FÍSICO-QUÍMICA EXPERIMENTAL
QFL-1444

Tensão Superficial e determinação da Concentração Micelar Crítica

A estrutura da superfície do líquido

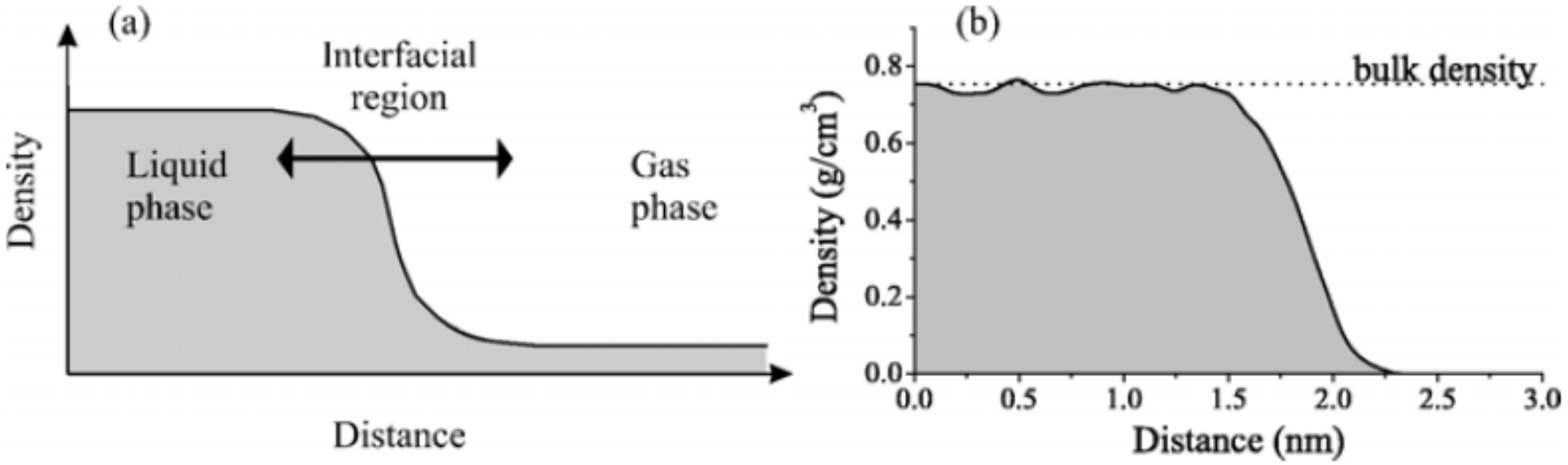
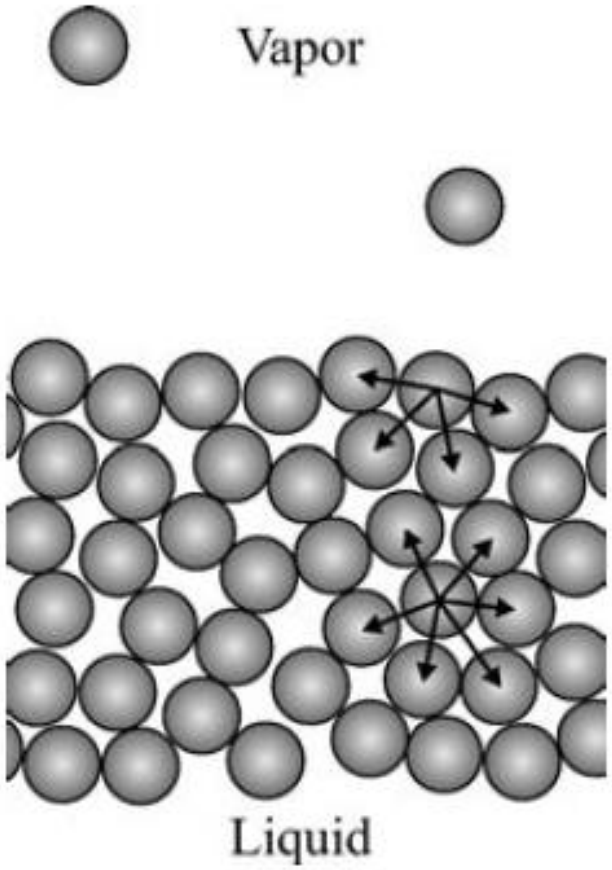


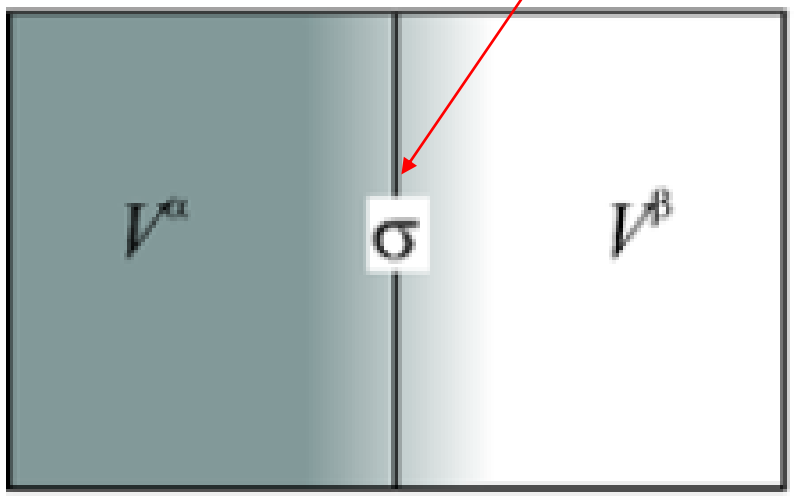
Figure 2.1: Density of a liquid versus the coordinate normal to its surface: (a) is a schematic plot; (b) results from molecular dynamics simulations of a n-tridecane ($C_{13}H_{28}$) at 27°C adapted from Ref. [11]. Tridecane is practically not volatile. For this reason the density in the vapor phase is negligible.

H. J. Butt, K. Graf, M. Kappl, *Physics and Chemistry of Interfaces*, Wiley-VCH, 2003.

A estrutura da superfície do líquido

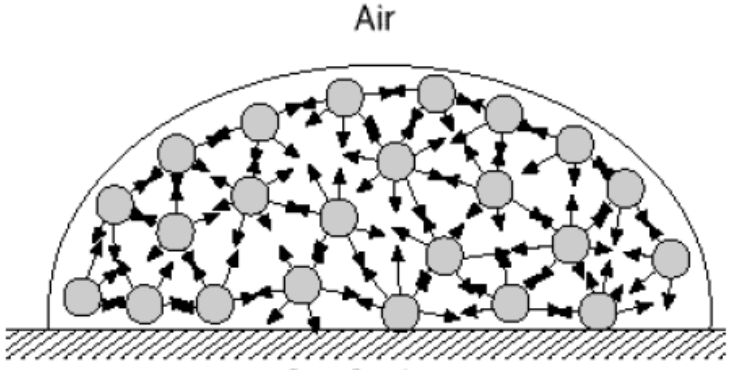


interface de área σ
e espessura infinitesimal



Gibbs ideal interface

H. J. Butt, K. Graf, M. Kappl, *Physics and Chemistry of Interfaces*, Wiley-VCH, 2003.



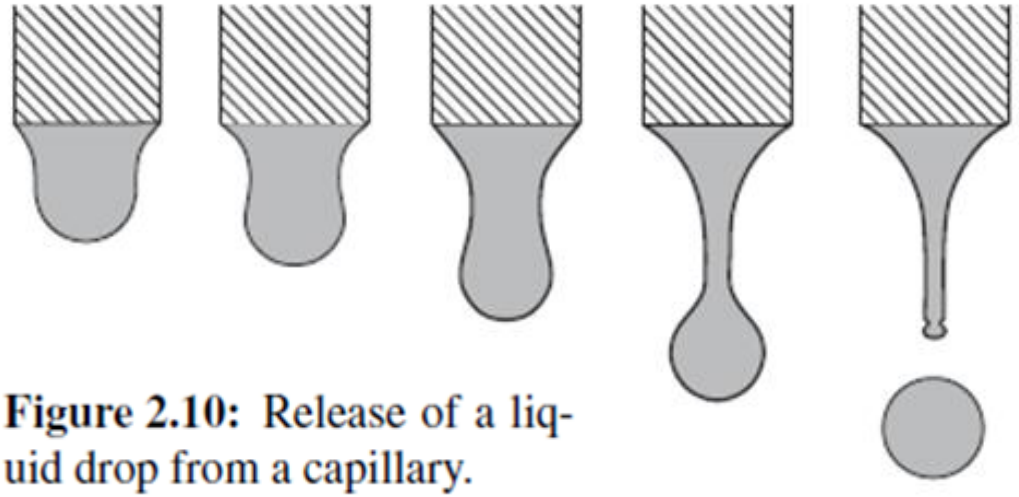


Figure 2.10: Release of a liquid drop from a capillary.

