Dynamic Surface Tensiometer
Bubble Pressure Method

BP-D5, BP-D5L

Kyowa Interface Science Co., Ltd.

Basics of Dynamic surface tension

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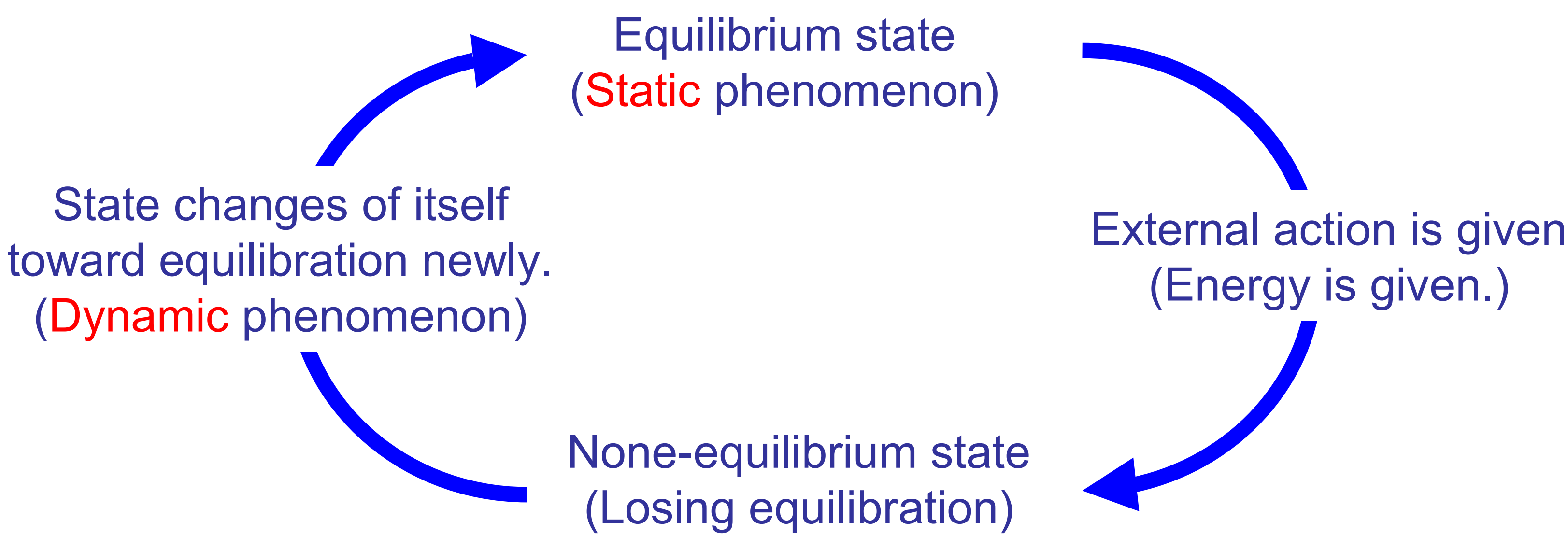
Bubble pressure method

What is Dynamic Surface Tension?

- If a state of equilibrium is once lost by external action, the state changes toward equilibration newly.



- **Dynamic surface tension** is the variations of surface tension over time caused in the process that none-equilibrium state changes toward equilibration.
- Target samples are liquids including surfactants.

Why surfactant solution changes surface tension?

- A molecule of surfactant has both hydrophilic and hydrophobic groups.
- When a surfactant solution is stirred, some molecules move for surface and the others create micelles in the liquid as time goes on.

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- The phenomenon continues until equilibration of the solution.

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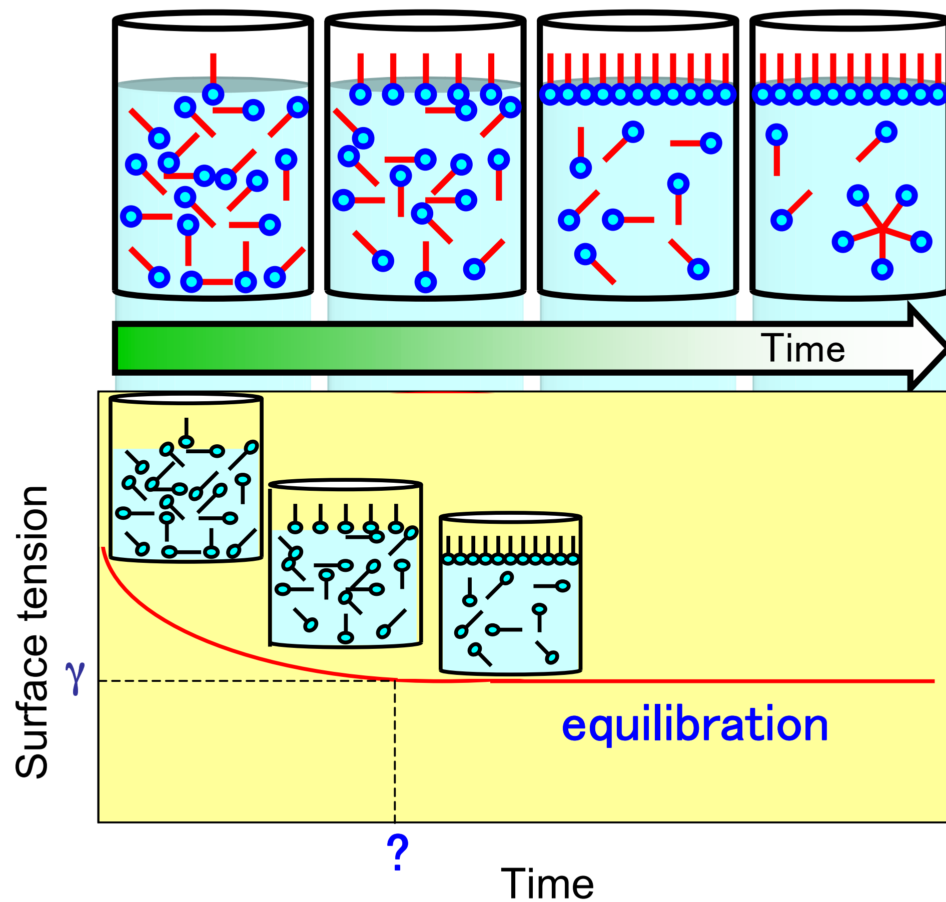
- Increase of the surfactant molecules of surface brings down the surface tension.



