent with a low dielectric permittivity resulting in only a weak screening of the electrostatic repulsion between head groups. Because their interaction will depend on the dielectric permittivity of the solvent, which make the interaction temperature dependent, this type of interaction will be referred to as an effective pair potential. Effective potential are frequently encountered in chemistry, the hydrophobic interaction and the screened coulomb interaction are typical examples. [19-21]

IV. HYDROPHOBIC INTERACTIONS

Water interaction is comparably strong due to the hydrogen bonds formed between the water molecules. Hence introducing a non-polar molecule into water strongly disturbs the hydrogen bond network with a loss of interaction energy. The loss in interaction energy can be minimized if the water molecules around the solute adjust themselves, but the price has to be paid

in lowered entropy. As a consequence, the free energy of transfer of a nonpolar molecule into water at room temperature contains a large entropy contribution.

When dissolving non-polar molecules the hydrocarbon tail of the surfactant molecules will try to minimize the damage to the water hydrogen bond network by aggregating. The attractive interaction between two atoms is due to solvation effect i.e. the two atoms are pushed together by solvent. Thus the hydrophobic interaction is the mechanism that promotes the formation of micelle. The longer the hydrocarbon tail a surfactant molecule carries, the more easily it will aggregate, as indicated by the lowered CMC.

The hydrophobic interaction can be of considerable strength and is a delicate balance of energetic (enthalpic) and entropic terms.

$$G^{\text{transfer}} = \gamma 4\pi R^2$$

where γ is the interfacial tension and R the solute radius. The same type of expression can also be used to estimate the hydrocarbon interaction between two non-polar solutes at contact:

$$G \text{ (at contact)} \approx -\gamma 4\pi Rr$$

where r is the radius of water molecule.

A semi quantitative measure of the solvent ability to dissolve non-polar molecules is given by the so called equation:

$$\text{Gorden parameter} = \gamma V^{-1/3} (\text{j/m}^3)$$

where γ is the surface tension of the solvent and V its molar volume.

Water has a very high Gorden parameter ≈ 2.7 while hexane has a very low value of ≈ 0.3 . Thus hydrophobic interaction is largely due to the high cohesive energy density in water. Water is actually a better solvent, as its high Gorden parameter implies, which means water to some extent is capable of compensating for the loss in cohesive energy when dissolving a non-polar solute.

At the separation of two surfaces comparable to the molecular size, packing effects will start to play a role in the interparticle force. This can under certain circumstances lead to an oscillatory density profile as well as an oscillatory force as a function of the distance between the surfaces. The oscillations could be superimposed on both a net attractive or net repulsive curve. [22-27]

V. REPULSIVE HYDRATION FORCES

A charged or zwitterionic surface immersed in aqueous solution achieves one or several well-defined layers of water molecules hydrating the surface in the same way as a dissolved ion has a hydration shell. Pushing two such surfaces together results in a dehydration and could be anticipated to be accompanied by a repulsive hydration force. Repulsive hydration forces seem to exist both between neutral and charged surfaces. Structural or H-bonding polarization at the surface has been suggested as the cause for the repulsion.

Monte-carlo simulation shows the existence of the short range repulsive forces even for perfectly smooth surfaces. A strong attractive solvent-surface interaction leads automatically to a repulsive surface-surface force. If the surfaces are inert i.e. no attractive surface-solvent interaction exist, then an attractive solvation force acts between the surfaces. The limitation in both cases of limited range, $< 100\text{\AA}$.

VI. ATTRACTIVE HYDROPHOBIC FORCES

Surprisingly long range attractive forces exist between hydrophobic surfaces. The attraction ranges several hundred \AA . The possible source for the attractive interaction between these surfaces is that they are locally non-neutral and that patches of negative and positive charges correlate and cause an attraction.

VII. CRITICAL PACKING PARAMETER

Critical packing parameter is an important property for self-assembled aggregate. Critical packing parameter CPP is a reflection of the balance of the interaction between the hydrophobic moieties and the polar part (Fig. 2). The estimation of critical packing parameter of amphiphilic compound is considered as hypothetical rather than empirical.

The geometric or packing properties of surfactants depend upon their optimal head group area 'a' as well as on the hydrocarbon volume 'v' and the extended length of the surfactant hydrophobic chain, l_{max} . The value of 'a' is governed by repulsive forces acting between the head groups and attractive hydrophobic forces between the hydrocarbon chains. It was observed that the magnitude of both 'v' and 'l' parameters can be estimated directly from quantum mechanical calculations. While the investigations found that the 'a' parameter is parallel to the Connolly solvent accessible surface area which could also be determined through theoretical computations.