Definição Termodinâmica da Tensão Superficial, γ

Energia livre de Gibbs $G = H - TS$

A ⇆ B

$\Delta G < 0$, espontâneo (A→B)

$\Delta G > 0$, não-espontâneo (A←B)

$\Delta G = 0$, equilíbrio

$G(p,T)$ $\quad dG = Vdp - SdT$

$\left(\frac{\partial G}{\partial p}\right)_T = V \qquad \left(\frac{\partial G}{\partial T}\right)_p = -S$

$G(p,T,n_A,n_B,\ldots)$ $\quad dG = Vdp - SdT + \mu_A dn_A + \mu_B dn_B + \cdots$

potencial químico $\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,n'}$

P. W. Atkins, *Physical Chemistry*, Oxford University Press, 5th ed., 1994.

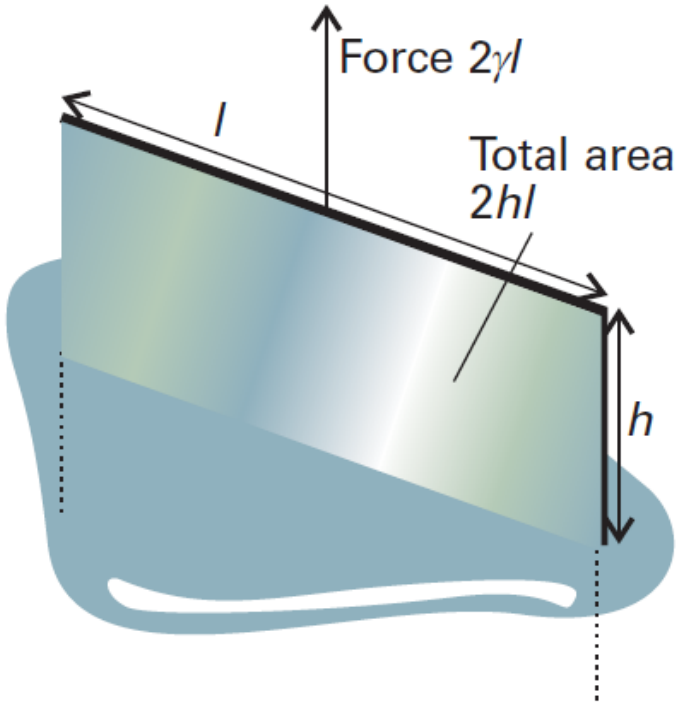
Definição Termodinâmica da Tensão Superficial, γ

$G(p,T,n_j,\sigma)$

$$dG = Vdp - SdT + \sum_J \mu_J dn_J + \gamma d\sigma$$

Maximum non-expansion work $dG = dw_{add,rev}$

$$\gamma = \left(\frac{\partial G}{\partial \sigma}\right)_{p,T,n_j}$$



trabalho para aumentar a área da superfície do líquido:

$$d\omega = \gamma . d\sigma$$

P. W. Atkins, *Physical Chemistry*, Oxford University Press, 5th ed., 1994.

$$d\omega = \gamma . d\sigma$$

Nm = Nm^{-1} m^2

Unidade SI de γ: Nm^{-1}

1 dyn/cm = 10^{-3} N/m

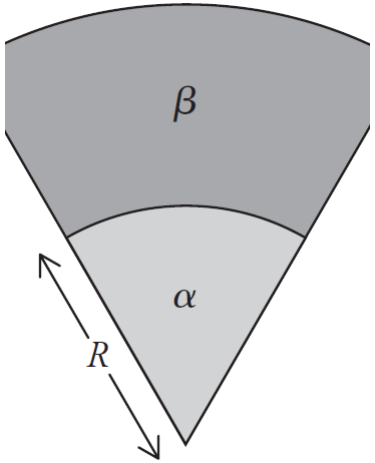
sistema cgs: 1 dyn = 1 g.cm/s^2 = 10^{-5} kg.m/s^2

Table 2.1: Surface tensions γ of some liquids at different temperatures T.

Substance	T	γ (mNm^{-1})	Substance	T	γ (mNm^{-1})
Water	10°C	74.23	Mercury	25°C	485.48
	25°C	71.99	Phenol	50°C	38.20
	50°C	67.94	Benzene	25°C	28.22
	75°C	63.57	Toluene	25°C	27.93
	100°C	58.91	Dichloromethane	25°C	27.20
Argon	90 K	11.90	*n*-pentane	25°C	15.49
Methanol	25°C	22.07	*n*-hexane	25°C	17.89
Ethanol	10°C	23.22	*n*-heptane	25°C	19.65
	25°C	21.97	*n*-octane	10°C	22.57
	50°C	19.89		25°C	21.14
1-propanol	25°C	23.32		50°C	18.77
1-butanol	25°C	24.93		75°C	16.39
2-butanol	25°C	22.54		100°C	14.01
Acetone	25°C	23.46	Formamide	25°C	57.03

