

Synthetic Chemistry of Fine Particles, 2023

Synthetic Chemistry of Fine Particles

<http://www3.tagen.tohoku.ac.jp/~mura/kogi/>
E-mail: mura@tohoku.ac.jp

Atsushi Muramatsu, IMRAM

Lecture Plan

- April 11, Introduction and Physical chemistry
- April 18, Nanoparticles and colloids in our daily experiences
- April 25, Nanoparticles and colloids in our daily experiences
- May 9, Dispersion and aggregation of particles
- May 16, Dispersion and aggregation of particles
- May 23, DLVO theory
- May 30, DLVO theory
- June 6, Theory of monodispersed particles synthesis
- June 13, Liquid-phase synthesis of functional nanoparticles
- June 20, Liquid-phase synthesis of functional nanoparticles
- June 27, Environmental catalysts
- July 4, Adsorption phenomena and catalytic reaction
- July 11, Catalyst preparation methods
- July 18, Catalyst preparation methods
- July 25, Summary

Basic Knowledges

Physical chemistry

- ▶ Physical (adjective)
- ▶ [1] material, material, material world, natural
- ▶ [2] bodily, physical, physical, human
- ▶ [3] Desire for the other's body, lustful
- ▶ [4] physics, physics, physical
- ▶ [5] Natural science according to the laws of nature

What is physical chemistry?

- ▶ Chemistry that captures the movement of materials
- ▶ Let's go to the world of equilibrium and kinetics!

Equilibrium and Kinetics

- ▶ The equilibrium theory is, so called, the story of the paradise utopia world. The energy difference between this world and the present is exactly the Gibbs free energy change. The equilibrium theory is a study that tries to define the most energetically stable situation under given conditions. The equilibrium theory is the numerical analysis of where we are now between the ideal and reality.

Equilibrium and Kinetics

- ▶ Kinetics expresses the degree of effort to reach the paradise. More details will be discussed later in the lecture.
- ▶ In short,
- ▶ Physical chemistry is to formulate and understand the movement of materials.

Invitation to Colloidal Chemistry

What is a Colloid?

- ▶ Colloid in physics and chemistry dictionary
- ▶ We can say, it is in a colloidal state when it is dispersed as particles larger than atoms or small molecules that cannot be seen by ordinary light microscopy.
- ▶ Colloidal particles themselves are difficult to define, and only when they are in a dispersed state can be defined as a colloidal state.
- ▶ Then, what is different from the dissolution of macromolecules?

Tyndall effect, Tyndall scattering

- ▶ A phenomenon in which light is scattered mainly by Mie scattering when it passes through a dispersion system, and the path of the light appears to shine even when viewed obliquely or sideways.
- ▶ It was discovered in the 19th century by British physicist, John Tyndale
- ▶ The intensity of Mie scattering is maximized when the particle size and wavelength are nearly equal.
- ▶ Since the intensity of Mie scattering does not particularly depend on the wavelength, it looks whitish in the case of sunlight.

サイズパラメータ α は

$$\alpha = \frac{\pi d}{\lambda}$$

$\alpha \ll 1$ レイリー散乱

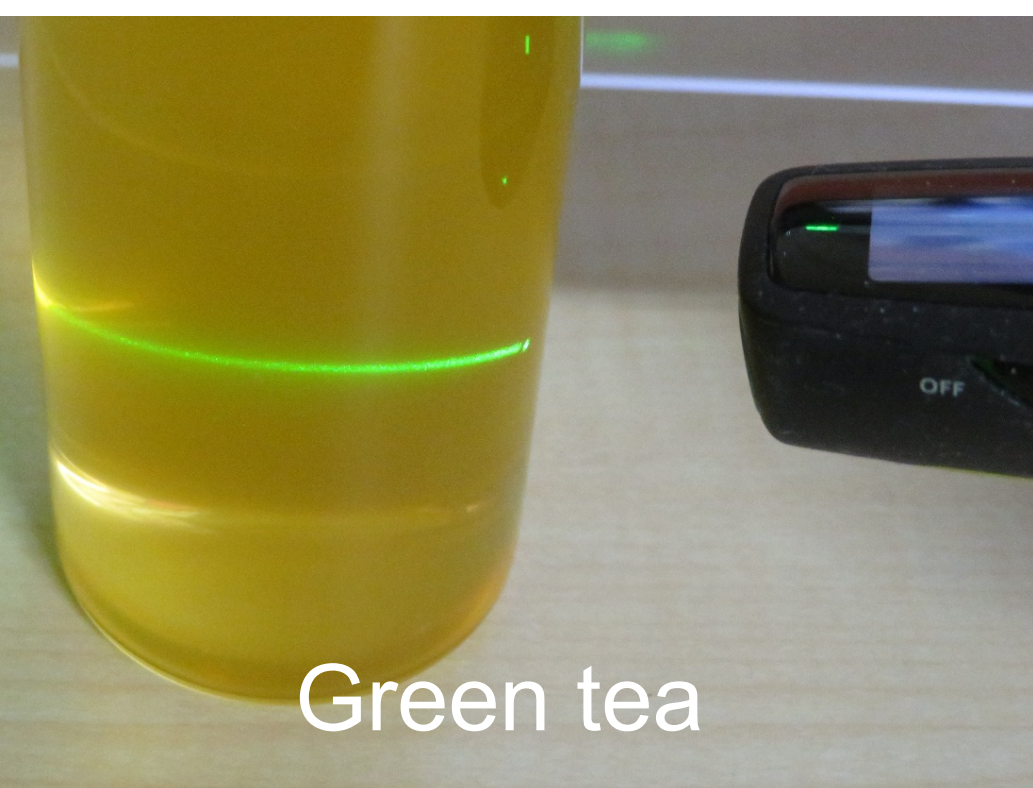
$\alpha \approx 1$ ミー散乱

$\alpha \gg 1$ 幾何光学近似

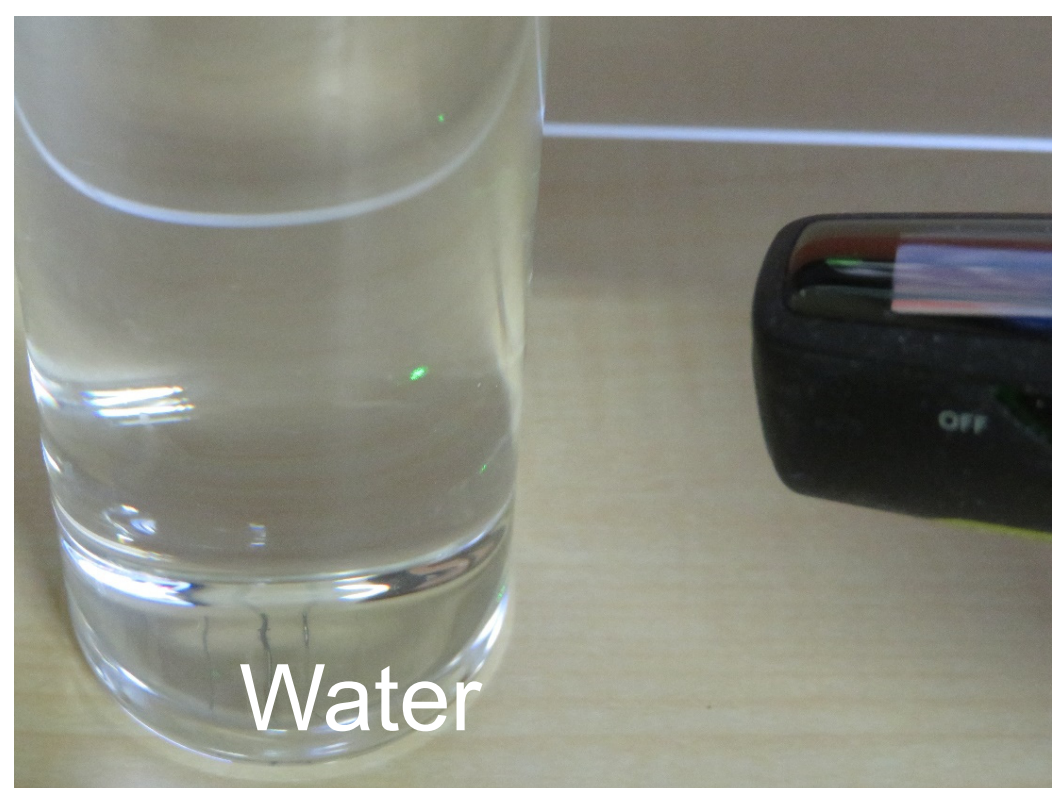
レイリー散乱の散乱係数 k_s は

$$k_s = \frac{2\pi^5}{3} n \left(\frac{m^2 - 1}{m^2 + 2} \right)^2 \frac{d^6}{\lambda^4}$$