Ideas on 0 sec. of some methods

To measure dynamic surface tension, starting point (0 sec.) is important.
How each method can get it?

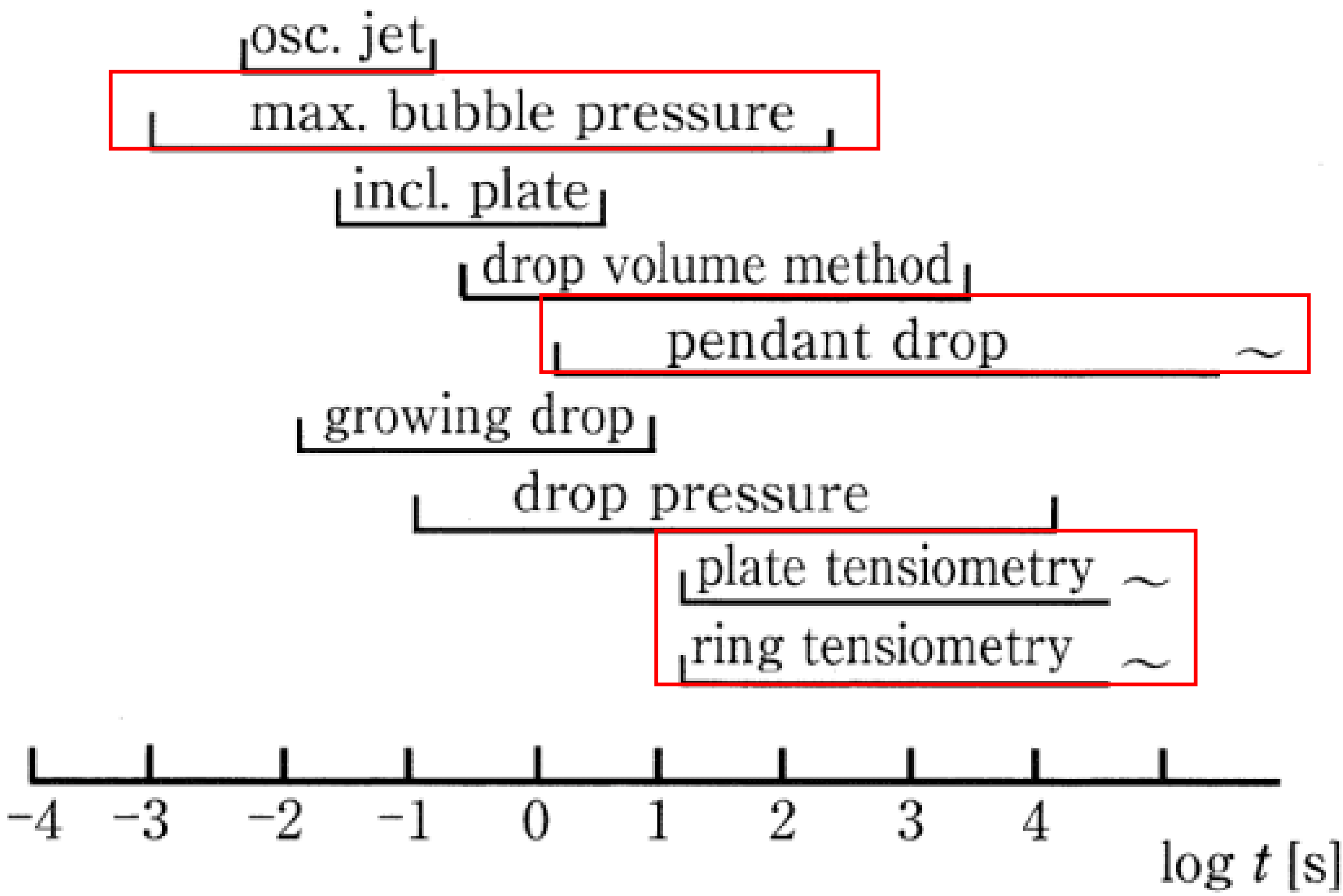
- Bubble Pressure method:
  Starting generating bubble is just starting creating new surface.
  → 0 sec. is comparatively precise.

- Pendant Drop method:
  The measurement is started after creating a certain amount of droplet.
  → 0 sec. is ambiguous. → Fits to measure over longer time range.