H. J. Butt, K. Graf, M. Kappl, *Physics and Chemistry of Interfaces*, Wiley-VCH, 2003.

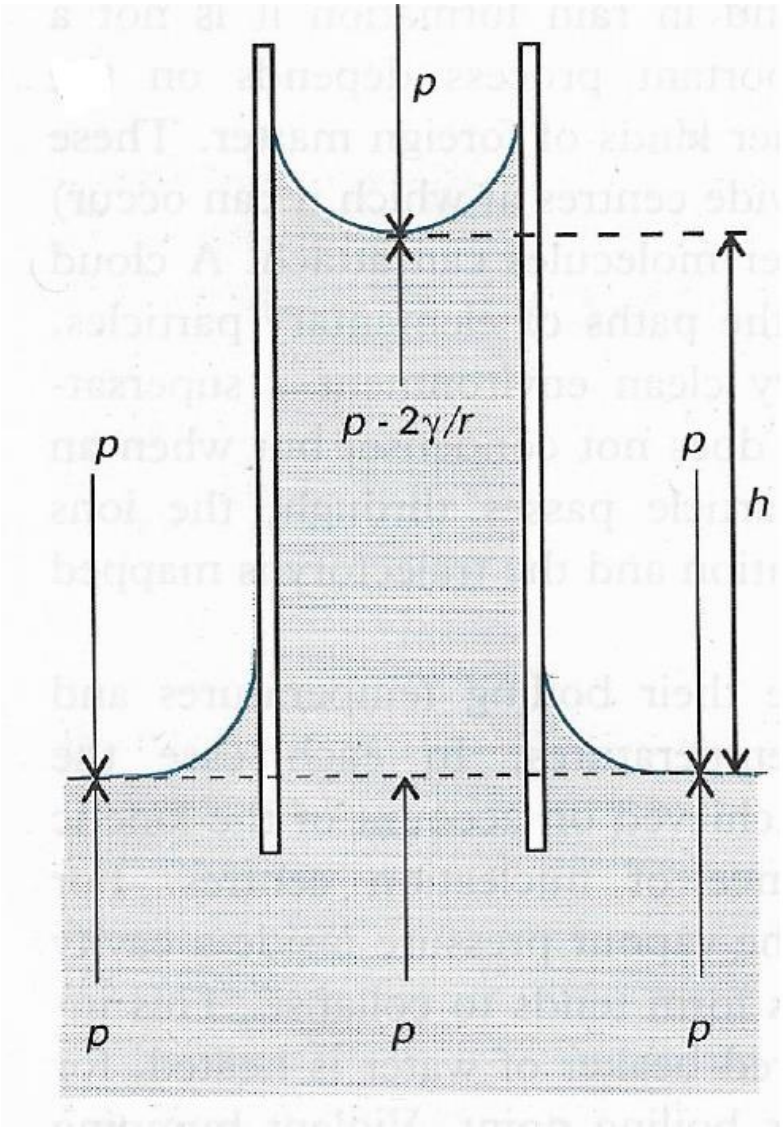
Ascensão capilar



superficies esféricas

Equação de Young-Laplace

$$P^{\alpha} - P^{\beta} = \frac{2\gamma}{R}$$



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

I. N. Levine, *Physical Chemistry*, McGraw-Hill, 6th ed., 2009.

P. W. Atkins, *Physical Chemistry*, Oxford University Press, 5th ed., 1994.

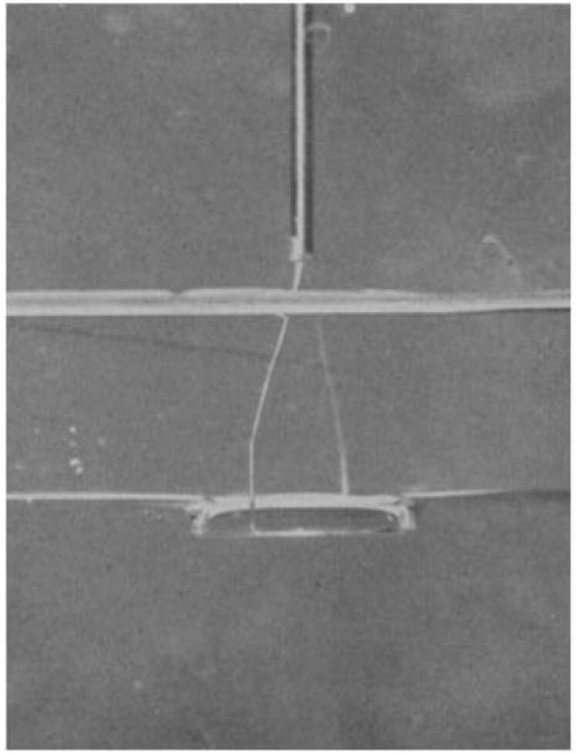
Tensiômetro de anel

AN INTERFACIAL TENSIOMETER FOR UNIVERSAL USE.

By P. LECOMTE DU NOÜY.

(*From the Laboratories of The Rockefeller Institute for Medical Research.*)

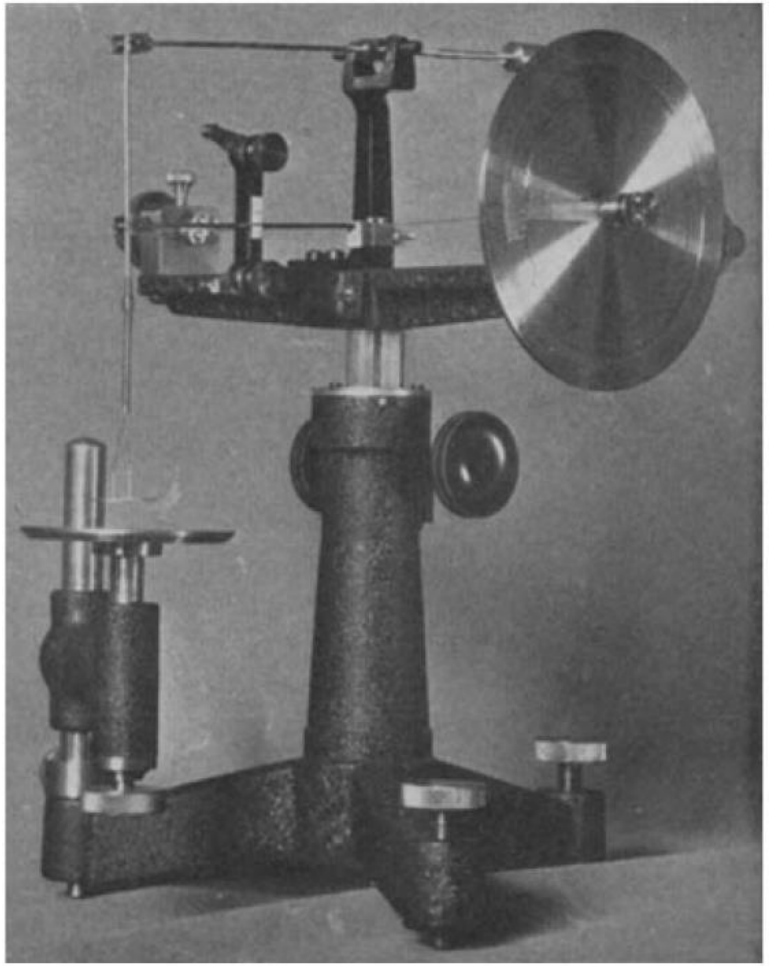
J. General Physiology **7**, 625-633 (1925)



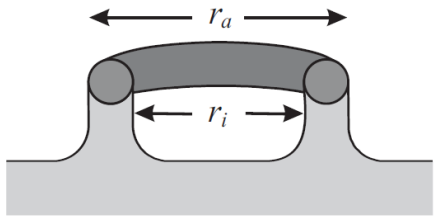
H_2O

CCl_4

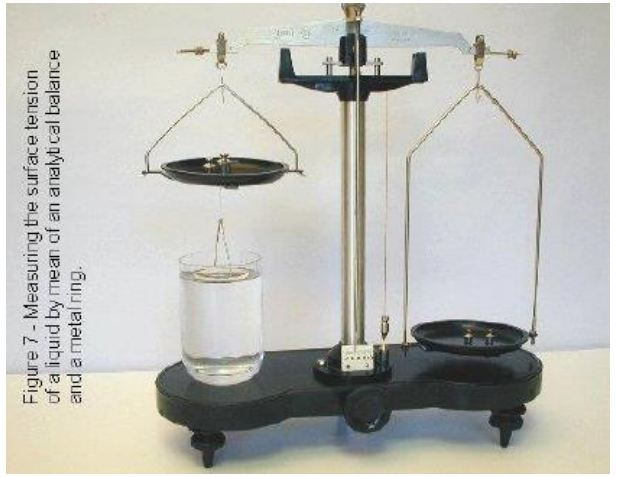
$$\gamma = \frac{M \cdot g}{2L}$$



Tensiômetro de anel



Du-Noüy ring tensiometer



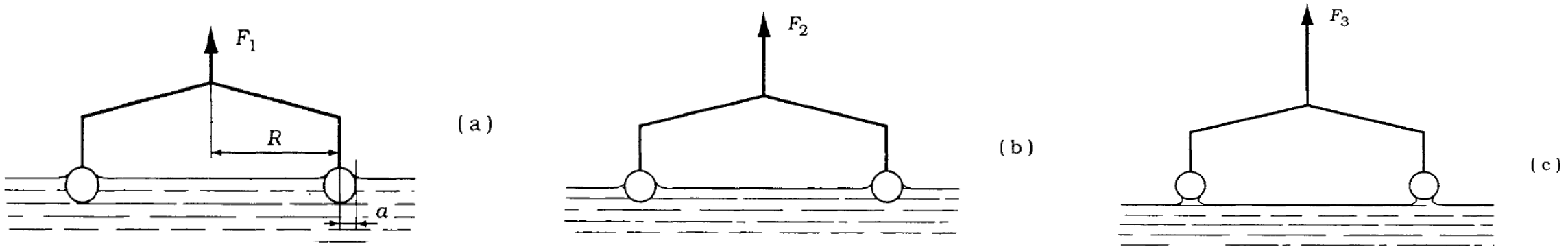


Figure 1.22. Three stadia in the detachment of a ring (idealized). Cross-section.