n :粒子数, d :粒子径, m :反射係数, λ :波長



Green tea



Water



Milk
diluted

緑色
レー
ザー

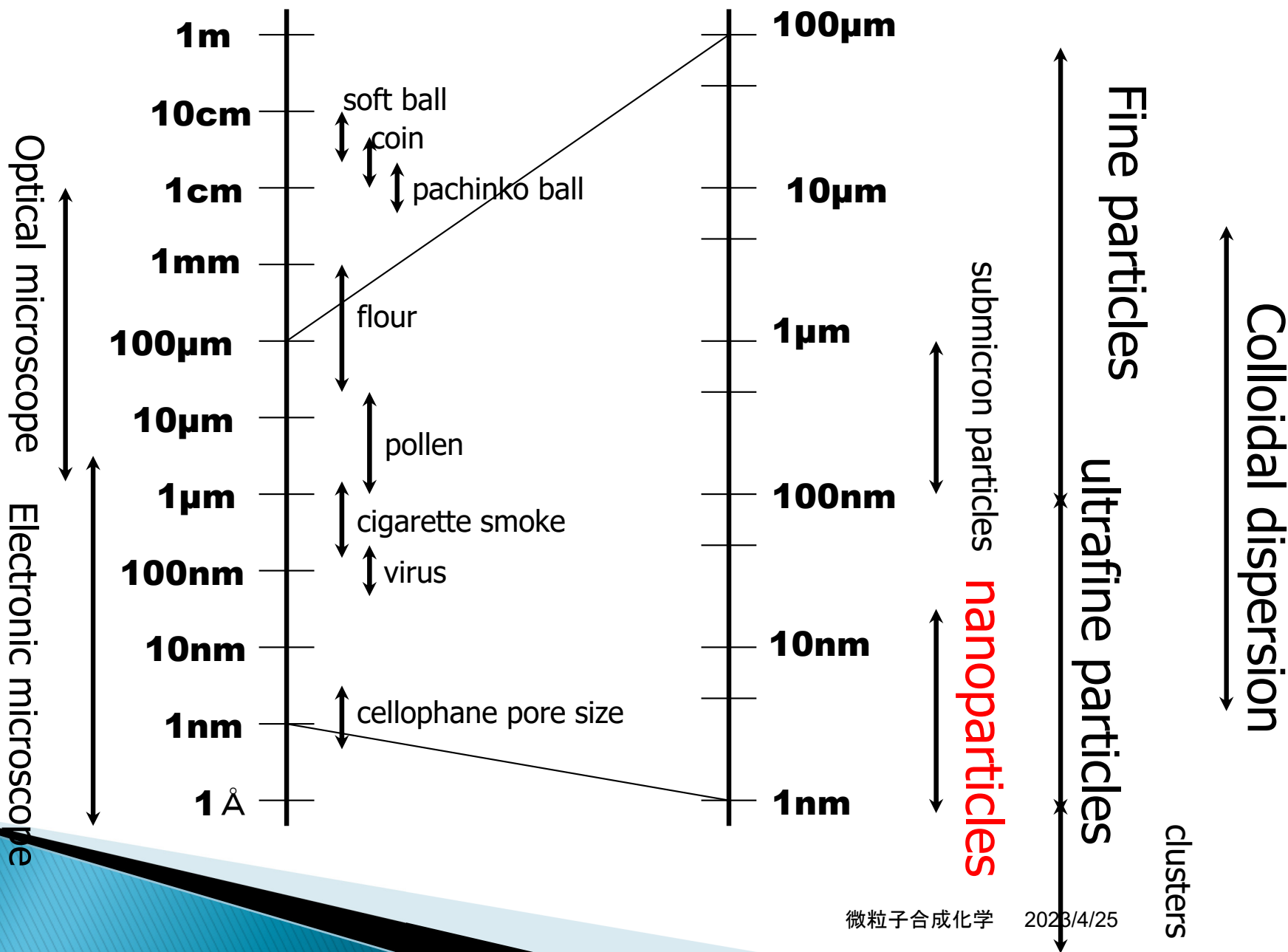
532
nm

微粒子合成化学



Coffee
diluted

Particle classification by particle size



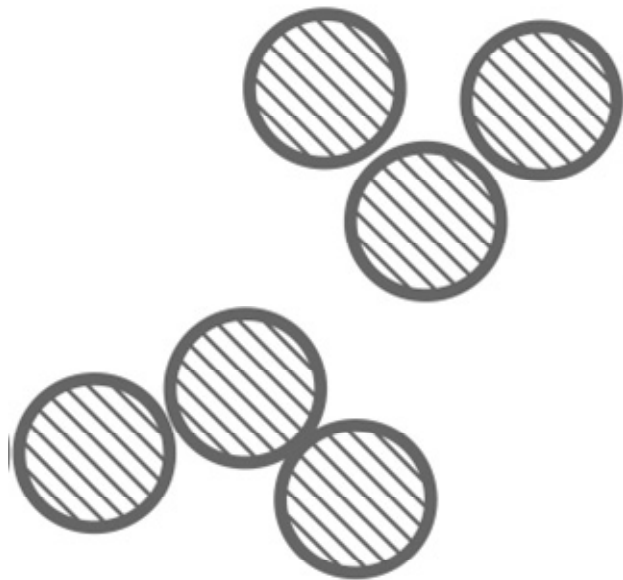
Colloid

Molecules form grains that cannot be seen with an ordinary microscope, and exist in a floating state.

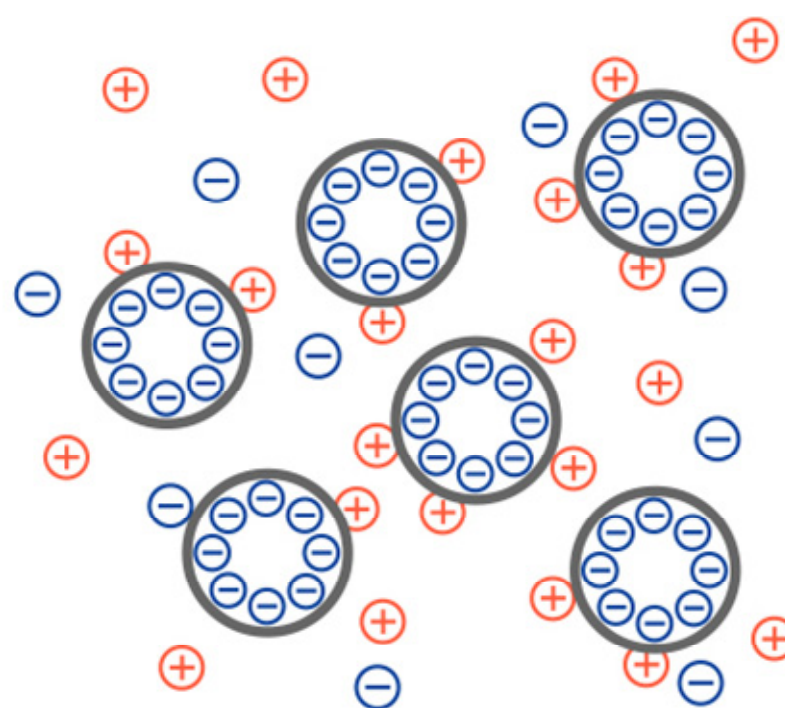
Dispersion and Aggregation

The state of drifting is "dispersion",
Aggregation is unstable state and becomes flocs.

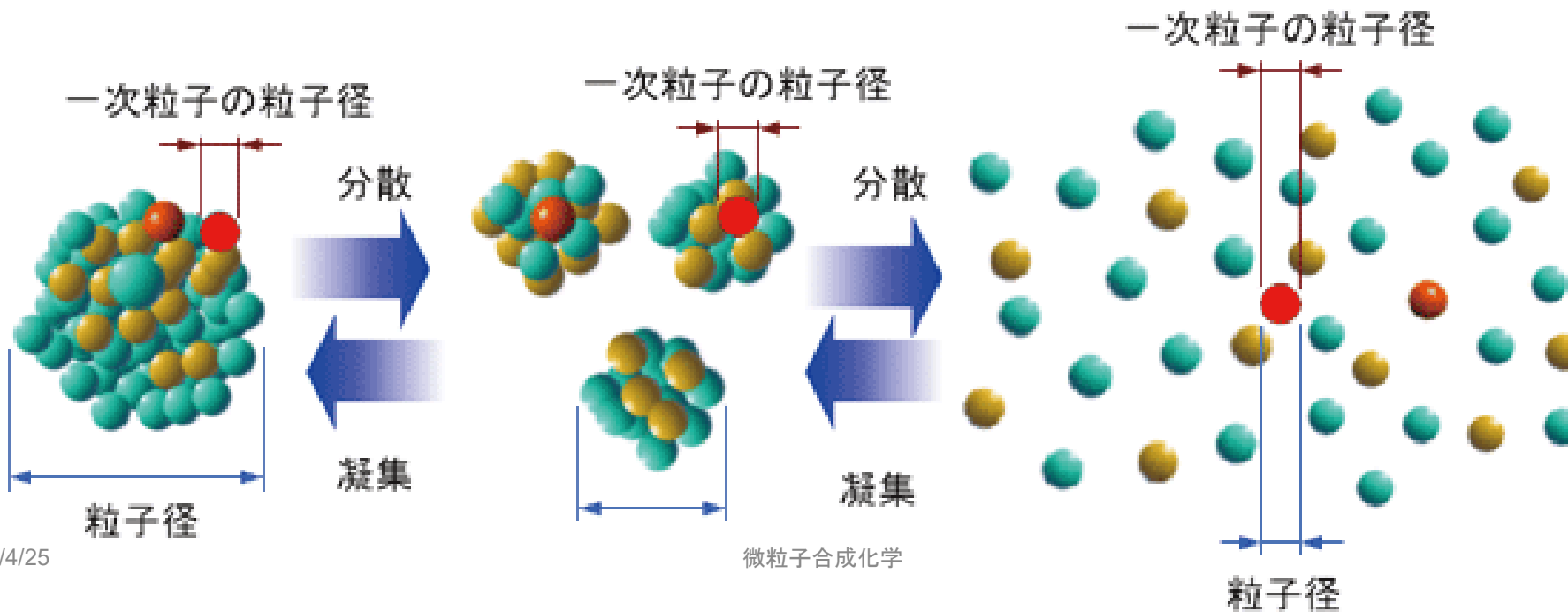
COLLOIDS IN LIFE



Aggregation



Colloid Dispersion



Let's take a look at the colloids around us !

- ▶ Focus on colloidal dispersion and aggregation!
- ▶ What is "dispersion"?
- ▶ What is "aggregation"?
- ▶ If "dispersion" and "aggregation" can be controlled, colloids can be manipulated freely!

Colloids around us

Hot spring

Beppu Hell Tour [Blood Pond Jigoku]



What is the cause of this red hot spring?

Beppu Hell Tour [Blood Pond Jigoku]

- ▶ Amount of discharge: about 1,800 kl/day
- ▶ Spring quality: Acidic meridian spring
- ▶ = Acidic-Fe(II)-sulfate spring
- ▶ Hot spring temperature: about 78 °C



The red color is caused by oxidation of ferrous ions (Fe(II)), hydrolysis, and then precipitation of solid-phase iron hydroxide $\text{Fe}(\text{OH})_3$ or hydrous iron oxide FeOOH . Part of it is hematite Fe_2O_3 .

They are particles of several microns to several millimeters, and are dispersed.

Beppu Sea Jigoku



What is the cause of this blue hot spring?

Beppu Sea Jigoku

- ▶ Conventionally, it was considered to be the blue color of ferrous sulfate (officially still)
- ▶ However, upon component analysis, there are almost no iron ions.
- ▶ why is it blue?
- ▶ In "Kanwaen" near Umi Jigoku, color is paler.