- Wilhelmy Plate method:
  The surface is created when liquid is prepared in a lab dish.
  → 0 sec. is ambiguous. → Fits to measure over longer time range.

- du Nouy Ring method:
  It is determined when the ring is detached from the surface, so the measurement status is not constant like Pendant drop and Wilhelmy.
  → Variations over time cannot be obtained.

Time range covered by each method



泡のエンジニリング，テクノシステム（2005）

Theory of Bubble Pressure method (1)

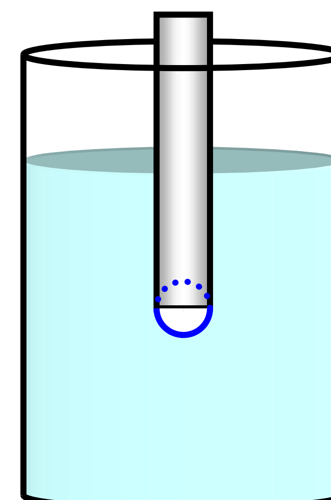
- Insert a probe (glass capillary) into a liquid sample and generate bubbles from the probe tip by pressing air or inert gas. Then, measure the inner pressure of air and convert it to surface tension.

  - Where, probe inner pressure p, curvature radius of bubble r, Liquid density ρ, gravitational acceleration g, depth of probe tip h
    The following is given from Laplace equation:

$$p = \frac{2\gamma}{r} + \rho g h$$

  - Surface tension γ is determined by the following equation:

$$\gamma = \frac{r}{2}\left(p - \rho g h\right)$$



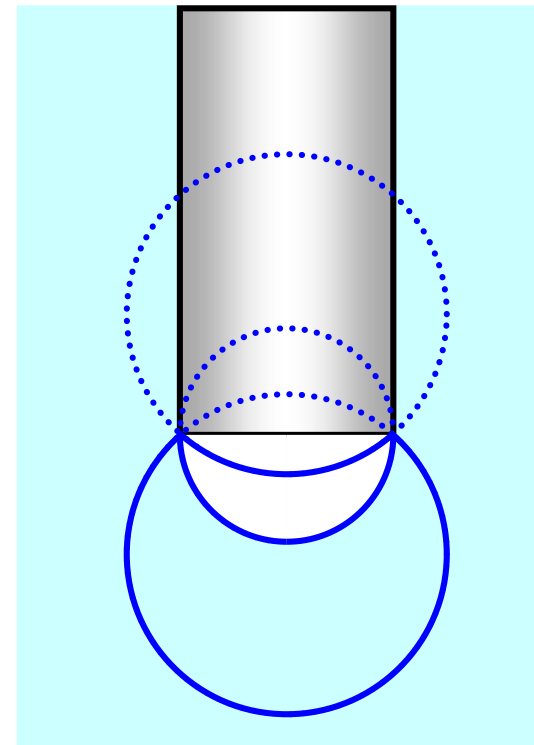
Theory of Bubble Pressure method (2)

- According to the generation of a bubble, curvature radius r of the bubble changes gradually.

- When r corresponds to the radius of probe hole r_{probe}, r becomes minimum.

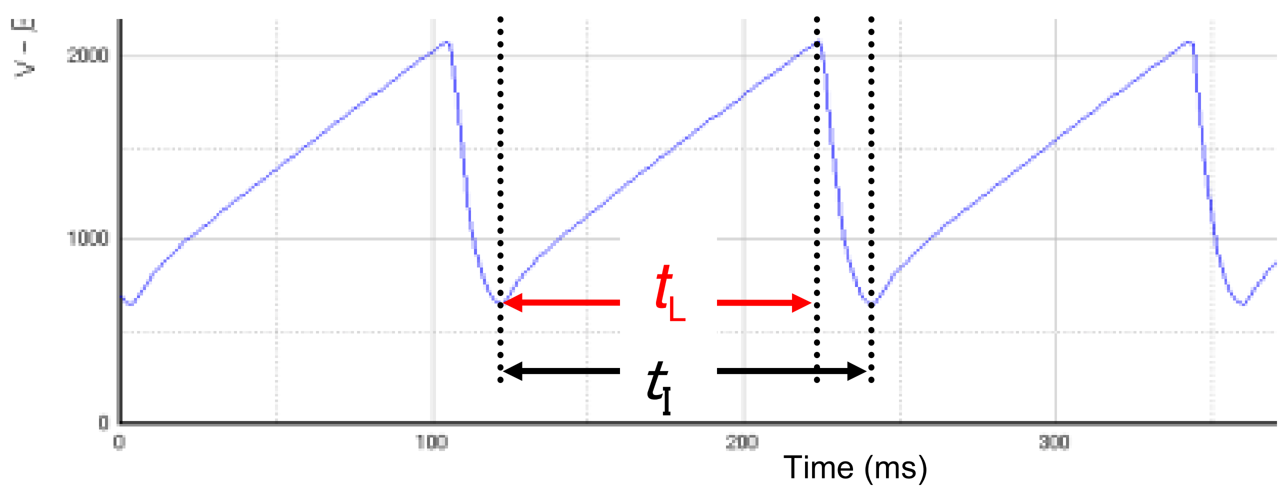
- When r becomes minimum, p attains maximum pressure based on Laplace equation.

