Experimental Methods in Interfacial Chemistry

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Outline

- Introduction to Interfaces
- Surface tension and CMC
- Self assembly structure and dynamics
- Applications

Surfactants as Interface modifiers

Solid-liquid interface:

Cleaning of oil droplet on floor or clothes Dispersion of particles in Paints and pigments





Interfaces

Liquid-liquid interface

Dispersion of one liquid in other



Bubbles and Foams, In Froth floatation, shaving creams, ice cream, fire fighting etc.

Free energy of the interface

Surface / interfacial tension – Free energy per unit area of the interface

Molecules at the surface behave differently from that at the bulk



Lesser number of nearest neighbours at the interface -Interaction energy is different.

 W_{11} – interaction energy of a pair

Energy per molecule is

For bulk, $E_b = n_b W_{11}/2$ For surface , $E_s = n_s W_{11}/2$

Energy and Force

Extra energy required to create a new surface of unit area,

$$\gamma = \frac{W_{11}(n_s - n_b)}{2a_0}$$

Energy/ area ; J/ m²

Molecules at the surface are under tension due to inward pull



An opposite force is required to expand the liquid film

Force/ length.; N/m

Surface tension and its consequences

Pressure across a curved surface is different

Surface tension tends to decrease the surface area and is counter balanced by a change in pressure

For sphere of radius r, changes in surface area and volume for a small change in radius (dr) is given by

$$dA = 8\pi r dr \qquad dV = 4\pi r^2 dr$$

Change in surface energy $= \gamma 8\pi r dr$ $\Delta P = \frac{2\gamma}{r}$ Pressure-volume work $= 4\pi r^2 dr \Delta P$

Laplace equation

Measuring surface tension – Capillary Rise

Changes in pressure across a curved surface leads to capillarity

Height h, radius r, contact angle q

Capillary pressure balanced by hydrostatic pressure

$$\frac{2\gamma\cos\theta}{r} = h\rho g$$

$$\gamma = \frac{hrg\rho}{2\cos\theta}$$

Flow of liquid in a capillary can be tuned by g





R.cos x = r

Solid-Liquid interface by Contact Angle



Contact angle and wetting can be tuned by g

Surface tension by Ring method

How to characterize the surface activity and aggregation?

1.By measuring surface tension

Drop weight (volume) method $mg = 2\pi r\gamma$

Measure the weight of a drop of liquid falling through a capillary tube

2. DuNuoy ring method

Measure the force or weight required to detach a ring from the surface

 $F = mg = 4\pi r\gamma \cos\theta$

Measuring surface tension



Courtesy: Kruss, GmbH

Measuring surface tension

Wilhelmy plate method - can measure the contact angle if g is known

Length I, thickness b and immersion height h

Can measure contact angle (advancing and receding)

Dynamic surface tension



A measure of diffusion of surfactant molecules to the interface

Bubble Pressure method





Dynamic surface tension



Langmuir 1998, 14, 979-981

$$\gamma(t)_{t \to \infty} = \gamma_{eq} + \frac{RT\Gamma^2}{2c} \left(\frac{\pi}{Dt}\right)^{1/2}$$



Surface activity and aggregation

Increasing surfactant concentration



- Tries to orient in such a way to evade water from the hydrophobic part
- Hydrophobic effect leads to surface adsorption and aggregation
- Since it sits on the surface/interface, it can change the surface tension! Useful to adjust capillarity and contact angle
- It can also change the charge on the surface if ionic head group is used Useful to prevent aggregation as like charges repel each other

Variation of surface tension with concentration



Gibbs equation

Gibbs equation predicts the variation of g with C using surface thermodynamics for adsorption

At equilibrium DG = 0 $Ad\gamma + \sum_{i} n_i d\mu_i = 0$

$$\Gamma_i = -\frac{1}{RT} \left(\frac{d\gamma}{d\ln c}\right)$$

- Surface tension decreases with surfactant concentration
- Above CMC, the chemical potential of the surfactant scarcely change.
- Thus S.T. vs. In C plot shows a break at CMC
- Surface saturation occurs much below CMC (see Gibbs equation)
- Huge change in surface area required to bring about change in CMC.

