Universidade de São Paulo
Instituto de Química

L4 - Determinação da concentração micelar crítica por **Tensiometria** e **Condutometria**

Prof. Vitor Leite Martins

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QFL1444 - 2023

Interface entre duas fases

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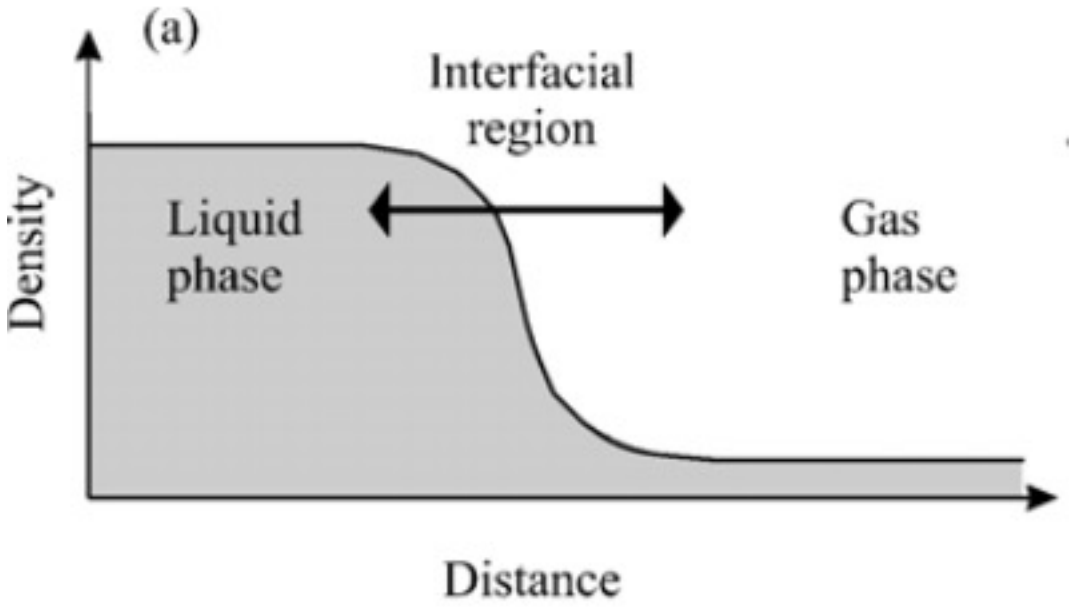
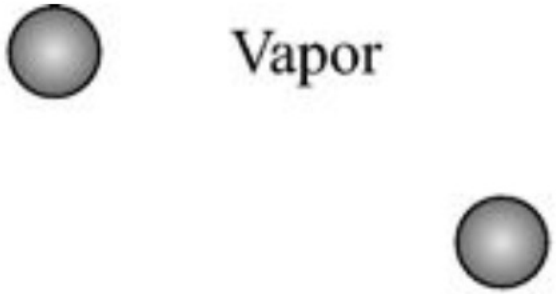
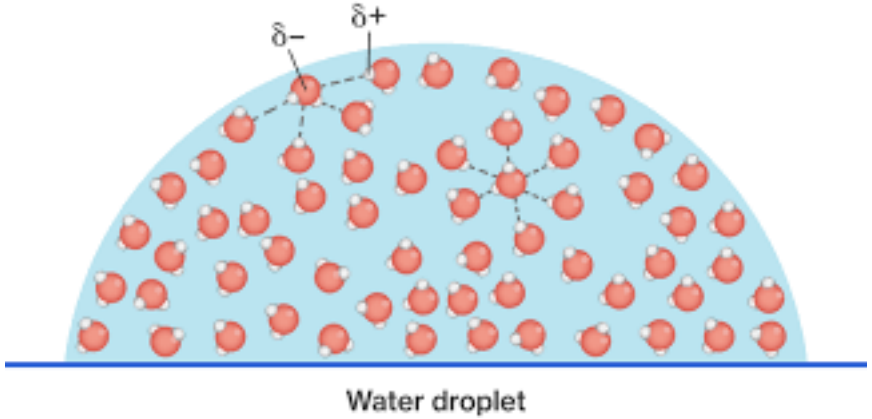
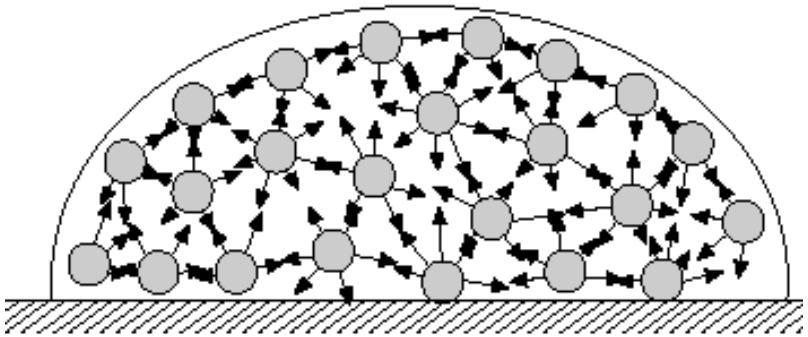


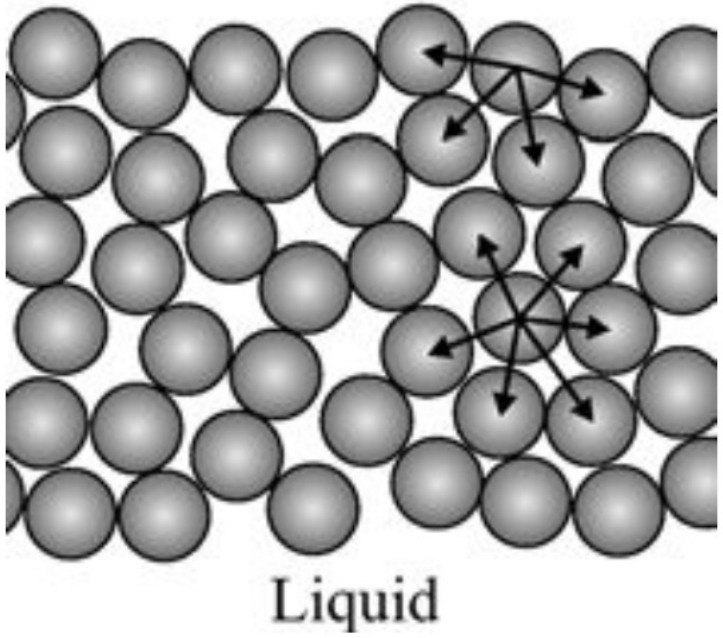
Butt, Graf, Kappl. Physics and Chemistry of Interfaces. 2003, Wiley-VCH

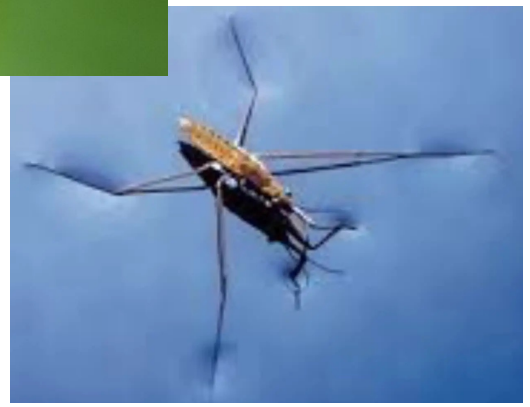
Interface entre duas fases

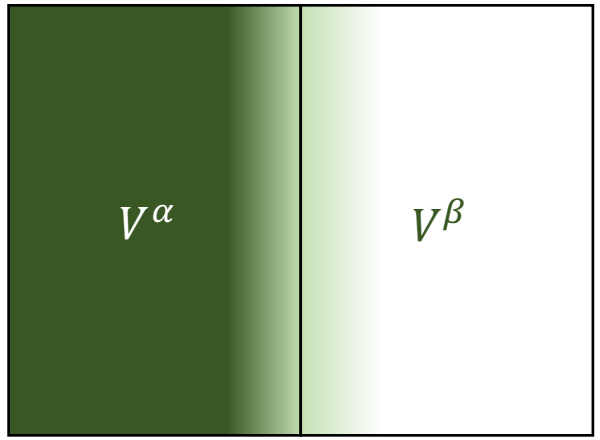












Interface de área σ

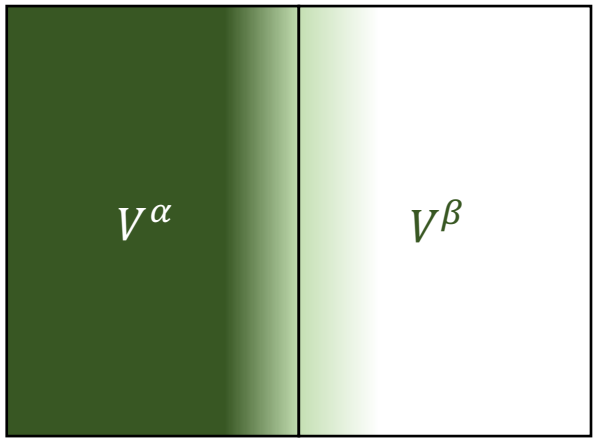
Butt, Graf, Kappl. Physics and Chemistry of Interfaces. 2003, Wiley-VCH

