Artery Academy

Done By amarat hamdeh

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# **Physical Pharmacy II**

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The DuNoüy Ring Method

- It is used for measuring surface and interfacial tensions.

- The principle of the instrument depends on the fact that the force necessary to detach a platinum–iridium ring immersed at the surface or interface is **proportional to the surface or interfacial tension**.

- The force is recorded in dynes on a calibrated dial.
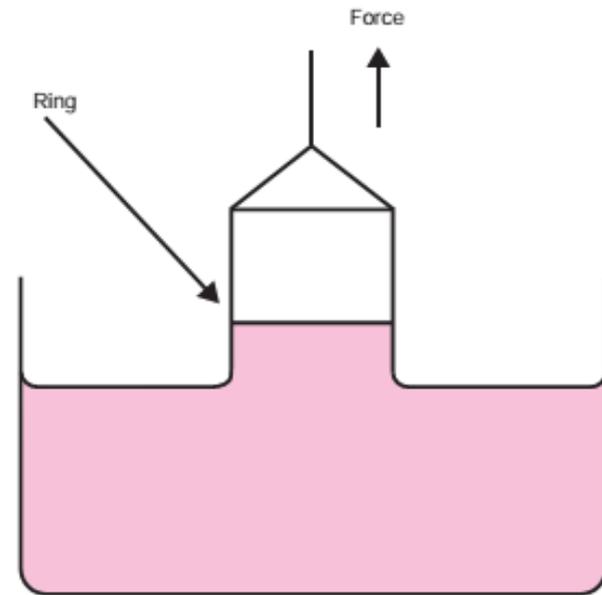
إحدى طرق قياس ال surface tension والـ interfacial tension غير طريقة الـ capillary method هي الـ dunouy ring method وهي دائرة مصنوعة من البلاتينيوم بنعملها immersion على سطح السائل فبتقيس الـ surface tension and interfacial tension وبنشغل الجهاز وهاد الجهاز بقيس القوة اللي لازمة حتى أعمل فصل لهاي الـ ring من السطح من خلال إنو الجهاز ببلش يرفعها فالسلايد اللي بعدو القانون اللي بحسب من خلالو الـ surface tension لهاد الجهاز الجهاز بعطيني القوة وبقسمها على المحيط تبع الدائرة نضروب بتنين لانو وجهين وهاد كلو بضربو بالـ correction factor

The DuNoüy Ring Method

- Surface tension=$\dfrac{dial\ reading\ in\ dynes}{2\times ring\ circumference}$×correction

  factor (ß)
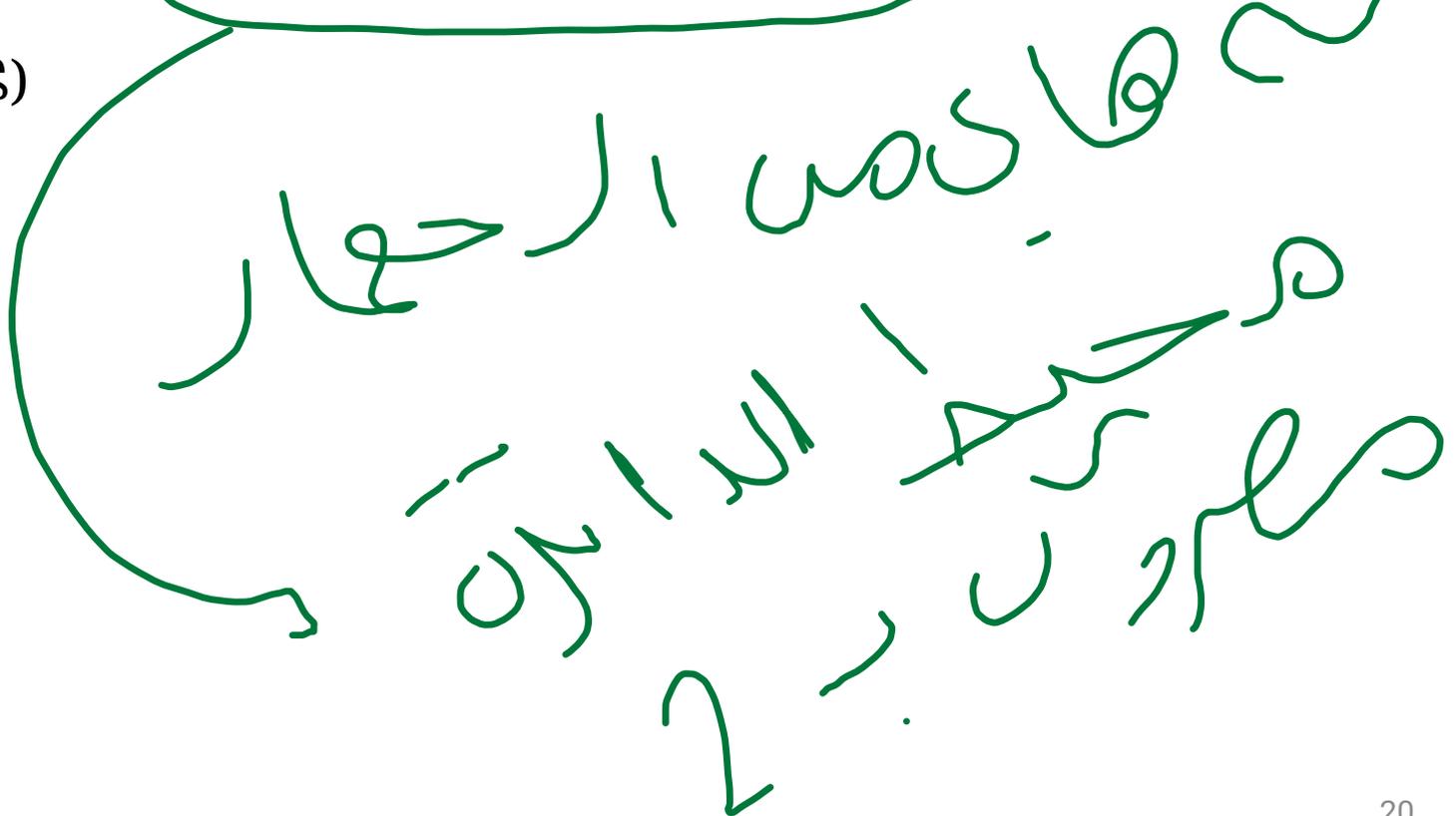
Correction factor must be used