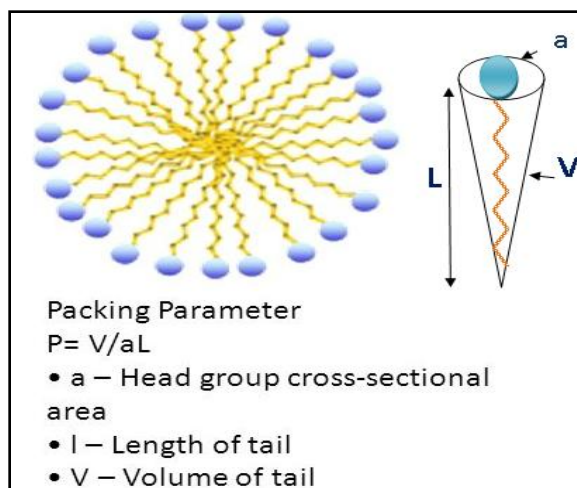


Fig. 2. Critical packing parameter

The ratio $v/l_{\text{max}}a$ which gives a geometric characterization of a surfactant molecule, will be seen to be very useful when discussing the type of structure formed by a given amphiphile. It is denoted as a critical packing parameter (CPP) or the surfactant number. The CPP of non-ionic surfactant is easily altered by changing the length of the chain or by changing the temperature. In ionic surfactant systems the CPP can be changed by altering the hydrocarbon chain length. Single chain surfactants tend to form micelles and other normal structures, while double chain surfactants prefer to form lamellar phases and reversed structures. On trying to pack space filling models of surfactant into different aggregate shape, find that due to bulkiness of the hydrophobic part, double chain molecules can't be packed into spherical micelles.

VIII. NANOSIZED SURFACTANTS

There are two factors that are not taken into account in the simple geometrical model but has a great influence on the aggregate structure. The first is the interaction between the head groups in the aggregates. Clearly a strong repulsive attraction between head groups will drive aggregates to the left in the Fontell scheme while the opposite applies for attractive interactions. This problem can be circumvented by estimating an effective head group area. E.g. for ionic surfactants, the head group interactions will be strongly affected by the electrolyte concentration so that a decrease on addition of electrolyte. Electrostatic calculations of distances between head groups can be made to estimate a CPP value or surfactant number in this case. For non-Ionics temperature rather than electrolyte concentration is very important for interaction between head groups and is decisive for aggregate structure.

As a bottom-up strategy to fabricate nanomaterials, surfactant self-assembly has received considerable attentions. Based on their diverse self-assembling behavior surfactants exhibit great potentials in many fields, including membrane protein stabilization, drug delivery, and tissue engineering. Since the surfactant-like peptide molecules can be easily designed and modified to form various nanostructures, they can be easily tailored for drug or gene delivery. Because of the unique amphiphilic structure of surfactant, and the hydrophobic tail could promote surfactant to self-assemble into the nanostructure with a hydrophobic core, which has potential to encapsulate water-insoluble molecules and deliver drugs and other biological molecules. On the other hand, the hydrophilic head could be modified as a functional group for cell-targeting. Although several attempts have been tried to obtain controllable self-assembling nanostructures. Nanosized surfactants have wide range of applications in the biomedical, clinical, pharmacological engineering products. [29-34]

IX. CONCLUSION

This article mainly focuses on the applications of the nanosized structured surfactant aggregates that are extensively used in various fields, depending upon the desired properties mainly in the fields of biomedical engineering, self assembled structures, desired structured nanomaterials etc. Surfactant aggregation is a spontaneous process and a delicate balance of forces governs the size and shapes of the structures at equilibrium. Aggregation is driven by the hydrophobic effect, the minimization of surfactant tail-water contact by transfer of the tail of the surfactant unimer from water to the aggregate core with the concomitant release of water of hydration, and an increase in the entropy of the system. Balance is provided by a combination of electrostatic, ion-specific, and hydration interactions in the interfacial region of the aggregates. In addition to lowering surface and interfacial tension, and rendering soluble what is insoluble, surfactants also have a number of useful properties including:

- Emulsifying or dispersing power
- Wetting
- Foaming
- Suspending/stabilizing power.

