Fundamental of Surface Tension

Kyowa Interface Science Co., Ltd.

Interfacial phenomena familiar with our life

- Natural phenomena
    - Barberpoles swim on water surface.
    - Dews remains on lotus leaves.
    - Windows are clouded over with condensation.
    - Hairs are bound with moisture.
    - Plants drink up water from the soil.

- Life environment
    - Detergents clean dishes and clothes.
    - Waxes on flooring materials to protect from soils
    - Ink-jet printers print.
    - Water/oil-repellent pan enables non-stick baking.
    - Hydrophilic finishing avoids condensation on windows.
    - Adhesive agents attach two objects.
    - Cosmetics are worn on skins
    - Cleaning up by water

Surface tension

- When filling a cup with water, water does not overflow even if its surface exceeds the level of cup border a little.

- Well, why water does not overflow?
- A reason is that water has force to round of itself and remains at the border of cup by shaping an arch. The force to round of itself (to reduce area of surface) is Surface Tension.
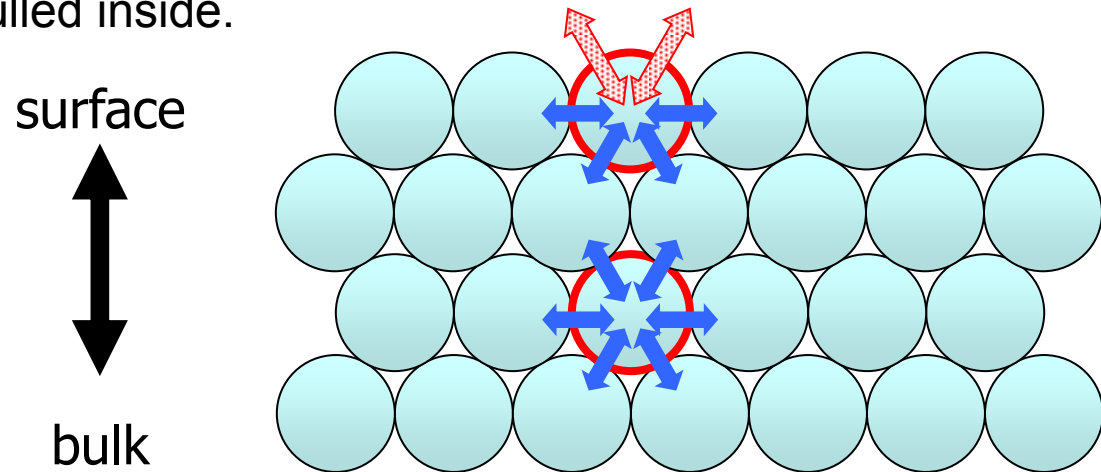- Unit of surface tension is "mN/m" now. Once "dyne/cm" was being used and the scale of those units are same.

- Why Japanese one Yen can float on water?

- Why the coin sinks when detergent is added?

Essentiality of Surface tension

- It originates in Intermolecular forces between molecules.
  - In the bulk, Intermolecular forces work every direction and keep balance.
  - On the surface, the balance is off and molecules exposed in the surface are pulled inside.

surface

bulk

- The surface molecules demand others for interaction and surplus energies generates there, which is Surface Tension.
- Surface tension is peculiar physical property of each material has.

Surface tension and Wettability

If the surface tension of a target liquid is large…

↓

● Force to make the liquid round of itself will be strong.

↓

● The liquid will be apt to be repelled by solid surfaces.

↓

● Contact angle results larger. → Wetting becomes worse.

If the surface tension of a target liquid is small…

↓

● The liquid will allow to wet over the solid surfaces.

↓
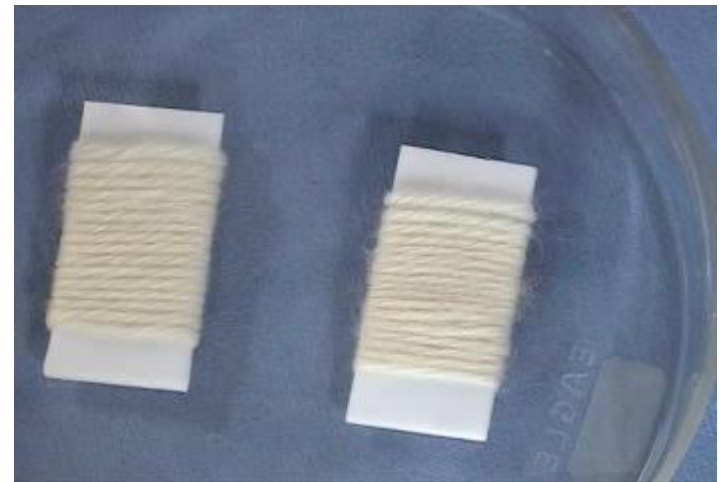
● Contact angle results smaller. → Wetting becomes better.

↓

● It will contribute better spreading and permeating.