- If the correction factor (ß) not used, error may reach 25%.

- ß depends on:
  - Radius of the wire r that form the ring
  - Radius R of the tensiometer
  - Volume of liquid raised out of the surface (V)

- Refer to Harkins and Jordan values of ß

ال correction factor بضرب في لانو عندي error بالتجربة إذا أنا ما حسبتها رح يطلع عندي خطأ بال surface tension والinterfacial tension بنسبة 25% فهاي ال correction factor عشان تصحح الخطأ وبعتمد ال correction factor على ال ال radius تبع ال ring اللي غمرناها بالماء وحجم ال liquid وال radius للجهاز اللي بقيس القوة اللي بدي ارفعها وهاد ال correction factor في إلو reference بقدر أخدها منو

Number of drops method

- It is a qualitative method to determine surface tension.

- It is based on the principle of "As surface tension reduced, the drop volume will decrease, and the number of drops for certain volume will increase".

- You need only a dropper for this method

- It cannot be applied for interfacial tension measurements,

- $ɣ=w/dA$

هاي الطريقة سهلة وهي qualitative إذا كان عندي بال dropper سائل ال surface tension إلو عالي هل رح تنزل ال drop بسرعة أكيد لا رح تتجمع هاي القطرات حتى تكون ال drop ال weight إلها يغلب ال surface tension عسان تنزل فعدد ال drop بقل كل ما زاد ال surface tension وبالمقابل ال volume تبعها بزيد لانو بتحتاج لقوة اكبر حتى تنتصر على ال surface tension فبالتالي لو عكست وجبت سائل إلو ال surface tension قليل ال drop رح تنزل بسرعة وال volume قليل فبالتالي حجم ال molecule قل لما يقل رح يزيد ال surface area فبنستنتج علاقة بين ال surface tension وال surface area وهي علاقة عكسية .... وهاي الطريقة بس لل surface tension مش لل interfacial tension

Wilhelmy Plate Method

plate

Liquid sample

θ

$$\gamma = \frac{F}{L cos\theta}$$
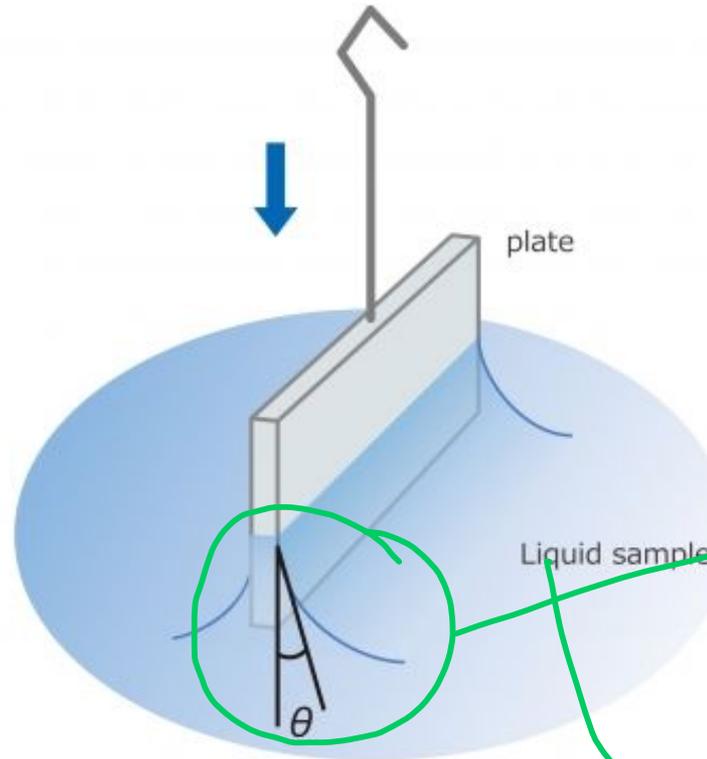
Where:

γ : Surface tension

F : Measuring force (force acting on the plate)

L : Perimeter of plate

θ : Contact angle of plate and the liquid

ال wihelmy plate method نفس ال dunouy لكن بدل ال ring مربع

مشكلة هاي الطريقة انو بتعمل زاوية ولازم ناخدها بعين الاعتبار

Spreading coefficient

- Upon placing a drop of insoluble oil on water
  - Oil remain as lens –No spreading
  - Oil spreads as a film- (duplex film)
  - Oleic acid in water (adhesive forces grater than cohesive)
  - Duplex films are sufficiently thick (100 A or more) -the surfaces and are independent of one another.
 - Oil spreads as a monolayer with excess oil forming lenses

هسا ال surface tension هي عبارة عن قوة adhesive اللي بتكون بين ال unlike وال cohesive اللي بتكون بين ال like molecules هسا إذا جبت وعاء من ال water وحطيت oil رح يضل على السطح على شكل قطرة ولما يكون في عندي oil بينو وبين ال water شوية interaction يعني في adhesion بعمل زي layer وأي زيادة رح تنزل ال oil على شكل قطرة

work of adhesion

- The work of adhesion, which is the energy required to break the attraction between the unlike molecule.