Surface excess concentration

Gibbs equation permits calculation of surface concentration from surface tension measurements



K and area per molecule can be calculated



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CMC of Mixed micelles

CMC – To measure interaction parameter

The interaction of two surfactant in a mixture can be expressed in terms of b

$$\beta = \frac{\left(w_{11} + w_{22} - 2w_{12}\right)}{kT}$$

b -ve : attractive interaction(synergism)b +ve : repulsive interaction(antagonism)

$$\frac{1}{CMC^*} = \sum_{i} \frac{\alpha_i}{CMC_i}$$

Ideal mixing

Monolayers at interface

A 2-D analog of P-V isotherm

Pressure, P is related to no. of molecules/unit volume Analogously surface pressure p is related to number/ unit area $\pi = \gamma_0 - \gamma$



Discontinuity in the gradient indicates a phase transition

Langmuir-Blodgett apparatus for measuring p-A isotherm

In the solid film the limiting area = cross section area of headgroup

Schematic of LB technique



Surfactants as monomers and micelles



CMC



Concentration of surfactant

Other methods of determining CMC

2. Conductivity of ionic micelles

Resistance R = (1/k).L/A L= length, A= area

K = sp. Conductance ; ohm⁻¹ cm⁻¹ Conductance of 1 cc of solution

Equivalent conductance is the conductance of one eq. wt. of the electrolyte. L = k.1000/C



The degree of dissociation is low above CMC: hence slope changes Useful for ionic surfactants



FIG. 1. Specific conductance (K) vs concentration of SDS in aqueous mixtures of DEG at 298 K.

Counter ion binding can also be obtained

CMC by spectral change method

I_{max} at different environments

Either the surfactant or an external indicator is used Eg: pinacyanol; rhodamine- 6G



FIG. 3. Visible absorption spectrum of 10^{-5} M PIN in several concentrations of TTAB (from 10^{-2} to 9.0×10^{-2} M) at pH 5.5 and 25°C.

I_{max} – solvent dielectric constant dependant



FIG. 4. λ_{max} values for the monomeric band of PIN in a series of *n*-alcohols (methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, and 1-octanol) as a function of the dielectric constants of the media at 25°C as taken from (26).

Dimer to monomer conversion



Figure 1. Absorption spectra at 0, 16 and 30 °C measured for a 5 wt % aqueous solution of P123 containing 1×10^{-3} mol/L R6G. The spectrum exhibits two peaks corresponding to the monomer and dimers of R6G in the solution.

CMC by dye solubilization

A suitable insoluble dye is used. Conc. determined by absorption Eg: Orange- OT, azobenzene etc.



Fig. 5. Dependence of amounts of dye solubilized, $C_{\text{solubilized}}$, on the surfactant concentration, C_{S} , for 4-PAA at 298 K: \bigcirc , DC3-12; \bigcirc , DC6-12; \triangle , C12C1NBr; \blacktriangle , C12C2NBr.

CMC by Fluorescence

Pyrene is a suitable fluorescent probe for identifying the microenvironment Excitation at 335 nm produces five vibronic peaks in fluorescence.

The ratio of $I_{1(372)} / I_{3(383)}$ is a measure of local polarity



In water, \sim 1.6, in micelle \sim 1.1; Can show excimer emission due to increased local conc.



Pyrene 1:3 ratio versus total concentration of surfactant in water (●) and in solutions with different KCl concentrations at 25.0 °C: ○, 0.5 M; ▲, 1.0 M; △, 1.5 M; and ■, 2.0 M.

Thermodynamics of micellization from CMC

The standard Gibbs free energy change of formation of micelles

$$\Delta G_{mic} = -RT \ln K \qquad \text{N} [S] \rightleftharpoons S_{\text{N}}$$
Per surfactant
$$\Delta G_{mic} = -\frac{RT}{N} \ln X_N + RT \ln X_1$$
Since N is high the first term is negligible
At CMC , X₁ = Xcmc
$$\Delta G_{mic} = RT \ln X_{cmc}$$

The enthalpy change can be obtained using Gibbs-Helmholtz equation

$$\left(\frac{\partial \Delta G/T}{\partial T}\right)_{p} = -\frac{\Delta H}{T^{2}} \qquad \Delta H_{m} = -RT^{2} \left(\frac{\partial \ln CMC}{\partial T}\right)_{p}$$

Isothermal titration calorimetry can also be used

Factors influencing CMC

- Nature of surfactant and length of chain

CMC decreases with increase in chain length; $Log(cmc) = a - b \cdot c_n$

Branching and unsaturation increases CMC

Fluorocarbons lower CMC

Counterions, electrolytes, alcohols etc. decreases the CMC
Factors influencing aggregation

Temperature – Kraft point and Cloud point

Ionic surfactants precipitates out as hydrated crystals below Kraft point.