Applications of Surface tension

- Evaluation focusing to liquids
- Ability of surfactant to decrease S.T.
- Wettability, permeability between solid and liquid
    - Permeation to clearance, fibers
    - Ink, surfactant
    - Coating
- Characterization of liquids
    - Ink, surfactant
- Emulsification
    - Dressing, mayonnaise, cosmetics
- Quality control of detergent, guilt
    - Management of change cycle

Emulsifying

Rolling up

Kyowa's Surface/Interfacial Tensiometers

- **DyneMaster series - Balance mechanical system**

  Available 3 types DY-700, DY-500, DY-300

  Measuring method: Wilhelmy Plate method (standard)

  du Noüy Ring method (option)

  Other characterization: Dynamic contact angle, Lamella length

  Powder contact angle, Liquid density

- **DropMaster series – Image analysis system**

  Available 4 types DM-701, DM-501, DM-CE2, DM-CE1

  Measuring method: Pendant Drop method

  Other characterization: Contact angle, Surface free energy

- **BP series - Dynamic surface tension measurement**

  Available 2 types BP-D5, BP-D5L

  Measuring method: Maximum Bubble Pressure method

  Other characterization: Decreasing slope by Rosen fitting

Principle of Wilhelmy Plate methods

- A detecting plate is hanged on the balance and the plate bottom is touched to the liquid surface .
Kyowa uses Platinum Plate as standard.

- Surface tension of liquid works along the plate bottom and causes a downward force.

- The downward force detected by the balance is converted to Surface tension.
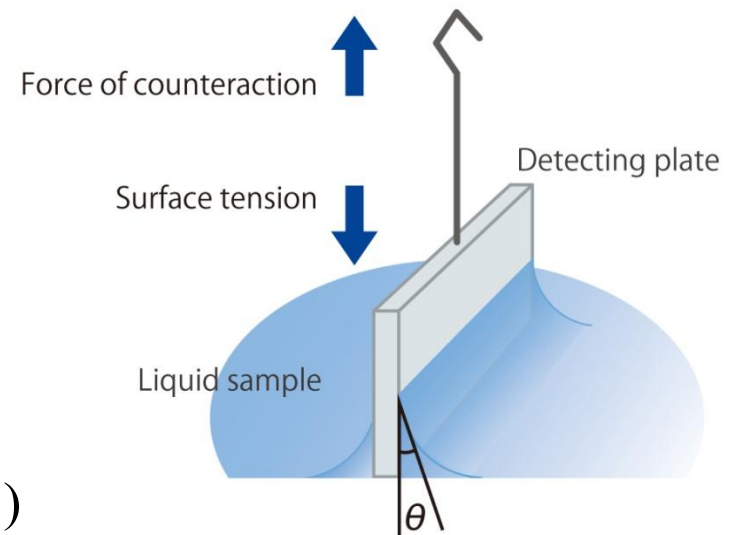The equation is given as below.

buoyancy

$$F = mg + L\gamma\cos\theta - Sx\rho g$$

mg : gravity worked on plate
L : plate peremeter
θ : C.A. (θ=0 is assumed generally.)

Force of counteraction

Surface tension

Detecting plate

Liquid sample

θ

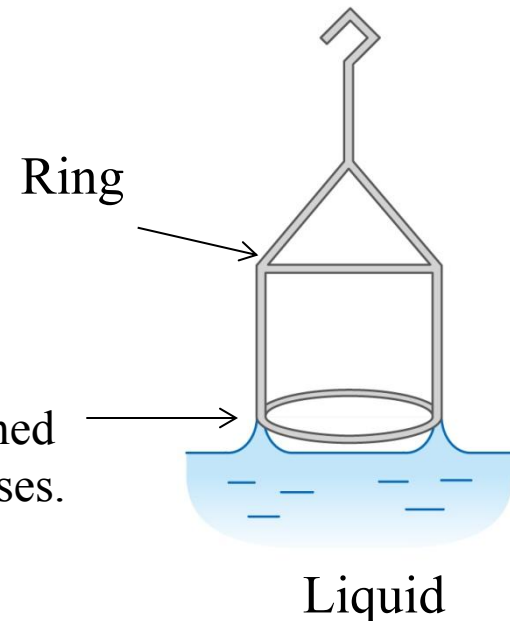# Principle of du Noüy Ring methods

- A detecting platinum ring is hanged on the balance and the ring bottom is touched to the liquid surface .
  Same system can be used for Plate and Ring in common.

- Surface tension of liquid does not work along the ring bottom at this condition. Then, let the liquid surface down to detach it from the ring.

- The peak downward force detected by the balance before detaching the ring from the liquid surface is converted to Surface tension. The equation is given as below.

Correction factor

$$\gamma = \frac{F}{4\pi R} k$$

Ring

Liquid is pulled down until detached from the ring and the force increases.

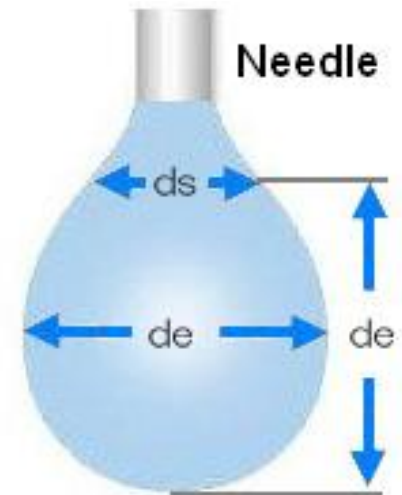Liquid

Principle of Pendant Drop methods

- A liquid is pushed our from the tip of needle toward the vertical direction. The hanging drop on the needle tip is called "Pendant Drop".

- The pendant drop shape is determined by the factors: droplet volume, density, surface tension.