- Lets imagine that we have a cylinder (cross-sectional area 1 cm^2) of the sublayer liquid, S, overlaid with a similar section of the spreading liquid, L.

- Surface or interfacial Work=ɣ×dA
  - Here the area increment being unity

- The work done is equal to the newly created surface tensions, γL and γS, minus the interfacial tension, γLS, that has been destroyed in the process.

- Wa=γL + γS − γLS

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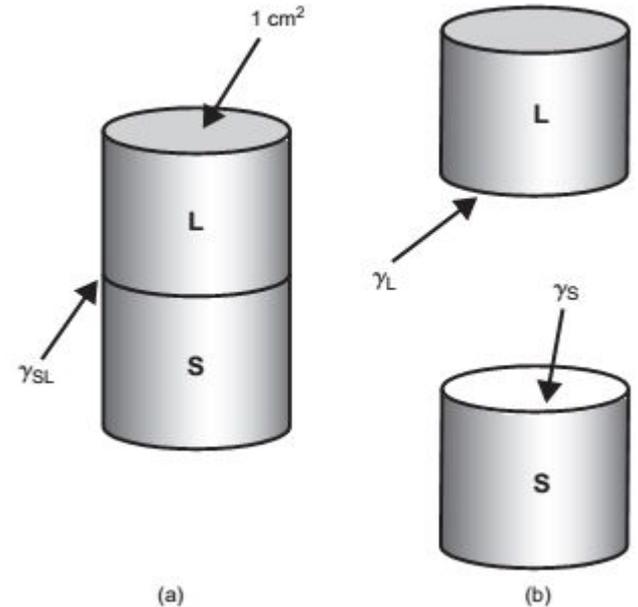
ال work of adhesion هي القوة اللي بدي إياها حتى أفصل ال unlike molecules عن بعض لنفرض عندي liquid عملتلو spread على liquid تاني وبعدها انا رجعت بدي افصلهم يعني بدي اخلي كل liquid لحال فال work بهاي الحالة تساوي ال surface tension لل liquid الأول زائد ال surface tension لل liquid التاني على ال interfacial tension بين ال tow liquid

$$W_a = \delta_L + \delta_d - \delta_{Ld}$$
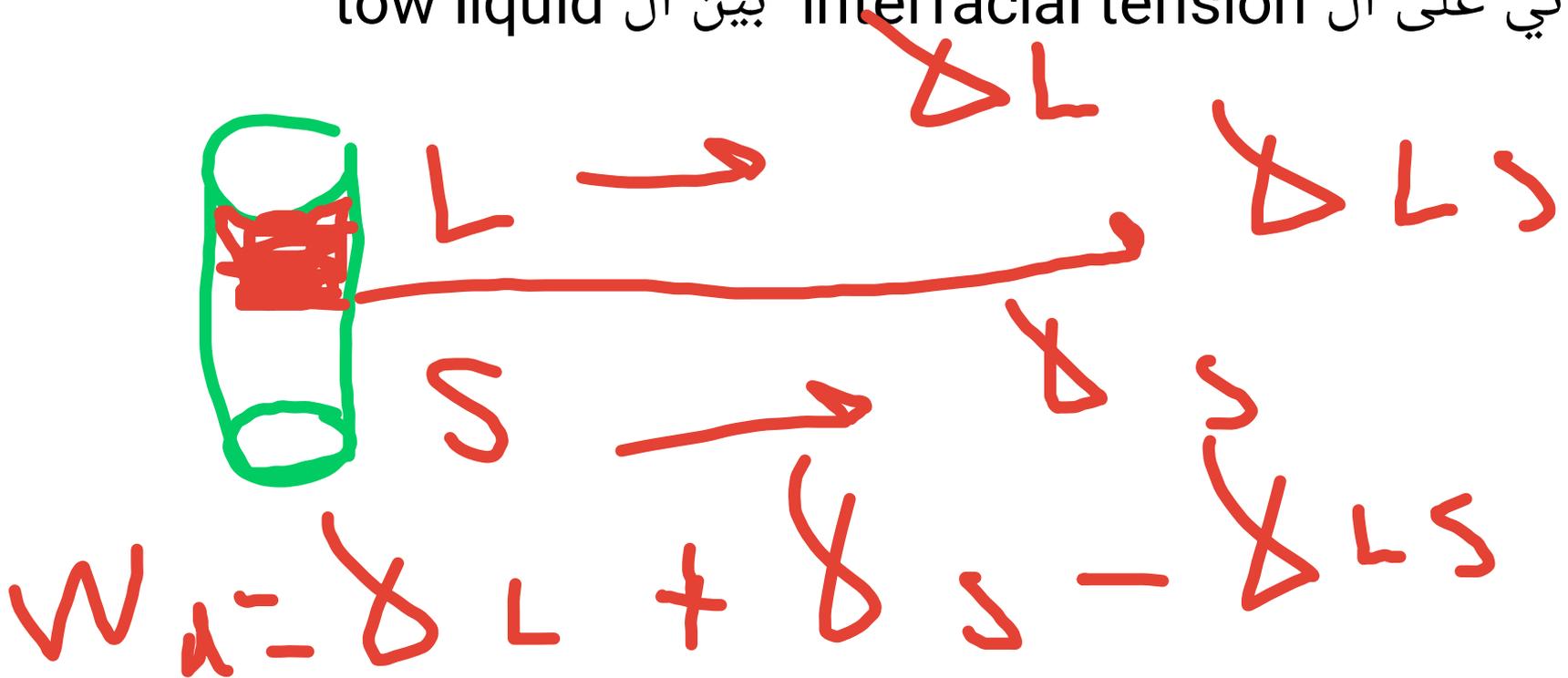
work of Cohesion