$$F \approx w(\text{ring}) + 4\pi R\gamma$$

H. J. Butt, K. Graf, M. Kappl, *Physics and Chemistry of Interfaces*, Wiley-VCH, 2003.

J. Lyklema, *Fundamentals of Interface and Colloid Science, Liquid-Fluid Interfaces*, Elsevier Academic Press, 2000.

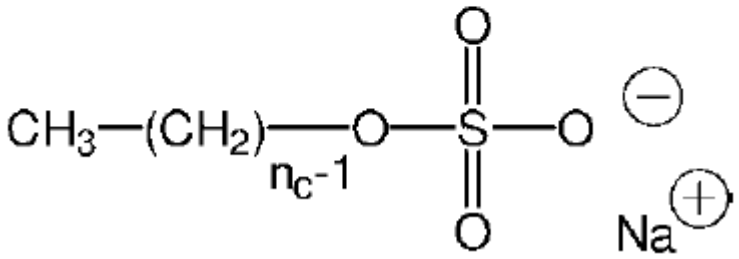
Surfactantes

Polar head →

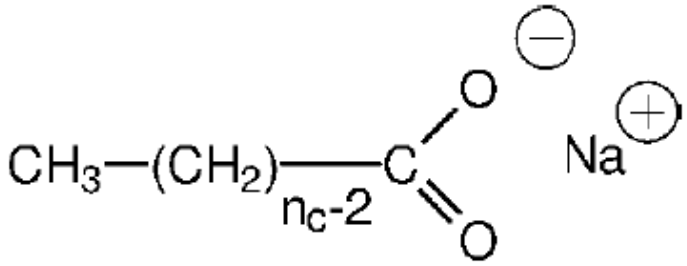
Hydrophobic tail →

Anionic

Sodium alkylsulfate



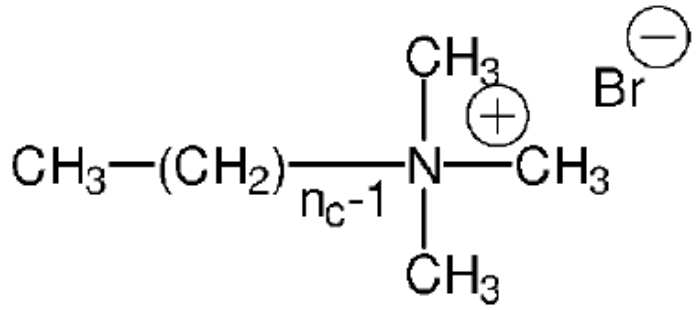
Sodium alkylcarboxylate



Stearic acid, $C_{17}H_{35}COOH$

Cationic

Alkyltrimethylammonium bromide



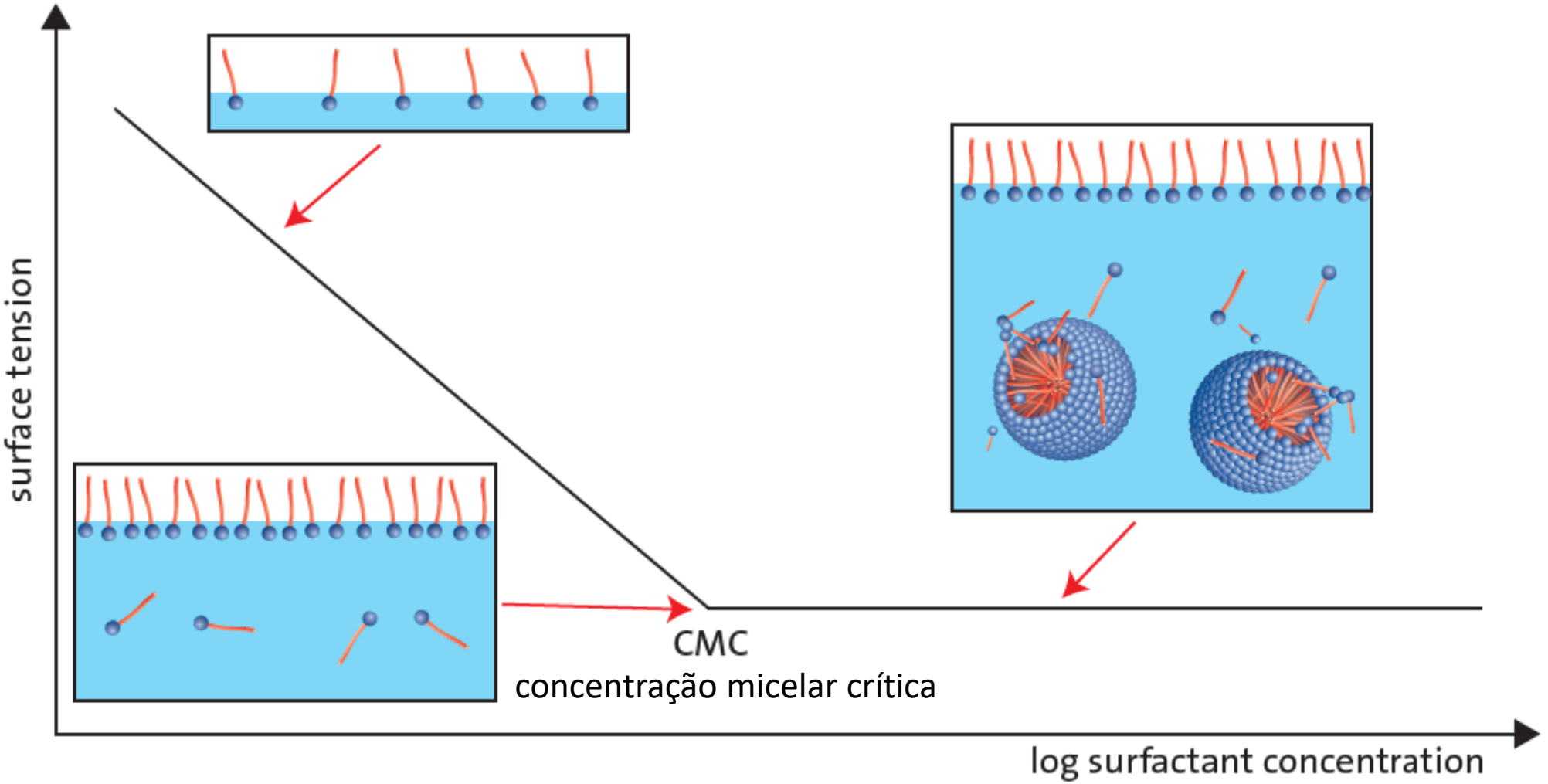
$n_C = 16$, hexadecyl trimethylammonium bromide (CTAB)