- This method analyzes the shape to compute out the surface tension. The following two methods are in general:

- d_s/d_e method:
Measures maximum diameter d_e of the drop and diameter d_s where has d_e risen from the lowest end.

$$\gamma = \Delta \rho g d_e^2 \frac{1}{H}$$

$\Delta \rho$: density difference
g: gravitational acceleration
$1/H$: correction coefficient
　　　determined by d_e/d_e

- Young-Laplace method：
Fits a curve of Young-Laplace equation on the drop profile.　(Equation omitted.)
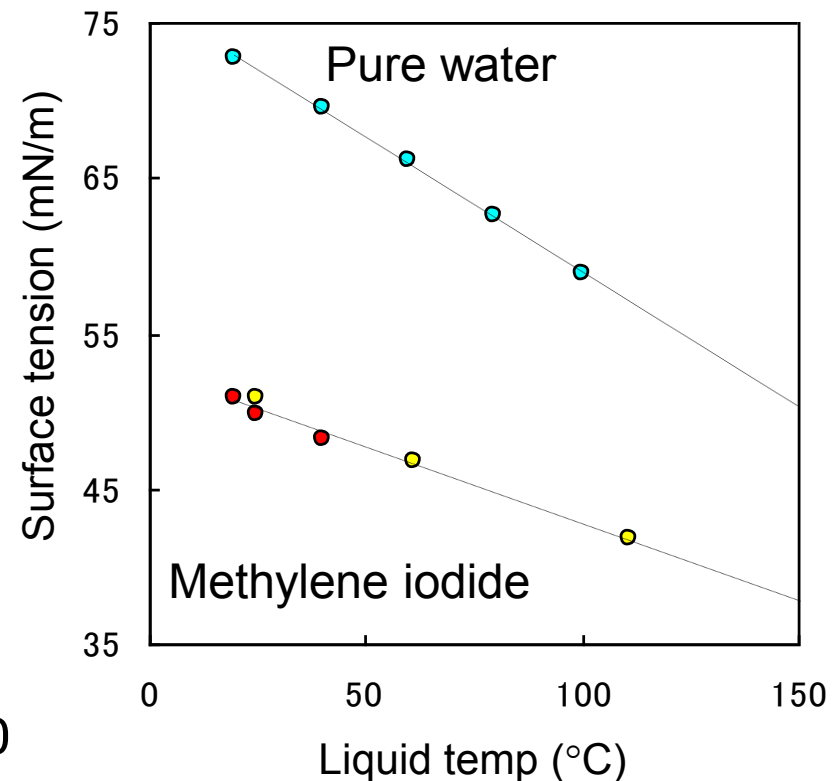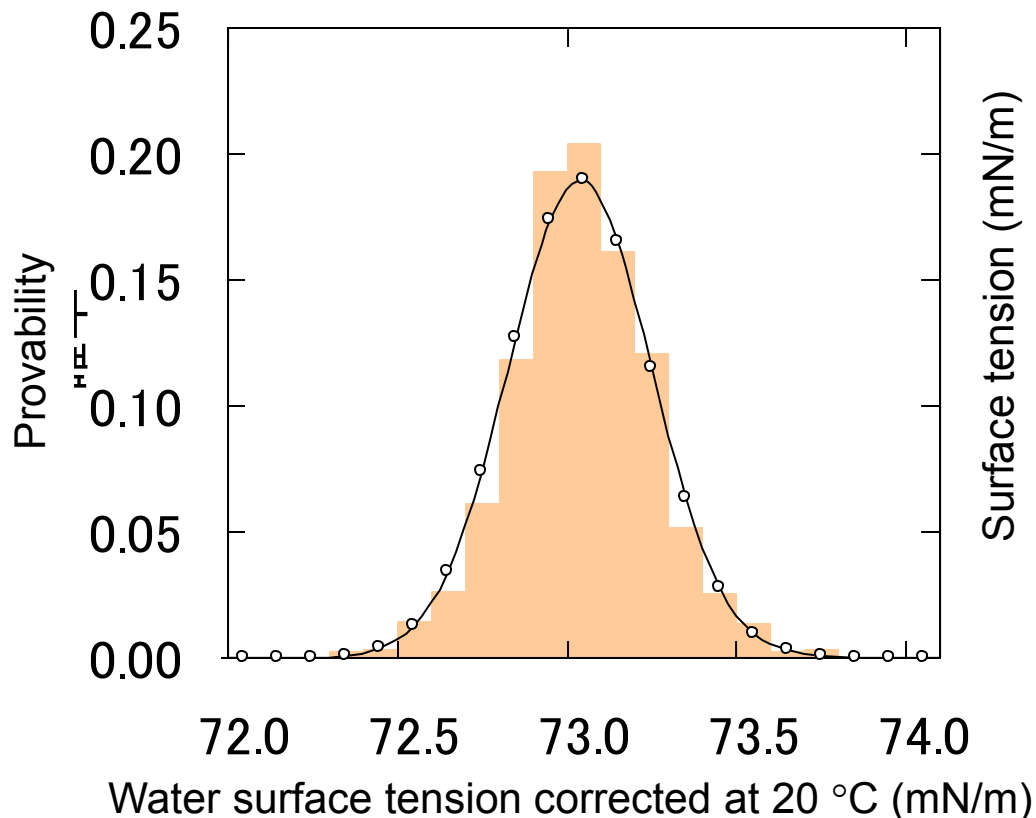
Surface tension of water

The following is an example of surface tension measurement of water.

Surface tension is specific physical property of each material but the accuracy is varied a little bit depended on measuring methods.

