Sistemi eterofasici:principi chimico-fisici

- **SISTEMI DISPERSI**

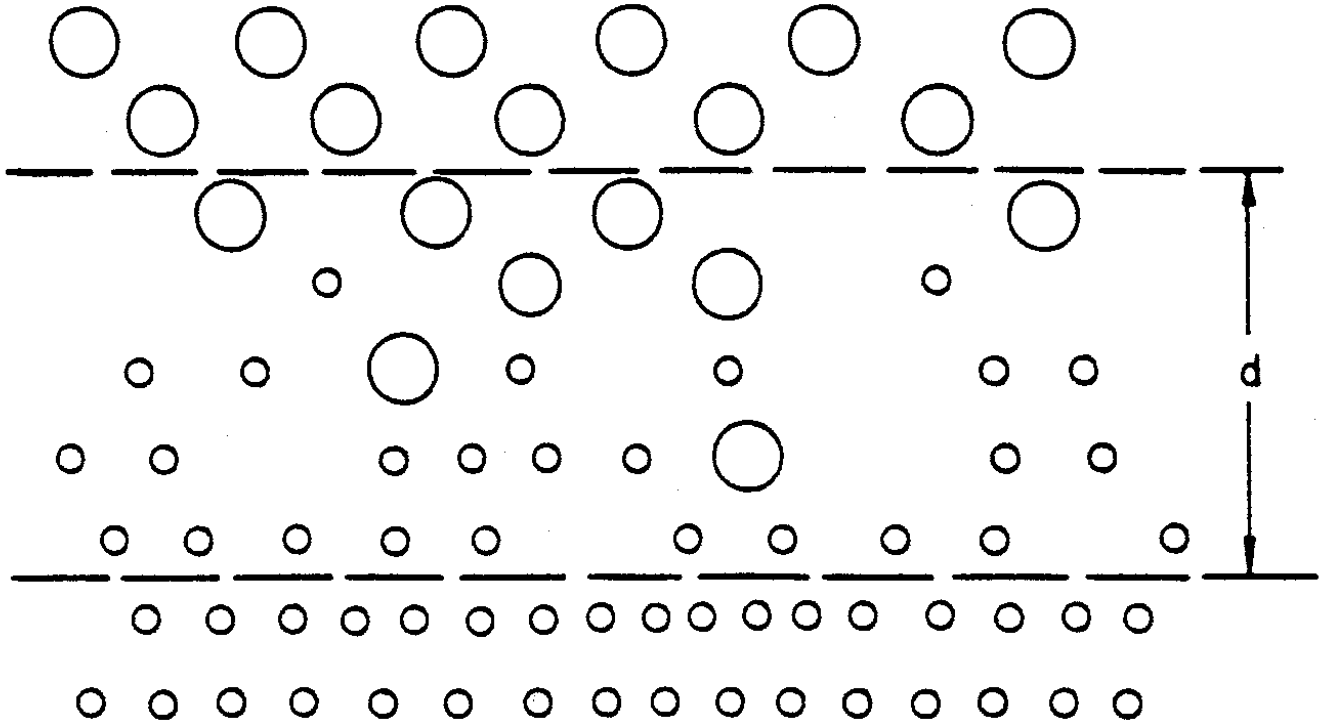


FIG. 5-4. *The interfacial region, d, between oil and water. Key: ○, oil molecule; ○, water molecule.*

FENOMENI INTERFACCIALI

TABLE 14–1. *Classification of Interfaces*

Phase	Interfacial Tension	Types and Examples of Interfaces
Gas–gas	—	No interface possible
Gas–liquid	γ_{LV}	Liquid surface, body of water exposed to atmosphere
Gas–solid	γ_{SV}	Solid surface, table top
Liquid–liquid	γ_{LL}	Liquid–liquid interface, emulsion
Liquid–solid	γ_{LS}	Liquid–solid interface, suspension
Solid–solid	γ_{SS}	Solid–solid interface, powder particles in contact

Interfacce liquide : g-l , l-l

Tensione interfacciale= F/l (dine/cm)

W = tensione interfacciale.A (erg)

TABLE 5-1. *Interfacial Tension with Water at 25°*

Liquid	*Interfacial Tension, dynes/cm*
Mercury	131
Hexadecane	54
Dodecane	53
Octane	52
Heptane	50
Carbon tetrachloride	45
Benzene	35
Nitrobenzene	25
Benzaldehyde	16
Diethyl ether	11
Octanol	9
Ethyl acetate	7
Heptanoic acid	7
Aminobenzene	6
Butanol	2

TABLE 5-2. *Surface Tension at 25°*

Liquid	*Surface Tension, dynes/cm*
Water, 5°	75
Water, 25°	72
Water, 50°	68
Glycerin	62
Dimethyl sulfoxide	44
Castor oil	39
Cottonseed oil	35
Liquid petrolatum	33
Benzene	29
Chloroform	27
Carbon tetrachloride	26
Methanol	23
Ethanol	22
Heptane	20

DETERMINAZIONE TENSIONE INTERFACCIALE

1)

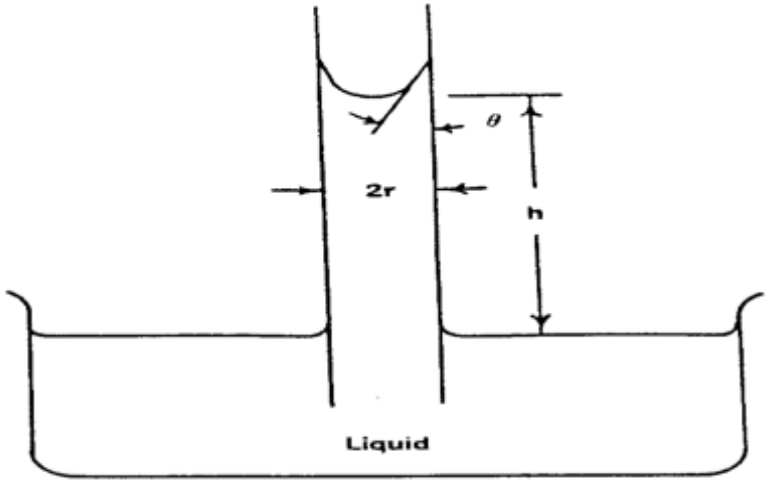
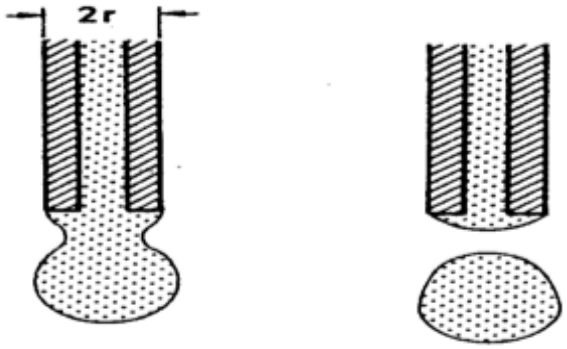


Fig. 14—5*a*. Measuring surface tension by means of the capillary rise principle.