Nonionic

Alkylethylene glycol

$C_{10}H_{21}(OCH_2CH_2)_4OH$

Tensão superficial × concentração surfactante



Dataphysics Instruments, https://www.dataphysics-instruments.com/

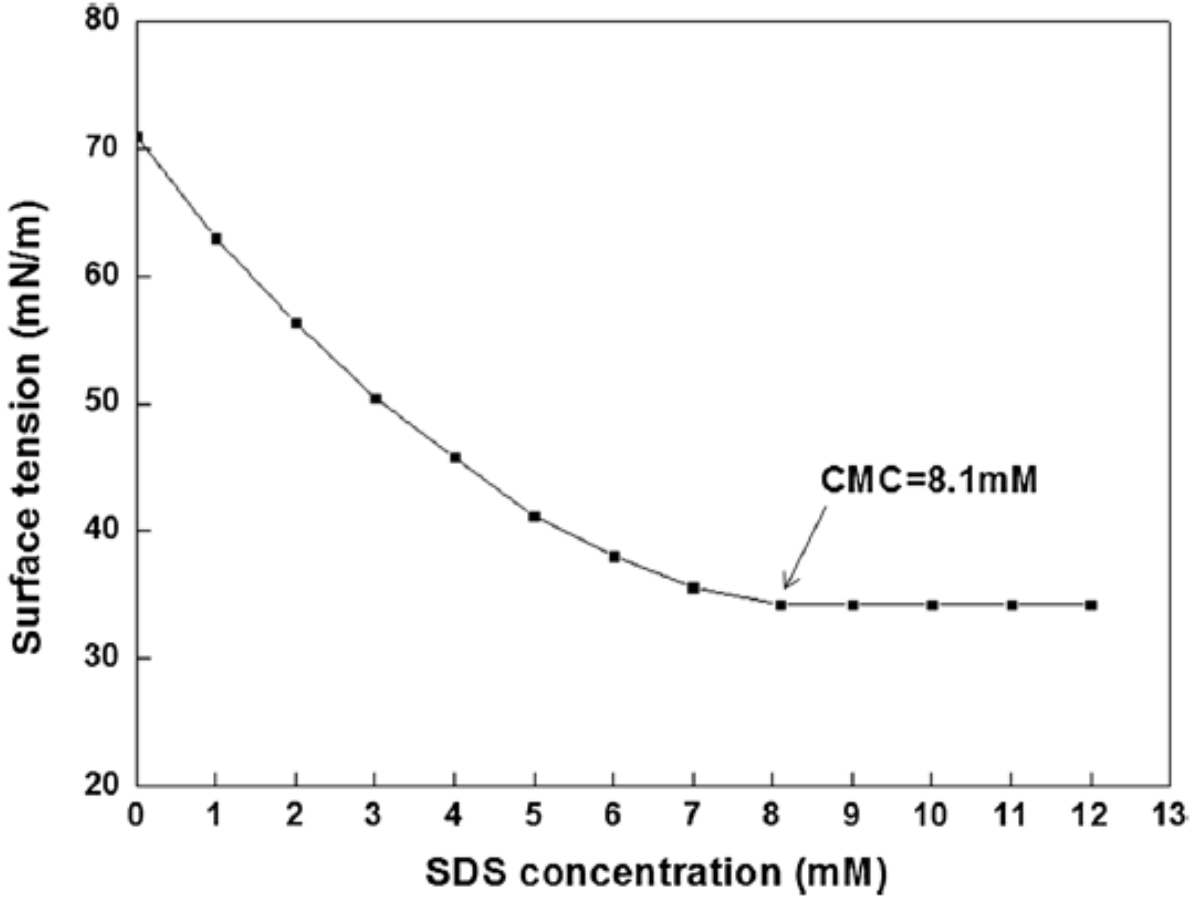
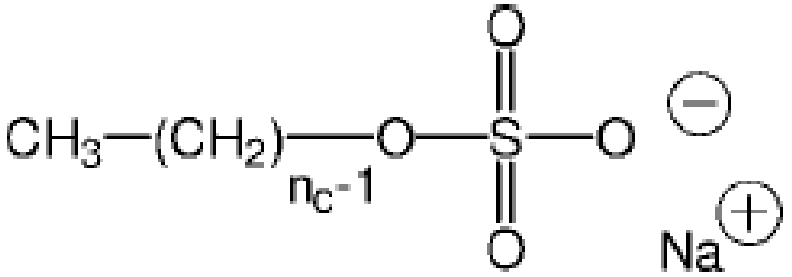


Fig. 1 Dependence of surface tension on concentration in SDS aqueous solutions

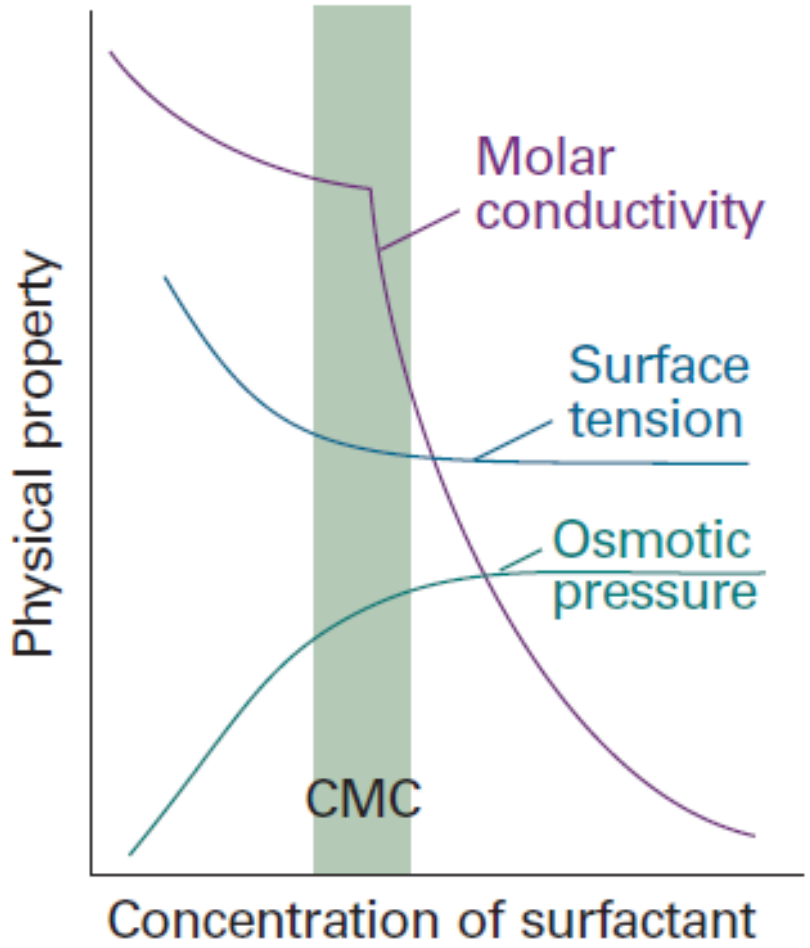


$n_C = 12$, sodium dodecylsulfate (SDS)

$$x_{cmc} = \frac{n_{surf}}{55{,}55} = \frac{8{,}1 \times 10^{-3}}{55{,}55} = 1{,}46 \times 10^{-4}$$

número de moles de 1 L H_2O

J. Zhang, Y. Meng, *Tribology Letters* **56**, 543-552 (2014).



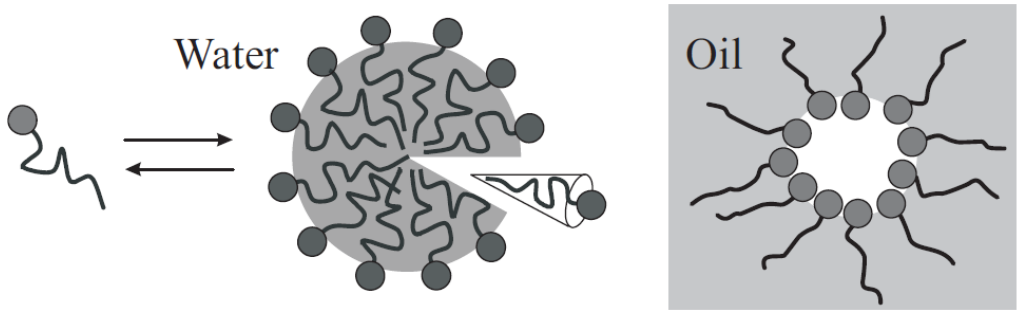
Surfactant	Solution	Critical micelle concentration (mole liter^{-1})	Aggregation number n
Sodium dodecyl sulfate	Water	0.00810	80
	0.02 M NaCl	0.00382	94
	0.03 M NaCl	0.00309	100
	0.10 M NaCl	0.00139	112
	0.20 M NaCl	0.00083	118
	0.40 M NaCl	0.00052	126

Fig. 19.40 The typical variation of some physical properties of an aqueous solution of sodium dodecylsulfate close to the critical micelle concentration (CMC).