- Sample: water (value in literature 72.8 mN/m at 20°C)
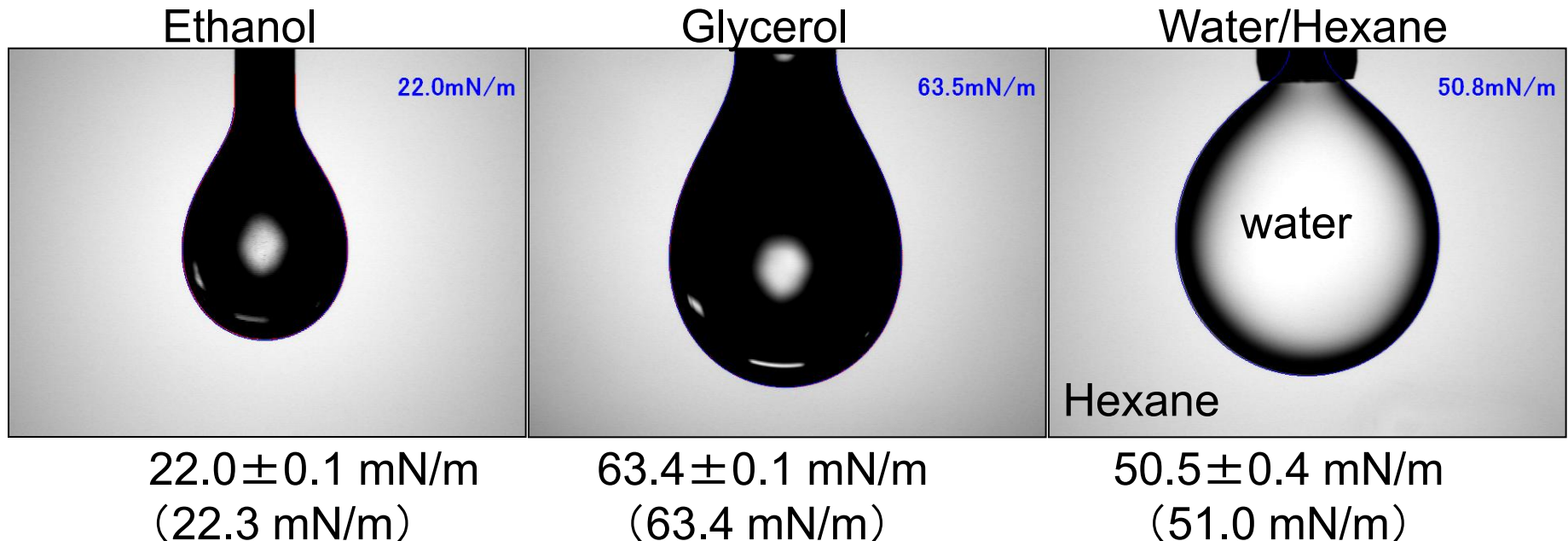- Room temperature: 19 - 21°C

Measuring method	Nos.	Average	S.D.	Min.	Max.	range
Wilhelmy plate	5	73.24	0.13	73.1	73.4	0.3
Pendant drop (Young-Laplace fitting)	5	73.00	0.48	72.3	73.6	1.3
Pendant drop (ds/de method)	5	73.16	1.36	71.2	74.4	3.2

Accuracy of pure water by Wilhelmy

- σ=0.2mN/m normal distribution
- Water has a temperature slope "-0.15[mN/m]/[°C]" around ambient temp.
- Optimized method for managing water surface tension.

Water surface tension corrected at 20 °C (mN/m)

Pure water

Methylene iodide

Liquid temp (°C)