Definição de Tensão Superficial, γ

Energia livre de Gibbs $G = H - TS$

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

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



Interface de área σ

$G(p,T,n_A)$ $\quad dG = Vdp - SdT + \mu_a dn_a$

$$\left(\frac{\partial G}{\partial n_A}\right)_{p,T}$$

$G(p,T,n_A,\sigma)$ $\quad dG = Vdp - SdT + \mu_a dn_a + \gamma d\sigma$

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

Atkins' Physical Chemistry 11th ed.
Butt, Graf, Kappl. Physics and Chemistry of Interfaces. 2003, Wiley-VCH

Definição de Tensão Superficial, γ

$$dG = Vdp - SdT + \mu_a dn_a + \gamma d\sigma$$

Trabalho máximo sem expansão: $dG = dw_{add,rev}$

$$dw = \gamma d\sigma$$

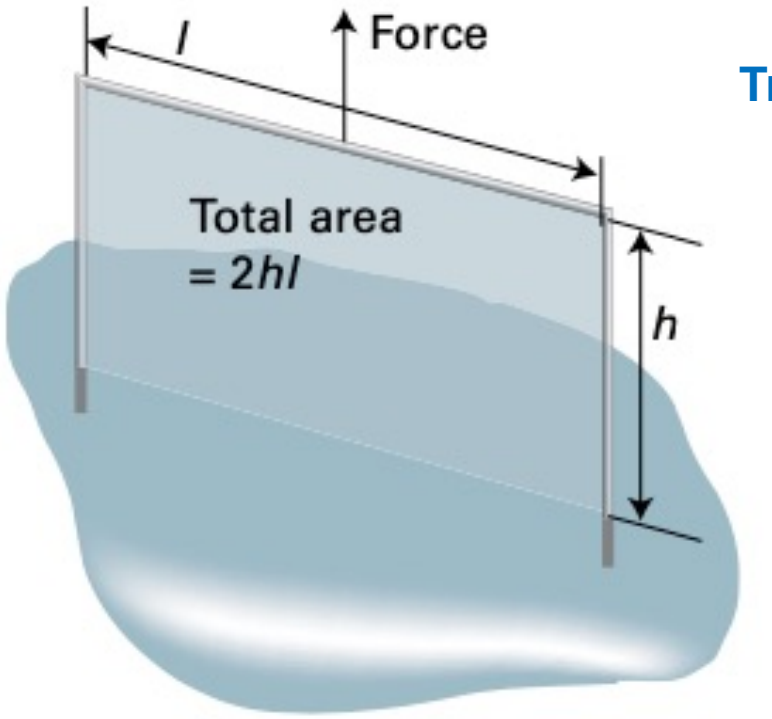
Trabalho para aumentar a área

$$Nm = Nm^{-1}\ m^2$$

unidade SI

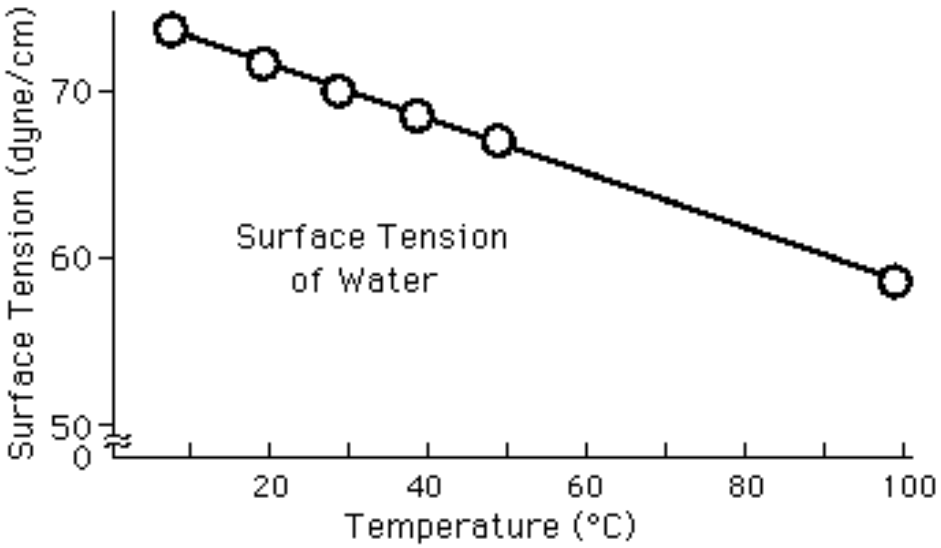
Também comum:

$$\frac{dyn}{cm} = \frac{10^{-3}N}{m} = \frac{mN}{m}$$



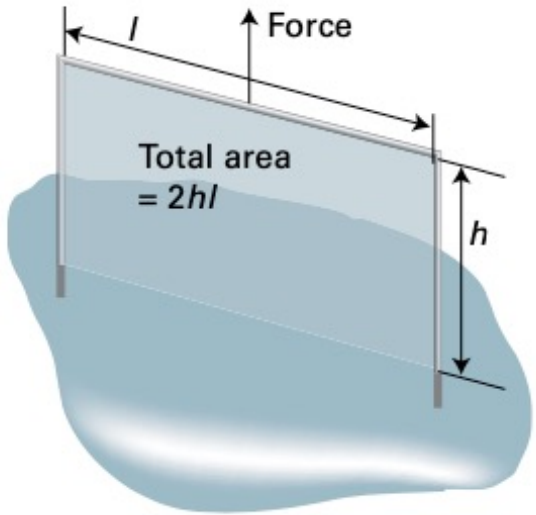
	$\gamma/(\mathrm{mN\,m^{-1}})$
Benzene	28.88
Mercury	472
Methanol	22.6
Water	72.75

a 293 K



Atkins' Physical Chemistry 11th ed.