P. W. Atkins, *Physical Chemistry*, Oxford University Press, 5th ed., 1994.

P. C. Hiemenz, R. Rajagopalan, *Principles of Colloid and Surface Chemistry*, Marcel Dekker, 3rd ed., 1997.

Estrutura dos agregados



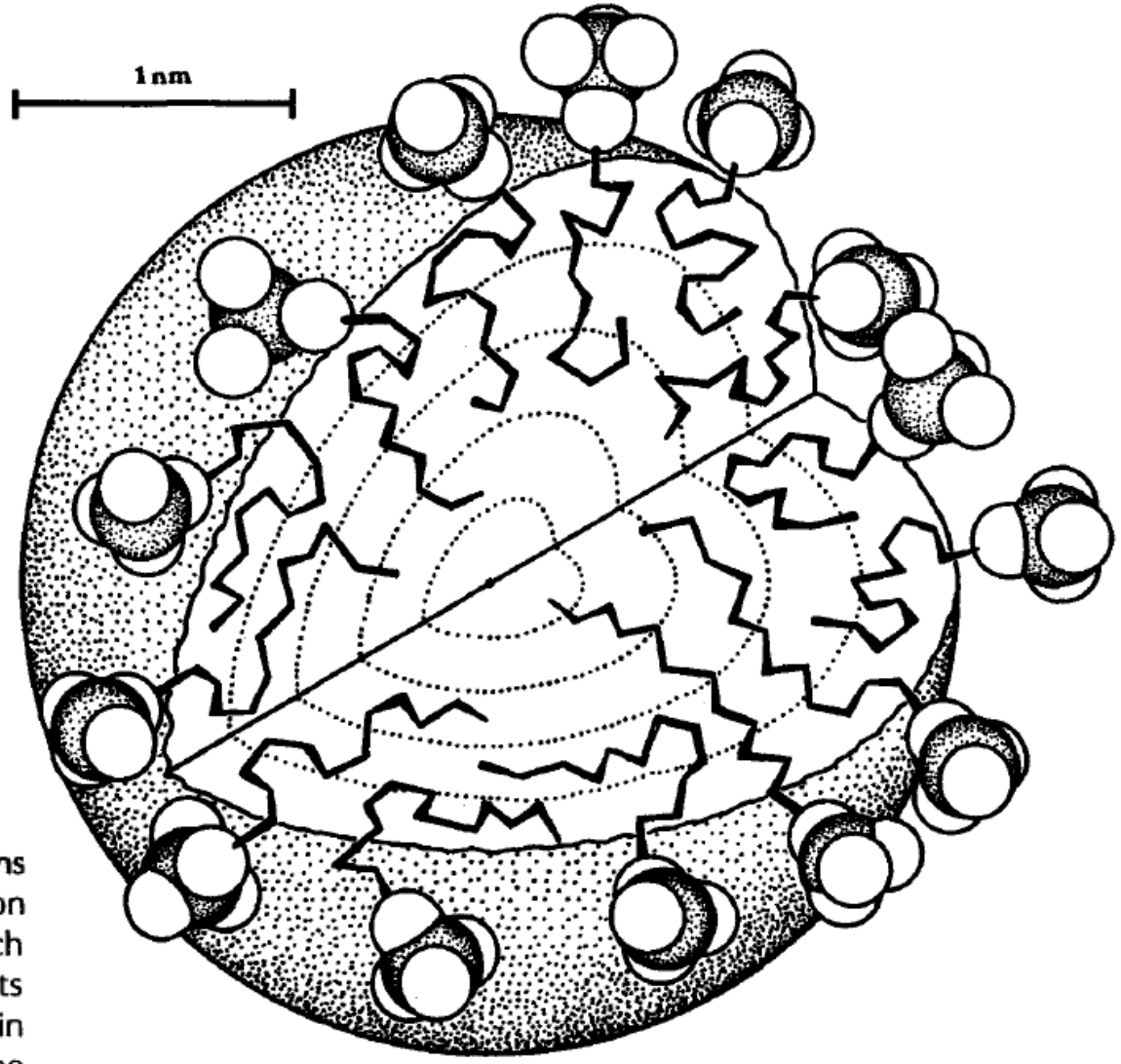
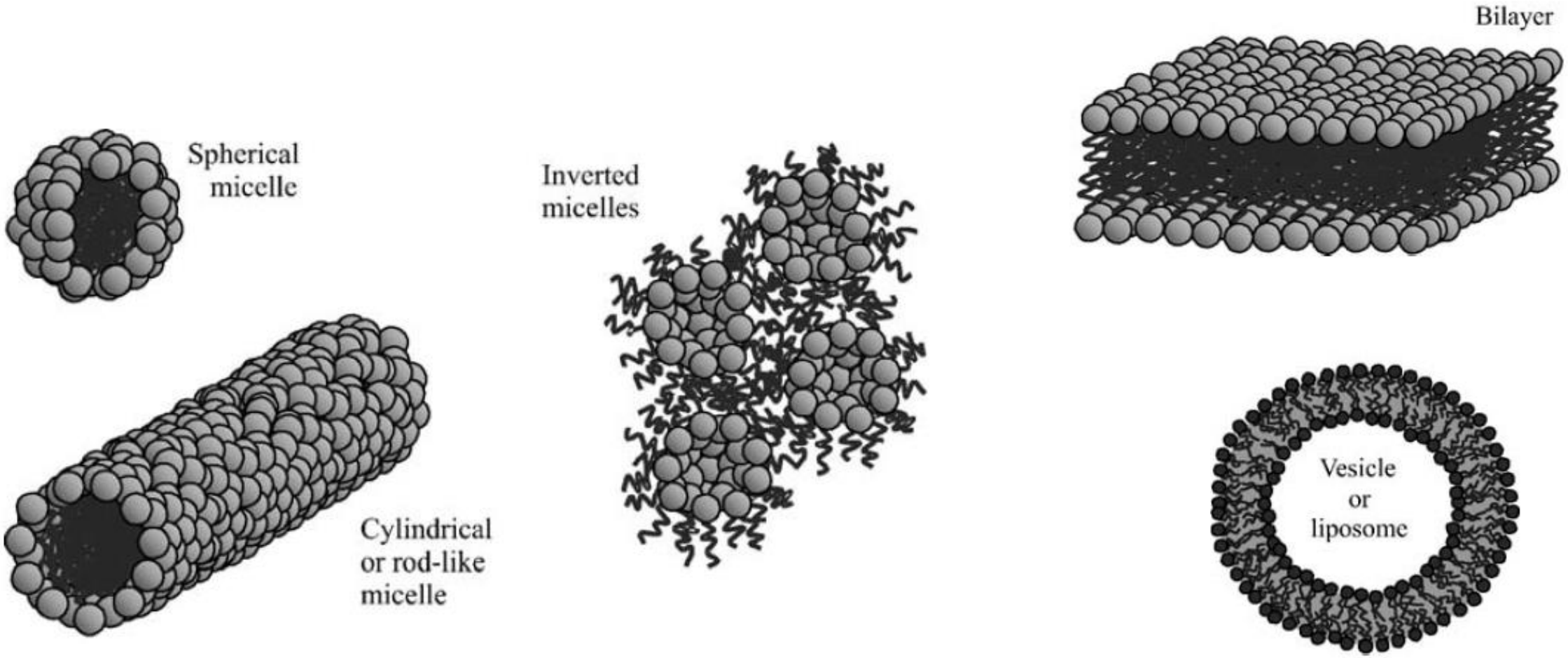


Fig. 17.3. A sodium dodecylsulphate (SDS) micelle drawn to scale. The micelle contains 60 sodium dodecylsulphate molecules. The hydrocarbon chains pack at liquid hydrocarbon density in the core where they are almost as disordered as in the bulk liquid state. Each of the five spherical shells contains approximately the correct number of chain segments to ensure even chain packing density throughout. Note that all segments of the chain spend an appreciable proportion of time near the micelle surface. Thus, even though the core is almost completely devoid of water each segment samples the hydrophilic environment. Drawing based on calculations by Gruen (1981) and Gruen and de Lacey (1984).