- If the radius of probe hole r_{probe} is known, surface tension γ can be determined by Laplace equation because of $r = r_{probe}$ at maximum bubble pressure.



Time scale (Aging time)

- The time scale (Aging time) is determined from starting generating a bubble at the probe tip to attaining maximum bubble pressure.
- Controlling bubble generating speed changes the time scale.
- Inner pressure changes as the graph below.
  - Interval time t_I: Full time between starting generating a bubble and the next one.
  - Life time t_L: The time after maximum pressure to starting generating bubble is ignored from the interval time.
  - Life time is used to determine the time scale of this method.



Data expressions by Bubble Pressure

- With the X axis as life time, comparing dynamic behaviors of surface tension depended on concentration (interpolation by Rosen approximation)
- With the X axis as concentration, comparing dynamic behaviors of surface tension depended on life time

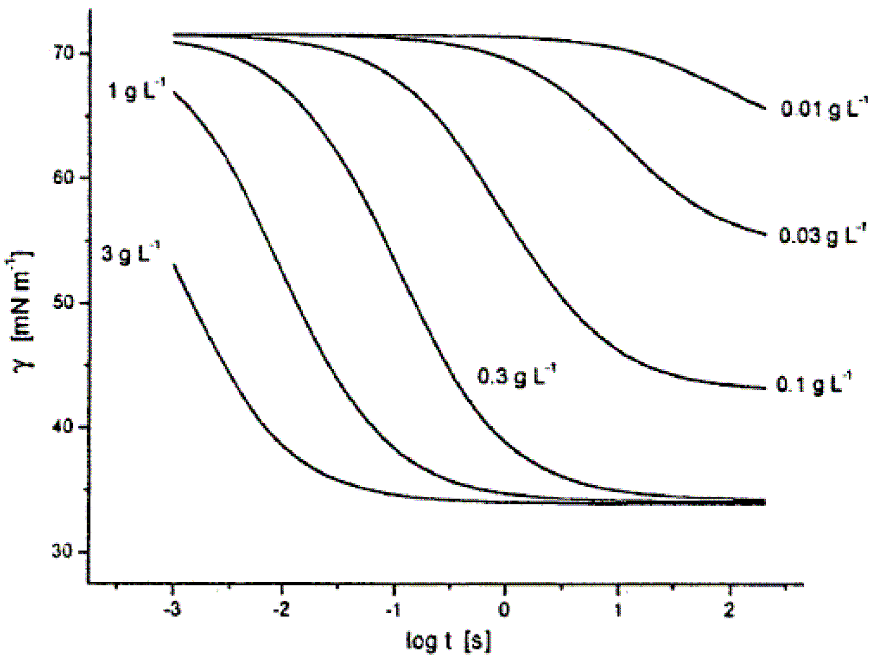


Figure 2 Example of surface tension vs. time curves for various surfactant concentrations. Time in seconds. Interpolated literature data for $C_{12}H_{25}O$-$C_2H_4OSO_3Na$ in 0.1 M NaCl [12, 13]