Pendant Drop method
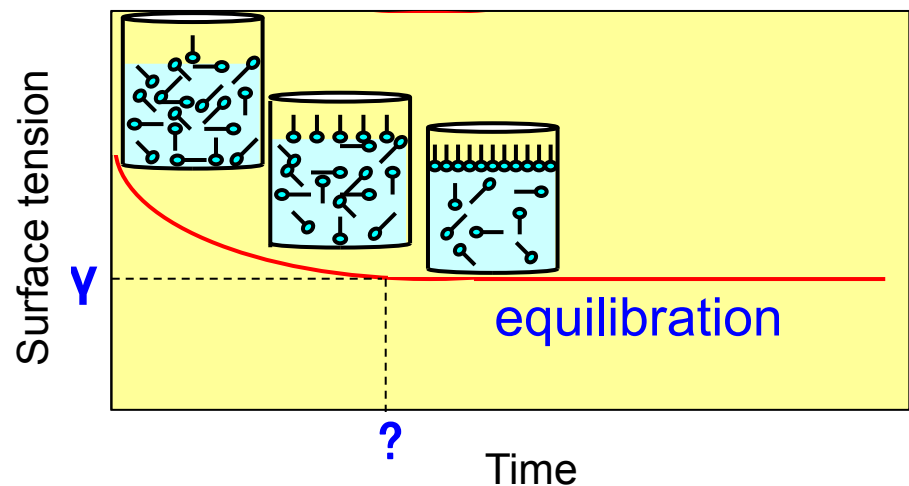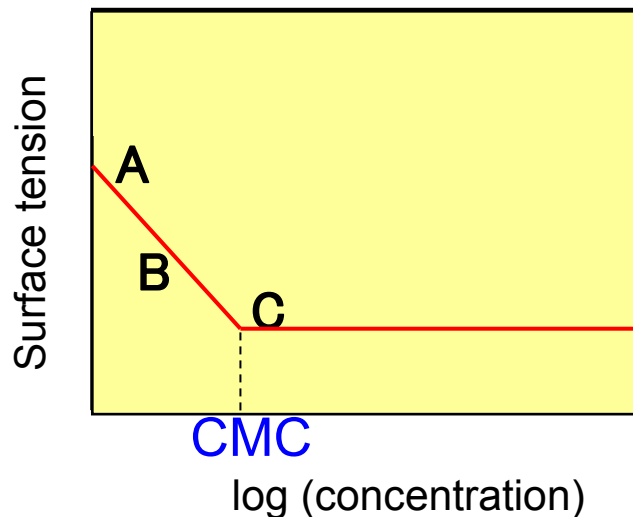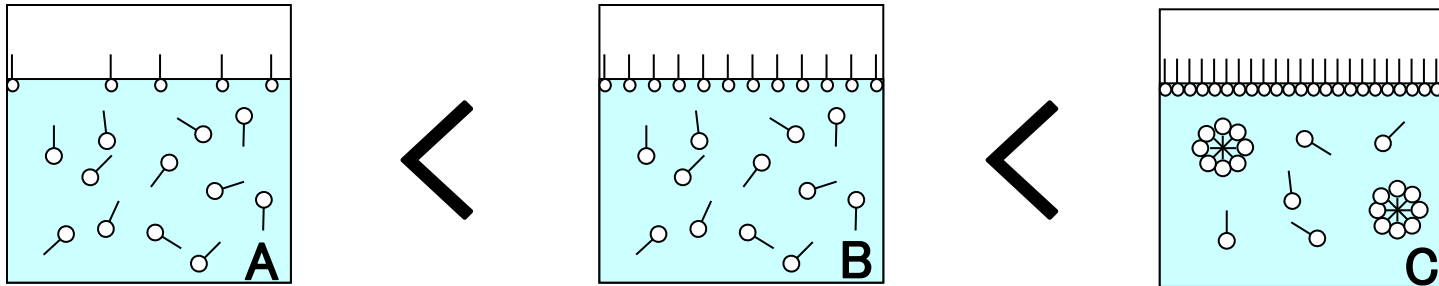
- Surface tension is figured out from the shape of pendant which is characterized by γ/ρ.

- Density is multiplied to the surface tension value figured out.

- With the optional heating chamber, surface tension measurement of molten polymers and solders are possible. But the surface should be shaped by itself.

Ethanol	Glycerol	Water/Hexane
22.0mN/m	63.5mN/m	50.8mN/m
22.0±0.1 mN/m (22.3 mN/m)	63.4±0.1 mN/m (63.4 mN/m)	50.5±0.4 mN/m (51.0 mN/m)

The data shown in case arc are from literatures.

Surface tension of Surfactant

- Surfactants have characteristics to change surface tension over time and the curves vary depended on surfactant concentration.
- Surfactants have a point of critical concentration that surface tension does not get lower. That point is called "CMC" (Critical Micelle Concentration).
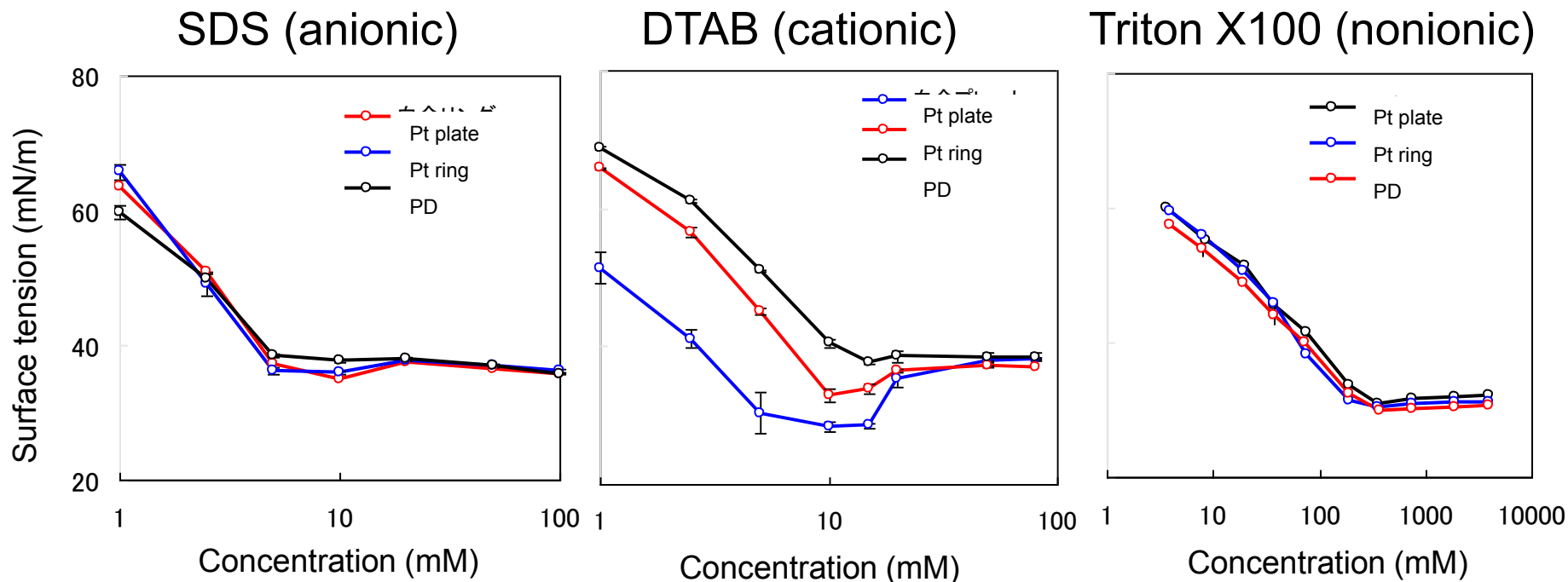- In the lower concentration than CMC, the surface tension will change until equilibration.