At Kraft point solubility= cmc

For nonionics, increasing the temperature causes clouding due to changes in the conformation and hydration of the oxyethylene groups as well as intermicellar interactions Clouding is followed by phase separation (critical phenomena)



Micelle formation

Size distribution of aggregates with increasing surfactant concentration



Self assembly beyond CMC



Concentration of surfactant

Structure of aggregates



1 nm = 1 nano meter - 1/10,00,000 of a mm

Microstructure of aggregates

How to characterize the structure in the sub-micron range? (size, shape, polydispersity etc)

- 1. Cryo Electron microscopy (SEM/TEM)
- 2. Indirect imaging possible with AFM, STM etc
- 3. Scattering of radiation (light, X-rays, Neutrons) (Similar to Crystal structure from X-ray diffraction)
- 4. Fluorescence quenching, Electrochemical methods, NMR

Fluorescence quenching method

A fluorophore(probe) and a quencher soluble in micelles is used Eg: $Ru(bpy)_3^{2=}$ and 9-methyl anthracene

Intensity of fluorescence decreases with quencher concentration.

$$I = I_0 e^{-[Q]/[M]}$$
 [M]= (c-CMC)/N Plot ln(I/I₀) vs [Q]

Assumptions:

Probe and quencher are totally soluble in micelles Residence time of the probe is higher than the life time of fluorescence Quenching rate is faster than the lifetime Only one probe per micelle.

The distribution is decided by Poisson statistics

 $P(x) = \frac{e^{-\mu}\mu^x}{x!}$

[M] >> [Q]

Aggregation number



Fig. 6. Plots of $\ln (I_0/I)$ against [Q] for the gemini surfactant micelles at 298 K: \bigcirc , DC3-12; \bigcirc , DC6-12.

 $\ln(I_0/I) = [Q]N/([C] - CMC)$

Time resolved fluorescence

Steady state fluorescence does not work for large aggregation numbers.

In the absence of quencher, $I(t) = I(0)e^{-t/\tau_0}$

In the presence of quencher

$$\ln \frac{I(t)}{I(0)} = \frac{-t}{\tau_0} + \overline{Q}[e^{-k_q t} - 1]$$

A rough estimate can be obtained from the long time behavior

$$\ln \frac{I(t)}{I(0)} = \frac{-t}{\tau_0} - \overline{Q}$$

Time resolved fluorescence

Dates and mingre



Electrochemical methods

Solubilization of electroactive molecules (probes)



Electrochemical methods

$$i_{\rm pa} = 0.4463 FAC (F/RT)^{1/2} v^{1/2} D^{1/2}$$



Figure 3. Plot of $t_{\rm pa}$ vs $v^{1/2}$ for ferrocene in aqueous CTAB solution in the absence and presence of various concentrations of SS. Scan rates vary from 10 to 80 mV/s.

NMR Line width



Fig. 1. Effect of KBr salt concentration on the ¹H NMR of CTAB molecules in the 0.01 mmol \cdot L⁻¹ micellar system. 1, ω -CH₃; 2, -(CH₂)₁₃; 3, β -CH₂; 4, N-(CH₃)₃; 5, α -CH₂.

Counterion Adsorption: ¹**H NMR**



Upfield shift of m- and p- protons while o- is unshifted

Line broadening ⇒ Formation of rod like micelles

Langmuir **2002**, 18, 2543

Scattering - Explore the nano world

Light, neutron and X-ray scattering

Size range of different scattering methods



Works in a range where optical microscopy fails !

Scattering from particles



Guinier regime

Dilute sphere with radius 50nm





P(q) at different length scale



Size Shape polydispersity

SANS is ideal for the length scale of micelles

SLS can be used to obtain R_g or R depending on size For SLS, P(q) ~ Guinier law S(q) ~ S(0)

Minima occurs at qR = tan(qR), for sphere qR = 4.49, 7.72 etc

S(q), Interparticle interference



Vol. Fraction Charge Ionic strength

As concentration increases, peak develops at $\sim 2p/d$ d is the average interparticle distance

SANS data for interacting micelles

SANS study of SDS micelles



SANS of micelles



SANS of drug loaded vesicles

with drug without drug

Drug solubilization increases the bilayer spacing from 72 Å to 79 Å



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Trapping micelles in biopolymer gels

System investigated : Alginate + triton X100



Ca²⁺ induced gelation



Courtesy: FMC Biopolymer

SANS



Micelle in a hydrogel



Light scattering under motion



Distance between particles changes with time due to motion The interference of scattered light changes with time. Net intensity of light fluctuates with time

Dynamic Light Scattering

Static light scattering – unable to probe micelles

Option – Look for the motion of scatterers (dynamic)