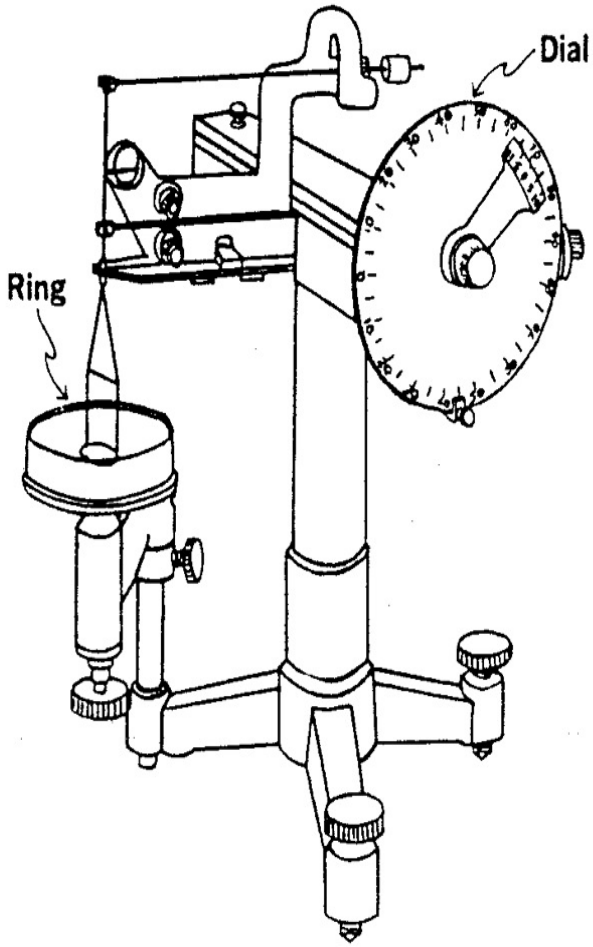
2)

Figura 16.3.
Formazione di una goccia da un contagocce con orifizio circolare di scolamento



DETERMINAZIONE TENSIONE INTERFACCIALE

3)



g. 14–6. Cenco DuNoüy tensiometer.

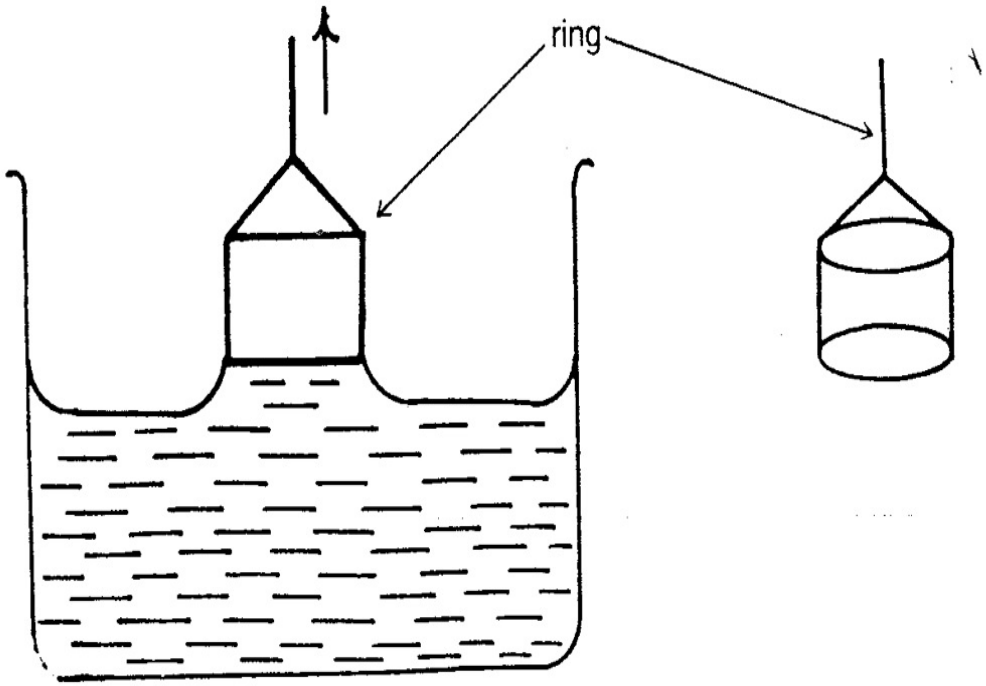
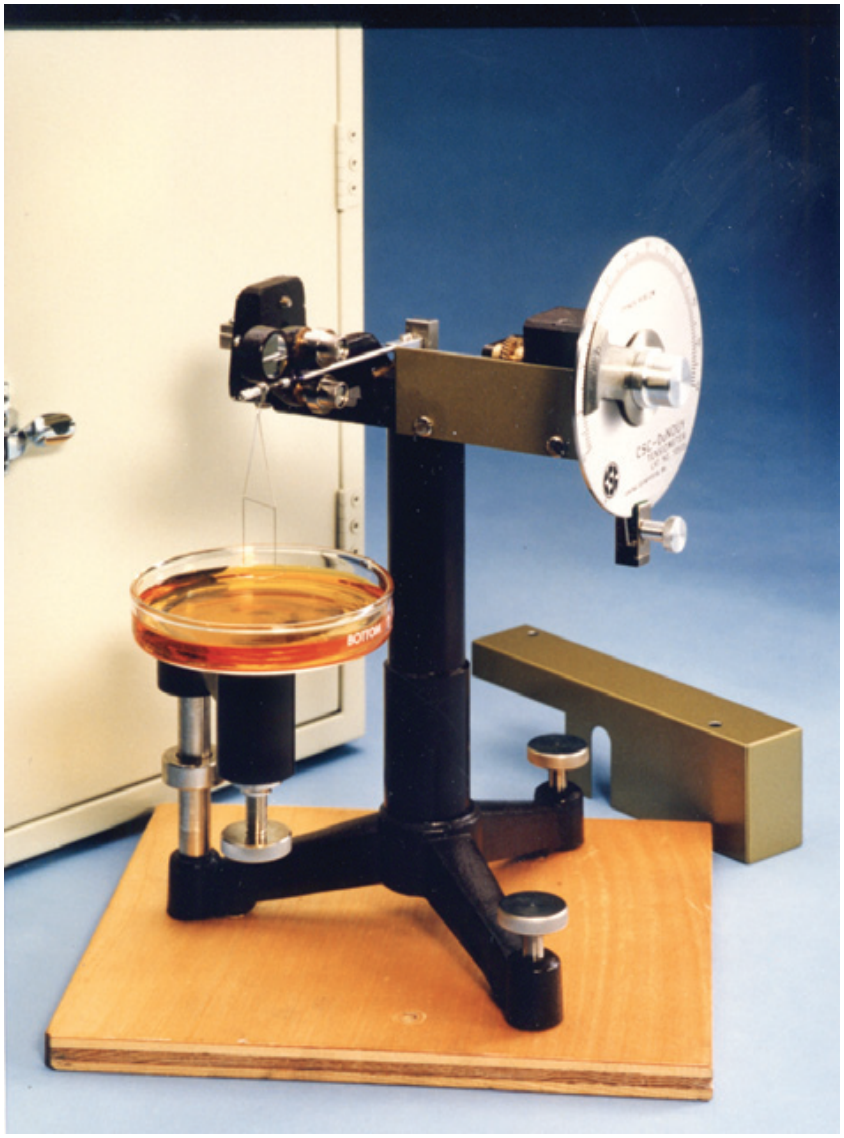
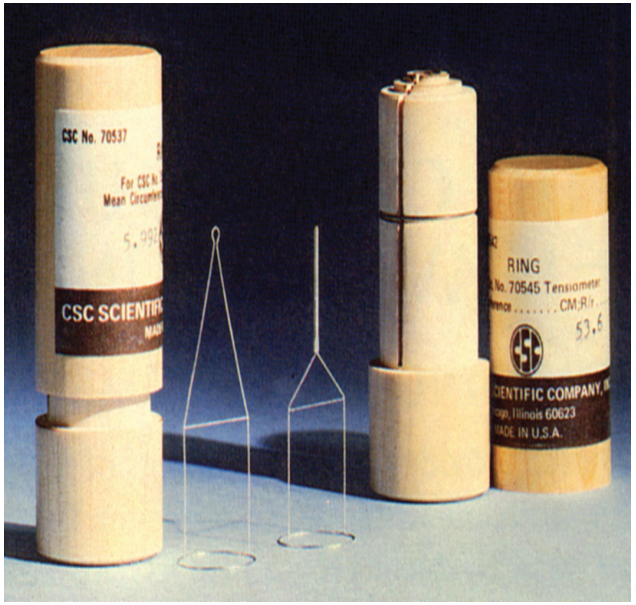