神和苑 温泉水 分析結果

京都大学地球熱学研究施設

	露天風呂流入口 (1997年11月4日)	露天風呂 #1 (1997年11月6日)	露天風呂 #2 (1997年11月9日)
水温 (°C)	75.6	42.1	43.5
pH	7.7	7.8	7.7
Na (mg/l)	1120	1140	1170
K (mg/l)	151	153	158
Ca (mg/l)	34.2	47.3	47.9
Mg (mg/l)	14.2	7.3	7.2
Cl (mg/l)	1680	1700	1700
SO ₄ (mg/l)	401	400	421
SiO ₂ #3 (mg/l)	466	444	406

#1 3日目: 透明感のある青色

#2 6日目: 白っぽい青色

#3 全シリカ

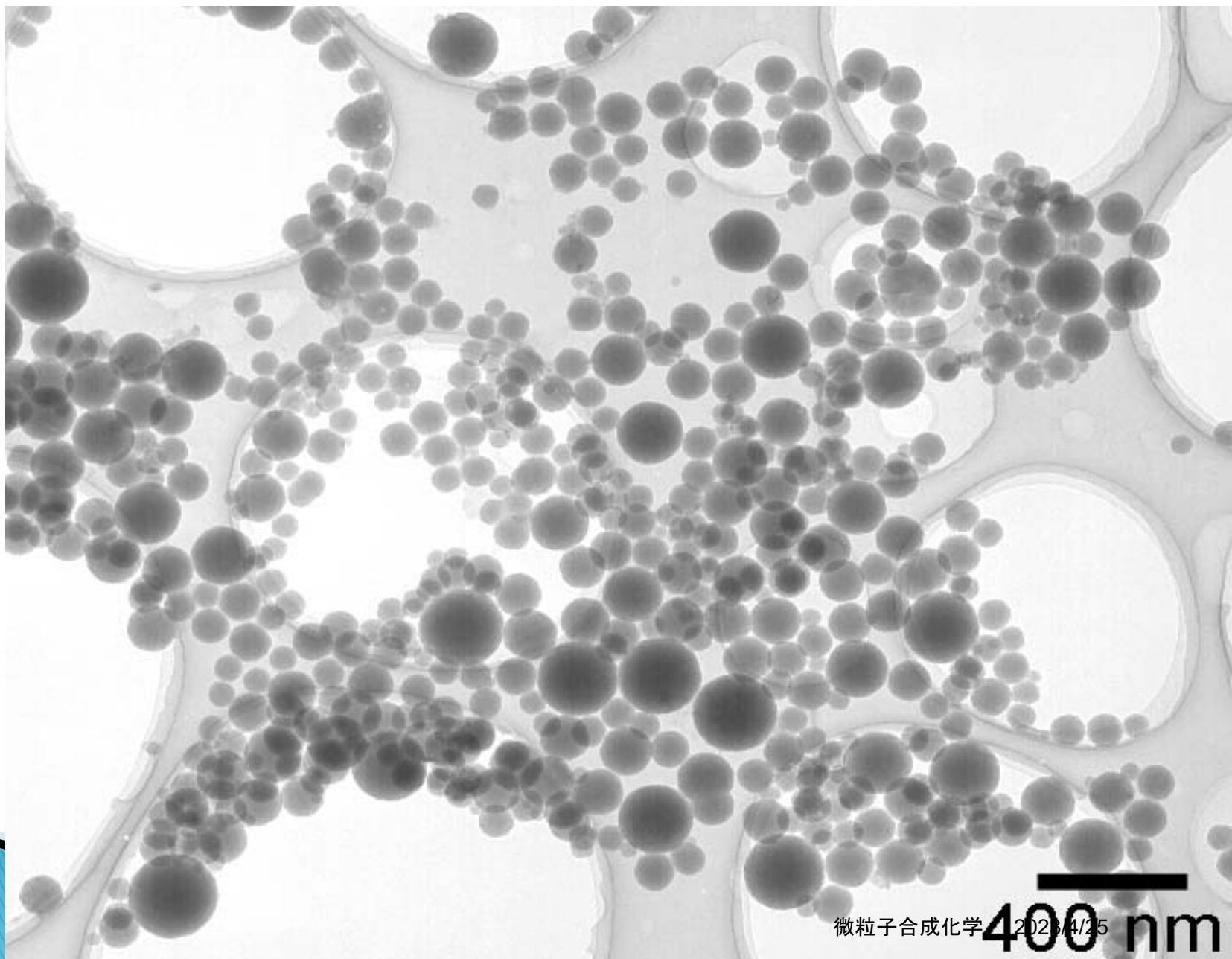
分析者: 大沢信二・川村隆夫



Blue = Silica colloid

- ▶ This silica colloid was so small that it looked like a solution.
- ▶ smaller than the wavelength of light.
- ▶ Could it be explained by the scattering phenomenon of light?

TEM photo of the silica colloid



SiO₂(silica) fine particles

- ▶ It was found by X-ray analysis that the particles were amorphous.
- ▶ FT-IR analysis revealed that it had a SiO₂ (silica) composition.
- ▶ Since spherical silica particles are synthesized by hydrolysis in a high alkali region, it is presumed that they are produced deep underground at high alkali and high temperature.

Why is it blue?

- ▶ It can be explained by the concept of Rayleigh scattering.
- ▶ The smaller the particle size, the easier it is to scatter short wavelengths, namely blue.
- ▶ Blue light is scattered by silica of several tens of nanometers or less
→ Suspension turns blue

Size parameter α is

$$\alpha = \frac{\pi d}{\lambda}$$

$\alpha \ll 1$ *Rayleigh scattering*

$\alpha \approx 1$ *Mie scattering*

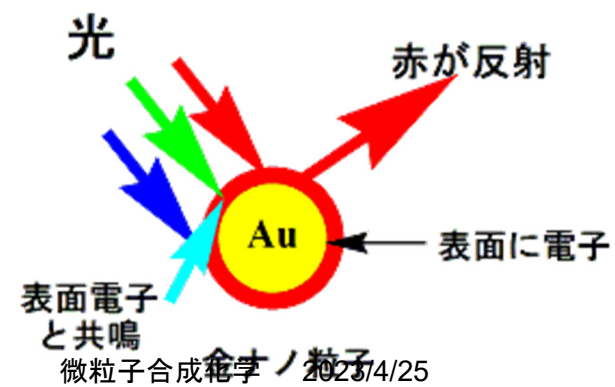
$\alpha \gg 1$ *geometric optics approximation*

Rayleigh scattering coefficient k_s

$$k_s = \frac{2\pi^5}{3} n \left(\frac{m^2 - 1}{m^2 + 2} \right)^2 \frac{d^6}{\lambda^4}$$

n :particle number, d :particle diameter,
 m :reflection constant, λ :wave length

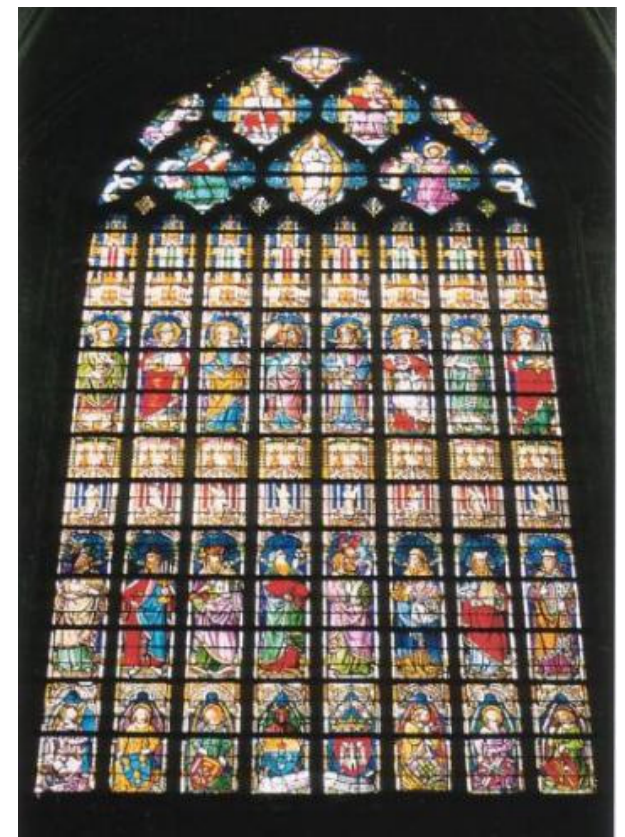
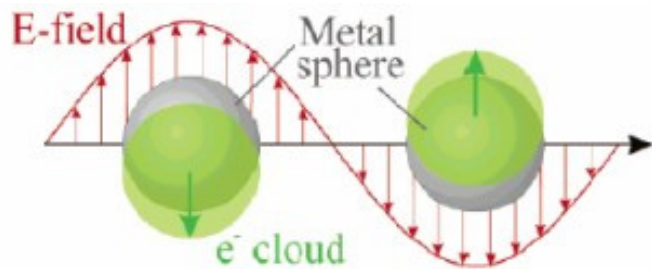
The color of the stained glass is due to surface plasmon resonance of gold nanoparticles...



Colored gold nanoparticles

Surface plasmon resonance

A phenomenon in which electrons in a metal interact with light. When a metal has a special structure in which the tips of nanometer-sized particles or needle-like protrusions are arranged periodically, conduction electrons and light resonate in these fine regions, It produces effects such as bringing a very high light output that overturns



