Physical characterisation of interfaces via surface tension / contact angle

Dr. Tapani Viitala

Outline

- Why should we be interested in ST/IFT and CA ?
- Basic concepts in surface chemistry
- Applications areas – Utilization of ST/IFT and CA properties
- Measuring techniques

Why – General ?

- Surfaces and interfaces are everywhere !!!
  - Many of the most interesting and important phenomena occur at interfaces
    - Heterogeneous Catalysis
    - Electron transport and scattering at semiconductor-metal or semiconcuctor-dielectric interfaces
    - Molecular Binding and Transport at Cell Membranes
    - Nanoscale Dynamics at Polymer Interfaces etc...
  - Fields that have impact on our everyday life:
    - ***Detergents, Pharmaceuticals, Paints and Lacquers, Adhesives, Paper coatings, Printing inks, Cosmetics, Textiles, Food, Packaging, Medical tests, Lubrication, Pesticides, various other coatings…and many more***
  - Growing interest and knowledge in conjunction with the advances in technology has increased the need for special surface science techniques that can be used in R&D applications, solve industrial problems, improve product quality, better productivity, longer equipment life and reduced waste

Why - Detailed ?

- The unbalance of forces at an interface forces the structure and composition of the interface to be different than in the bulk:
  - special orientations of molecules
  - accumulation of certain types of molecules
  - separation of positive and negative charges
- Interface properties often completely different from bulk material properties ⇒ determine the behavior of the whole system
  - 1 cm^3 solid particle ⇒ 1 mm^3 ⇒ 1 μm^3
    Surface area: 6 cm^2 ⇒ 60 cm^2 ⇒ 60 000 cm^2 (6 m^2)
  - 0.1 M micellar solution of amphiphile ⇒ 40 000 m^2 micellar-water interface
- Basic measurement properties (ST/IFT and CA) gives information about the properties of the outermost layer of a surface/interface in a simple way

CA & ST vs. other surface characterization techniques

- Technically advanced and expensive techniqes widely used: XPS or ESCA, SIMS, SAXS, Raman, IR spectrometry and TOF-SIMS
  - Penetrates more or less into the surface
- CA and ST techniques only way to access the properties of the outermost layer of the surface/interface in an in-expensive way
- Goniometry and Tensiometry are fast, simple and accurate techniques for checking for example surface treatments of solids or liquid formulations
- Goniometry enables to determine visco-elastic properties of interfaces

⇒ Goniometry and Tensiometry:
1) Complementary techniques used to give supporting information to other surface characterizations techniques
2) Used to guideline the researcher in the right direction before a more elaborate analysis is started with a more advanced and expensive surface characterization technique

What Is Surface Chemistry and What Does It Do?

- *”Physical” surface chemistry* – controls the properties of multiphase systems (i.e. the interfaces)
- *”Synthetic” surface chemistry (surface modification)* – modifies the properties of interesting surfaces in a controlled manner

→ *to change e.g. wetting / porosity/ colour / chemical nature*

Macroscopic Interfaces
- Thermodynamics of the Boundary between Phases

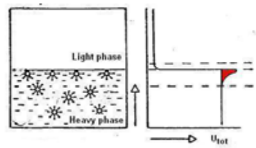
The Interface

- liquid/gas
- liquid/liquid
- liquid/solid
- solid/gas
- solid/solid

Each interface is defined by an *"interfacial tension"*

Surface/Interfacial tension, γ

- Surface/Interfacial is a measurement of the cohesive energy present at an interface arising from the imbalance of forces between molecules at an interface (gas/liquid, liquid/liquid, gas/solid, liquid/solid).
- Force involved in stretching a film (force/unit length, mN/m), or work involved in increasing the surface by a length ($J/m^2 = N/m$)
- Solid surfaces also may be described to have an interfacial tension normally referred to as Surface Free Energy (SFE)



Force: $F = \gamma L \Rightarrow \gamma = F/L$

Work: $dW = dG = \gamma L dx = \gamma\, dA$
$\Rightarrow \gamma = dG/dA$

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Effect of Substances Dissolved in the Liquid Phase

- Some molecules/particles have affinity for both phases – "amphiphilic"

→ **SURFACE ACTIVE AGENTS = SURFACTANTS**

Driving force – to reduce interfacial tension!