Medindo a tensão superficial



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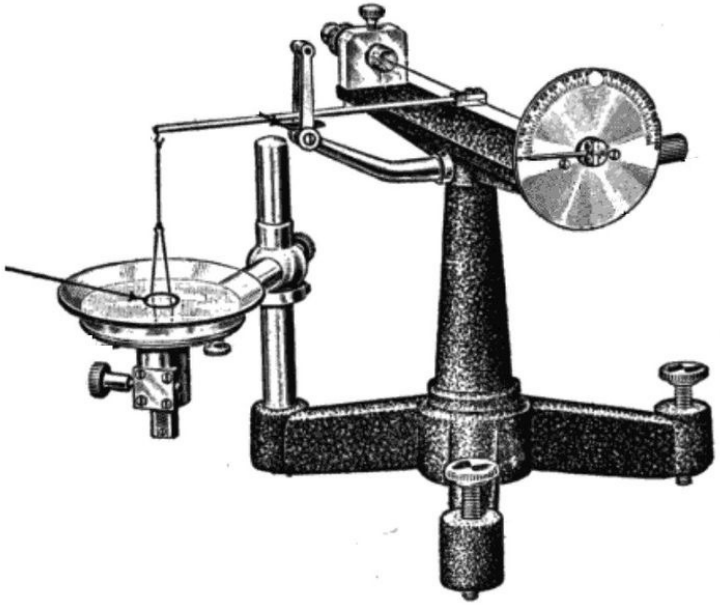
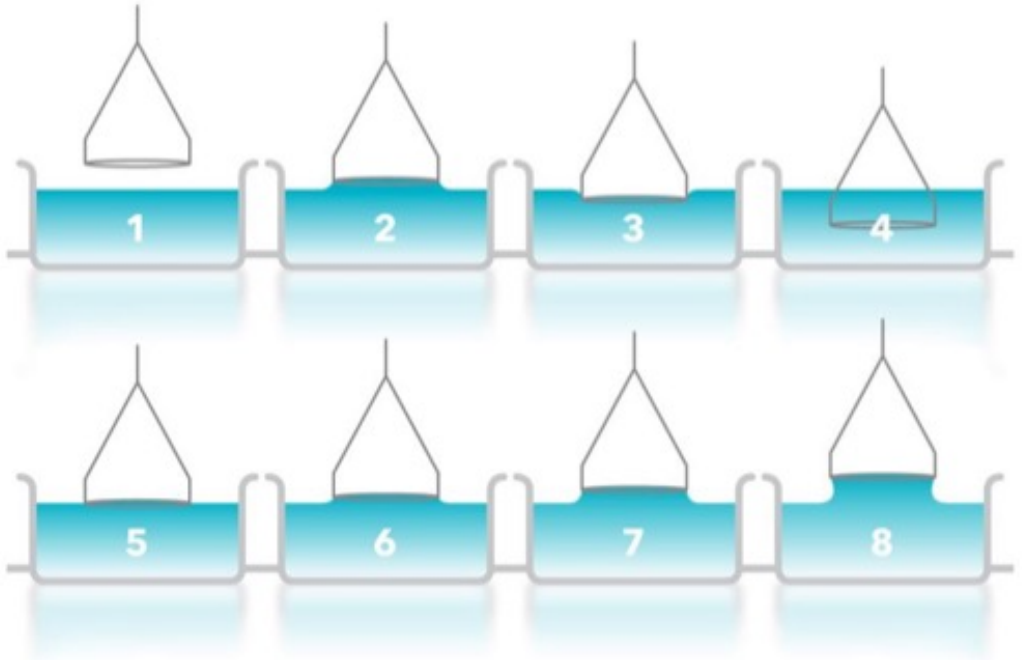
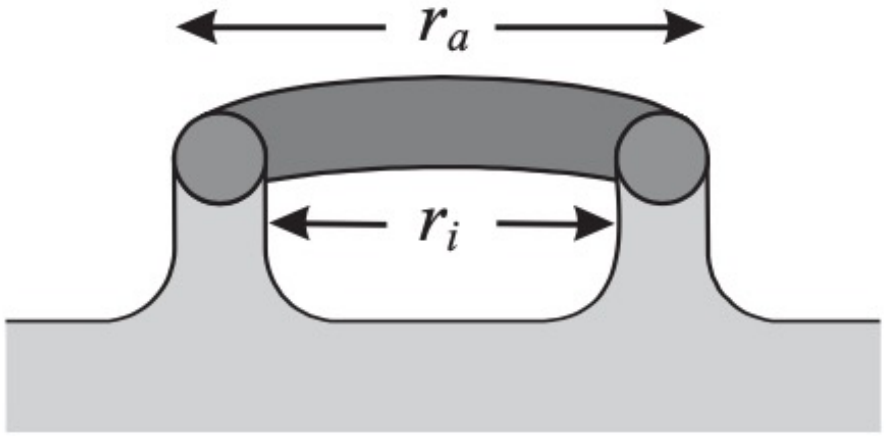
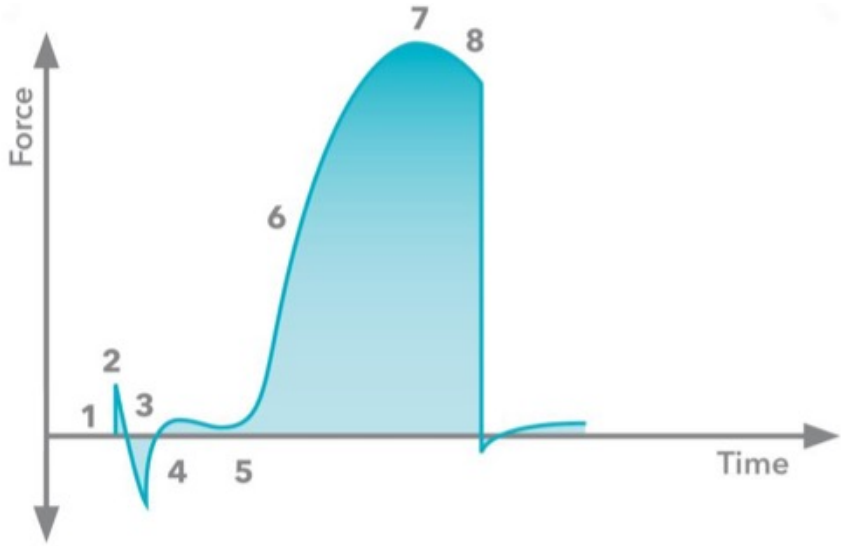


Tensiômetro de anel (du Noüy)



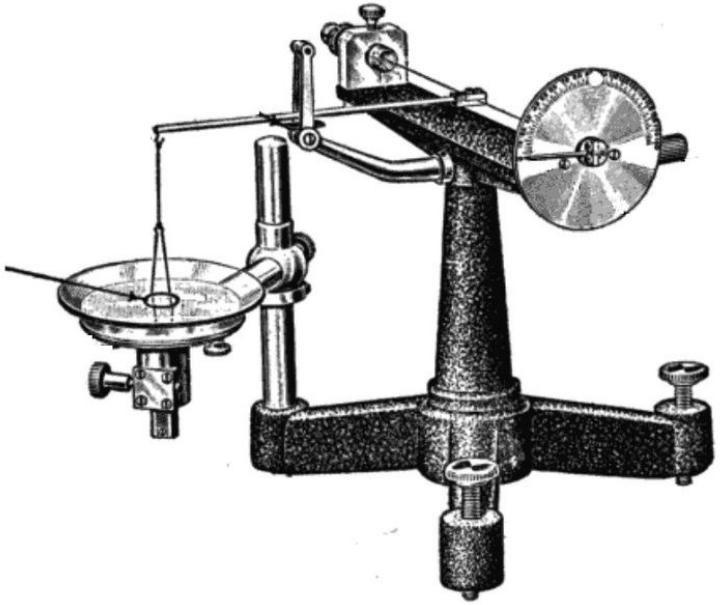


$$F = 2\pi(r_i + r_a)\gamma$$



Butt, Graf, Kappl. Physics and Chemistry of Interfaces. 2003, Wiley-VCH

Medindo a tensão superficial



Tensiômetro de anel (du Noüy)

AN INTERFACIAL TENSIOMETER FOR UNIVERSAL USE.

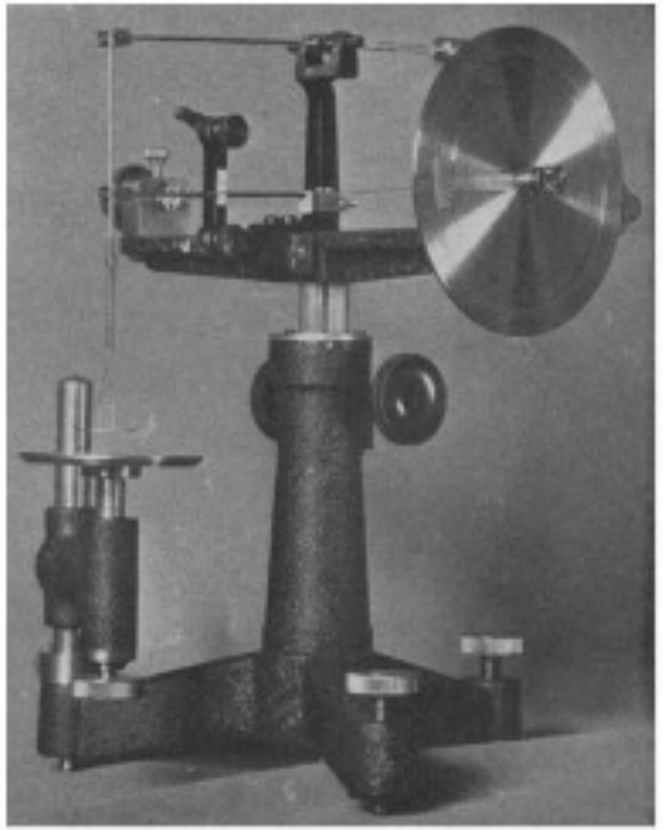
By P. LECOMTE du NOÜY.

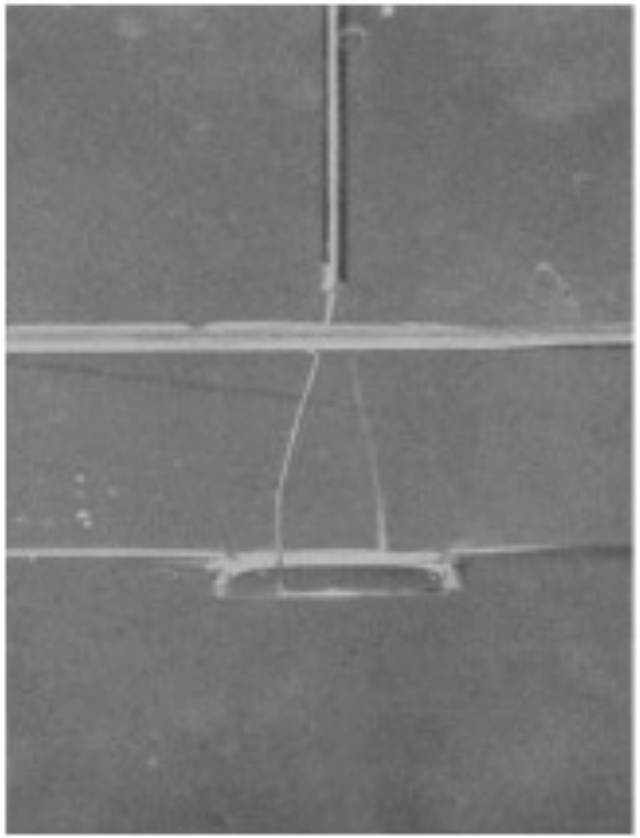
(*From the Laboratories of The Rockefeller Institute for Medical Research.*)

PLATE 5.

(Accepted for publication, April 6, 1925.)

J Gen Physiol (1925) 7 (5): 625–631.