church stained glass



Late Roman
Lycurgus Cup

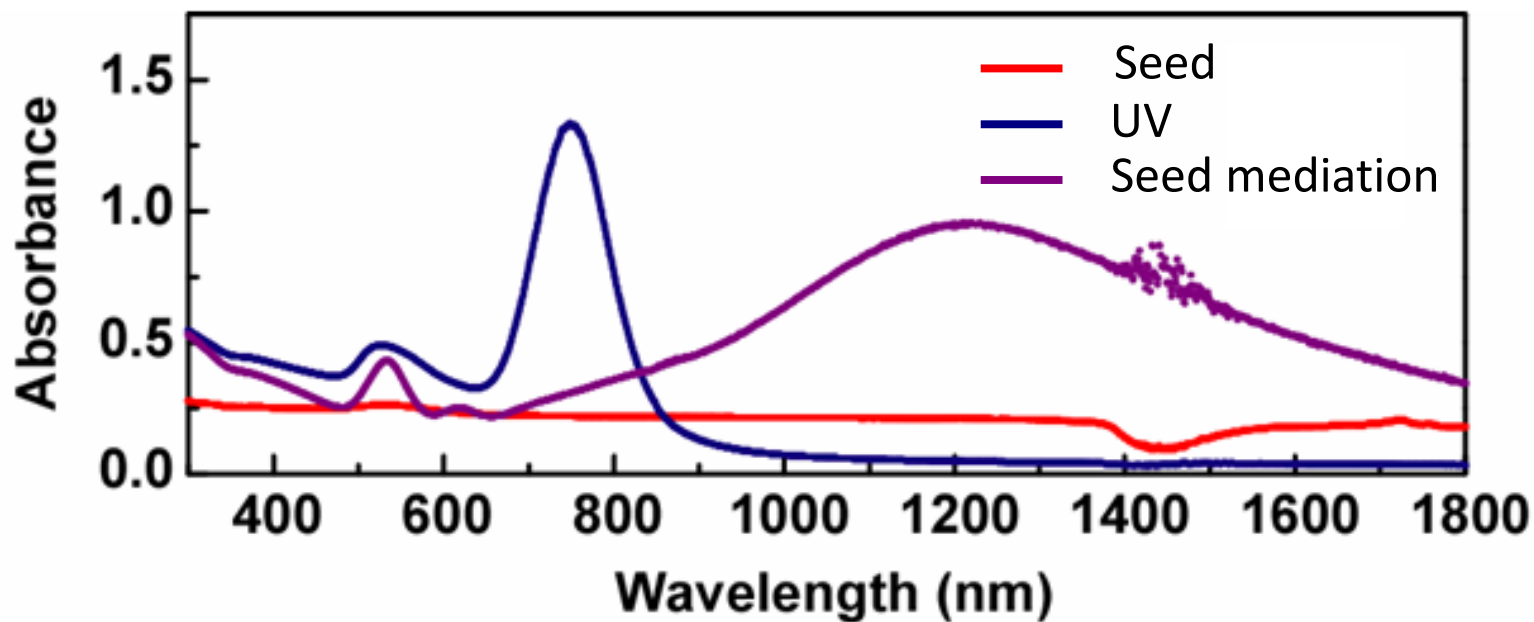
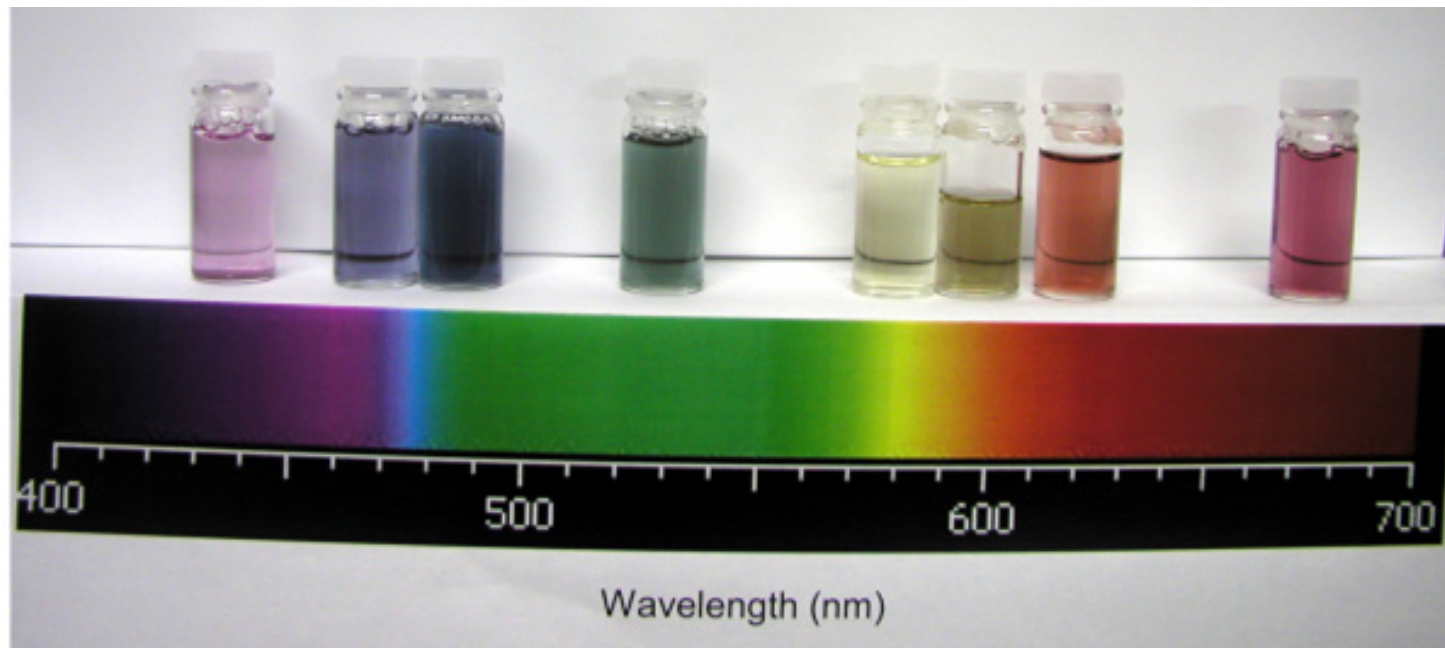
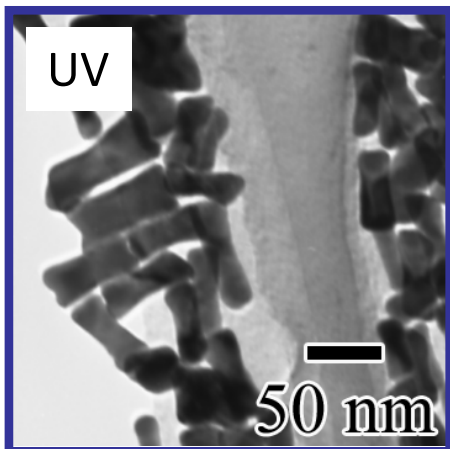
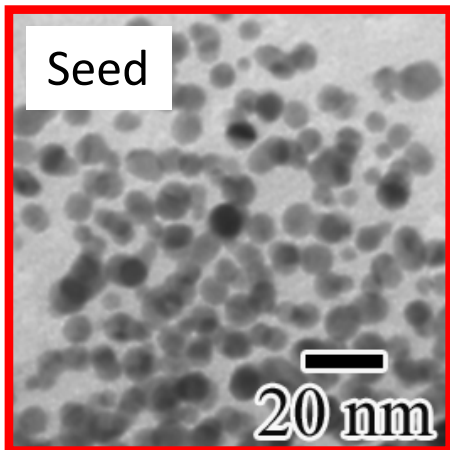


Baroque Ruby Glass 微粒子合成化学



Colloidal dispersion of gold nanoparticles

Color change due to change in morphology of gold nanoparticles



2023/4/25

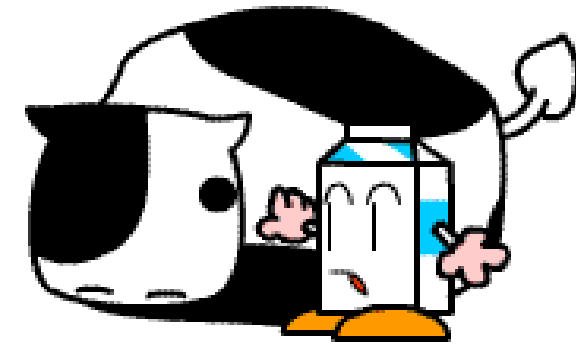
微粒子合成化学

Absorption wavelength shifts to longer as aspect ratio increases

Colloids around us

Milk

Milk



Nutrient energy value	Cow's milk	Human milk
Protein (% of energy)	3.25	1.42
Fat (% of energy)	3.61	3.64
Lactose (% of energy)	4.88	6.71
Casein (% of protein)	2.51	0.37
Whey (% of protein)	0.57	0.76
Energy value (kcal/g)	674	677
Vitamin A (ug/100 ml)	35.2	60
Vitamin D (ug/100 ml)	0.29	0.01
Vitamin E (ug/100 ml)	113.5	0.35
Vitamin C (ug/100 ml)	1530	380
K (mg/l)	1204	491
Na (mg/l)	504	15
Ca (mg/l)	1287	35
P (mg/l)	996	15
Mg (mg/l)	134	2.8

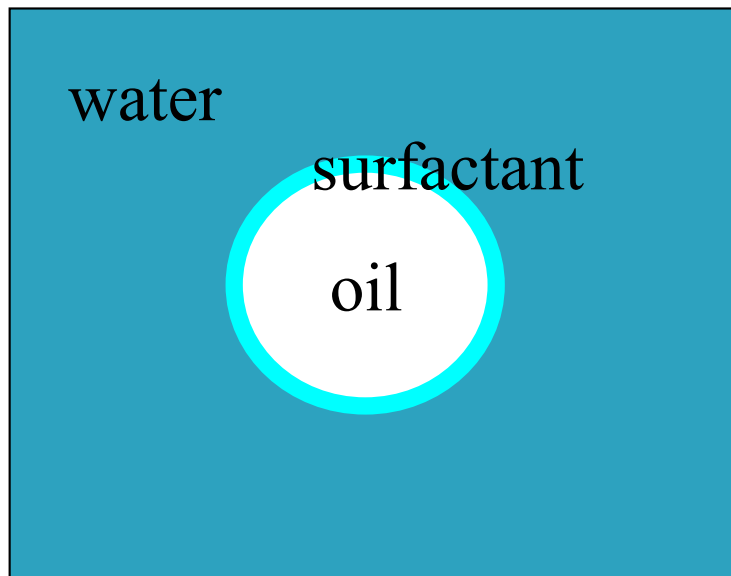
Water

milk fat

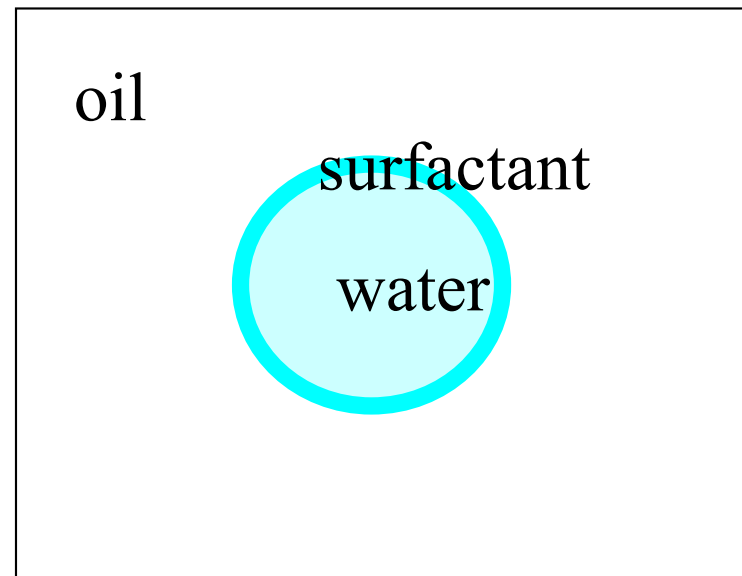
protein



Milk is an O/W emulsion



O/W emulsion



W/O emulsion



water



Salad oil

Three clear plastic vials with white caps are shown side-by-side. The first vial on the left contains a clear, colorless liquid. The middle vial contains a bright blue liquid with some white foam on top. The third vial on the right contains a clear, yellowish liquid. The labels 'Water', 'Soap', and 'Salad oil' are printed in white with black outlines over each vial respectively.