Similar effect from gas phase
→ e.g. adventitious carbon

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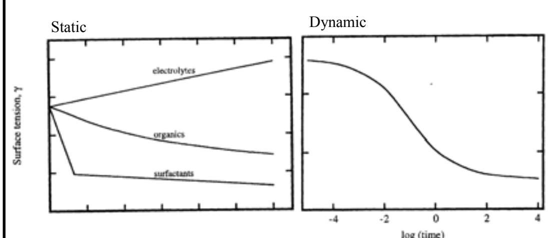
Surface/Interfacial tension, γ

- Effect of solutes & time



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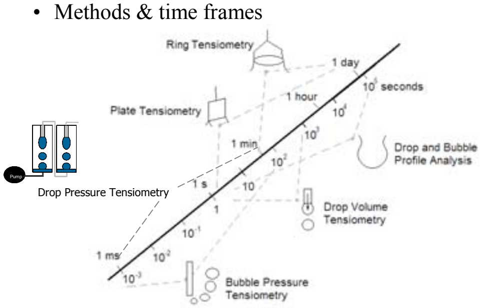
Surface/Interfacial tension, γ

- Methods & time frames



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Dilational visco-elastic properties of interfacial layers

- The formation of stable colloidal dispersion (emulsions, foams etc.) is extremely important in many industries: **Pharmaceutical**, **Cosmetic**, **Food**, Paint, Petroleum
- Emulsifiers like lipids, phospholipids and proteins is widely used to stabilize pharmaceutical, cosmetic and food emulsions and foams
- Interfacial rheology is an important factor for stability of emulsions and foams and thin films containing lipids, phospholipids and proteins
- The stablizing role is based on the formation of a strong visco-elastic network in which the molecules are essentially immobile
- This visco-elastic network opposes film stretching, damps the interfacial fluctuations and slows down thinning
- The dilational visco-elastic properties gives information about the state of the interfacial layer and its changes; **molecular arrangement**, **phase structure**, **phase transition** and **relaxation behaviour**

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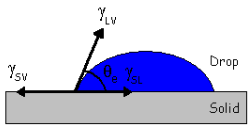
Contact angle, θ

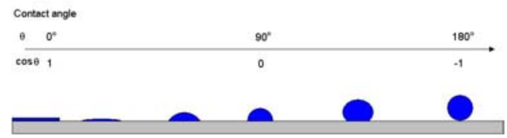
- Quantitative measure of the wetting of a solid by a liquid
- Angle formed by the liquid at the three phase boundary where a liquid, gas (or a second immiscible liquid) and solid intersect
- The shape of the drop and the magnitude of the contact angle are controlled by three interaction forces of interfacial tension of each participating phase (gas, liquid and solid)
- Young equation apply for homogeneous, smooth and rigid solids



$\gamma_{LV} \cos\theta = \gamma_{SV} - \gamma_{SL}$ Young equation

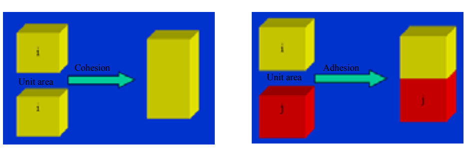
Wetting

- The primary focus of contact angle studies is in assessing the wetting characteristics of solid/liquid interactions
- Contact angle is commonly used as the most direct measure of wetting
- Low contact angles this means good wetting, and when the contact angles are high this means non-wetting conditions



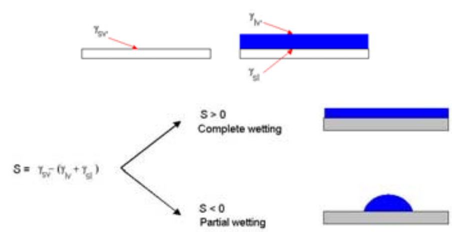
Cohesion & Adhesion

- The surface tension is correlated with the cohesion energy: $\Delta G^C = -2\gamma_i = -W^C$. Measure of the strength of molecular interactions within the liquid
- The interaction of 2 immiscible phases correlates with the adhesion energy: $\Delta G^A = \gamma_{ij} - \gamma_i - \gamma_j = -\gamma_j(1+\cos\Theta) = -W_{ij}^A$. Strength of the interaction between two immiscible phases



Spreading

- A quantitative measure of wetting is the Spreading coefficient, which is the energy difference between the solid substrate with the contacting gas and liquid phases

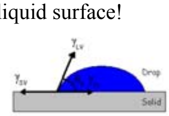


Surface Free Energy

α "work of cohesion"

Solid surface cannot be stretched as liquid surface!