Fig. 14–7. Schematic of the tensiometer ring pulling a column of water above the surface before it breaks away.

DETERMINAZIONE TENSIONE INTERFACCIALE

3)





DETERMINAZIONE TENSIONE INTERFACCIALE

tensiometro digitale

ADSORBIMENTO ALL'INTERFACCIA LIQUIDA

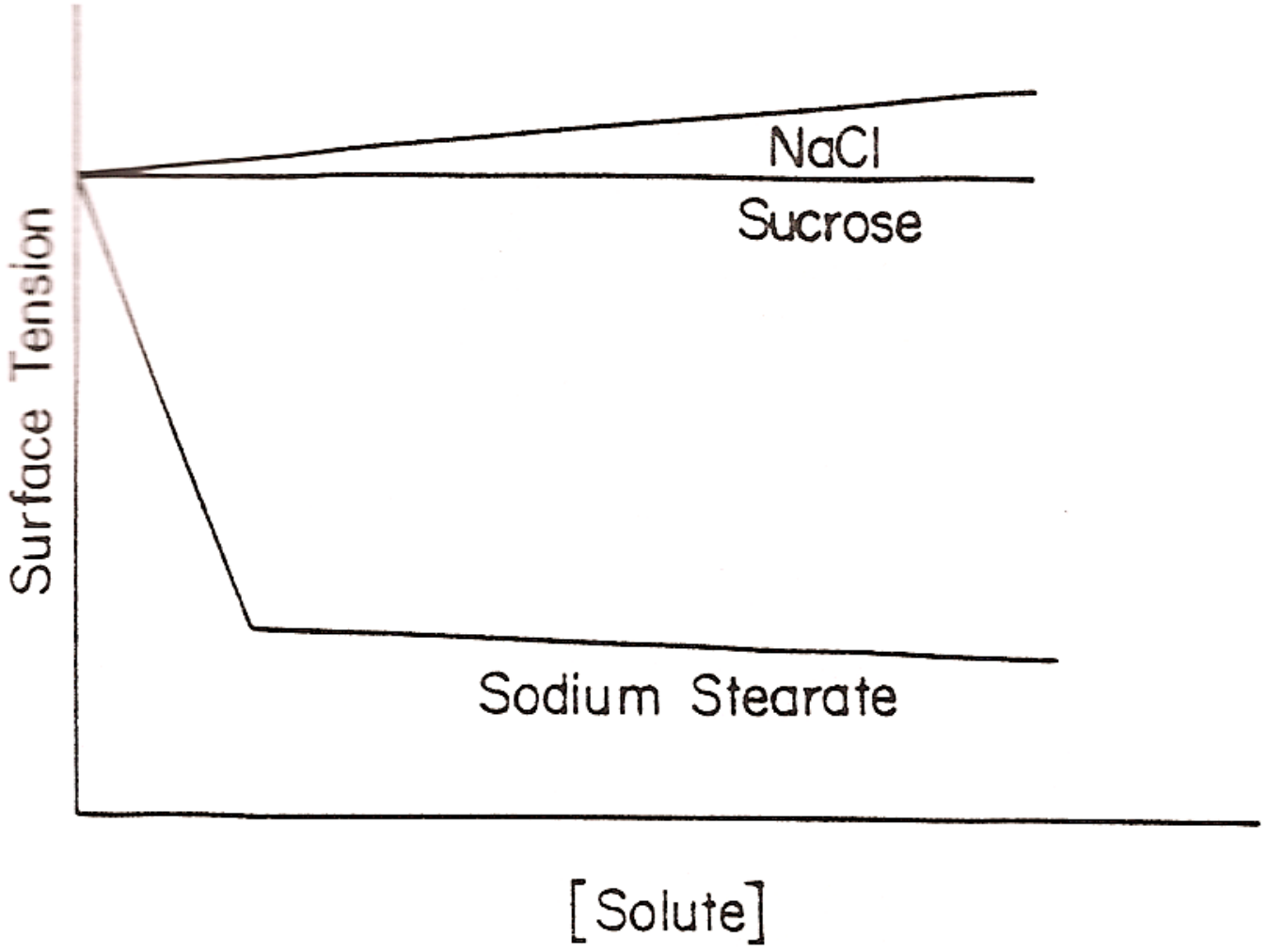
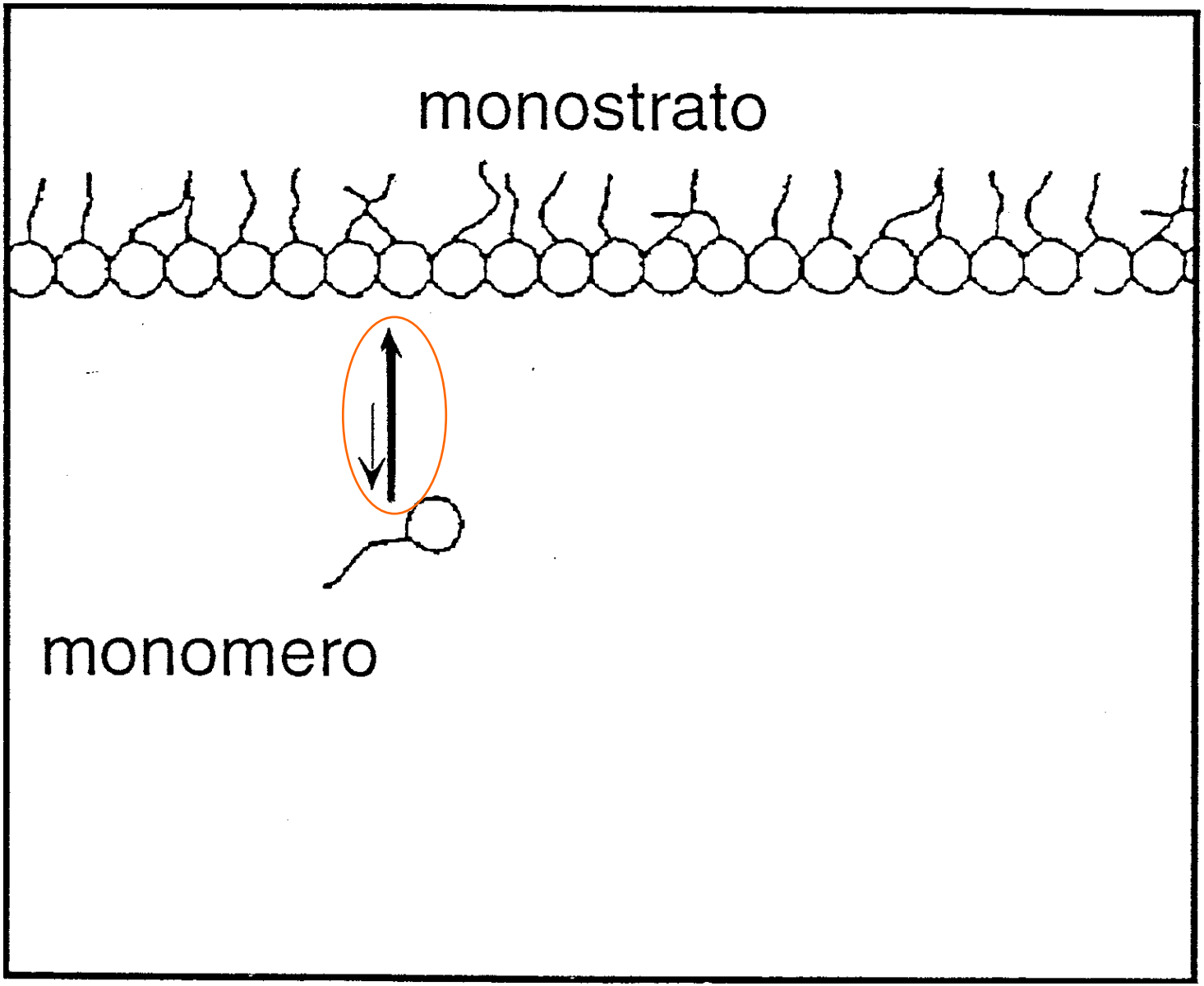