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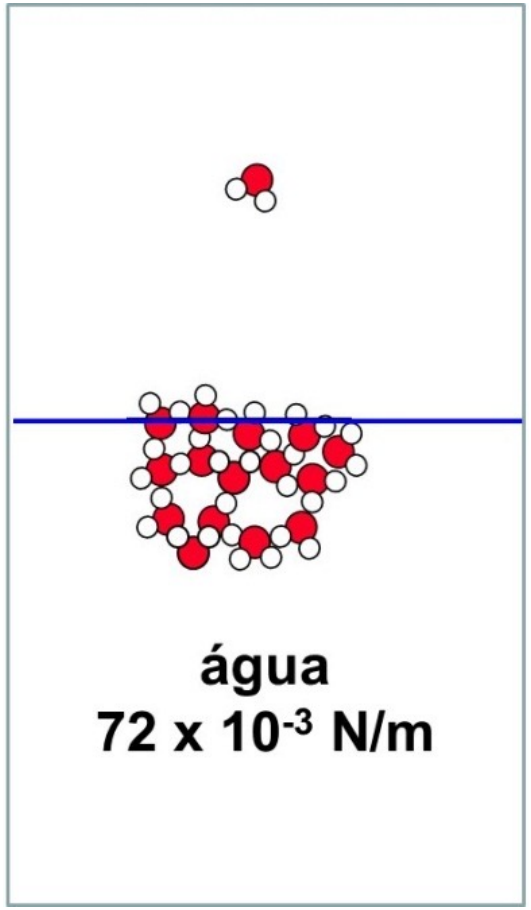
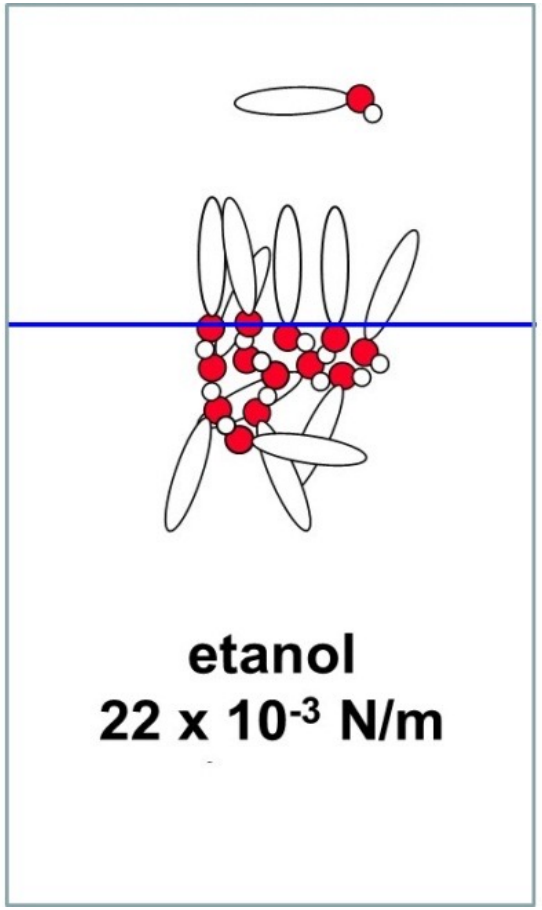
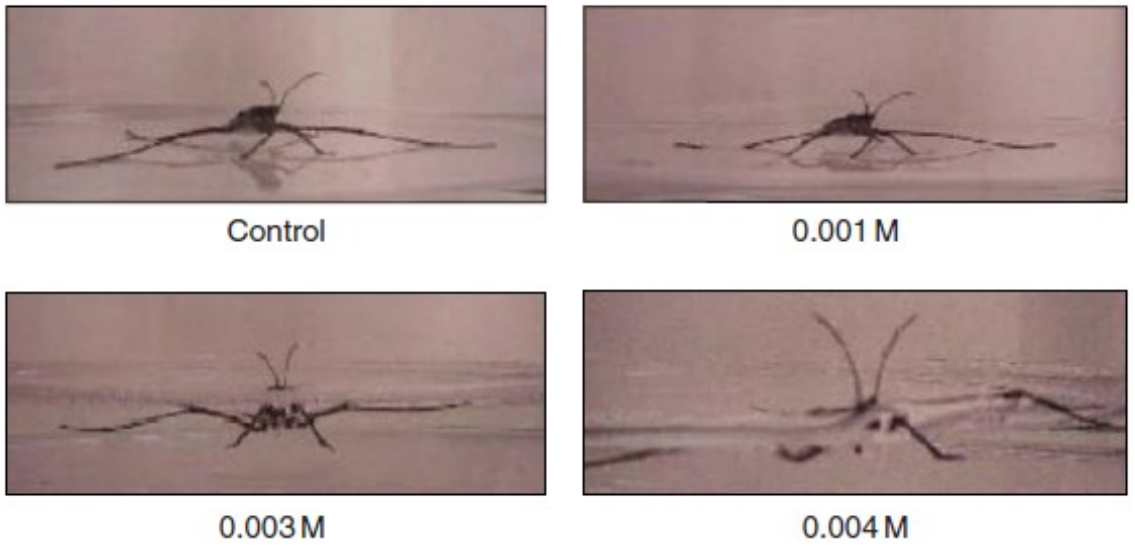




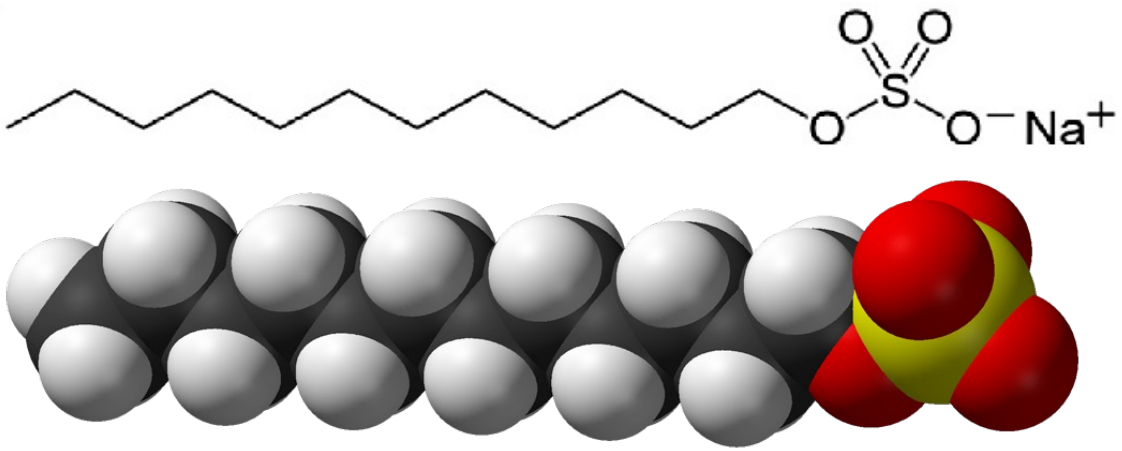
E soluções de surfactante!

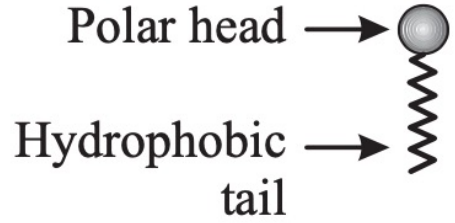
Surfactantes



Inseto-jesus em soluções aquosas de SDS

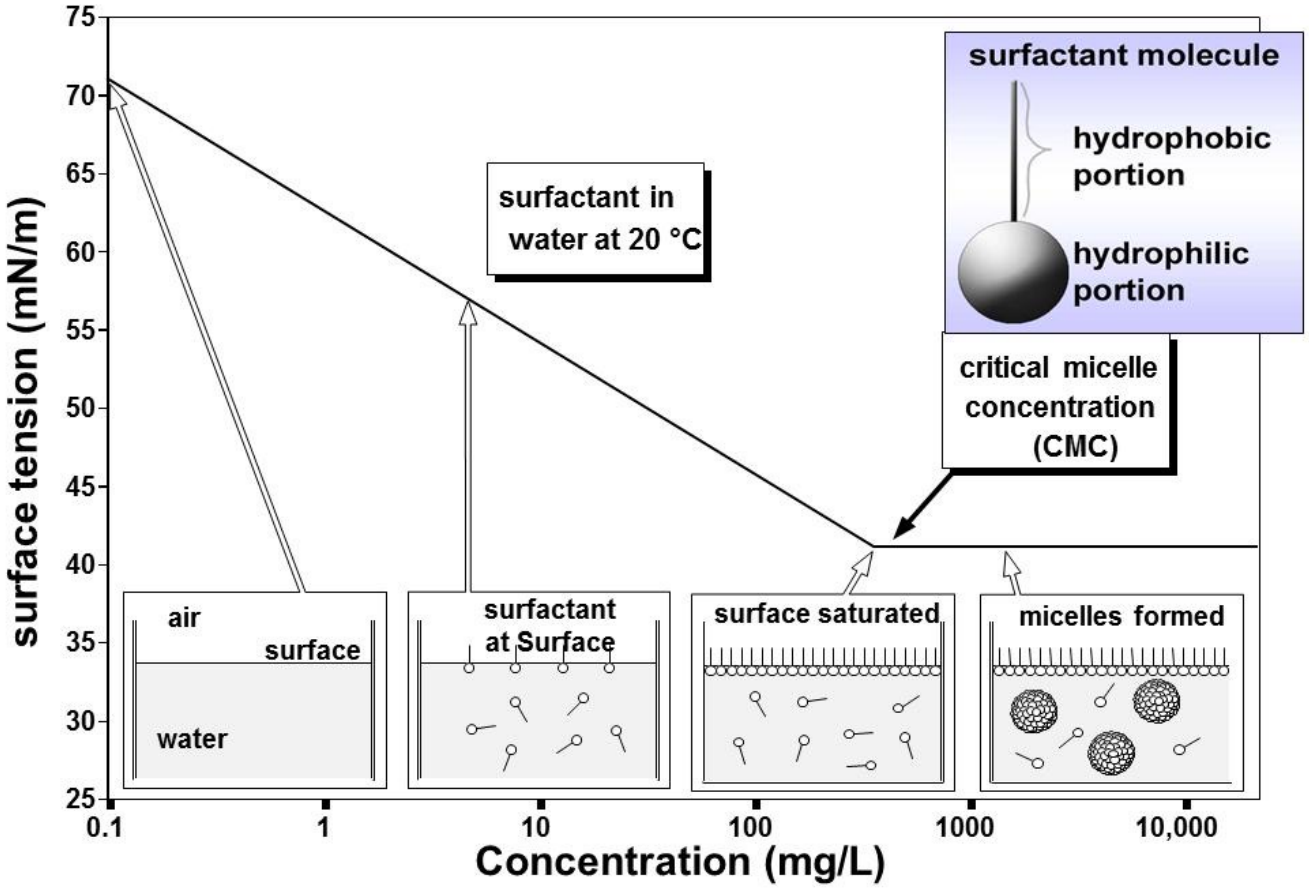
Kontogeorgis & Kiil, *Introduction to Applied Colloid and Surface Chemistry*- John Wiley & Sons (2016)