REFERENCES

- [1] LOMAX, E.G. (ed.), Amphoteric Surfactants, Surfactant science series 59, Marcel Dekker, New York, 1996
- [2] Rosen, M.J., Surfactants and interfacial phenomena, 2nd edn John Wiley, New York, 1989.
- [3] Evans, D.F. and H. Wennerstrom, the colloidal domain, where physics, chemistry, biology and technology meet, VCH Publishers Inc., New York 1994, Chs. 1 and 4.
- [4] Friberg, S.E. and B Lindman(eds), Organised solutions, Surfactant science series, vol. 44, Marcel Dekker Inc., New York, 1992.
- [5] Israelachvili, J., intermolecular and surface forces, Academic press, London, 1991.
- [6] Lindman, B. and H. Wennerstrom, micelles: Topics in current chemistry, vol. 87, Springer-verlag, Berlin, 1980.
- [7] Lindman, B., O. Soderman and H. Wennerstrom, NMR of surfactant systems, in surfactant solutions. New methods of investigation (ed. R Zana), Marcel Dekker Inc., New York, 1987, ch 6.
- [8] Shinoda, K., Principles of solution and solubility, Marcel Dekker, New York, 1978.
- [9] Tanford, C, the hydrophobic effect. Formation of micelles and biological membranes, John Wiley, New York 1980.
- [10] Fontell, K., Some aspects on the cubic phases in surfactant and surfactant-like lipid systems, Adv. Colloidal Interface sci. 41 (1992) 127-47.
- [11] Larsson, K., Lipids molecular organization, physical functions and technical applications, the oily press limited, Scotland, 1994.
- [12] Laughlin, R. G., The aqu. Phase behavior of surfactants, Academic press London 1994.
- [13] J. Israelachvili, D. Mitchell, and B. Ninham, "Theory of self-assembly of hydrocarbon amphiphiles into micelles and bilayers," Journal of the Chemical Society Faraday Transactions II., vol. 72, pp. 1525-1568, 1975.
- [14] D. Langevin, "Structure of reverse micelles," in Structure and Reactivity in Reverse Micelles, Elsevier, Ed. New York, 1989, pp. 13-43.
- [15] P. Hiemenz and R. Rajagopalan, Principles of Colloid and Surface Chemistry, Third ed, 1997.
- [16] D. F. Evans and H. Wennerstrom, The Colloidal Domain: Where Physics, Chemistry, Biology, and Technology meet., Second ed. Canada, 1999.
- [17] A Model for Monomer and Micellar Concentrations in Surfactant Solutions. Application to Conductivity, NMR, Diffusion and Surface Tension data, Wajih Al-Soufi, Lucas Piñeiro, Mercedes Novo, Journal of Colloid and Interface Science 2012, 370, 102–110 DOI: 10.1016/j.jcis.2011.12.037.
- [18] P. Jokela, B. Jönsson, and A. Khan, "Phase equilibria of cationic surfactant-water systems," Journal of Physical Chemistry, vol. 91, no. 12, pp. 3291–3298, 1987.
- [19] E. Clementi, J. Chem. Phys. 46, 3851 (1967).
- [20] Calculation of Intermolecular Interaction Energies by Direct Numerical Integration over Electron Densities. 2. An Improved Polarization Model and the Evaluation of Dispersion and Repulsion Energies, A. Gavezzotti, J. Phys. Chem. B, 2003, 107 (10), pp 2344–2353.
- [21] S. Tsuzuki, T. Uchimar, K. Matsumura, M. Mikami, and K. Tanabe, Chem. Phys. Lett. 547, 319 (2000).
- [22] Rehfeld SJ. Adsorption of sodium dodecyl sulfate at various hydrocarbon-water interfaces. J Phys Chem. 1967;71:738–745.
- [23] Israelachvili J. Intermolecular and Surface Forces. 3rd Ed. San Diego: Elsevier; 2011. pp. 291–314. pp. 361–378. pp. 536–626.
- [24] Acharya H, Vembanur S, Jamadagni SN, Garde S. Mapping hydrophobicity at the nanoscale: Applications to heterogeneous surfaces and proteins. Faraday Discuss. 2010;146:353–365.
- [25] Christenson HK, Claesson PM. Direct measurements of the force between hydrophobic surfaces in water. Adv Colloid

- Interface Sci. 2001;91:391–436.
- [26] Chen YL, Chen S, Frank C, Israelachvili J. Molecular mechanisms and kinetics during the self-assembly of surfactant layers. *J Colloid Interface Sci.* 1992;153:244–265.
- [27] Interactions Between Nonionic Surfactant Monomers, Hydrophobic Organic Compounds and Soil D. A. Edwards, Z. Liu, R. G. Luthy, July 1992, 26 (1-2) 147-158.
- [28] Molecular Packing Parameter and Surfactant Self-Assembly: The Neglected Role of the Surfactant Tail R. Nagarajan, *Langmuir*, 2002, 18 (1), pp 31–38.
- [29] Theoretical estimation of the critical packing parameter of amphiphilic self-assembled aggregates, Khalil, Rabah A.; Zarari, Al-hakam A., *Applied Surface Science*, Volume 318, p. 85-89, 11/2014.
- [30] Micelle Formation and the Hydrophobic Effect, L. Maibaum, A. R. Dinner, D. Chandler, *J. Phys. Chem. B* 2004, 108, 6778 – 6781.
- [31] Two-Detector System for Small- Angle Neutron Scattering Instrument, A. I. Kuklin, A. Kh. Islamov, V. I. Gordeliy, *Scientific Reviews*, 2005, 16, 16-18.
- [32] Murray, C. B.; Kagan, C. R.; Bawendi, M. G. (2000). "Synthesis and Characterization of Monodisperse Nanocrystals and Close-Packed Nanocrystal Assemblies". *Annual Review of Materials Research*. 30 (1): 545–610.
- [33] Zhrebetsky D, Scheele M, Zhang Y, Bronstein N, Thompson C, Britt D, Salmeron M, Alivisatos P, Wang LW (2014). "Hydroxylation of the surface of PbS nanocrystals passivated with oleic acid". *Science*. 344 (6190): 1380–1384.
- [34] Hakiki, F.; Maharsi, D.A.; Marhaendrajana, T. (2016). "Surfactant-Polymer Coreflood Simulation and Uncertainty Analysis Derived from Laboratory Study". *Journal of Engineering and Technological Sciences*. 47 (6): 706–724.