FIG. 5-6. *Effect of solutes on the surface tension of water.*

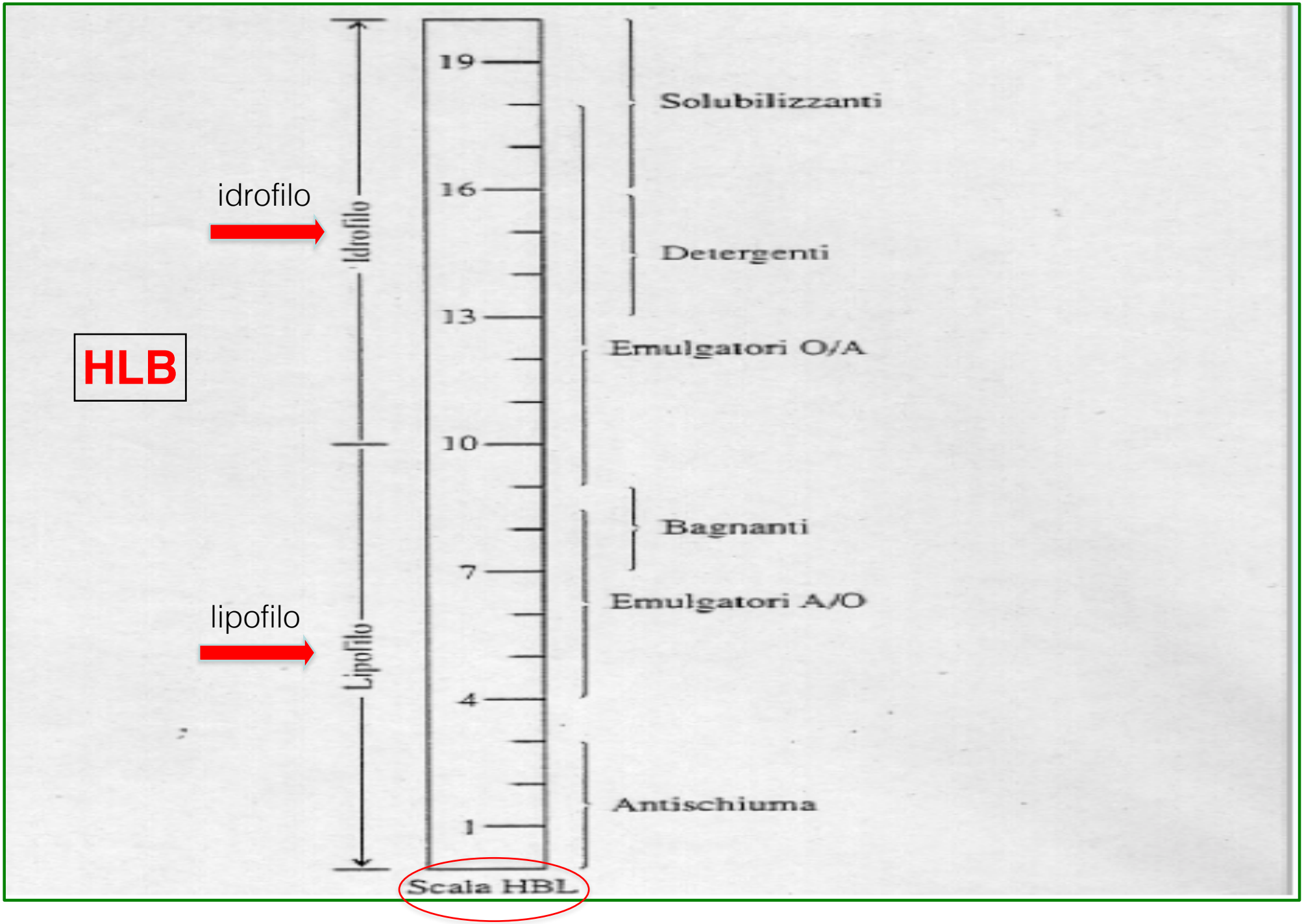
ADSORBIMENTO ALL'INTERFACCIA LIQUIDA



TENSIOATTIVI

HLB (hydrophilic-lipophilic balance)

- *Griffin (1950): scala arbitraria di valori per misurare la natura prevalentemente idrofila o lipofila di un emulsionante*


HLB
idrofilo
lipofilo
Idrofilo
Lipofilo
19
16
13
10
7
4
1
Solubilizzanti
Detergenti
Emulgatori O/A
Bagnanti
Emulgatori A/O
Antischiuma
Scala HBL