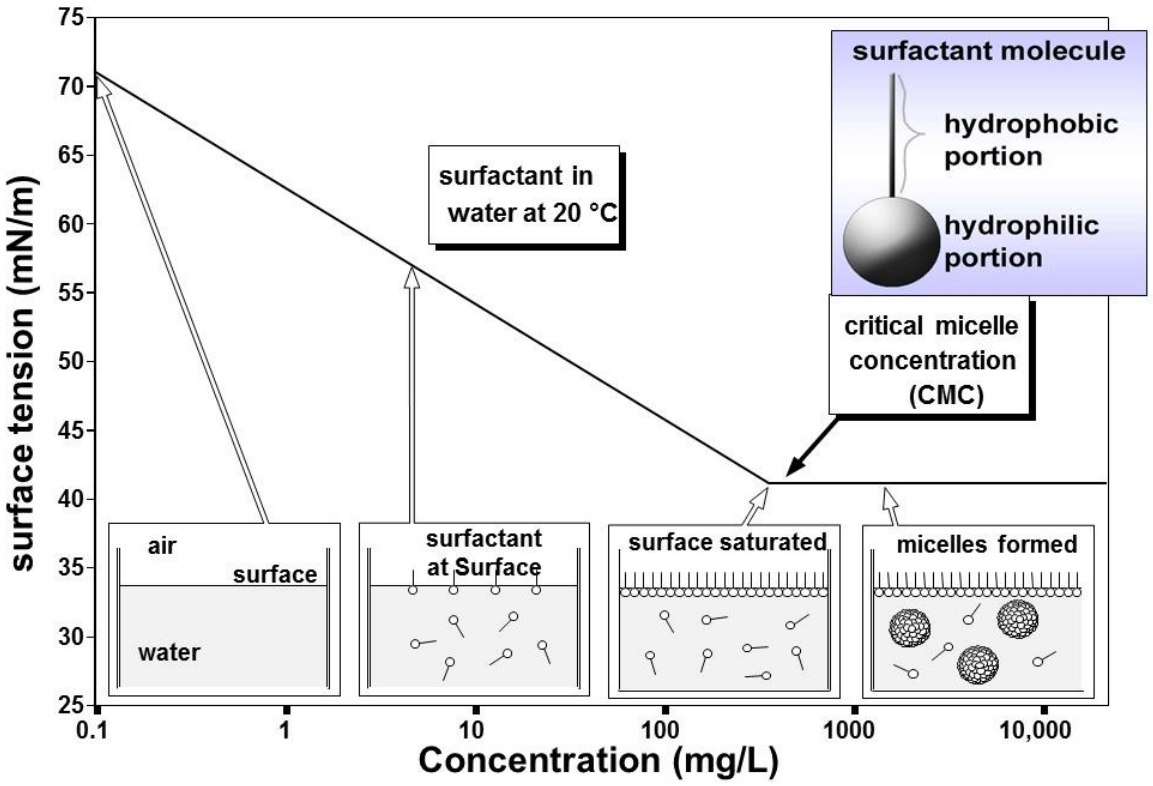


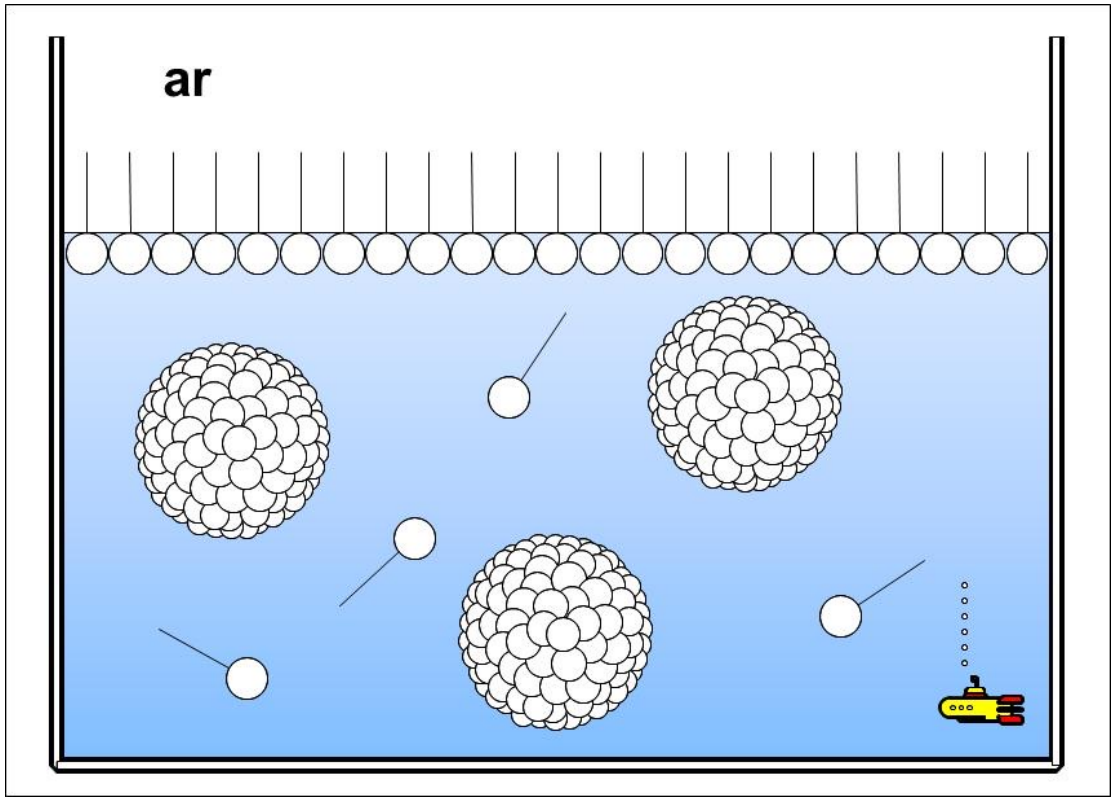
Interação com a água?

Depende da concentração!