Water

Soap

Salad oil



Salad oil

Water

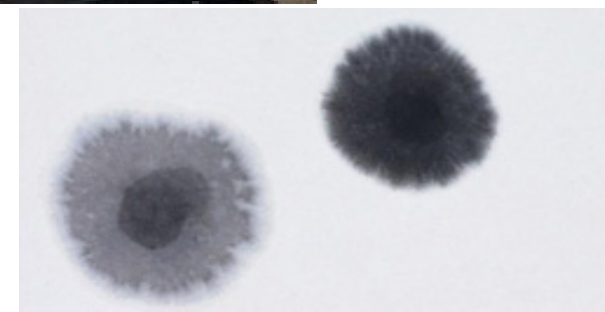
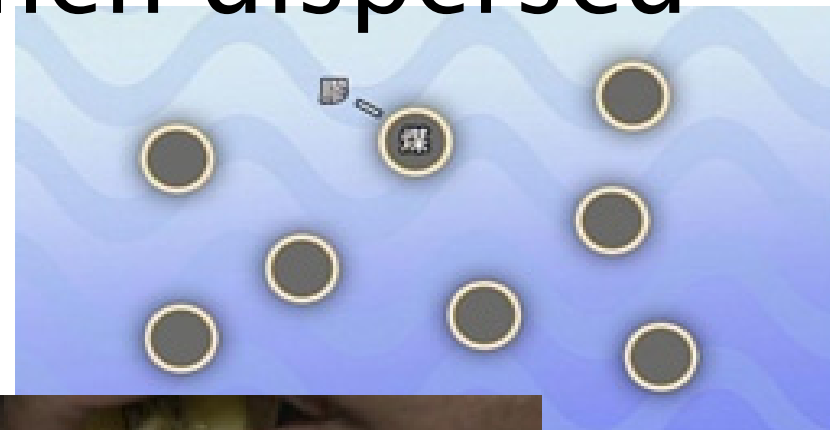


Without soap



With soap

India ink is also an O/W emulsion ~ Glue is adsorbed and then dispersed ~

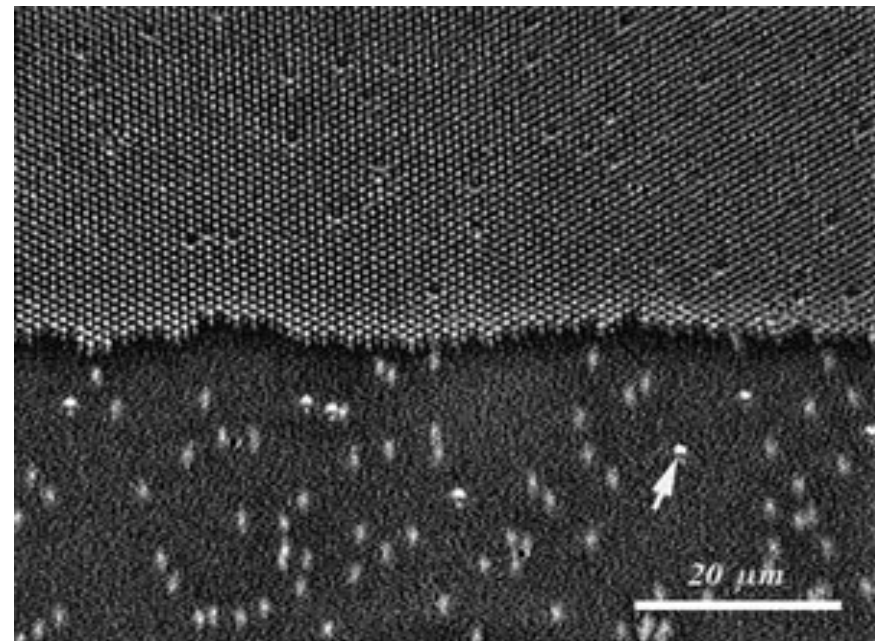


Colloids around us

Beer

beer foam

Nagayama Project Beer

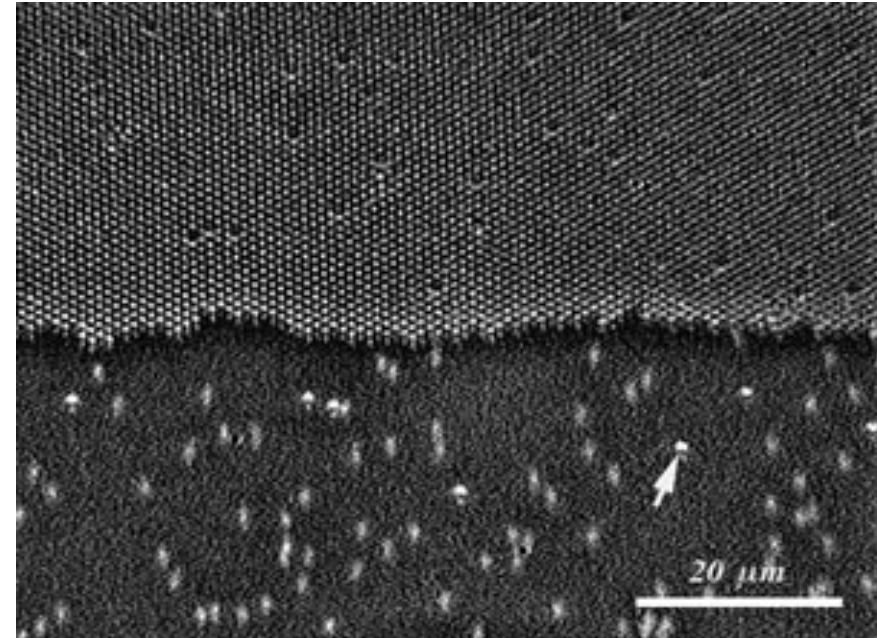


Colloids that are transported from bottom to top by advective accumulation to form a two-dimensional crystal structure. The lower colloid is blurred because it is moving.

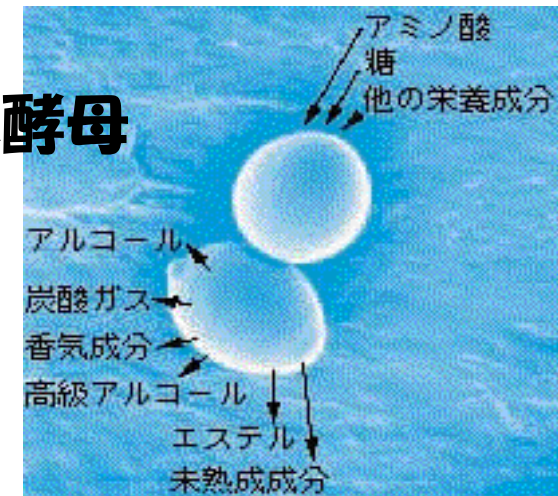


ビールの泡

- なぜ合一しにくいのか？
 - 分散安定化への指針
 - 泡の表面にホップと麦芽由来のフムロンや塩基性アミノ酸が吸着し、分散剂的な働きをしている



ビール酵母



How to pour beer properly

Pure malt



Open can



pour it to 1/3



Pour slowly and gently without foaming





**Homogeneous nucleation:
Bubbles come out of the solution**

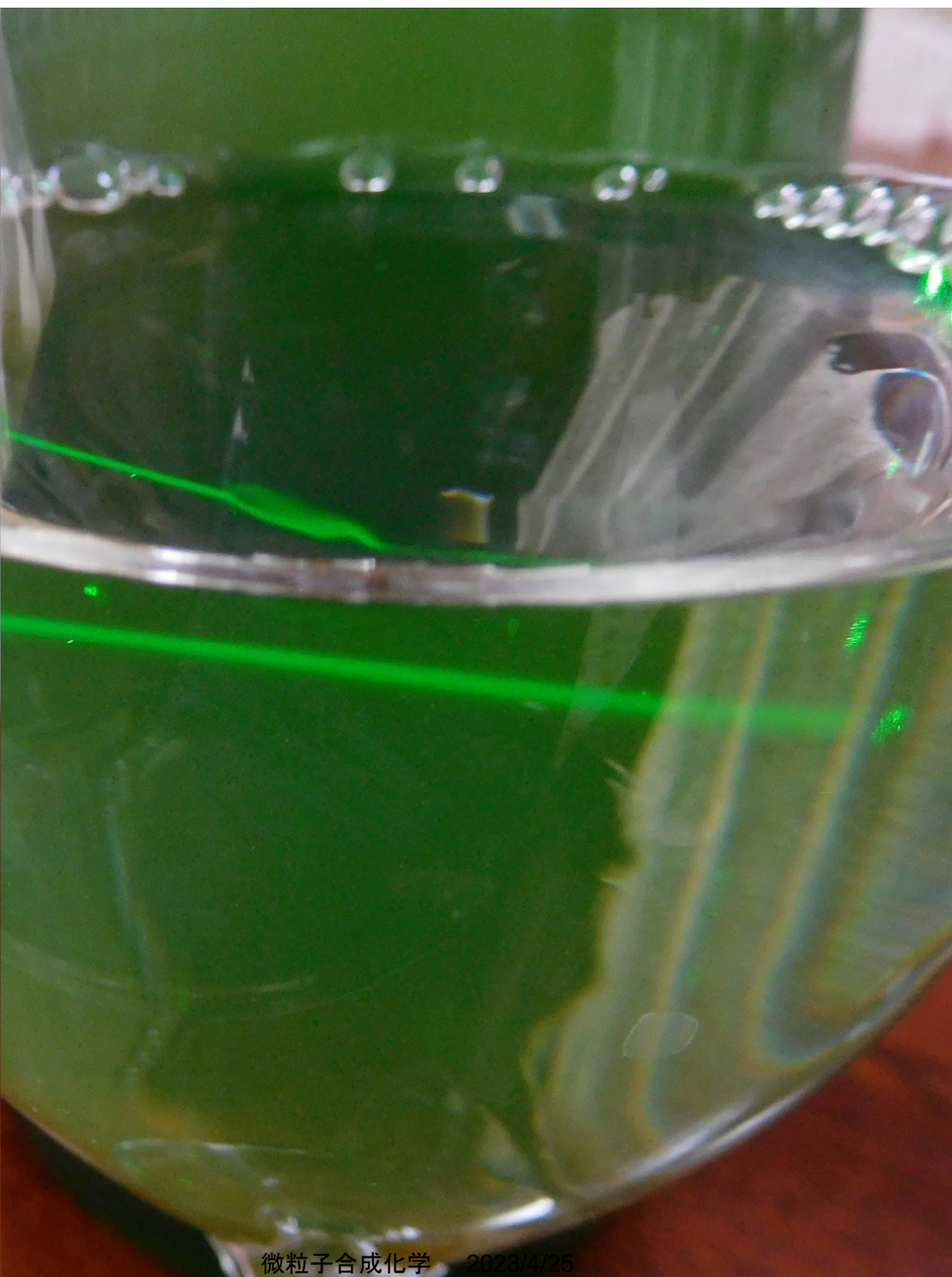


Heterogeneous nucleation:
Bubbles come out of disposable chopsticks when inserted

WHAT IS THE THEORY BEHIND ?