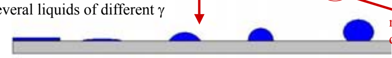
Cannot measure "interfacial tension" (γ_{SV}) directly



$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta$

modelled in different ways

Measure contact angle with several liquids of different γ



Calculate surface free energy!
(9 different theories)

Utilization of γ and θ

- Lowering the surface/interfacial tension is the driving force for solubilizing non-soluble compounds into each other
- Visco-elastic properties of liquid interfaces can predict emulsion and interface stabilities
- Modifying the surface free energy (wettability) of solid surfaces is the driving for "solubilizing" and stabilizing particles in solutions.
- Modifying surface free energy (wettability) of solid surfaces can be used for enhancing or decreasing the wetting ability of the surface for specific applications

Industries Dealing Daily With Interfaces

- ***Foods*** – emulsions, foams, dispersions, fouling etc.
- ***Pharmaceuticals*** – as above!
- ***Household products*** – dirt removal, foam control etc.
- ***Paints & coatings*** – cleanliness, wetting, adhesion, wicking, dispersion stability
- ***Mineral Processing*** – froth flotation
- ***Semi-conductors*** – cleanliness, adhesion of thin layers, characterisation of surface treatments
- ***Heavy industry*** – lubrication/wear, degreasing
- ***Crude oil*** – oil recovery
- ***Paper*** – printing, adhesion in packaging etc.
- ***Biomaterials*** – fouling, tissue adhesion

What Can Be Measured?

Instruments

Property	*Method*
Surface/interfacial tension	**tensiometry, drop shape analysis, max. bubble pressure, drop volume**
Contact angle, Surface Free Energy	**tensiometry, drop shape analysis**
Surface Forces	Surface force apparatus, thin film balance, AFM, MASIF etc.
Adsorbed mass/thickness	**QCM**, ellipsometry, SPR, reflectometry
Adsorbed layer rheology	**ISR, LB, Pulsating Drop, Dissipative QCM**
Morphology of surface layers	**BAM**, AFM
Chemical composition and nature of first few nm	ESCA, **IR (e.g. PM-IRRAS)**
Particle Size	Light scattering

(KSV techniques)

Sigma Instruments

- Sigma 700 – fully automated, computer-controlled instrument
- Sigma 701 – extra sensitive balance
- Sigma 702 – stand-alone automatic unit, for quick and simple on-site operation
- Sigma 702ET – stand-alone automatic unit for determining water in transformer oils via interfacial tension (ASTMD-971 and IEC-60422)
- Sigma703 – simple manual instrument



Force based Contact Angle/Surface and Interfacial Tension Meters

- Surface and Interfacial Tensions
- Dynamic Contact Angles
- Critical Micellar Concentration
- Powder Wettability
- Surface Free Energy Calculations
- Force Curves
- Density of Liquids

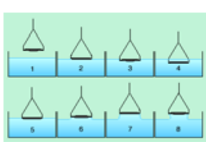
Measuring methods of Sigma Tensiometers

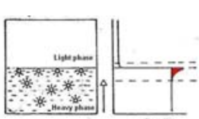
- Du Nouy Ring Surface/Interfacial tension

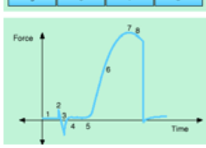
$\gamma = (F_{max}/4\pi R) \times f(R^3/V, R/r)$

• Huh and Mason used by WinSigma softw.

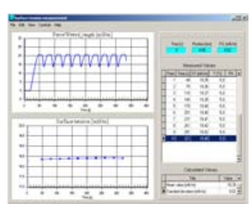
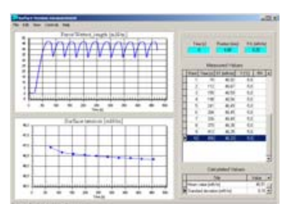
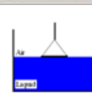
• Harkins and Jordan or Zuidema and Waters also available

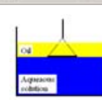






Surface Tension: Hexane (Ring)
Interfacial Tension: Hexane/Water (Ring)

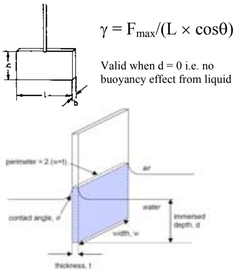


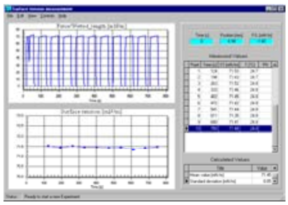
Measuring methods of Sigma Tensiometers

- Wilhelmy Plate Surface/Interfacial tension

$\gamma = F_{max}/(L \times \cos\theta)$

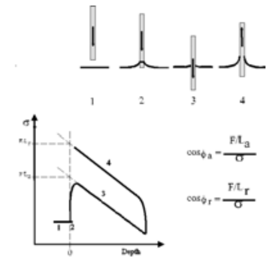
Valid when d = 0 i.e. no buoyancy effect from liquid