TENSIOATTIVI

Classi di tensioattivi :

anionici, cationici, anfoteri, non ionici

La parte lipofila è comune ed è costituita da catene alifatiche lineari o ramificate di derivazione sintetica o petrolchimica o di derivazione naturale di grassi vegetali o animali (gliceridi, acidi grassi, alcoli grassi)
La parte idrofila distingue le classi

- Anionici −
- Cationici +
- Anfoteri − +
- Non ionici

TENSIOATTIVI ANIONICI

Tipo	Formula	Esempi
Carbossilati	$R\text{-}COO^{-}\ Me^{+}$	Sapone, sarcosinati, acilglutammati, alcoilpolipeptidi, alchileterecarbossilati, solfosuccinati*
Solfati	$R\text{-}O\text{-}SO^{-}_{3}\ Me^{+}$	Alchilsolfati, alchileteresolfati, (solfoacetati)
Solfonati	$R\text{-}SO^{-}_{3}\ Me^{+}$	aciltaurati, solfosuccinati * (Alchilarilsolfonati, α-olefinsolfonati, alchilisetionati)

* i solfosuccinati contengono un terminale carbossilico ed uno solfonico

Alchilsolfati e Alchiletere solfati

Per la parte lipofila della catena la frazione alcolica più impiegata deriva **dall'olio di cocco**. Si preferisce usare grassi vegetali (cocco, palma), naturali o sintetici, piuttosto che sego animale per i problemi di BSE.

Gli acidi grassi dell'olio di cocco, ridotti successivamente ad alcoli, hanno la seguente composizione:

- caproico C6, caprilico C8, caprico C10 15%
- laurico C12 48%
- miristico C14 17%
- palmitico C16 9 %
- stearico C18 2 %
- oleico C18/1 7 %
- linoleico C18/2 < 1 %

La frazione maggiore è costituita da laurico perciò, anche se sono miscele, si definiscono lauril e laurileteresolfato di Na+, TEA, NH_4, MEA, Mg++

Tensioattivi anionici delicati

- **Solfosuccinati**

Ben tollerati dalla pelle, buoni schiumogeni e relativamente poco costosi.

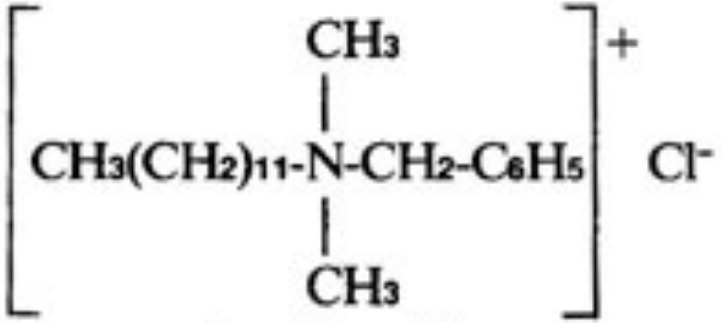
- **Alchil-taurati, -sarcosinati**

anionici delicati derivati da taurina, sarcosina, ben tollerati dalla pelle

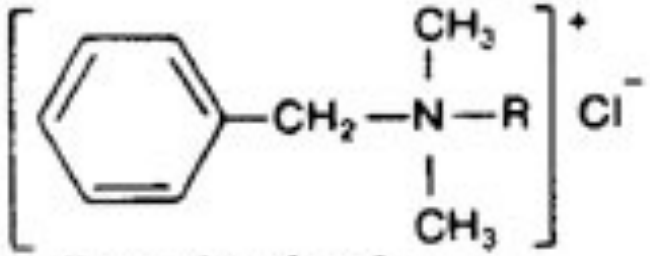
- **Acil-glutammati**

anionici delicati derivati da aa. ben tollerati dalla pelle

TENSIOATTIVI CATIONICI



laurildimetil
benzil ammonio
cloruro



Benzalconio cloruro

TENSIOATTIVI ANFOTERI

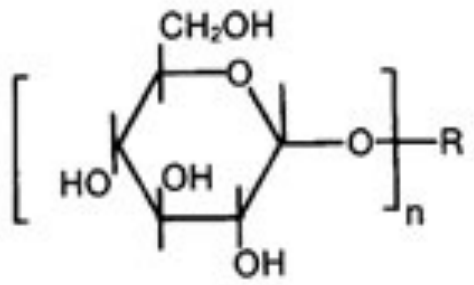
• ***BETAINE***: *Alchilbetaine, alchilamidopropilbetaine, solfobetaine*.
Il prodotto più impiegato è ***l'alchilamido propilbetaina di cocco***

• ***LECITINE :***

TENSIOATTIVI NON-IONICI

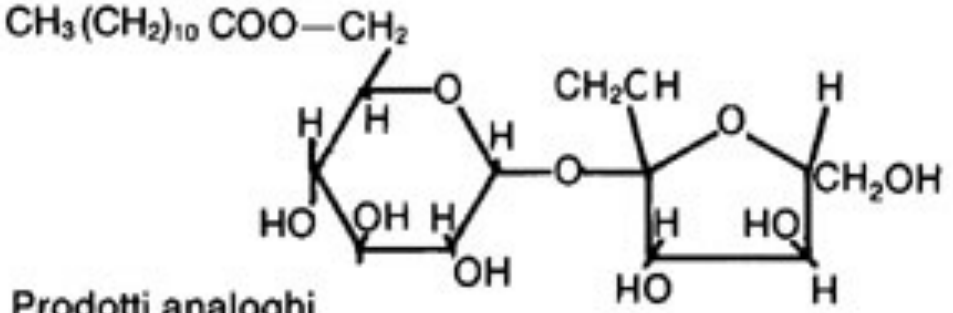
- ALCOLI ETOSSILATI
- ACIDI GRASSI ETOSSILATI
- ESTERI DI POLIALCOLI
- ESTERI O ETERI DI ZUCCHERI

$C_{8\text{-}10}$ Glucoside
($C_{8\text{-}10}$Glucosyde)



dove R è il radicale di alcoli in C_8 e C_{10}.