2023/4/25

Essence of Particle Dispersion and Aggregation



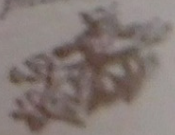
Penfolds®

KOONUNGA
HILL

CHARDONNAY
SOUTH AUSTRALIA

2014

*In 1976, Penfolds released the first wine to bear the name
Koonunga Hill. By applying our long held philosophy of
blending select parcels of grapes from South
Australia's wine regions, Penfolds wine
makers are able to craft wines of distinction
without ever compromising on quality.*



375ML





お酒は20歳を過ぎてから。・スーパ
る酒は適量を。・開封時にこぼれ





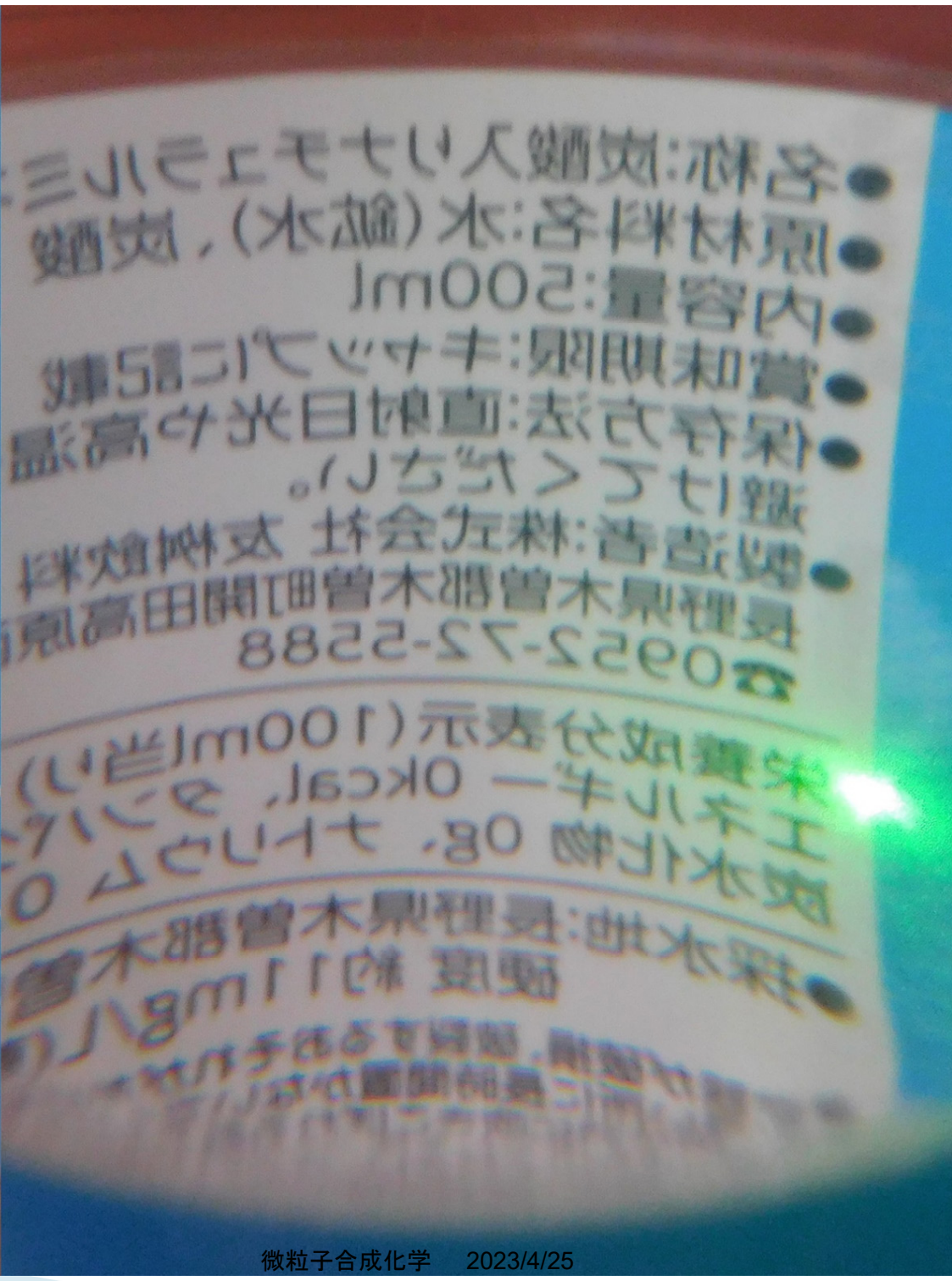


SPARKLING
WATER

アサヒ
炭酸水

高田高原
開田高原
曾木郡
木曾郡
天然水使用

0 kcal
500ml



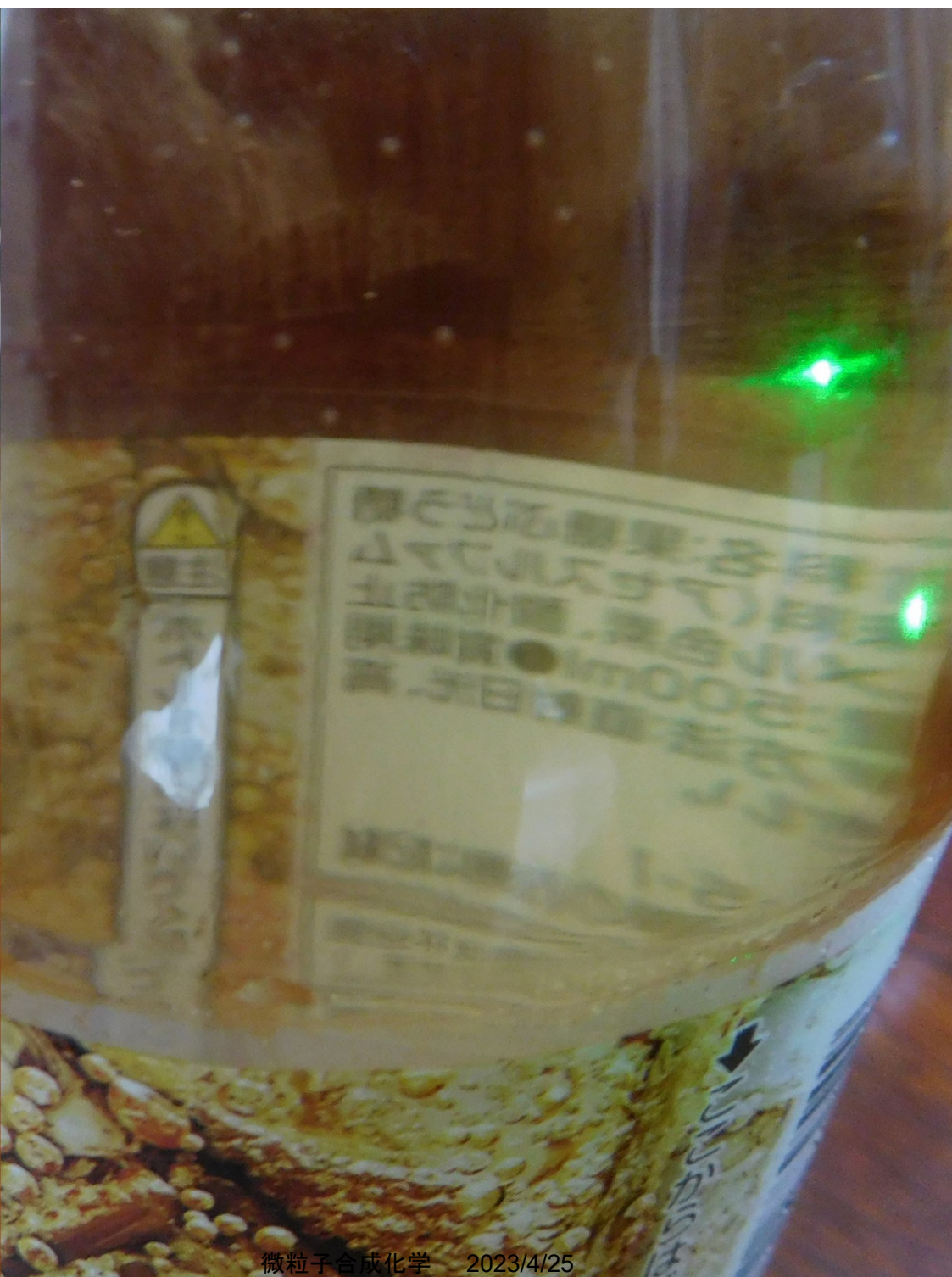
三小エモセい人 麵炭: 群各 ●
麵炭, (木論) 木: 各 群 林 煎 ●
1m002: 量 容 内 ●
姉 58 21 て ッ マ キ: 卵 卵 和 賞 ●
盛 高 の 光 日 娘 直: 表 式 群 呆 ●
。 1 ち 式 > 3 ち 麵 ●
群 類 姉 式 并 会 左 林: 香 香 麵 ●
煎 高 田 開 田 曾 木 郡 曾 木 郡 群 呆 ●
8822-57-5288

(1 当 1m001) 示 表 代 如 養 朱 ●
7 1 2 3 4 5 6 7 8 9 0 一 半 小 本 工 ●
0 kcal, マ ン 1 ●
0 4 0 1 7 8 0 群 小 本 工 ●

曾 木 郡 曾 木 郡 群 呆: 世 本 群 ●
1 8 m l 1 味 爽 野 ●
... 手 ち ろ る ... ●
... 手 ち ろ る ... ●







Let's take a look at the colloids around us !

- ▶ Focus on colloidal dispersion and aggregation!
- ▶ What is "dispersion"?
- ▶ What is "aggregation"?
- ▶ The keyword to controlling "dispersion" and "aggregation" is the zeta potential!