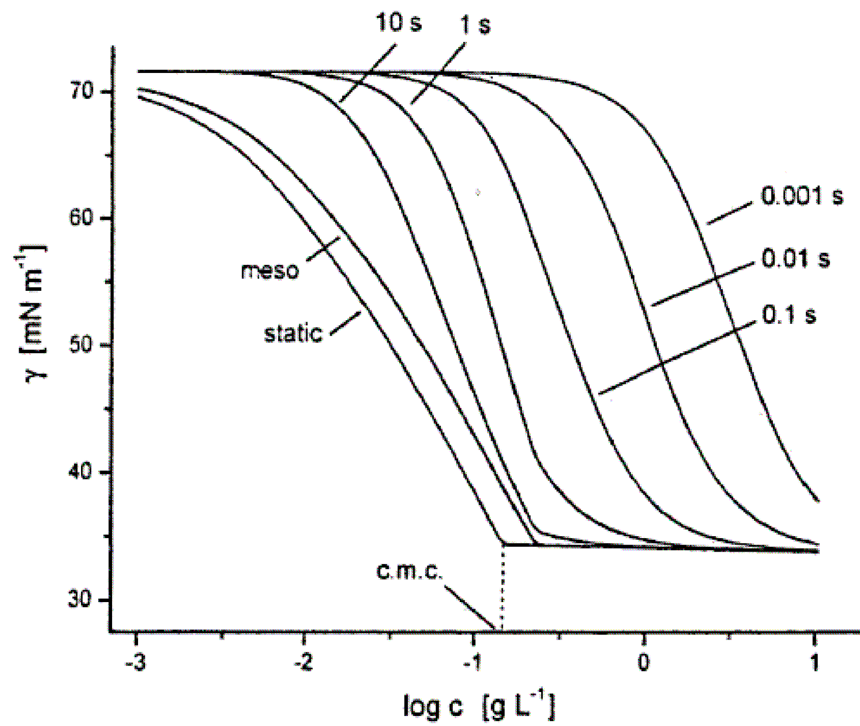
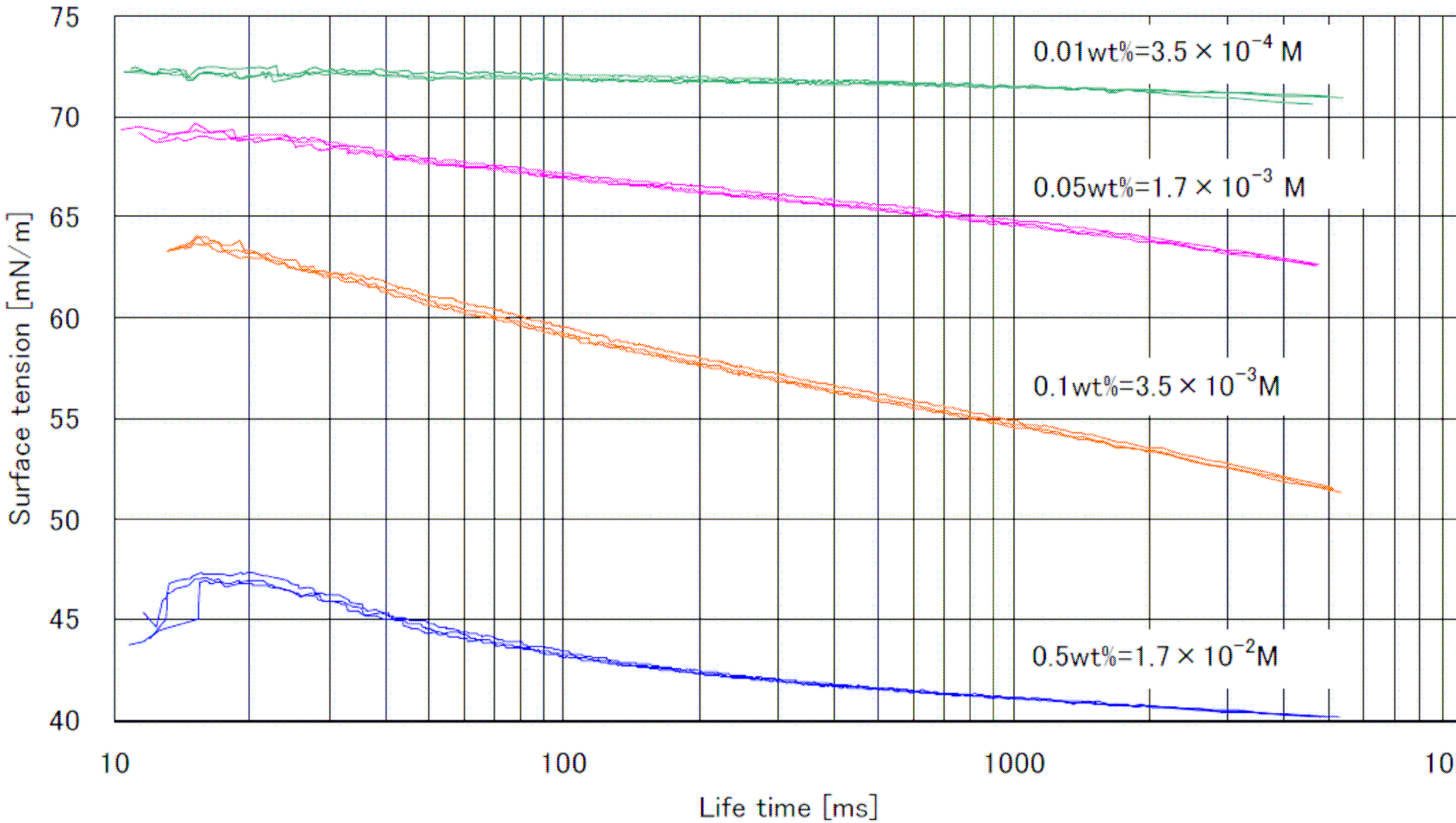


Figure 3 Data in Fig. 2 replotted as surface tension vs. log c

(held by Dennis Miller, Clariant GmbH,Tenside Surf.Det.42(2005),pp204−209)

Data examples obtained by BP-D5

- 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%



Typical Applications

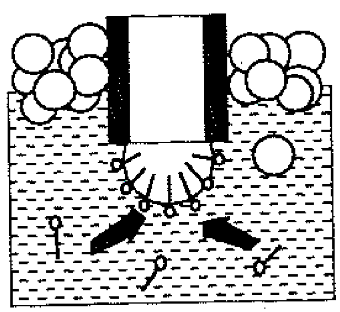
1. Evaluation of detergents for dish washing machines

2. Evaluation of additives for foaming, sprayer

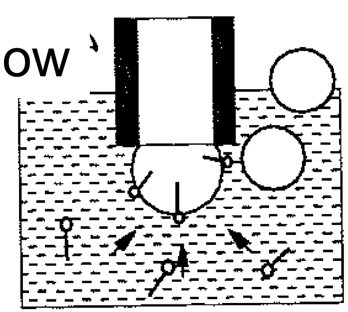
Ex-1: Detergents for dish washing machine

- Household product users have sense to evaluate cleaning efficiency from foaming of detergent, and study of foaming is significant for the suppliers.
- Dynamic surface tension and stability of film creating foams are evaluated for foaming of detergents.
  - If movement speed of surfactant is quick, surface tension falls off in short time and foams are created comparatively small. As the result, surface area of foams in total increases and total volume of foams increases. (Creating layers of foams)