- The work of cohesion, required to separate the molecules of the spreading liquid so that it can flow over the sublayer

- There is no interfacial tension exists between the like molecules of the liquid and when the hypothetical 1-cm2 cylinder is divided, two new surfaces are created each with a surface tension of γ_L
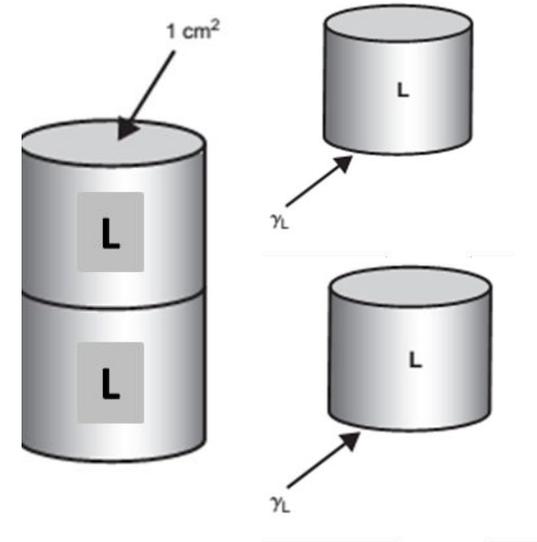
- Wc= $2\gamma_L$

ال work of cohesion هي القوة اللي بدي أفصل ال like molecules عن بعض هون ما في interfacial tension لانو ال liquid نفس الأشي لكن في surface tension موجود

$$\gamma_L + \gamma_L - \boxed{\gamma_{LL}}$$

يعني هيي عنتَ نيبتن حسر لأ بوس رس

$$W_c = 2\gamma_L$$

Spreading coefficient (S)

- Spreading occurs if the work of adhesion (a measure of the force of attraction between the oil and the water) is greater than the work of cohesion (oil molecules).

- S=Wa − Wc

- S=$(\gamma_L + \gamma_S − \gamma_{LS}) − 2\gamma_L$

- S = $\gamma_S − (\gamma_l + \gamma_{LS})$

- S= $\gamma_S − \gamma_L - \gamma_{LS}$

- So if S is positive, spreading occurs

- If $(\gamma_S + \gamma_{LS})> \gamma_S$ The substance forms globules or a floating lens and fails to spread over the surface. (e.g. mineral oil in water)

ال spreading بحدث لما يكون في interaction between different molecules فمن هاد الأشي بنستنتج إنو لازم تكون ال adhesion لانها بين different molecules أكبر من ال cohesion ومن خلالها بقدر أعرف قانون ال spreading

$$S = W_a - W_c$$

$$S = \gamma$$

$$S = \gamma$$

ءادكن الحواب (١)

spread جا ماد

دا ا ك نوص ص

جا spread
-

Spreading coefficient (S)

- Evaluate the ability of simple liquids to spread on water

$$S_{wo} = \gamma_w - \gamma_o - \gamma_{wo}$$

	γ_w	γ_{wo}	γ_o	S	
n- hexadecane	72.8	52.1	30	-9.3	Non-spreading
n-octane	72.8	50.8	21.8	+0.2	Just spreading
n-octanol	72.8	8.5	27.5	+36.8	Easily spreads

Reversal spreading

- The initial spreading may change after equilibrium.

- The water surface becomes saturated with the spreading material, which in turn becomes saturated with water so the surface tension will change

- $\gamma_{S'}$ and $\gamma_{L'}$ are the new surface tensions following equilibrium.

- Example: water has a surface tension of 72.8 dyne/cm, benzene has a surface tension of 28.9 dyne/cm and the interfacial tension between water and benzene is 35 dyne/cm .

  - Will benzene spread on water?

- After sometime, the benzene will begin to saturate the water and the surface tension of water-saturated benzene layer is 62.2 dyne/cm

  - What will happen to the spreading factor?

- **When mutual saturation has taken place, the spreading coefficient (S') may be reduced or may even become negative.**

- γ_{LS} **does not change** because the interfacial tension is determined under conditions of **mutual saturation**.