**There is an electric charge on the surface of all the materials.
(It is called "surface potential" or "zeta potential")**

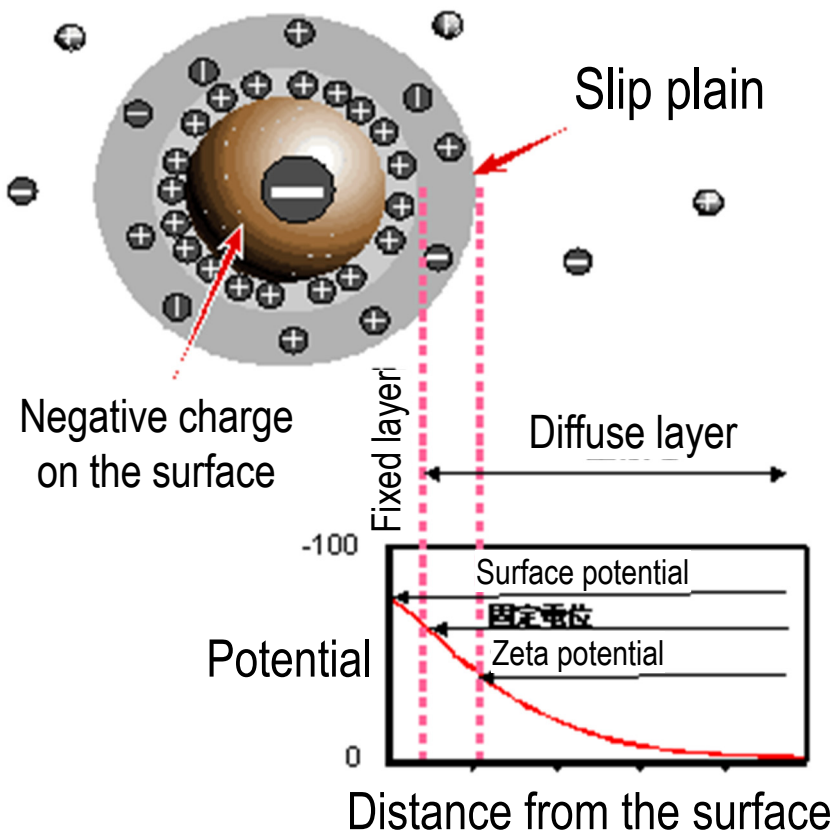
It's on your face, on your desk, on your foam, on everything!

WHAT IS THE THEORY BEHIND THIS

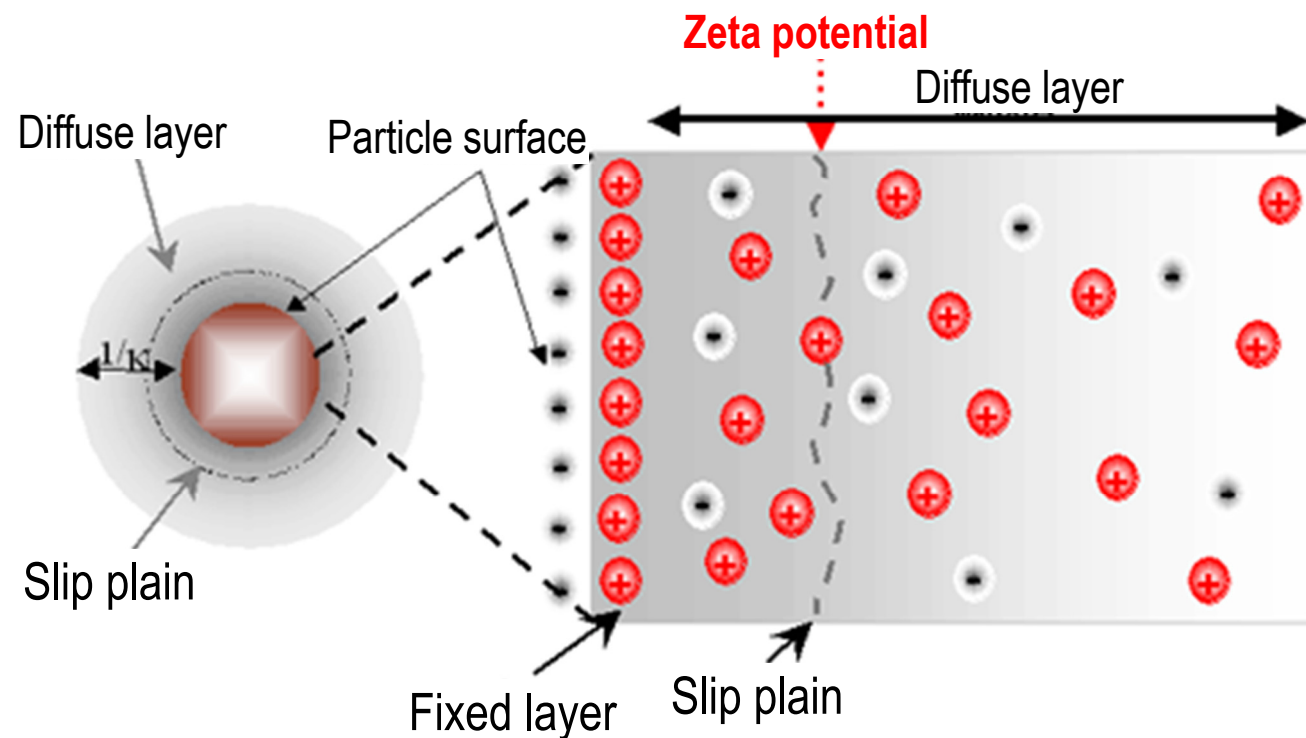
Zeta potential

- ▶ Zeta potential is a unique physical character of each material.
- ▶ Zeta potential changes with pH of aqueous solution.
- ▶ Zeta potential is a clue for dispersion/aggregation.
- ▶ Low zeta potential usually results in aggregation, called homocoagulation.

Zeta potential



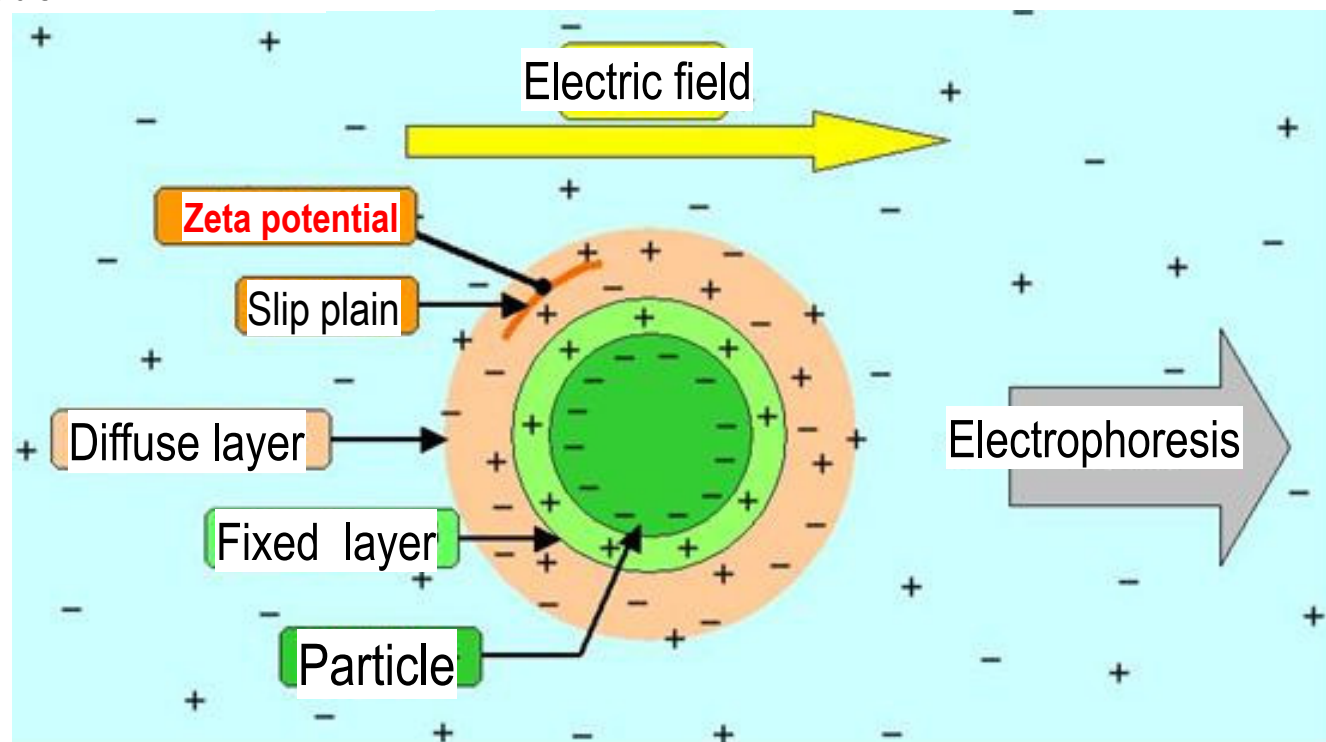
Zeta potential at slip plane



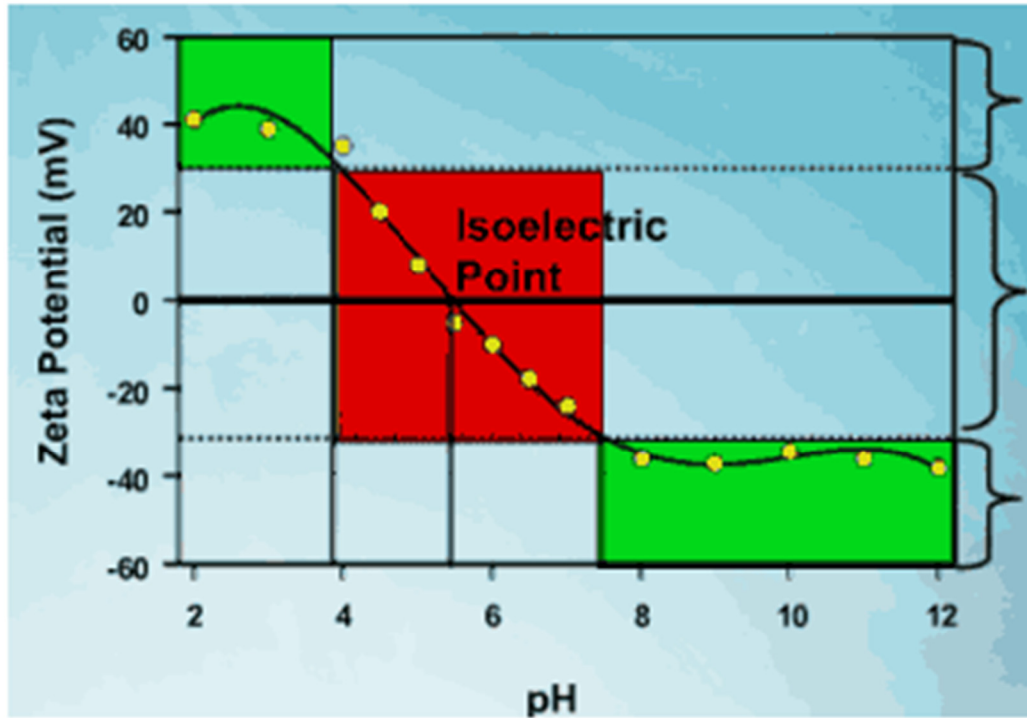
6 Electrophoresis



Particles with the same negative charge are moving to the positive electrode.