Measuring methods of Sigma Tensiometers

- Advancing & Receding CA – Dynamic Wilhelmy method
  - Sheets
  - Plates
  - Round rods
  - Square rods
  - Single fibers



$\cos\phi_a = \frac{F/l_a}{\sigma}$

$\cos\phi_r = \frac{F/l_r}{\sigma}$

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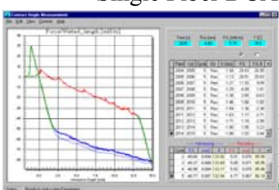
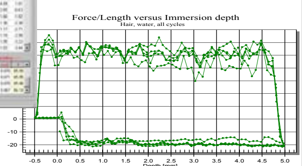
Dynamic Contact Angle: Teflon/Water
Single Fiber DCA: Single Hair/Water





–Sheets
–Plates
–Round rods
–Square rods
–Single fibers

Cycle	Advancing F/L [mN/m]	Advancing Cos ()	Advancing θ	Receding F/L [mN/m]	Receding Cos ()	Receding θ
1	-16.94	-0.237	103.72	49.95	0.699	45.65
2	-19.79	-0.277	106.08	54.88	0.768	39.83
3	-18.00	-0.252	104.59	53.64	0.751	41.36
4	-17.41	-0.244	104.10	53.06	0.743	42.06
5	-17.51	-0.245	104.18	54.78	0.767	39.96

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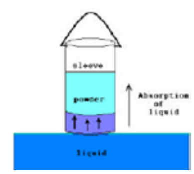
Measuring methods of Sigma Tensiometers

- Washburn method: Powder, Porous solid, fabric CA

$T = [\eta / C \rho^2 \ \gamma \cos\theta]\, M^2$

The terms are defined as follows:

T = time after contact
η = viscosity of liquid
C = material constant characteristic of solid sample
ρ = density of liquid
γ = surface tension of liquid
θ = contact angle
M = mass of liquid adsorbed on solid



A graph of Time vs Mass^2 should yield a straight line whose slope is $\eta / C \rho^2 \ \gamma \cos\theta$.

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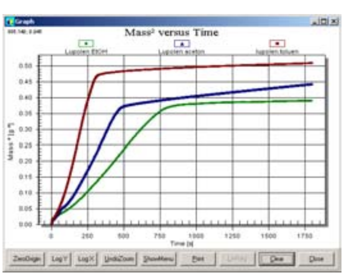
Powder Wettabililty:Lupolen/Different liquids



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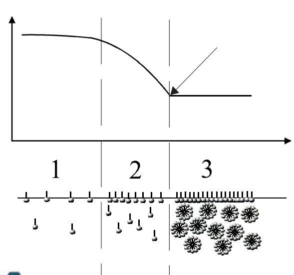
Measuring methods of Sigma Tensiometers

CMC Critical Micellar Concentration

-Surface excess
-Area per molecule
-Synergy



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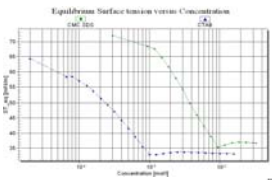
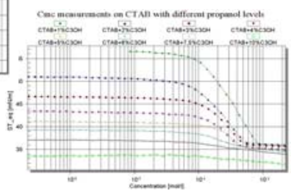
Critical Micelle Concentration, CMC





2 dispensing units for dilution CMC
→ Infinite dilution

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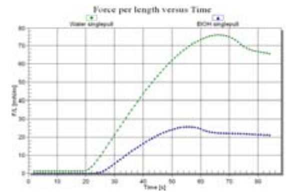
Measuring methods of Sigma Tensiometers

Single force curve ring measurement or continuous Wilhelmy plate ST/IT measurement



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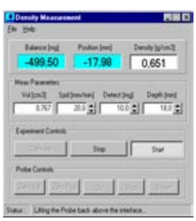
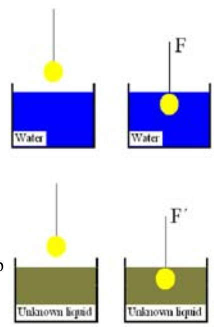
Measuring methods of Sigma Tensiometers