Micelas e CMC

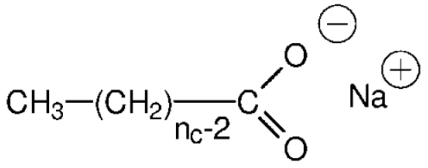




Tipos de Surfactantes

Aniônicos

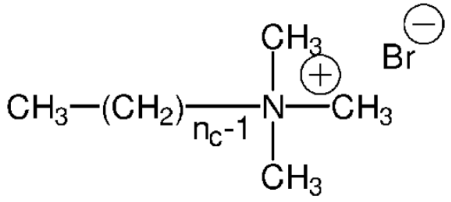
Sodium alkylcarboxylate



	CMC
Sodium salt of	
$n_C = 10$, decanoic acid	100
$n_C = 11$, undecanoic acid	50
$n_C = 12$, dodecanoic (lauric) acid	25
$n_C = 13$, tridecanoic acid	13
$n_C = 14$, tetradecanoic (myristic) acid	6.3
$n_C = 16$, hexadecanoic (palmitic) acid	1.8
$n_C = 18$, octadecanoic (stearic) acid	
$n_C = 20$, eicosanoic (arachidic) acid	
$n_C = 22$, docosanoic (behenic) acid	

Catiônico

Alkyltrimethylammonium bromide



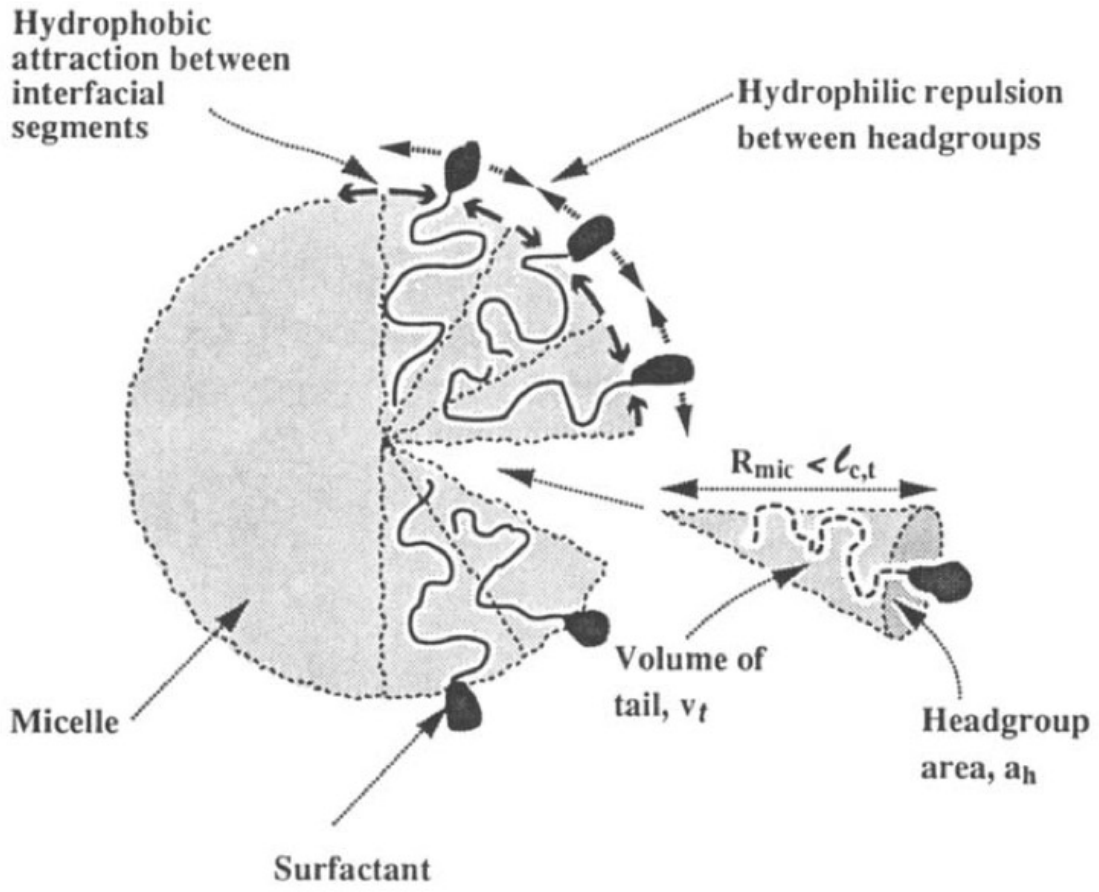
$n_C = 10$, decyl trimethylammonium bromide	66
$n_C = 12$, dodecyl trimethylammonium bromide	15
$n_C = 14$, tetradecyl trimethylammonium bromide (TTAB)	3.5
$n_C = 16$, hexadecyl trimethylammonium bromide (CTAB)	0.9

Não-iônico

Alkylethylene glycol		
$C_{10}H_{21}(OCH_2CH_2)_4OH$	$C_{10}E_4$	0.79
$C_{10}H_{21}(OCH_2CH_2)_6OH$	$C_{10}E_6$	0.9
$C_{10}H_{21}(OCH_2CH_2)_8OH$	$C_{10}E_8$	1.0
$C_{12}H_{25}(OCH_2CH_2)_8OH$	$C_{12}E_8$	0.071
$C_{14}H_{29}(OCH_2CH_2)_8OH$	$C_{14}E_8$	0.009

Estrutura dos agregados

Parâmetro de empacotamento: $$P = \frac{V}{l_c a}$$



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
~ 1	Cylinder	Planar bilayers
> 1	Inverted truncated cone or wedge	Inverted micelles

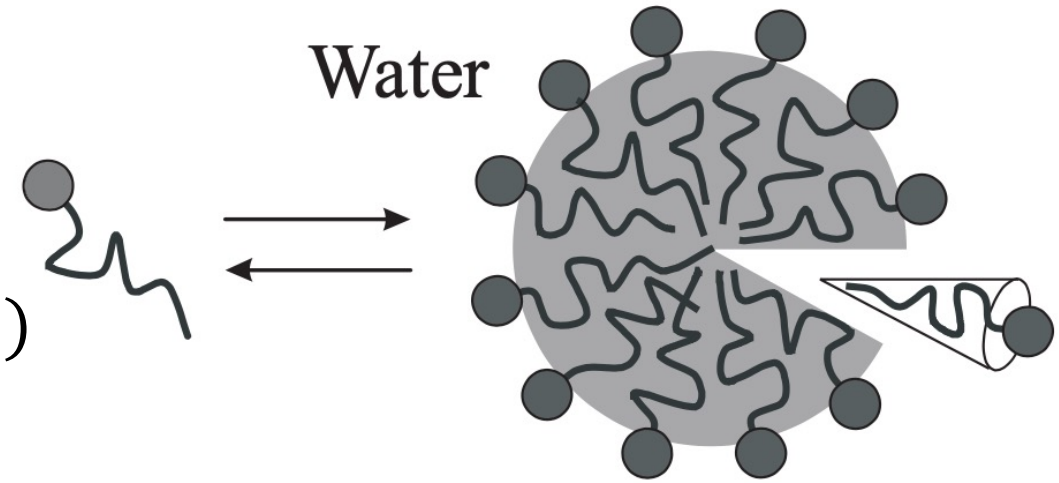
Hiemenz, Rajagopalan. Principles of Colloid and Surface Chemistry. 1998, Marcel Dekker Inc.

Termodinâmica da micelização

$$nS \rightleftharpoons S_n$$

Equilíbrio!

Na CMC temos o eq. da micelização:



Podemos encontrar ΔG ?

$$\Delta G_{mic} = \mu_{surf,mic} - \mu^0_{surf} = RT \ln(x_{cmc})$$

Podemos encontrar ΔS_{mic} ?

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

Podemos encontrar ΔH_{mic} ?

$$\Delta G_{mic} = \Delta H_{mic} - T\Delta S_{mic}$$

Exemplo:
SDS a 25 ºC

$$\Delta G_{mic} = -21\ kJ\ mol^{-1}$$

$$\Delta H_{mic} = +2{,}54\ kJ\ mol^{-1}$$

$$\Delta S_{mic} = +81{,}9\ kJ\ mol^{-1}$$

Qual a força motriz da micelização?

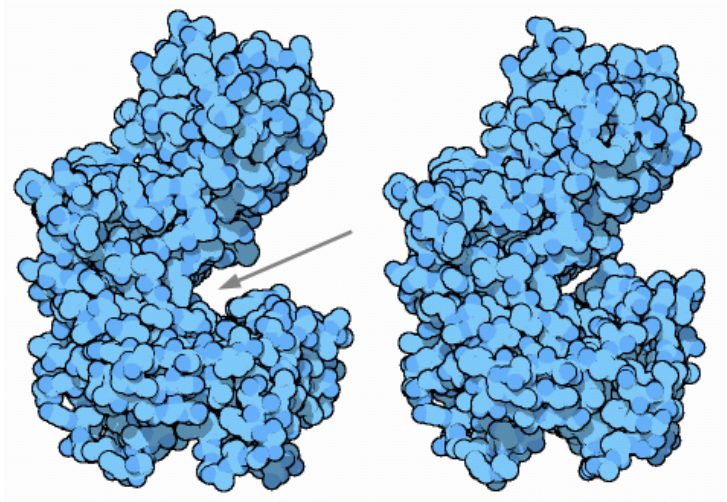
Butt, Graf, Kappl. Physics and Chemistry of Interfaces. 2003, Wiley-VCH