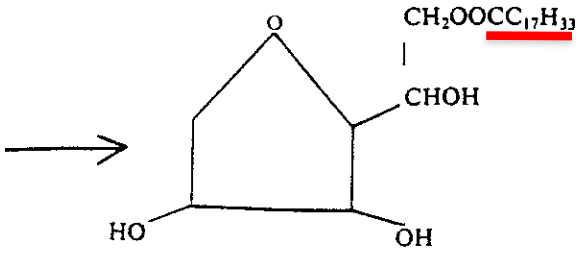
Saccarosio laurato
(Sucrose Laurate)



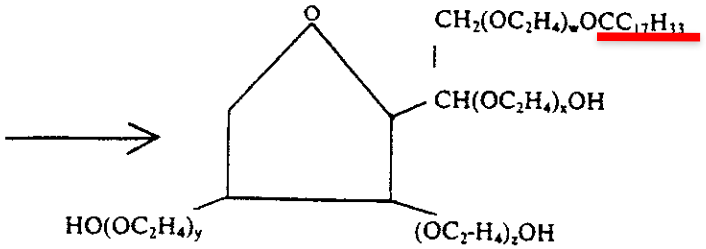
Prodotti analoghi
— saccarosio coccoato
— saccarosio stearato

TENSIOATTIVI NON-IONICI

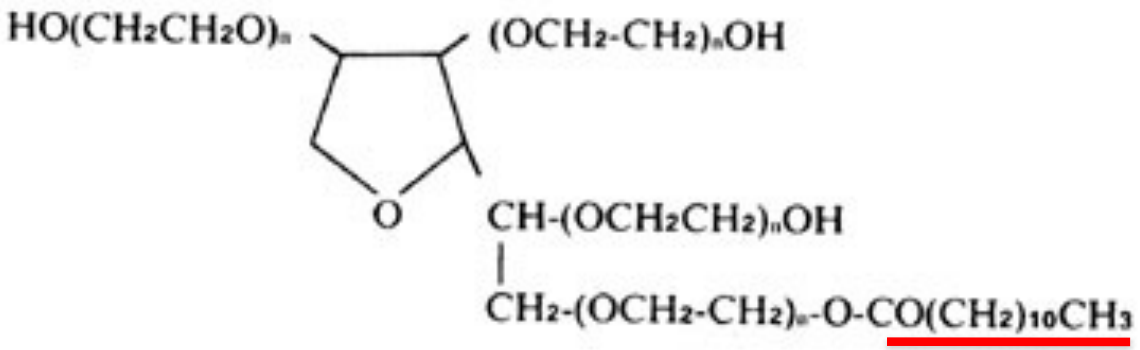
ESTERI DEL SORBITANO



SORBITAN MONO-OLEATE
(a *Span*)



POLYSORBATE 80
(a *Tween*)



es. sorbitan (20)OE mono-laurato

TENSIOATTIVI NON-IONICI

HLB di esteri del sorbitano (span)

Nome chimico	Nome commerciale	**HLB**
Sorbitan monolaurato	**Span 20**	**8,6**
Sorbitan monopalmitato	**Span 40**	**6,7**
Sorbitan monostearato	**Span 60**	**4,7**
Sorbitan tristearato	**Span 65**	**2,1**
Sorbitan monooleato	**Span 80**	**4,3**

TENSIOATTIVI NON-IONICI

HLB di polisorbati (tween)

Nome chimico	Nome commerciale	**HLB**
Sorbitan monolaurato poliossietilenato (20)	**Polisorbato (Tween) 20**	**16,7**
Sorbitan monopalmitato poliossietilenato (20)	**Polisorbato(Tween) 40**	**15,6**
Sorbitan monostearato poliossietilenato (20)	**Polisorbato (Tween) 60**	**14,9**
Sorbitan tristearato poliossietilenato (20)	**Polisorbato (Tween) 65**	**10,5**
Sorbitan monooleato poliossietilenato (20)	**Polisorbato (Tween) 80**	**15**

Physical:

	Solubility				Specific Gravity @ 25°C	Viscosity (cps)	HLB #
	H2O	EtOH	Veg. Oil	Mineral Oil			
Polysorbate 20	L	L	U	U	1.1	400	16.7
Polysorbate 21	D	L	U	U	1.1	500	13.3
Polysorbate 40	L	L	U	U	1.08	500	15.6
Polysorbate 60	L	L	U	U	1.1	600	14.9
Polysorbate 61	D	LW	LWT	LW	1.06	solid	9.6
Polysorbate 65	D	L	D	L	1.05	solid	10.5
Polysorbate 80	L	L	U	U	1.08	425	15.0
Polysorbate 81	D	L	LT	L	—	450	10.0
Polysorbate 85	D	L	LT	U	1.00	300	11.0

Note: Abbreviations: D = dispersible; L = soluble; T = turbid; U = insoluble; W = in the warm. Both the fire point and the flash point for all polysorbates listed above are approximately 149°C.

12. Stability and Storage Conditions

Polysorbates are stable to electrolytes as well as to weak acids and bases. There is gradual saponification by strong acids and bases. The oleic acid esters are sensitive to oxidation. Preserve in a tight container protected from light, and store in cool conditions.

13. Incompatibilities

Discoloration and/or precipitation occurs with various substances, especially with phenols, tannins, tars and/or tar-like compounds.

14. Safety

Polysorbates are well tolerated, practically non-irritating and of very low toxicity.

17. Applications in Pharmaceutical Formulation or Technology

Use	Concentration (%)
Emulsifiers	
Used alone in water-in-oil emulsions	1-15
Used in combination with hydrophilic emulsifiers in oil-in-water emulsions	1-10
Used to increase the water-holding properties of ointments	1-10
Solubilizers	
For poorly soluble active constituents in lipophilic bases	1-10
Wetting Agents	
For insoluble active constituents in lipophilic bases	0.1-3

18. Related Substances

None

19. Comments

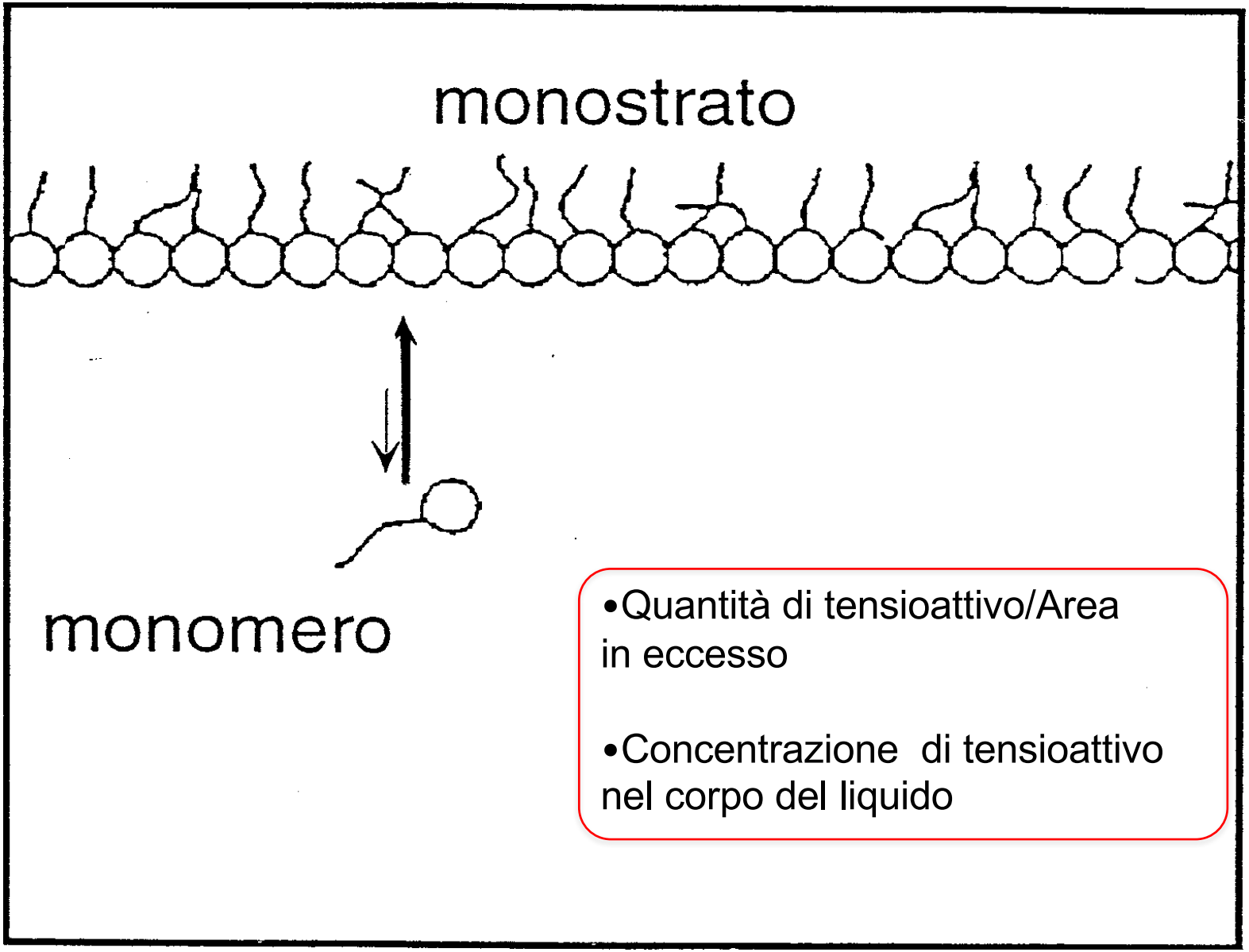
Tweens 20, 60 and 80 are obtainable in a specially deodorized form as *Tween* 20 SD, 60 SD, and 80 SD.