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هسا بين ال tow phase بصير مع الوقت saturation يعني الماء مثلا بدخل جواها molecules من السائل الثاني فبنصير نسميها water rich layer وكذلك الامر للسائل الآخر بتدخله حزيئات الماء هسا هون بصير في عندي equilibrium وبتغير فيها ال surface tension لل tow face لكن ما بتتغير ال interfacial tension لانو المواد ضلت نفس ما هي وممكن يتحول ال spreading coefficient من - لل + او العكس

ما بتتغير على الحرحلة
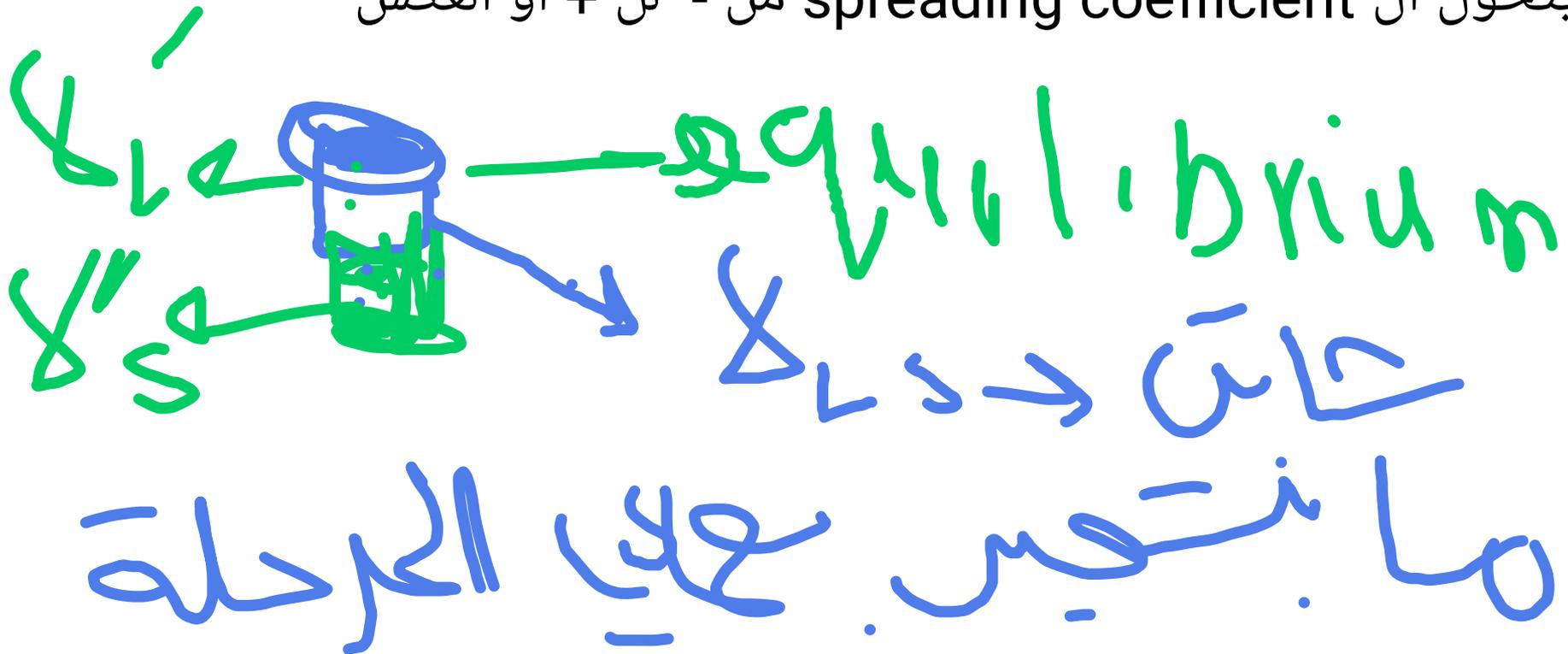
Initial spreading coefficient of organic liquid on water at 20 °C

Substance	Formula	S (dyne/cm)
Ethyl alcohol	C_2H_5OH	50.40
Diethyl ether	$(C_2H_5)_2O$	45.5
Oleic acid	$C_{17}H_{33}COOH$	24.62
Methylene chloride	CH_2Cl_2	17.97
Benzene	C_6H_6	8.94
Hexane	C_6H_{14}	3.41
Octane	C_8H_{18}	0.22
Carbon disulfide	CS_2	6.94
Ethylene dibromide	$C_2H_4Br_2$	−3.19
Liquid petrolatum	$C_{15}H_{11}ClO_7$	−13.4

# Factors affecting surface and interfacial tension values

1. Adsorption at liquid interface:

    A. Positive adsorption: molecules are partitioned in favor of the interface (e.g SAA and amphiphile). These tends to decrease surface and interfacial tension

    B. Negative adsorption: molecules are partitioned in favor of the bulk (e.g. inorganic electrolytes). These tends to increase surface and interfacial tension

2. Temperature

3. Presence of impurities

    - Impurities affect the surface tension, so cleanliness is a very important factor in determining surface tension.

العوامل اللي بتأثر على ال surface tension and interfacial tension هي : إذا كان عندي surfactant وراح على السطح رح يقلل ال surface tension لانو صارلو إمتزاز على السطح وبقلل ال surface tension وبنسميه positive adsorption لانو وصل للسطح وقلل ال surface tension.... ال negative adsorption هو إنو لو أضيق nacl رح تنتقل لمنطقة الwater وتعمل ionic bonds وبالتالي رح تزيد قوة الربطة ورح يزيد ال surface tension.... درجة الحرارة بتقلل قوة الرابطة فبتقلل ال surface tension ووجود الشوائب حسب نوعها ممكن تزيد ال surface tension وممكن تقللو