Quick



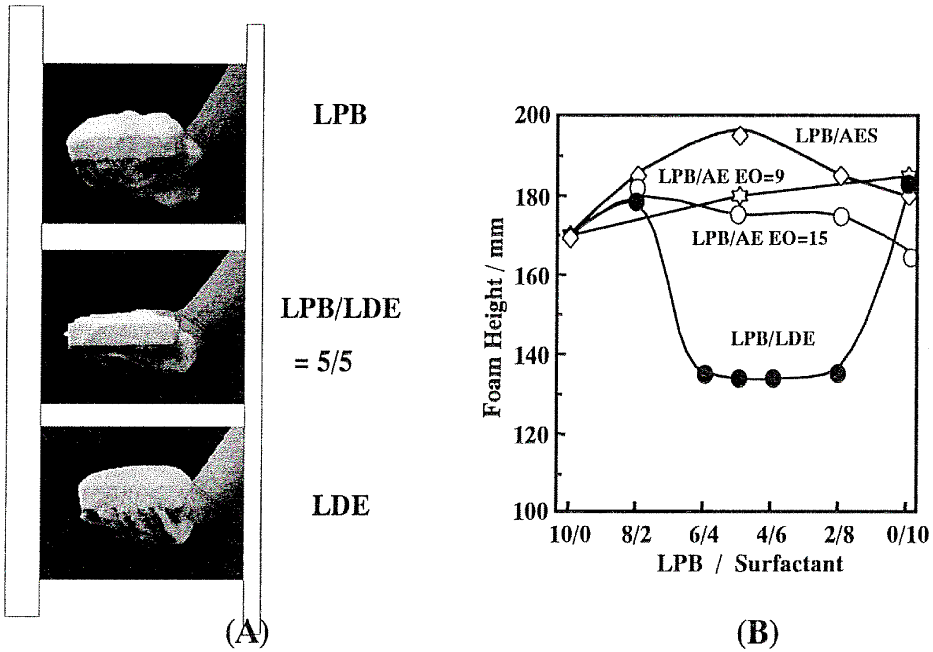
Slow



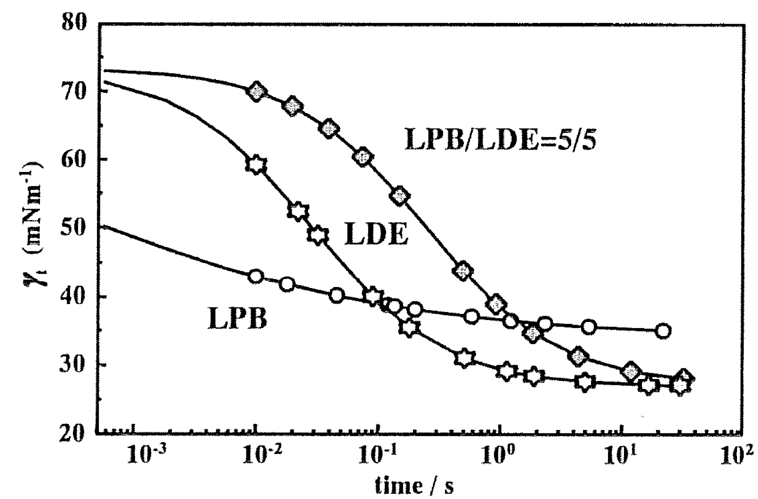
Takamitsu Tamura
Engineering of foams, 19, (2005)

Ex-1: Detergents for dish washing machine

[Relation between foaming and Dynamic surface tension]



Initial foaming of LPB/LDE group and quantity of washed Ross dishes



Measurement results of dynamic surface tension of LPB/LDE group

Takamitsu Tamura, Engineering of foams, 19,（2005）

Ex-2: Additives for foaming, sprayer

- Spray mechanism of foaming additives are briefly summarized as the following 3 steps:

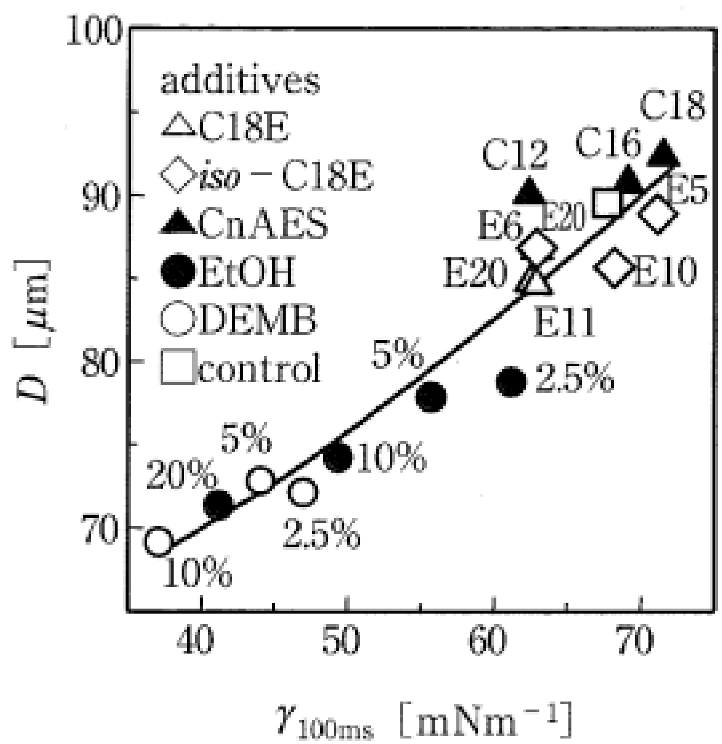
  Step-1: Producing O/W emulsion (additive and low-boiling hydro carbon) by shaking the bottle.