J. Israelachvili, *Intermolecular & Surface Forces*, Academic Press, 2nd ed., 1991.
H. J. Butt, K. Graf, M. Kappl, *Physics and Chemistry of Interfaces*, Wiley-VCH, 2003.

Estrutura dos agregados

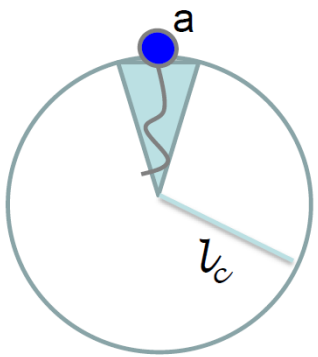


H. J. Butt, K. Graf, M. Kappl, *Physics and Chemistry of Interfaces*, Wiley-VCH, 2003.

Estrutura dos agregados

Parâmetro de empacotamento

$$P = \frac{V}{l_c a}$$



V = volume da cauda hidrofóbica
l_c = comprimento da causa hidrofóbica
a = área da cabeça hidrofílica na interface

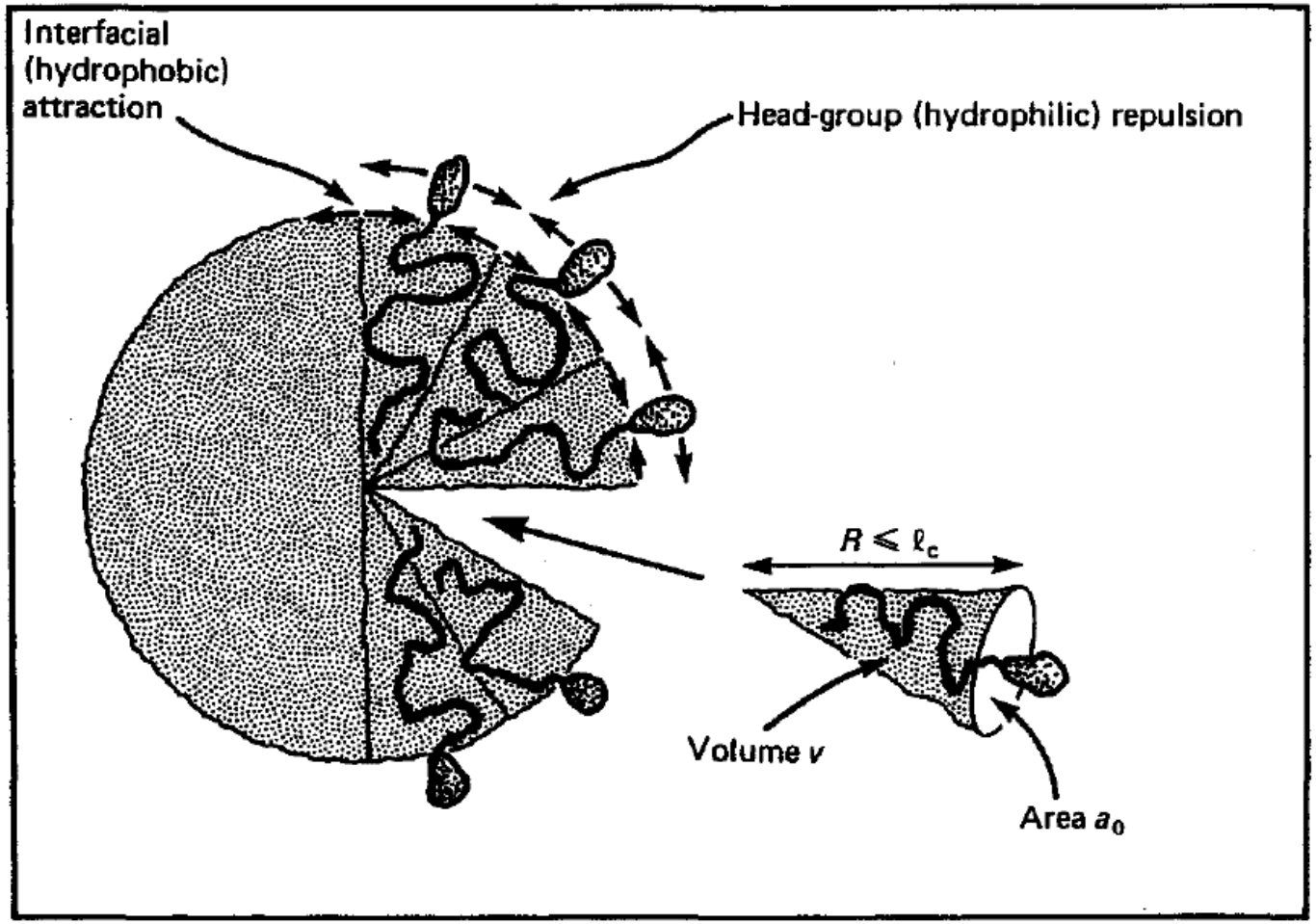
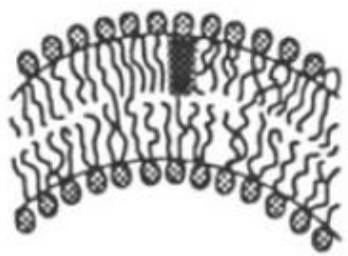
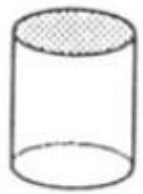
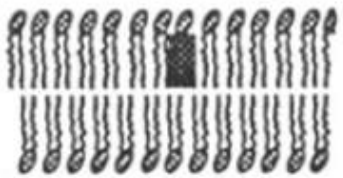
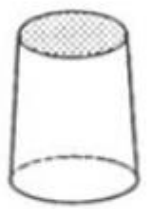
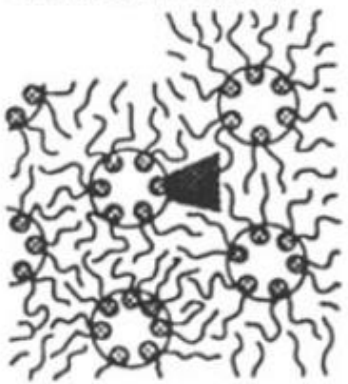


Fig. 17.1. The hydrocarbon interiors in both micelles and bilayers are normally in the fluid state (Shinitzky *et al.*, 1971; Lindblom and Wennerström, 1977). Repulsive headgroup forces and attractive hydrophobic interfacial forces determine the optimum headgroup area a_0 at which μ_N^0 is a minimum (see Fig. 17.2). The chain volume v and chain length l_c set limits on how the fluid chains can pack together, on average, inside an aggregate. Thus, the mean molecular conformation depends on a_0, v and l_c.