Adsorption at liquid interface

Y-Values

- Electrolytes

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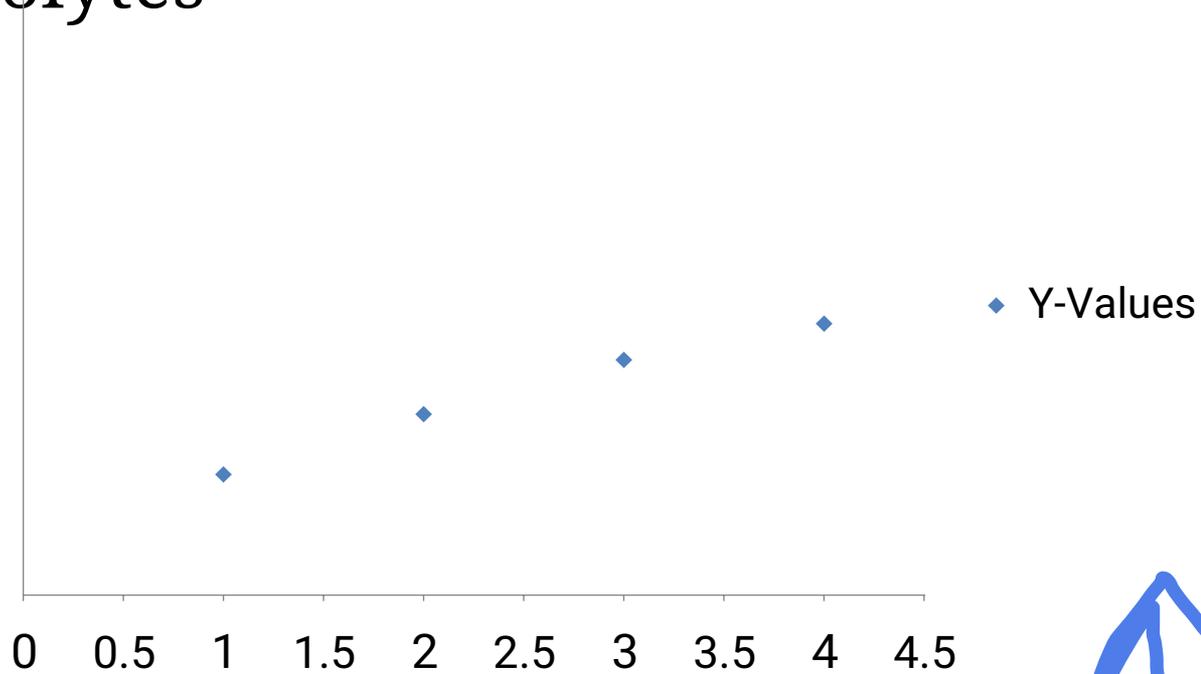
Adsorption at liquid interface surfactants

- Substances which have a tendency to concentrate at the surface or interface are called surface active agent (SAA)

- They have a number of effects on the nature of the surface

- They decrease surface tension

ال surface active agent او ال surfactant
polar إلهم surface tension وظيفتهم يقللو ال
head و nonpolar tail فبترتبو على السطح بجيث
يعملو balance بين ال water وال oil وبزبطو حتى
بين liquid and gas

Nonpolar polar

Adsorption at liquid interfaces Surfactants

- SAA or surfactants are amphiphilic agents are absorbed at interfaces (adsorbed).

  - Gas-liquid interfaces
  - liquid–liquid interfaces

- For the amphiphile to be concentrated at the interface, it must be balanced with the proper amount of water- and oil-soluble groups.

Classification of Surfactants

Non-ionic surfactants → uy st stable

- Have low toxicity and high stability and compatibility, e.g.

- Sorbitan esters (spans) and Polysorbates (tweens).

Anionic surfactants

- Have bacteriostatic action

- e.g. Sodium Lauryl Sulphate

Cationic surfactants

- Have bactericidal activity
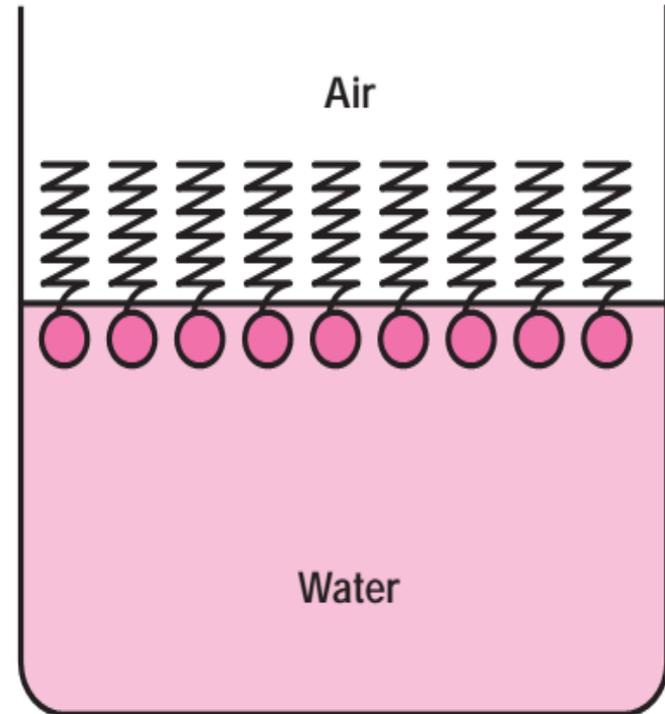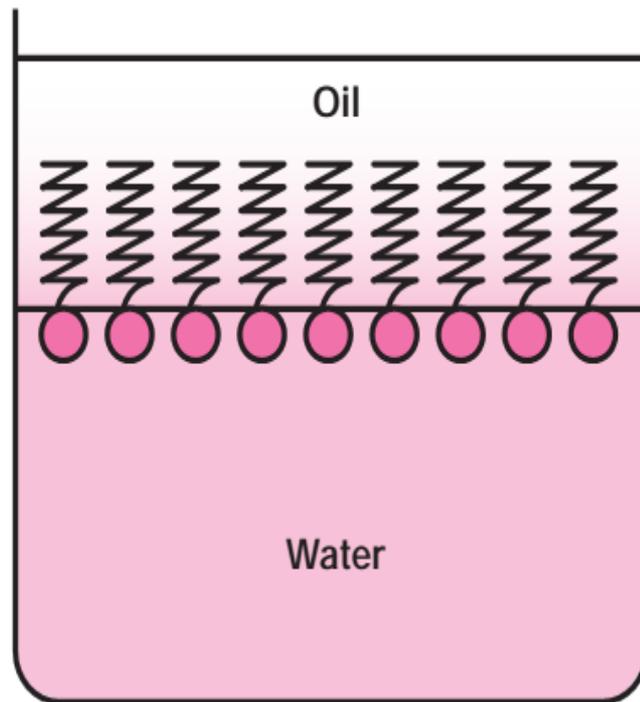
- e.g. benzalkonium chloride