Density of Liquids



1st Step

2nd Step



$\rho'_{\text{unknown liquid}} = (F'/F) \times \rho_{\text{water}}$

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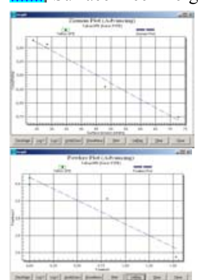
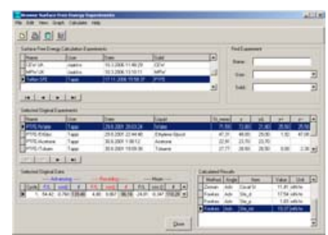
Measuring methods of Sigma Tensiometers

Surface Free Energy Calculations





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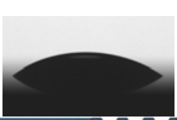
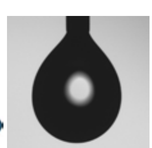
CAM 100 Series Instruments

- CAM 100 – simple contact angle meter, can measure surface energy
- CAM 101 – same instrument as above, but with software to measure surface/interfacial tension





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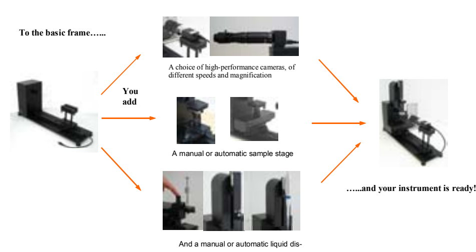
CAM 200 – The Modular High Performance Instrument



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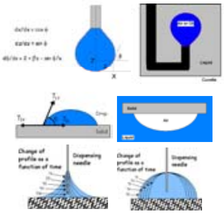
CAM 200 – The Modular High Performance Instrument

Optical Contact Angle/Surface and Interfacial Tension Meters



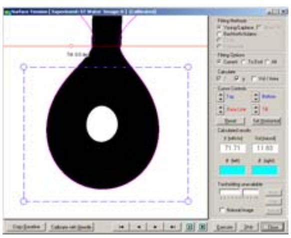
Surface and Interfacial Tensions by Pendant Drop or Bubble Method

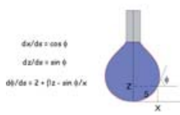
Static and Dynamic Contact Angles

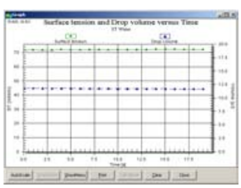
Surface Free Energy Calculations

Dilational visco-elastic measurements on interfacial layers

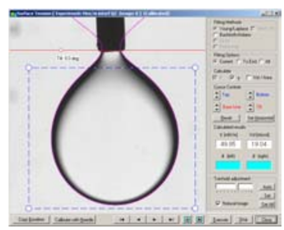
Surface tension of liquids

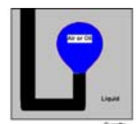




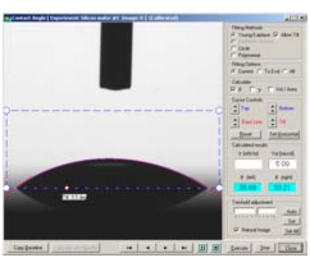


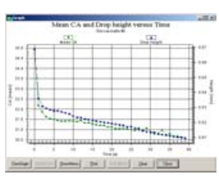
Interfacial tension of 2 immiscible liquids



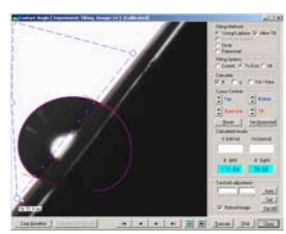


Static Contact Angle: Water/SiO_2 wafer

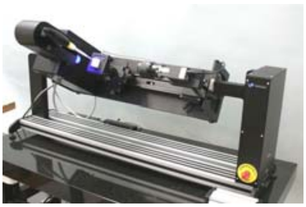




DCA Manual Tilting Stage



DCA Motorized Tilting Cradle



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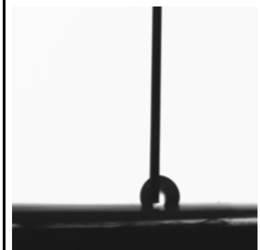
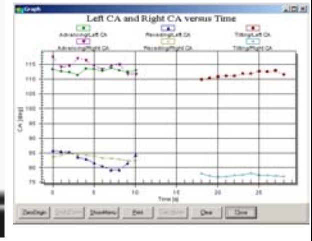
DCA Increasing/Decreasing drop size