Time dependence of scattered intensity is measured

Brownian motion of colloidal particles due to collision with solvent molecules



Measures dynamic structure factor

Brownian motion depends on size, viscosity and temperature

Timescale of intensity fluctuation



t



As size increases, motion become slower and the decay time increases

Micellar growth probed by DLS



Decreases the apparent diffusion coefficient of the micelles

Micelle length from DLS



Block copolymers

Surfactants for "macro" micelles



Thermoreversible gels in block copolymer micelles

J. Phys. Chem. B, **2005**, 109, 5653

J. Phys. Chem. B 2006, 110, 9843

Effect of PPO block length



Particle Interactions

 $D = D_0 (1 + k_d C)$ Thermodynamic + hydrodynamic



Small q limit No hydrodynamics,

 $\mathsf{D}=\mathsf{D}_0/\mathsf{S}(0)$

For repulsive S(0) < 1, D increases

With hydrodynamics, $D = D_0 H(0)/S(0)$

Concentration

Measuring interparticle interaction


Rheology

Rheology - Study of flow and deformation of matter Microstructure can alter the flow behavior- soft materials

Shear modulus (G) – a measure of softness



Solids vs liquids

Shear stress, **s** (force/area) = F/A

Shear strain, **g** (deformation) = dy/dx

Solid are elastic

 $\sigma \!=\! G \gamma$ Hooke's law

Liquids are viscous

 $\sigma = \eta \gamma$

Newton's law

Soft materials are viscoelastic

Self assembled polymers



- Break and recombine with change in temperature
- Equilibrium polymers (living polymers)
- Thickness of chain ~ 20 50 Å

Practical Examples

Foods, Pharmaceuticals, Personal care products, Life science etc.













Viscoelastic behavior



Langmuir **2002**, 18, 2543.

Microscopy



Why electrons?

Resolving power

$$db = \frac{1.22 \text{ x } \lambda}{2n \text{ x } \sin \alpha} \text{ or } db = \frac{1.22 \text{ x } \lambda}{2 \text{ x } \text{ N.A}}$$

Charged particle – focused by electric or magnetic fields Small mass- accelerated and thus energy can be changed, de Broglie wavelength ~ Å Visible on a fluorescent screen – detection Availability of sources

Drawback - Needs vacuum – cryo fixation of samples!

Cryo-TEM Spherical micelles

CTAB 0.01M and NaNO₃ 0.01M, 30°C



3 - 4 nm spheres – (viscosity similar to that of water)

Polymer-like micelles



Length ~ microns Viscoelastic fluid

1000 times more viscous than water

CTAB 0.01M and NaNO₃ 0. 5M, 30°C

Applications in Industry

Soaps and Detergents

All household and industrial cleaners contain surfactant.

Cleaning – a three phase system





To detach a drop of oil from cloth fiber, capillary action, wetting and contact angle are important. Surfactant formulations are made to do that job

Textiles finish

Synthetic fiber yarns need "spin finish" liquids to modify the surface

Abrasion protection during weaving Lubrication- enhances the speed of weaving

Typically an emulsion of polymers and wax in water are used as spin finish liquid

Surfactant is used as an emulsifier and as a coating material

A contact angle 20- 40° with water is prefered for fibers



Surfactant as a wetting agent

Dyeing of fabrics:

Printing of polymers (polyolefin – packaging material) Highly hydrophobic - difficult to wet with water based inks Surfactants help to improve wetting

Other applications include:

Flux cleaning in electronic circuit boards Lubricants in watch industry

Cell adhesion enhancement of culture cells in pathology Removal of bubbles in electroplating industry Tertiary oil recovery in oil fields

Pesticide formulations

Pesticides are organic compounds – insoluble in water

Emulsifiable concentrates A mixture of surfactant and active ingredient in hydrocarbon - forms emulsion when mixed with water

Droplets should not fly off from leaves – good wetting

Wettable or water dispersible powders – contain surfactant as dispersing agent and stabilizer



Mineral processing



Surfactants are used as collector (to make the ore hydrophobic) and foamer (stabilize the foam)

Pharmaceutical formulations

Many drugs are hydrophobic in nature

They can be solubilized and administered using surfactants

Typical formulations include:

Emulsions Microemulsions Micelles Vesicles (liposomes) – uni and multi lamellar

Vesicles can incorporate both hydrophilic and hydrophobic drugs





Miscellaneous applications

Personal Care products - Looking good and feeling good

Shampoos – quarternary amine surfactants Skin creams – emulsion and gels

Thickeners (viscosity modifier)Enhanced absorption through skin Stability of particles

Foam Fire fighting – fluorocarbon and polymeric surfactants are used. Mainly used for oil fire – foam act as a mask for O_2

Foam stability – depends on interfacial tension, viscosity (bulk and surface), film drainage, surface charge etc.