Dynamic surface tension & its necessity

- In the most fields of R&D or QC purposes, measurements of equilibrated surface tension are done. → Static status

- But the most liquids are actually used under circulating or being stirred. → Dynamic status

- In that condition, the concentration distribution and the absorbing amount to surface of surfactant should be uneven and not appear equilibrated conditions. These may cause troubles.

- Study of dynamic surface tension is important to select proper adding agents and the quantity.
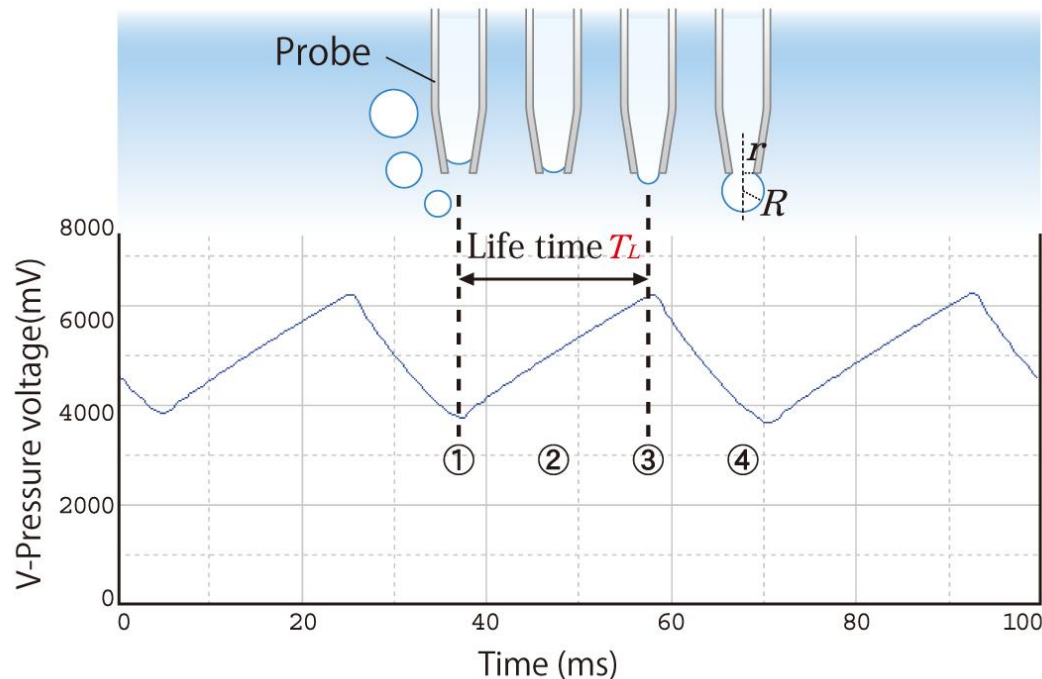
Measurements of CMC of surfactants

The below charts are the plotting of CMC (Critical Micelle Concentration) by three different methods: Wilhelmy Plate, du Noüy Ring, Pendant Drop

Cationic surfactant causes problem of wetting to the Wilhelmy plate, which causes inaccurate results.

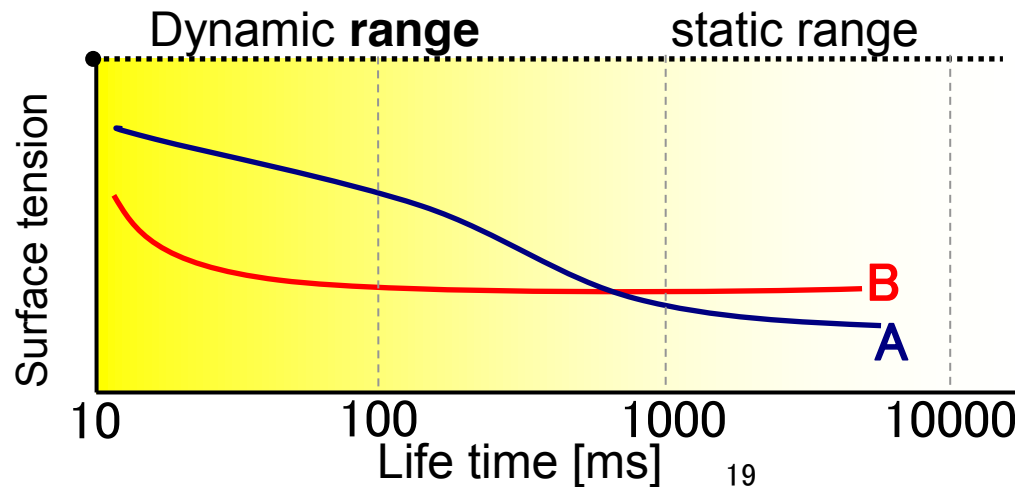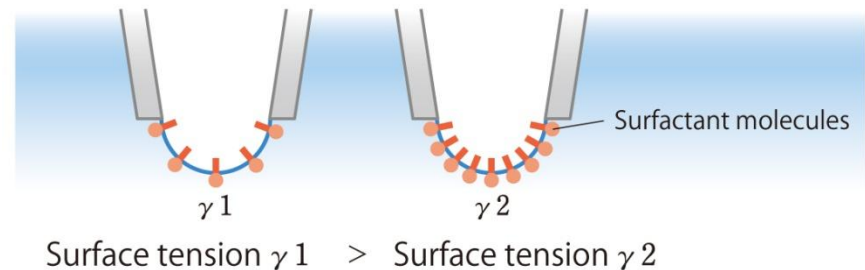SDS (anionic)   DTAB (cationic)   Triton X100 (nonionic)