Concentração superficial em excesso, Γ

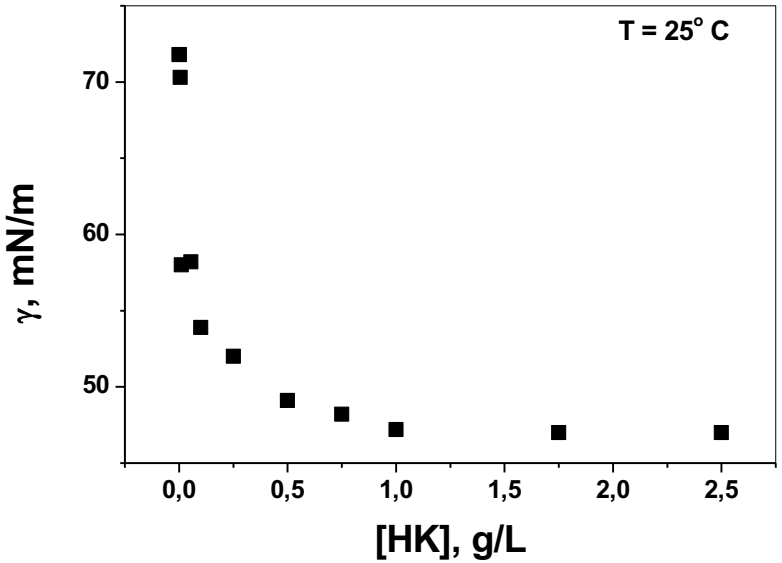
nº de moléculas na superfície

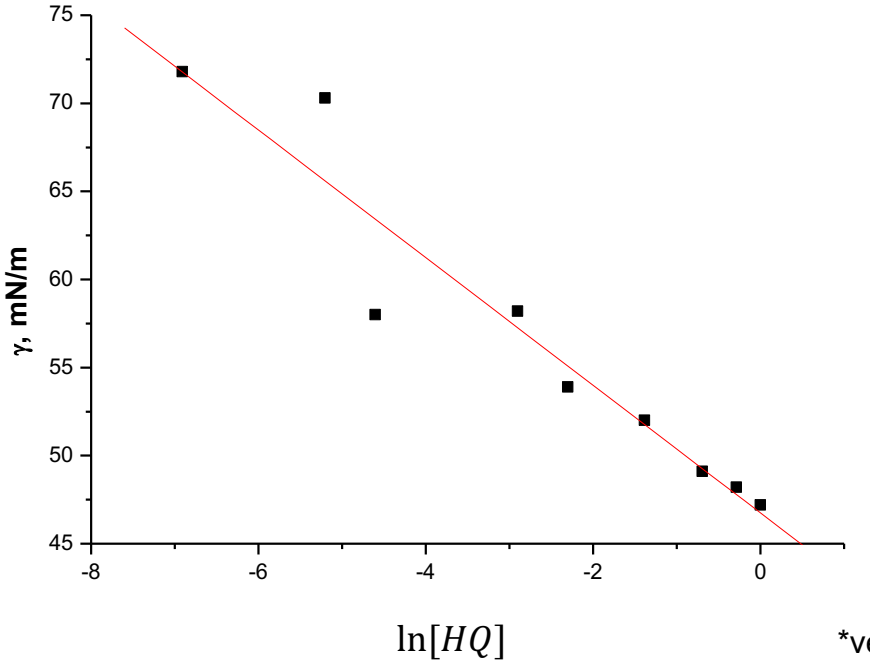
$$\Gamma = \frac{n_{surf}}{\sigma}$$

área da superfície



Hexokinase: catalisa a fosforilação da glicose





Isoterma de adsorção de Gibbs*

$$\Gamma = -\frac{1}{\mathrm{RT}}\left(\frac{\mathrm{d}\gamma}{d\ \ln(c)}\right)_{\mathrm{p,T}}$$

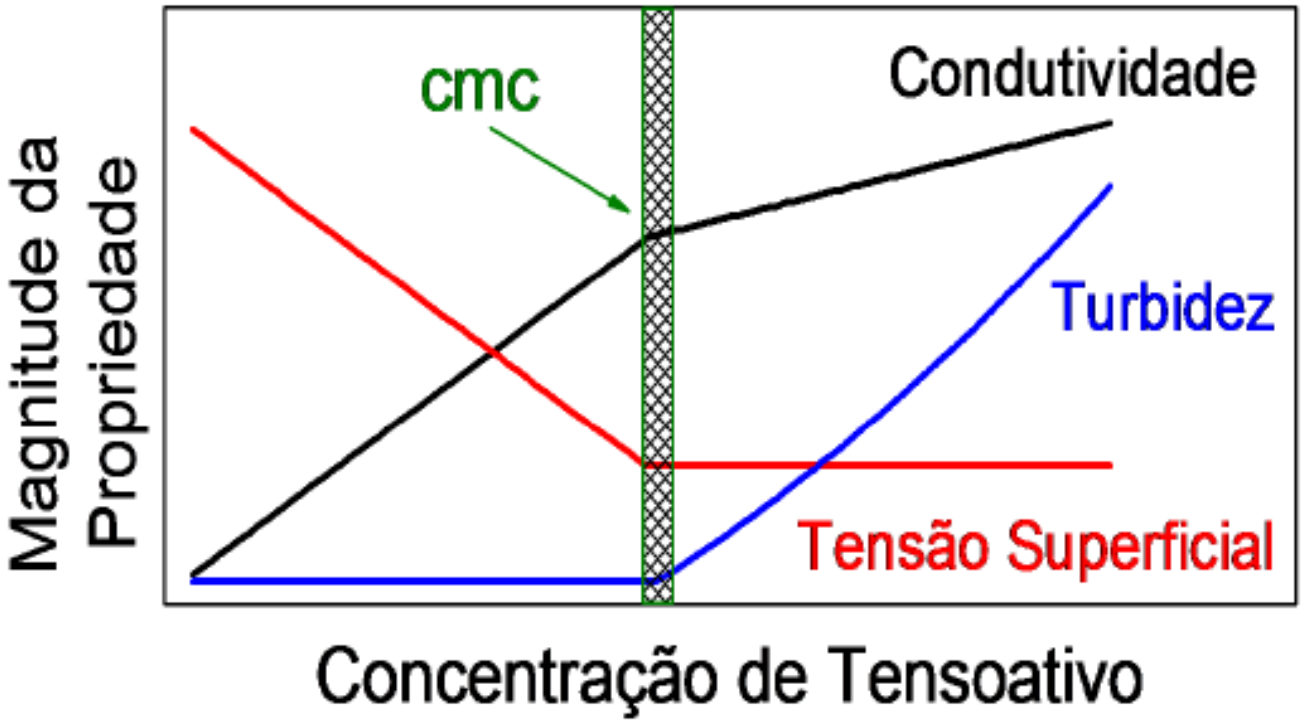
$$\left(\frac{\mathrm{d}\gamma}{d\ \ln(c)}\right)_{\mathrm{p,T}} = -\mathrm{RT}\ \Gamma$$

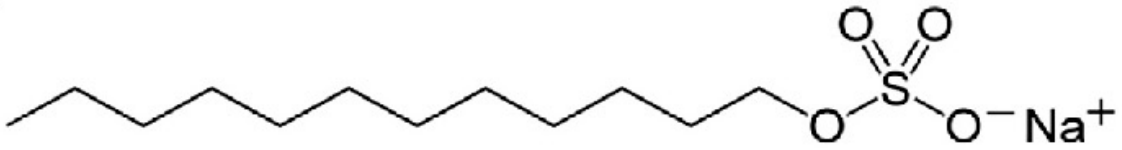
$$\gamma \times \ln(c)$$

$$\Gamma = 8{,}80 \cdot 10^{17}\ \text{moléculas/m}^2$$

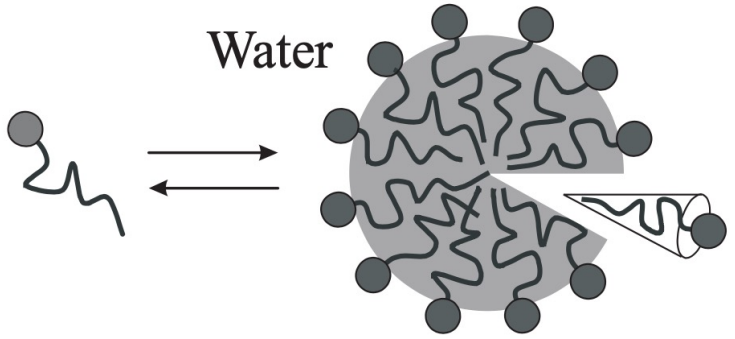
*ver pag. 610 Atkins' Physical Chemistry 11th ed.

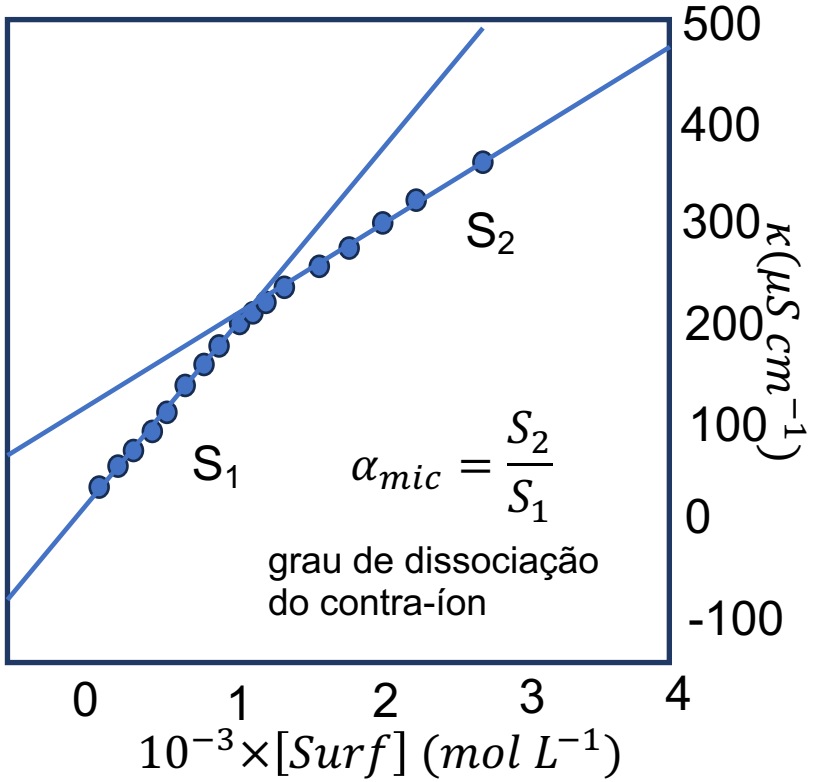
Outras propriedades





O que afeta a condutividade?