J. Israelachvili, *Intermolecular & Surface Forces*, Academic Press, 2nd ed., 1991.

Critical packing parameter	Critical packing shape	Structures formed
< 1/3	Cone 	Spherical micelles 
1/3–1/2	Truncated cone 	Cylindrical micelles 
1/2–1	Truncated cone 	Flexible bilayers, vesicles 

Critical packing parameter	Critical packing shape	Structures formed
~ 1	Cylinder 	Planar bilayers 
> 1	Inverted truncated cone or wedge 	Inverted micelles 

P. C. Hiemenz, R. Rajagopalan, *Principles of Colloid and Surface Chemistry*, Marcel Dekker, 3rd ed., 1997.

Termodinâmica da micelização

$$nS \leftrightarrows S_n$$

$$\Delta G_{mic} = \mu_{surf}(mic) - \mu^o_{surf} = RTln(x_{CMC})$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S$$

$$\Delta G = \Delta H - T\Delta S$$

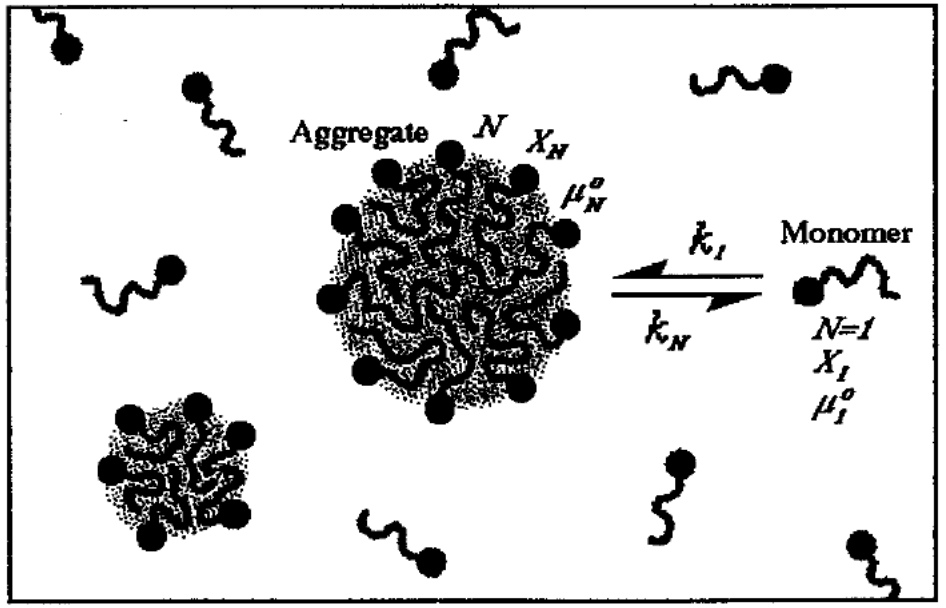


Fig. 16.3. Association of *N* monomers into an aggregate (e.g., a micelle). The mean lifetime of an amphiphilic molecule in a small micelle is very short, typically 10^{-5}–10^{-3} s.

Exemplo, se CMC = 1 mM

ΔG_{mic} = -17,1 kJ/mol a 25 °C

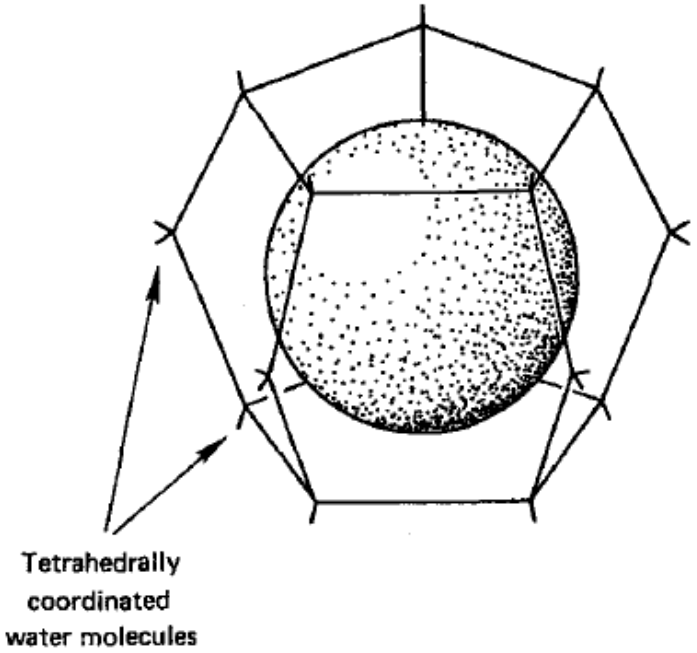
típico ΔH_{mic} ~ +2 kJ/mol

então, ΔS_{mic} ~ +65 J/Kmol

H. J. Butt, K. Graf, M. Kappl, *Physics and Chemistry of Interfaces*, Wiley-VCH, 2003.

J. Israelachvili, *Intermolecular & Surface Forces*, Academic Press, 2nd ed., 1991.

Efeito Hidrofóbico

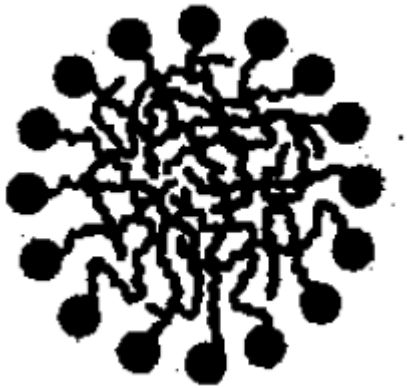


Ordenamento de moléculas de água em torno de uma molécula de soluto apolar é entropicamente desfavorável. (Note que a interação é atrativa entre o soluto hidrofóbico e água).

Fig. 8.4. Clathrate 'cages' formed by water molecules around a dissolved non-polar solute molecule. Such structures are not rigid but labile, and their H bonds are not stronger than in pure water, but the water molecules forming these cages are more ordered than in the bulk liquid.

Interação Hidrofóbica

Segregação de muitas moléculas do soluto apolar numa única estrutura demanda menos ordenamento (entropia maior) das moléculas de água ao redor.

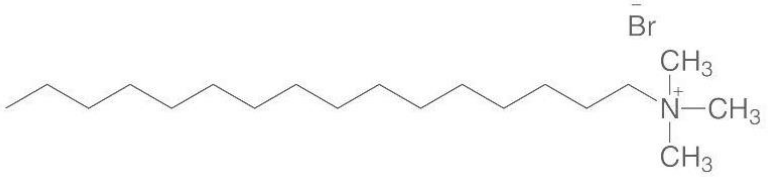


J. Israelachvili, *Intermolecular & Surface Forces*, Academic Press, 2nd ed., 1991.

Tensão superficial e CMC do brometo de cetiltrimetilamônio

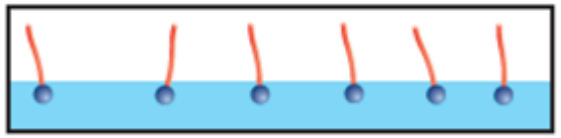
(CTAB, brometo de hexadeciltrimetilamônio, $[(C_{16}H_{33})N(CH_3)_3]Br$)

Tensão Superficial (N/m)	1ª medição	2ª medição	3ª medição
H_2O			
CTAB (0,3 mmol/L)			
CTAB (0,4 mmol/L)			
CTAB (0,5 mmol/L)			
CTAB (0,6 mmol/L)			
CTAB (1,0 mmol/L)			
CTAB (2,0 mmol/L)			
CTAB (4,0 mmol/L)			
CTAB (8,0 mmol/L)			
CTAB (10,0 mmol/L)			



M = 364,45 g/mol

Concentração superficial em excesso, Γ



$$\Gamma_{surf} = \frac{n_{surf}}{\sigma}$$

n_{surf}: número de moléculas de surfactante na superfície

σ: área

equação de Gibbs da tensão superficial $\quad d\gamma = -\sum_j \Gamma_j d\mu_j$

$$d\gamma = -\Gamma_{surf} d\mu_{surf}$$

$$d\mu_{surf} = RT\, d\ln c$$

isoterma de adsorção de Gibbs

$$\left(\frac{\partial \gamma}{\partial \ln c}\right)_T = -RT\Gamma_{surf}$$

$\gamma \times \ln c$

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