  Step-2: Generating mist droplets to be sprayed from the nozzle

  Step-3: Accreting the mist droplets onto work by evaporating the low-boiling solvent

- Dynamic surface tension is effective for the evaluation of emulsifying and stability of foam as worked in the above step 1 and 2.

Ex-2: Additives for foaming, sprayer



Relation between dynamic surface tension at 100ms
and diameter of sprayed mist

Takamitsu Tamura, Engineering of foams, 19,（2005）

Introduction of BP-D5 series

Introduction of BP-D5 series

BP-D5 series are the special tensiometers to measure *dynamic surface tension* by the technique of *Maximum Bubble Pressure method*.
KYOWA provides the following two models.

BP-D5

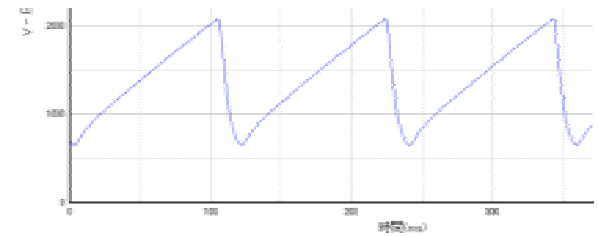
- Automatic operation from measurement processes to data acquisition

BP-D5L

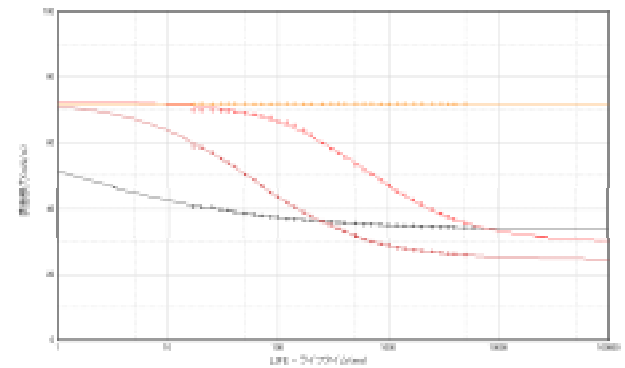
- Automatic data acquisition but manual measurement processes (Economy model)

Features of BP-D5 series

1. Pressure conditions of bubble generations are monitored by waveform.
   Unstable bubble generations lead unsuccessful results.In the short life time range, the software monitors the waveform and starts measurement after adjusting the stable waveform.



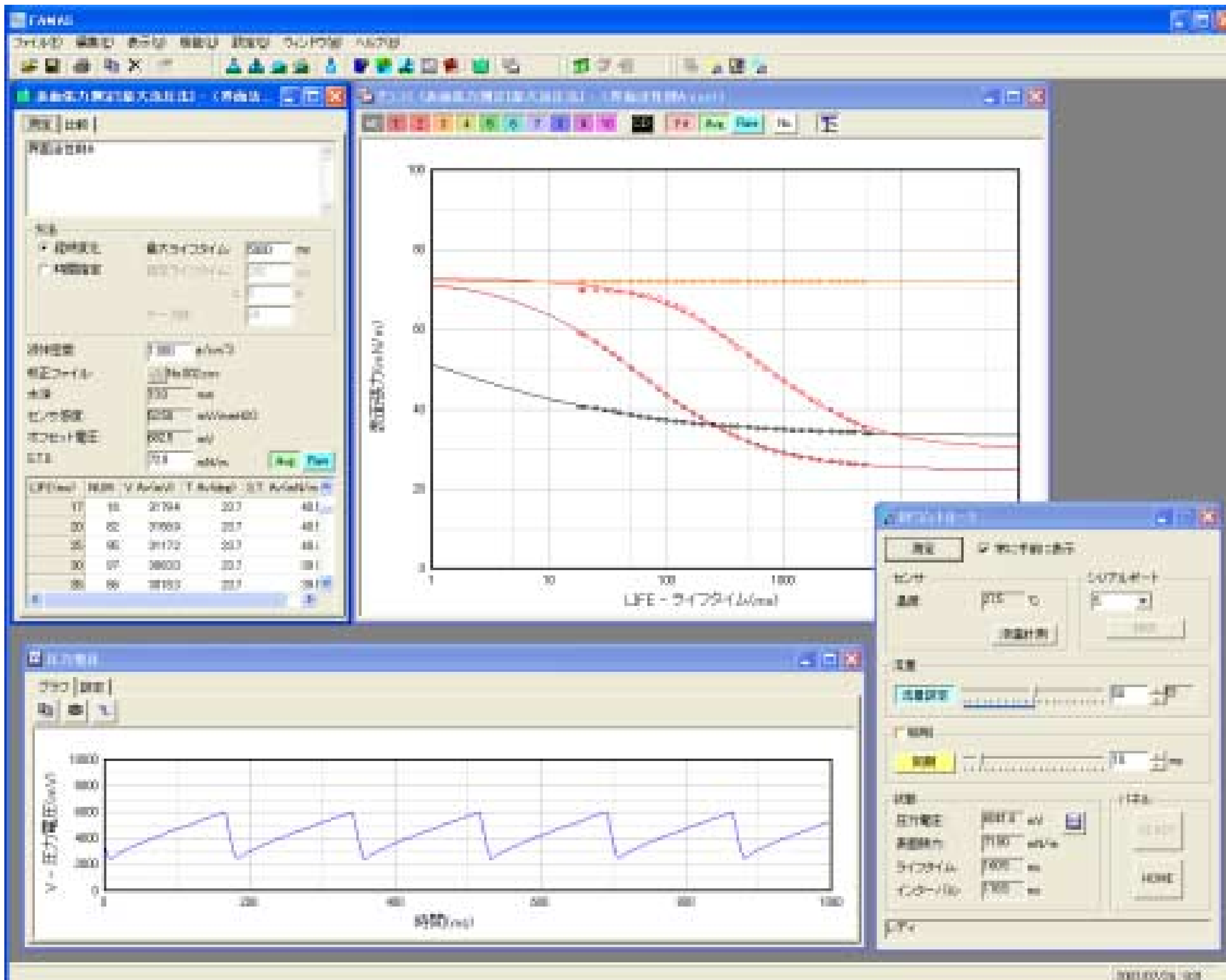
2. Rosen fitting is applied to the plots of data.
   The Rosen fitting determines a slop $(d\gamma_t/dt)_{max}$ of lowering surface tension, which can be used indexes of surface adsorbing speed and foaming.
   $(d\gamma_t/dt)_{max}$ Larger → foaming better