1. When pressurized air is flown constantly through the probe, the pressure inside the probe changes periodically. (1) – (2)
2. When the curvature radius of bubble R equals to the radius of capillary tip r, the pressure should reach maximum. (3)
3. After that, the pressure drops rapidly by expansion of the bubble. (4)
4. The Maximum Bubble Pressure technique is a method for determining the surface tension form the maximum pressure.
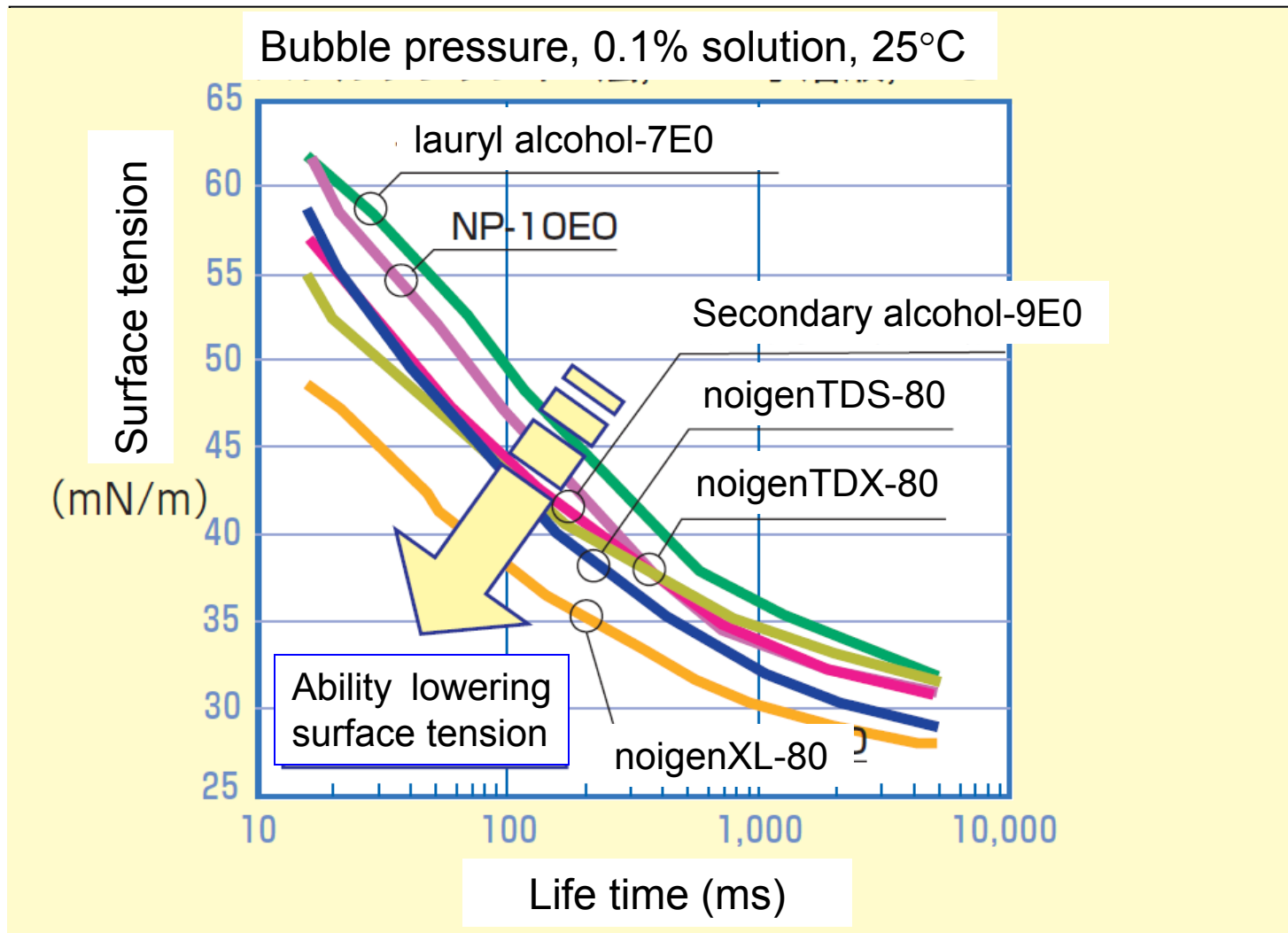
1. The cycle (1) - (3) of previous slide refers to the life time (life time of bubbles), from the time that the new interface has been generated in the probe tip until the maxim bubble pressure is reached.