Ampholytic Surfactants

- Zwitterionic: -ve and +ve charges (phosphatidylcholine

hydrophil   hydrophob
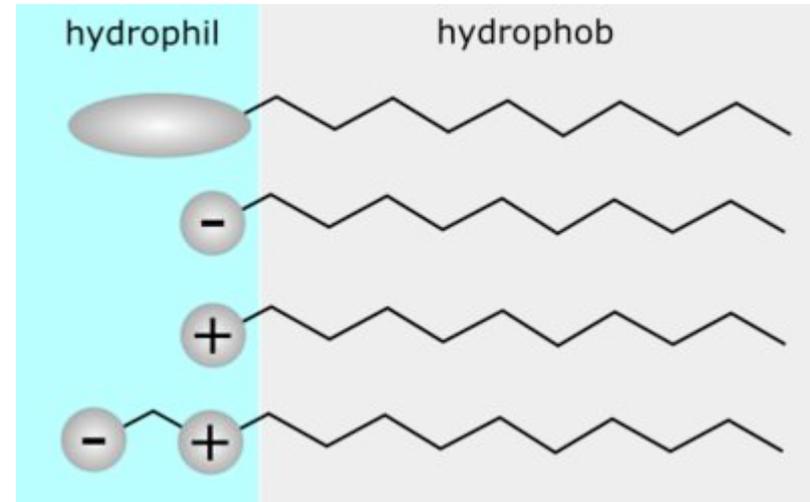
Adsorption at liquid interfaces Surfactants

Reduction of Surface Tension
Effect of Structure on Surface Activity

- The surface activity (surface tension reduction) of a particular surfactant depends on the balance between its hydrophilic and hydrophobic properties.

- An increase in the length of the hydrocarbon chain (hydrophobic) of a surfactant increases the surface activity.

- Conversely, an increase in the length of the ethylene oxide chain (hydrophilic) of a non-ionic surfactant results in a decrease of surface activity.

فكون ال surfactant بترتبو على ال surface بأثرو على ال surface tension من خلال إنو ببطل ال interaction مع ال phase التاني لأ بصير بينها وبين ال surfactant... هسا كل ما زدنا ال hydrophobic part رح يروح على السطح لانو ما رح يحب الماء ورح تزيد فعاليتو لانو ضل على ال surface وبالتالي رح يكون تقليلو لل surface tension أعلى والعكس صحيح لما ازيد ال hydrophilic part رح يحب الماء وما رح يقلل ال surface tension بشكل صحيح عشان هيك لازم يكون في balance between the hydrophobic part and hydrophilic part
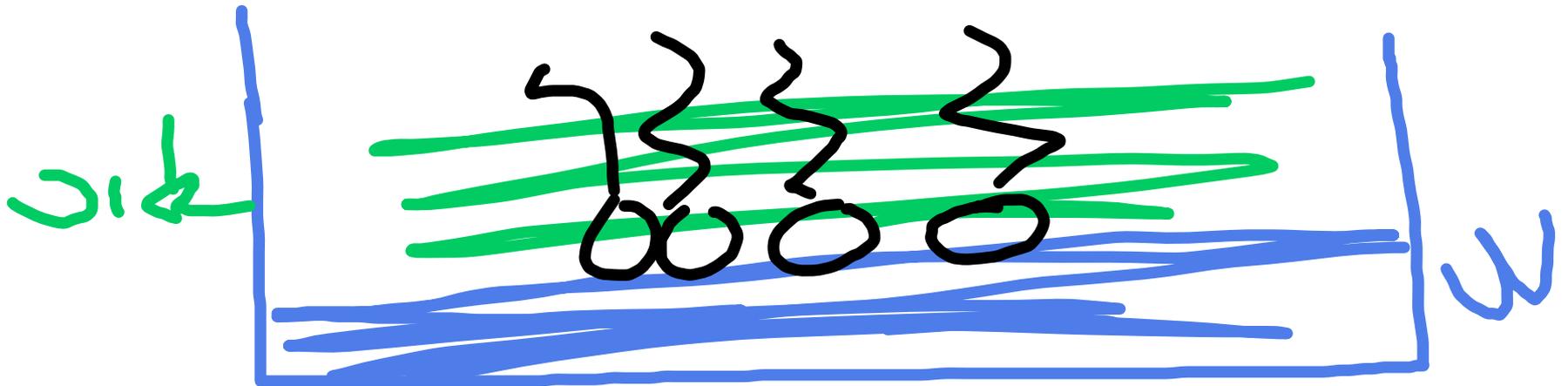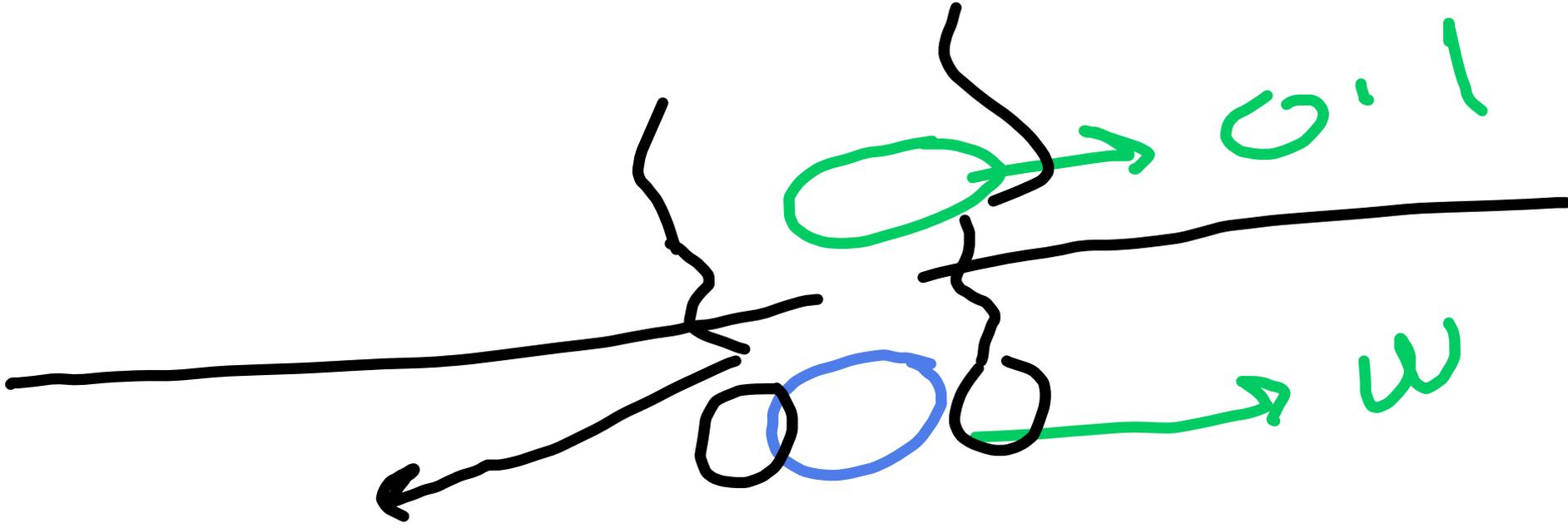
oil