3. Fully automatic operation (BP-D5)
   One-touching the start button determines the probe immersion depth precisely, adjusts stable bubble rate, controls bubble rate from high frequency to low, and plots the results.

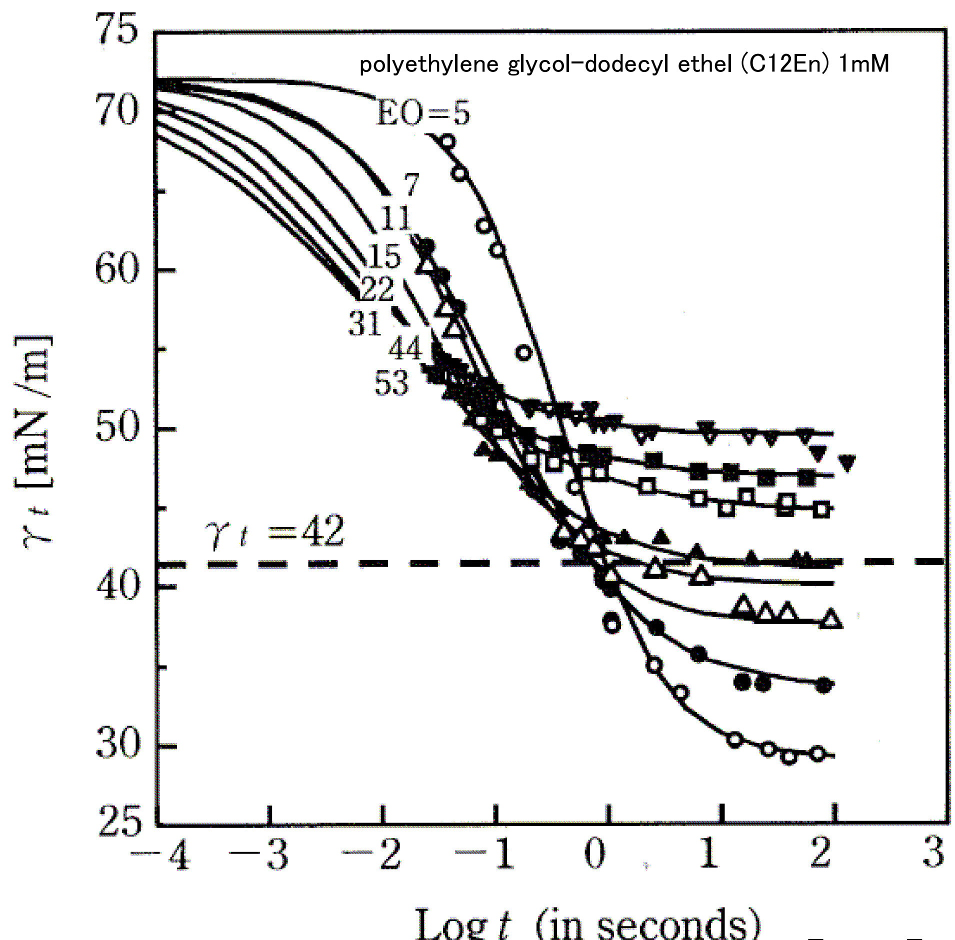
Application software FAMAS

Data table & parameter setting sheet, graph, waveform for monitoring bubble generating condition, and instrument controller are displayed.



Rosen approximate curve fitting

- Approximate curve is fit to the measurement curve of dynamic surface tension by Rosen's (1988) equation $\gamma(t) = \gamma_m + (\gamma_0 - \gamma_m)/\{1 + (t / t_*)^n\}$. Then, the result $(d\gamma_t/dt)_{max} = n(\gamma_0 - \gamma_m)/4t_*$ become an effective index to know the lowering ability of dynamic surface tension.



Tamura T, *et al. J.Colloid Interface Sci.* **173**,493(1995)

Rosen fitting obtained by BP-D5