2. Surfactant absorbed during the lifetime will determine the surface tension.

3. Data chart as in the below is obtained.
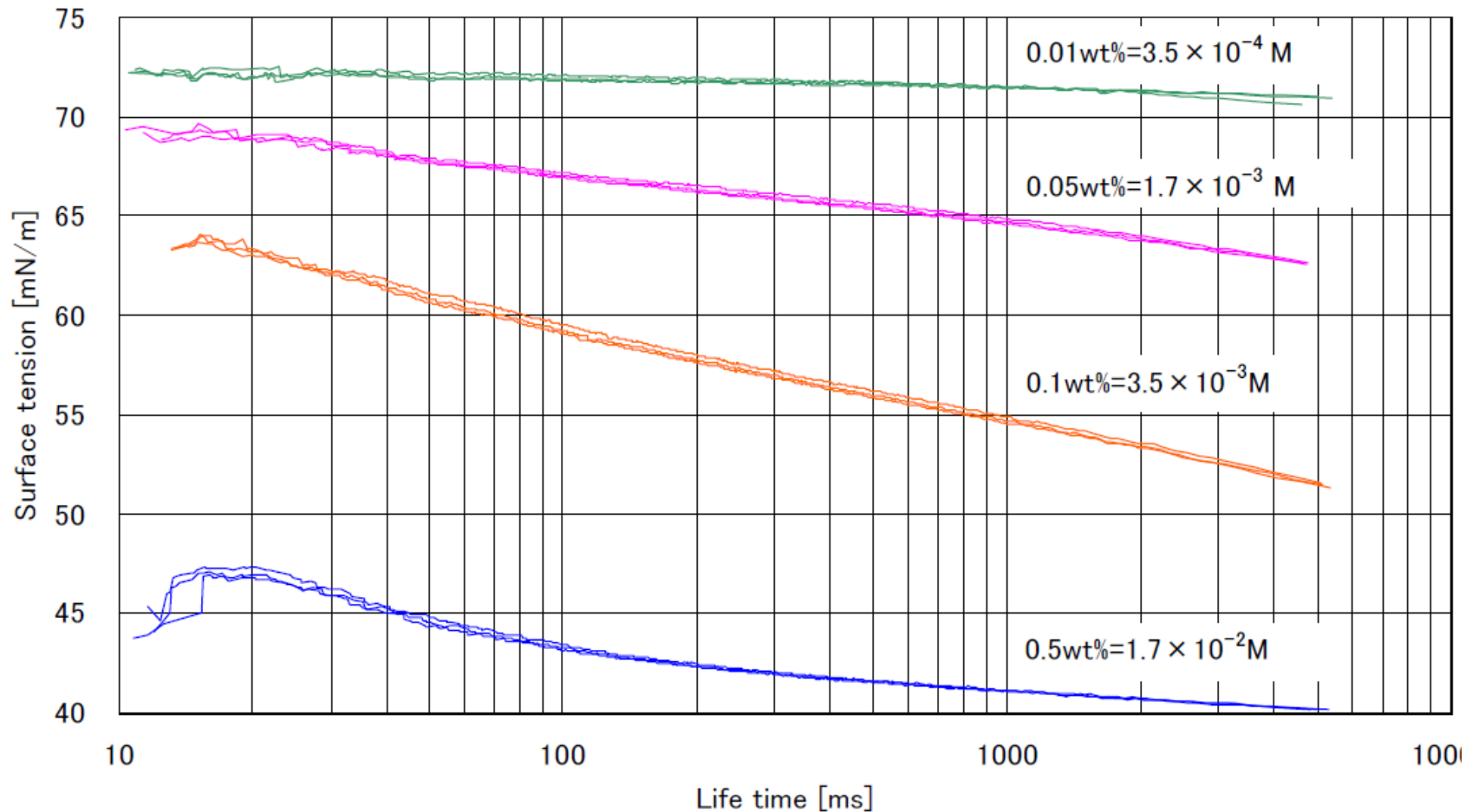
Surfactant molecules

$\gamma 1$ $\gamma 2$

Surface tension $\gamma 1$ > Surface tension $\gamma 2$

Dynamic **range**   static range

Surface tension

B

A

10   100   1000   10000

Life time [ms]

Ability of surfactant lowering surface tension

Bubble pressure, 0.1% solution, 25°C

lauryl alcohol-7E0

NP-10EO

Secondary alcohol-9E0

noigenTDS-80

noigenTDX-80

noigenXL-80

Ability lowering surface tension

Surface tension (mN/m)

Life time (ms)

（held on http://www00.wipenetworks.com/dks/j/pdf_products/542_1.pdf）

Data examples of dynamic surface tension

- Dynamic surface tension of 4 concentration level of SDS solution.
- Ability of lowering surface tension does not progress in the range of concentration more than 0.5wt% → Dynamic CMC?

Remarks for measuring surface tension

- Surface tension value is very sensitive to contamination. Take care throughout the measurement processes not to touch or contaminate the sample.

- Contamination on measuring tools are also effective to the data. Take care as well not to use contaminated tools like sample container , lab dish, measuring unit (plate or ring), needle, probe, etc. Remained detergent may be also effective much.

- Surface tension has temperature dependency. Generally, the higher temperature is, the lower surface tension is. Data should be always reported with temperature, and controlling temperature of liquid surface is recommendable.

- Every Kyowa's surface/interfacial tensiometer requires periodical calibration and has functions enable to do calibration by users themselves.

Thank you for your company