w

سي inter
action يعني
oil و w

Reduction of Surface Tension
Surface Excess Concentration

- **Surface excess concentration (Γ)** is the extra amount per unit area of the solute that is present in the surface

- It represents the difference between the amount per unit area of a solute in the surface of a real system and that of a hypothetical system (without adsorption).
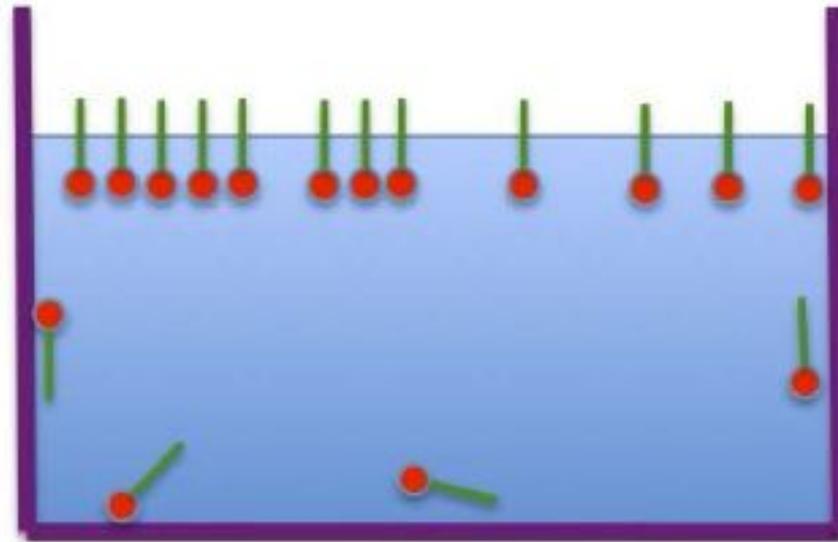
- Surface excess is expressed by the Gibbs equation:

$$\Gamma = \frac{1}{RT} \times \frac{d\gamma}{d\,lnc}$$

Γ = surface excess (g/cm^2)
R = gas constant (8.314 J mol^{-1} K^{-1})
T = absolute temperature (kelvins)
c = concentration (mol m^{-3})

هسا أي زيادة على ال concentration لل surfactant رح يصير supersaturation ال surface ورح ينزل ال surfactant لتحت ويكون micelle... فالقانون اللي بالسلايد اللي فوق بحسبلي ال surface excess ومن هاد القانون عملو قانون تاني اللي هو بالسلايد اللي تحت حتى أحسب المساحة اللي عندي كم لازم يكون فيها surfactant

Reduction of Surface Tension
Surface Area

- The **surface area (A)** is the area occupied by one surfactant molecule at the solution surface.

- It can be calculated from the equation:

$$A = \frac{1}{N_a \times}$$

N_a = Avogadro number (6.023×10^{23} molecules mol^{-}')

بتحسب مساحة كل
surface