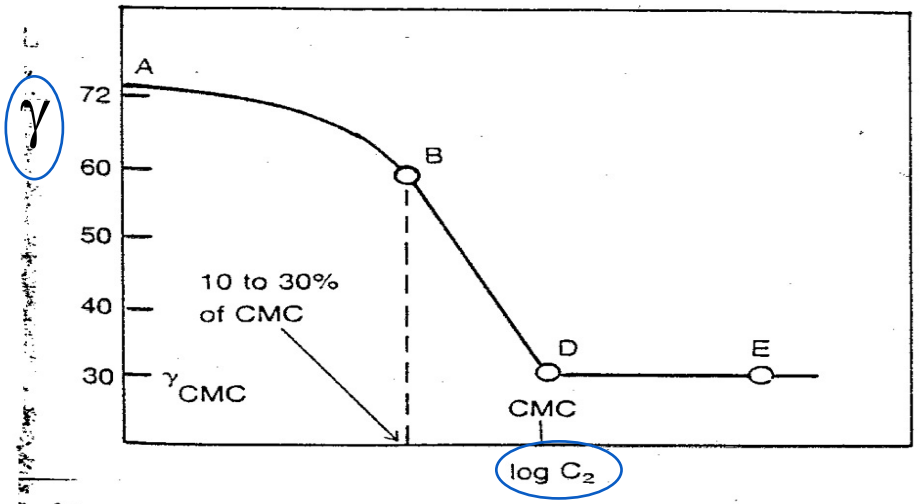
TENSIOATTIVI

HLB (hydrophilic-lipophilic balance)

- *tensioattivi non-ionici : HLB= % p/p catena POE/5*
- *metodi cromatografici*
- *HLB grandezza additiva*

ADSORBIMENTO ALL'INTERFACCIA LIQUIDA





Equazione di GIBBS

FIG. 14–14. Decrease in the surface tension of water when a straight-chain amphiphile is added. (From H. Schott, J. Pharm. Sci. 69, 852, 1980, reproduced with permission of the copyright owner.)

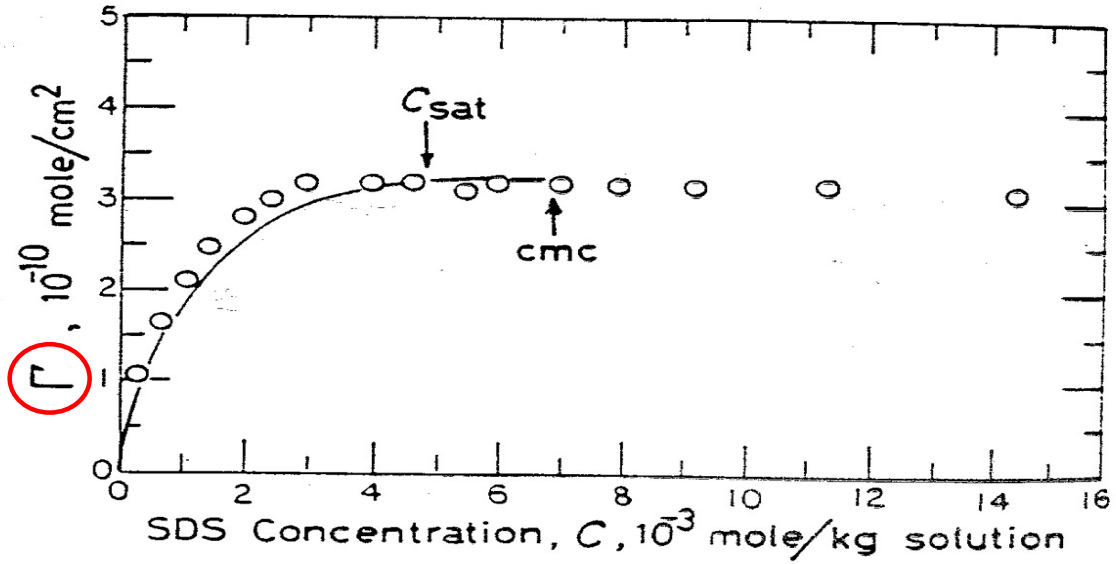
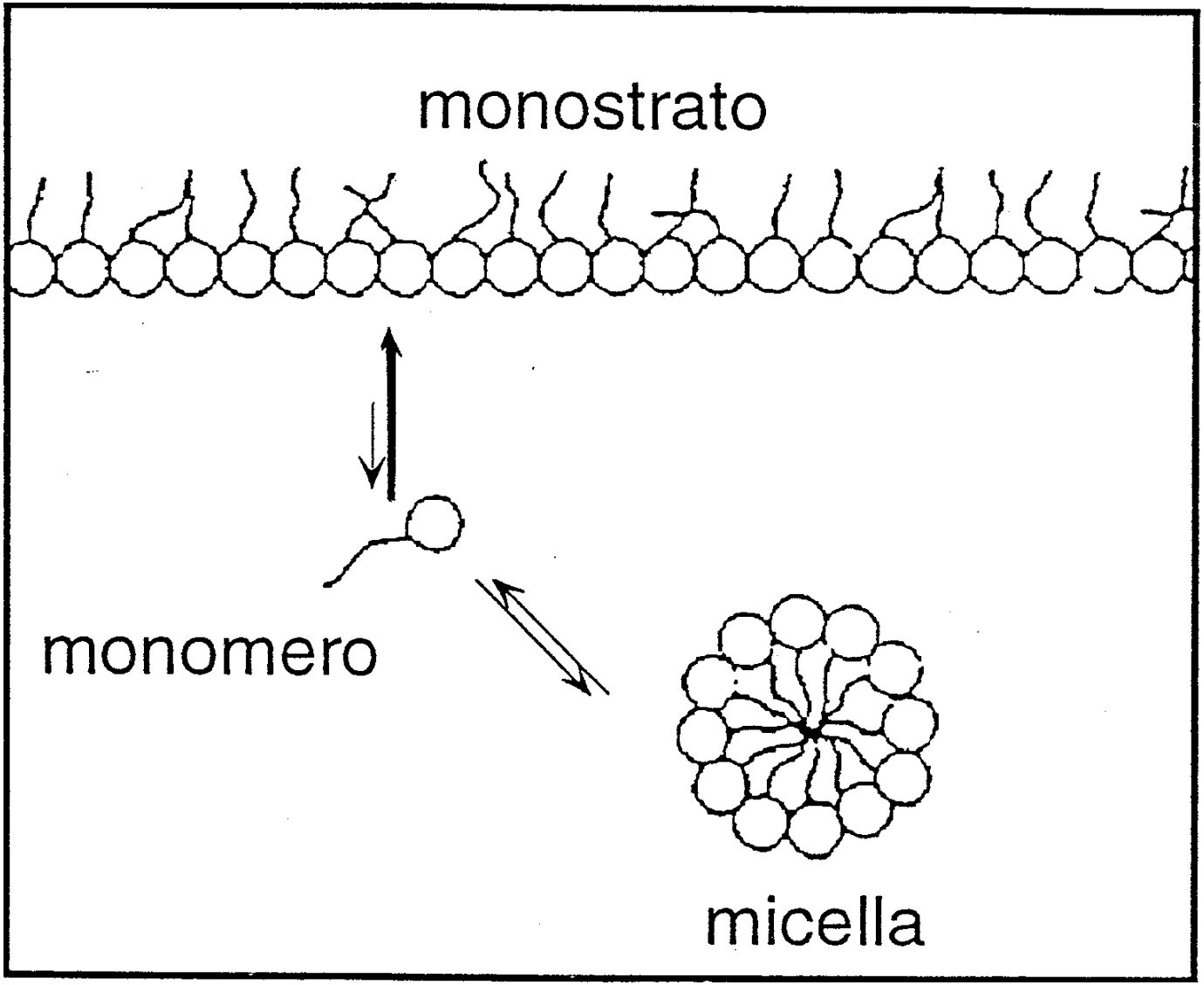