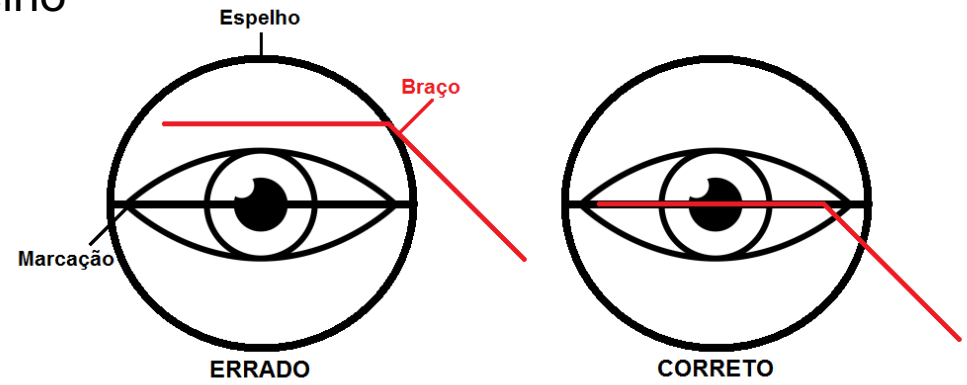


No lab.

Medidas de tensão superficial

Assista ao vídeo de operação disponibilizado no e-disciplinas antes da aula prática.

1. Limpeza do anel em Etanol antes do experimento e em água antes de todas as medidas
2. Colocar o anel no braço do aparelho. A cuba onde serão realizadas as medidas deverá ser preenchida aproximadamente com o mesmo volume em cada experimento (metade de sua capacidade). Coloque a cuba sobre a plataforma do aparelho e ajuste a altura da plataforma até que o anel entre no líquido. Verifique se o tensiômetro está no zero de sua escala e ajuste a altura da plataforma até que o braço esteja posicionado horizontalmente, dentro da marcação do aparelho



3. Fator de correção: $F = \frac{\gamma^{H_2O}_{literatura}}{\gamma^{H_2O}_{medido}}$

No lab.

Medidas de tensão superficial

Amostras	M1	M2	Média ± s	Temperatura
H_2O				
SDS 0,25 mmol L^{-1}				
SDS 0,50 mmol L^{-1}				
SDS 1,0 mmol L^{-1}				
SDS 2,0 mmol L^{-1}				
SDS 4,0 mmol L^{-1}				
SDS 6,0 mmol L^{-1}				
SDS 8,0 mmol L^{-1}				
SDS 10 mmol L^{-1}				
SDS 20 mmol L^{-1}				
Álcool comercial				

Cada grupo irá medir 3-4 concentrações.
Todos devem realizar medidas.
Medir da mais diluída para a mais concentrada

- Estimar CMC do SDS
- Calcular Γ e área ocupada por cada molécula
- Comparar e explicar os valores de tensão superficial da água, etanol comercial e solução de SDS 8 mmol L^{-1}.

No lab.

Medidas de condutividade

Antes de cada medida, lavar o eletrodo com água deionizada e secar bem com papel absorvente.
Insira e retire o eletrodo da solução de 2-3 vezes, Aguarde estabilizar.
Meça da mais diluída para a mais concentrada.
Meça todas as soluções.

Amostras	M1	M2	Média ± s	Temperatura
H_2O				
SDS 0,50 mmol L^{-1}				
SDS 1,0 mmol L^{-1}				
SDS 2,0 mmol L^{-1}				
SDS 4,0 mmol L^{-1}				
SDS 6,0 mmol L^{-1}				
SDS 8,0 mmol L^{-1}				
SDS 10 mmol L^{-1}				
SDS 12 mmol L^{-1}				
SDS 16 mmol L^{-1}				
SDS 20 mmol L^{-1}				

Relatório

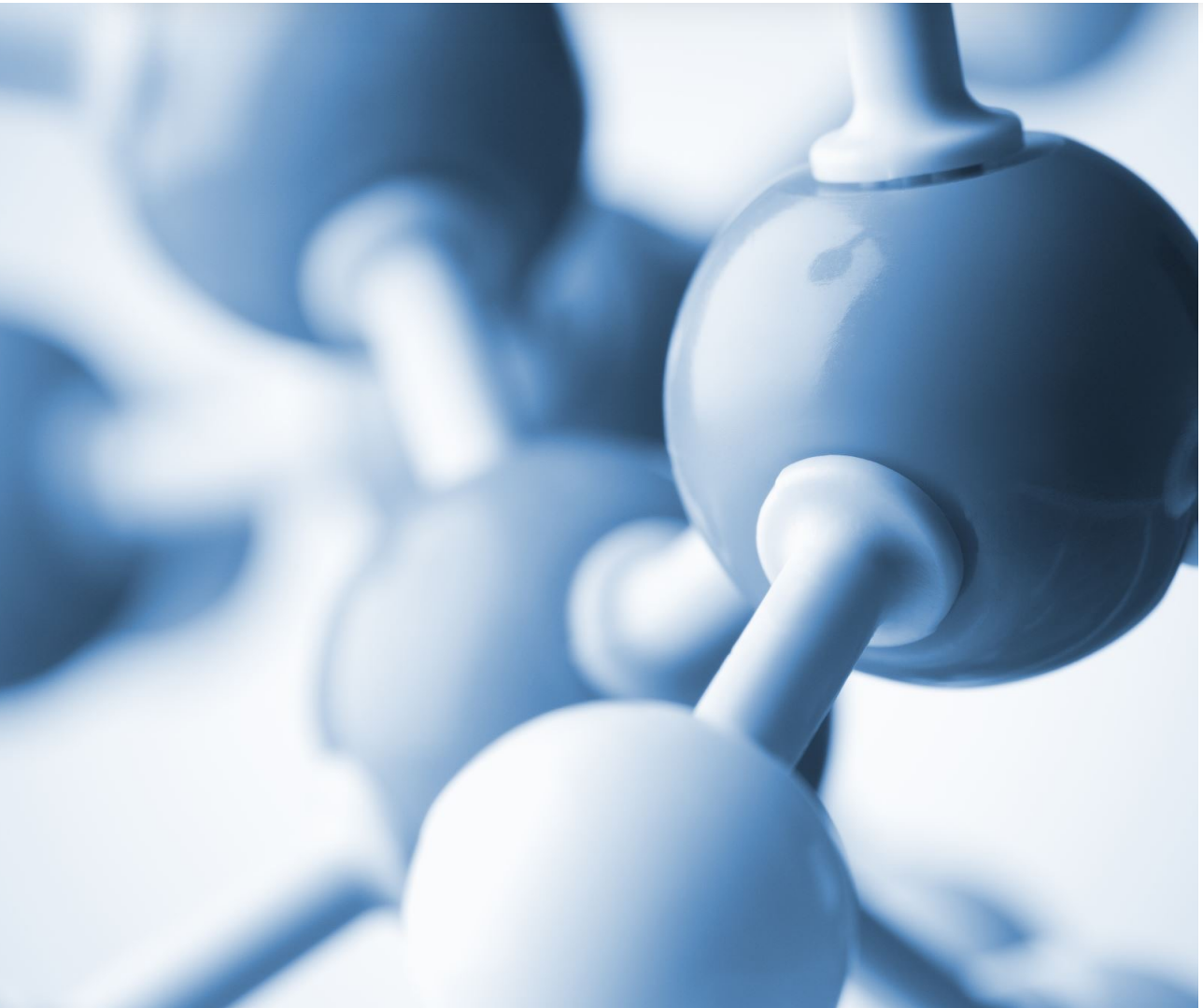
Seguir modelo pedido na apresentação do curso:

Objetivos
Resultados e Discussão
    Tensiometria
    Condutometria
Conclusões
Referências

Algarismos Significativos

Parâmetros que devem ser calculados e comparações que devem ser feitas estão no roteiro e na descrição da tarefa de entrega do relatório.

Referências



- Butt, Graf, Kappl. Physics and Chemistry of Interfaces. 2003, Wiley-VCH.
- Atkins' Physical Chemistry 11th ed.
- Hiemenz, Rajagopalan. Principles of Colloid and Surface Chemistry. 1998, Marcel Dekker Inc.
- Introdução da química dos colóides e de superfícies, D. J. Shaw, Ed. Edgard Blücher Ltda, 1975.