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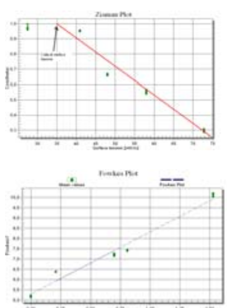
Surface Free Energy Calculations

- Zisman plot, Fowkes, OWRK / Ext. Fowkes, Wu, Acid-Base, Equation of state, Schultz theories



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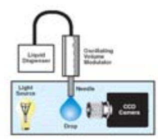
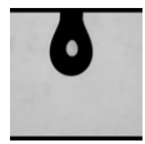
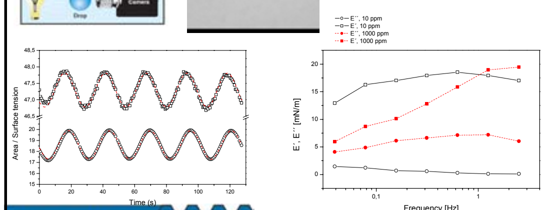
Dilational visco-elastic measurements of interfacial layers





$$E^* = E' + iE'' = |E| \times \cos\phi + i|E| \times \sin\phi$$

$$|E| = \gamma_A / [A_A/A_{mean}]$$



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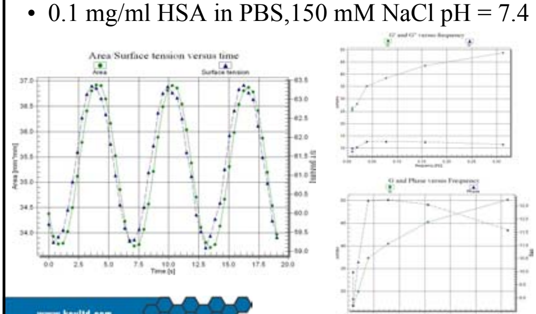
Dilational elasticity example

- 0.1 mg/ml HSA in PBS,150 mM NaCl pH = 7.4



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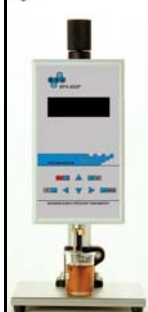
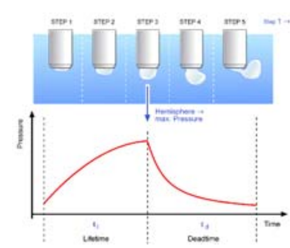
Dynamic Surface Tension
- BPA-800P





$$\gamma = f \frac{r \cdot P}{2}$$

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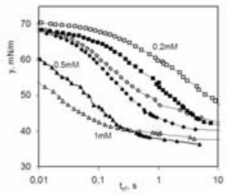
Dynamic surface tension

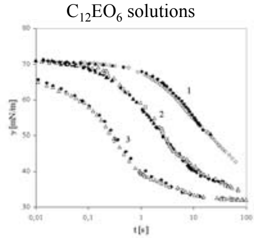
• Provide dynamic surface tension information important for many fields of applications, where the dynamics of adsorption of surface-active compounds is a vital property of the involved surface layers

Cationic surfactant CTAB



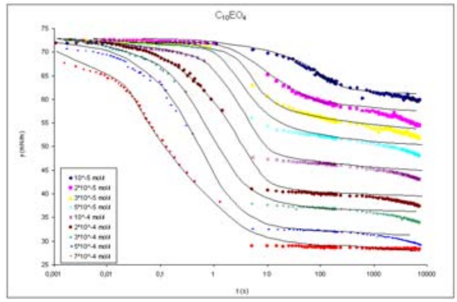
With 0.01 M NaCl (closed symbols) and without NaCl (open symbols)

$C_{12}EO_6$ solutions



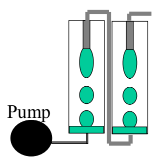
1) 10^{-4} mol/l (1),
2) $3{\cdot}10^{-4}$ mol/l (2)
3) 10^{-3} mol/l (3)

Combining Dynamic and Optical



Continuous On-line monitoring of process parameters based on bubble pressure or drop volume

- Online measurement of surface tension
- Automatic chemical dosing – optional
- Online measurement of pH – optional
- Online measurement of conductivity – optional
- Online measurement of process temperature



$$\gamma = \frac{\Delta\rho g V}{2\pi\, r_{cap}\, f}$$

2 weeks monitoring period of degreasing bath