FIG. 5-7. *Surface excess of tritium-labeled sodium dodecyl sulfate (SDS) determined by radiotracer method (○) and calculated by the Gibbs equation from surface tension data (——). (From Muramatsu, M., Tajima, K. M.,*

MICELLE



Equazione di GIBBS

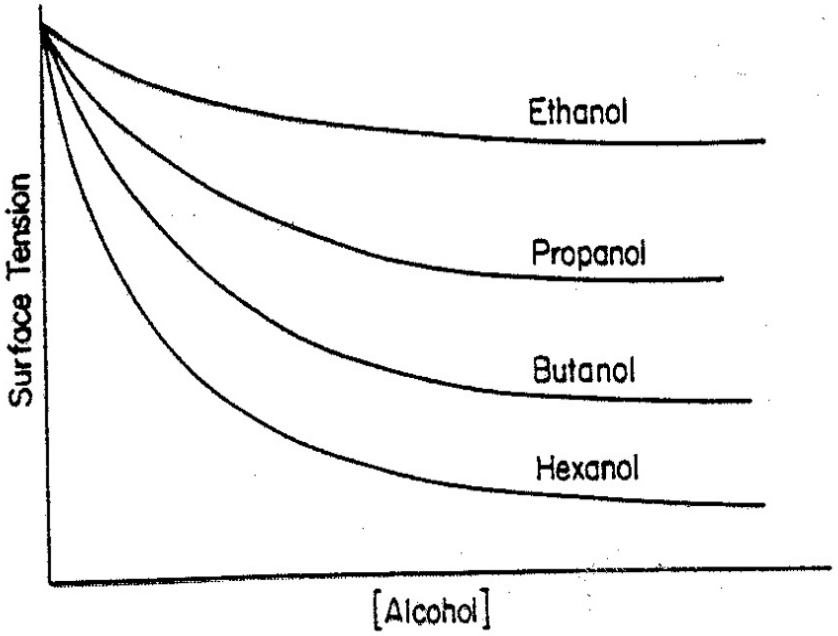


FIG. 5-8. *Effect of a series of alcohols on the surface tension of water.*

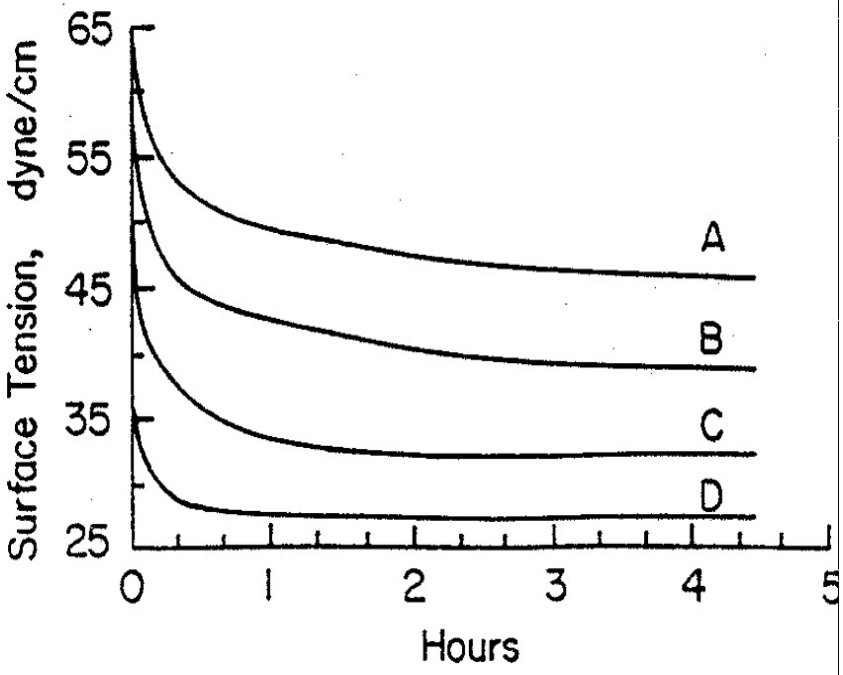


FIG. 5-9. *Change in surface tension with time following the addition of sodium dodecyl sulfate to water. Key:* A, 4×10^{-4} *M;* B, 8×10^{-4} *M;* C, 1.6×10^{-3} *M;* D, 4×10^{-3} *M. (From Neumann, A. W., and Tanner, W.: Tenside, 4:220, 1967.)*