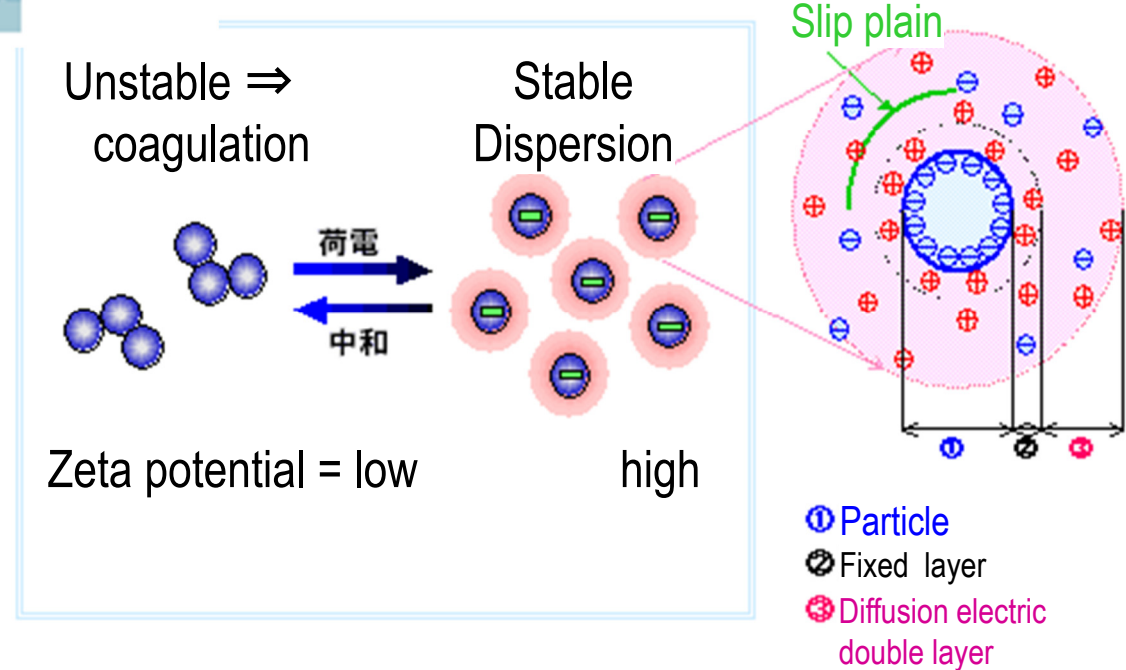


Zeta potential as a function of pH

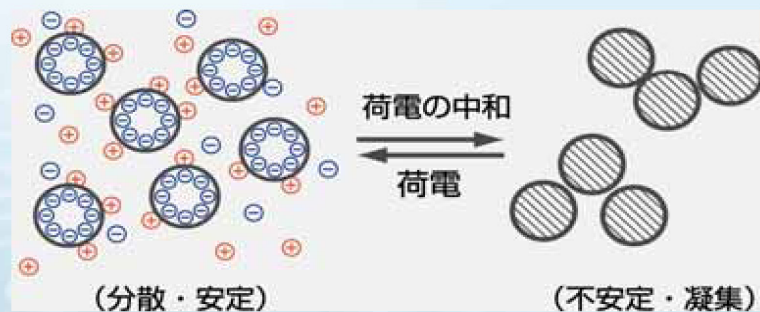


Stable
Unstable
Stable

Zeta potential and dispersion



What can we learn from zeta potential?

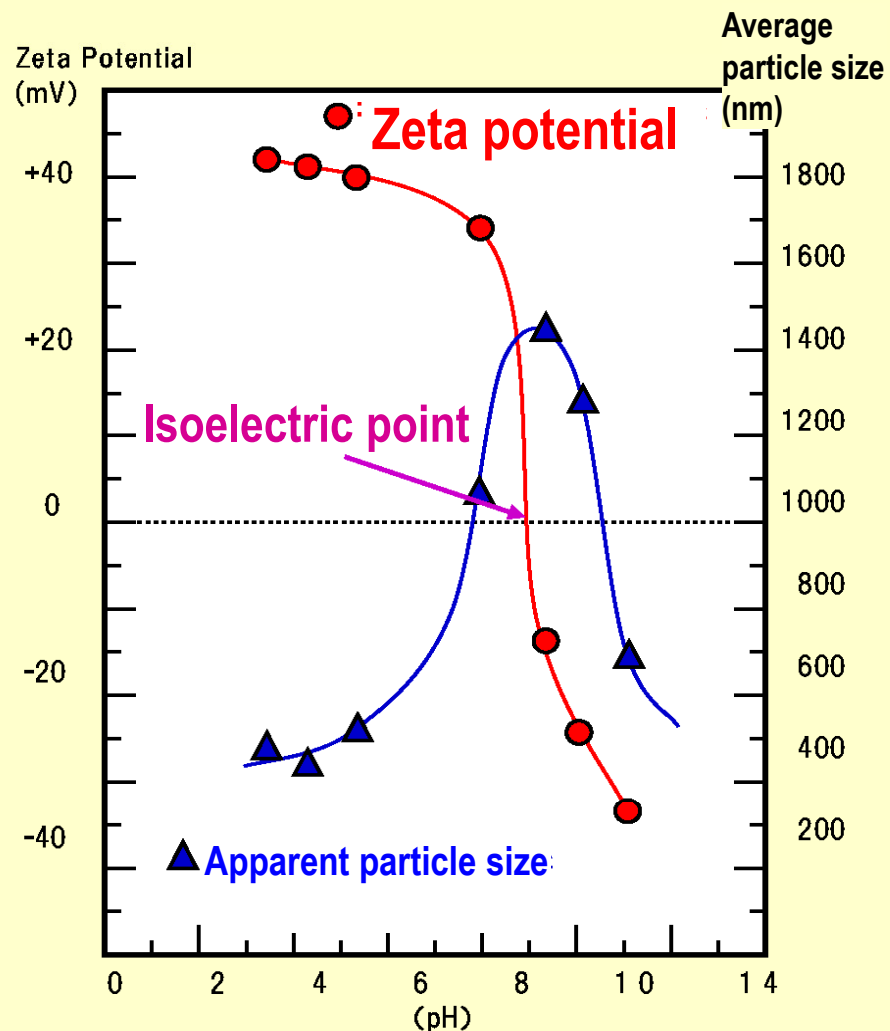


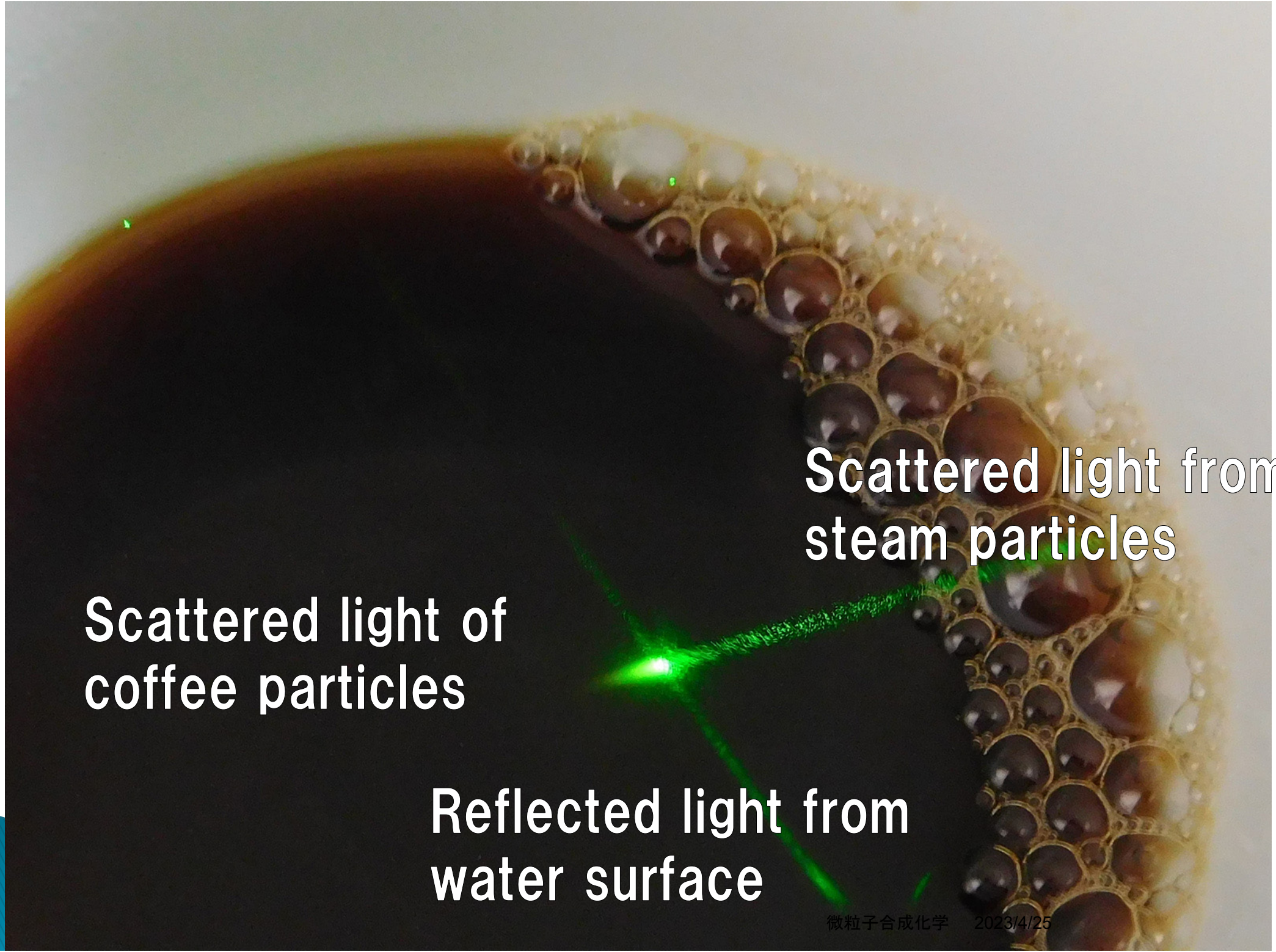
The larger the absolute value of the zeta potential, the better the dispersibility. However, if it is small, it is unstable and tends to aggregate.

The alumina particles in the right figure have a **positive charge** on the acidic side. The isoelectric point is around pH 9. It has a **negative charge** on the alkaline side.

The average particle size is small in the pH region where the absolute value of the zeta potential is large. In the vicinity of the isoelectric point, they aggregate and have a large particle size.

The larger the absolute value of the zeta potential, the better the dispersibility. If it is small, it is unstable and tends to aggregate.





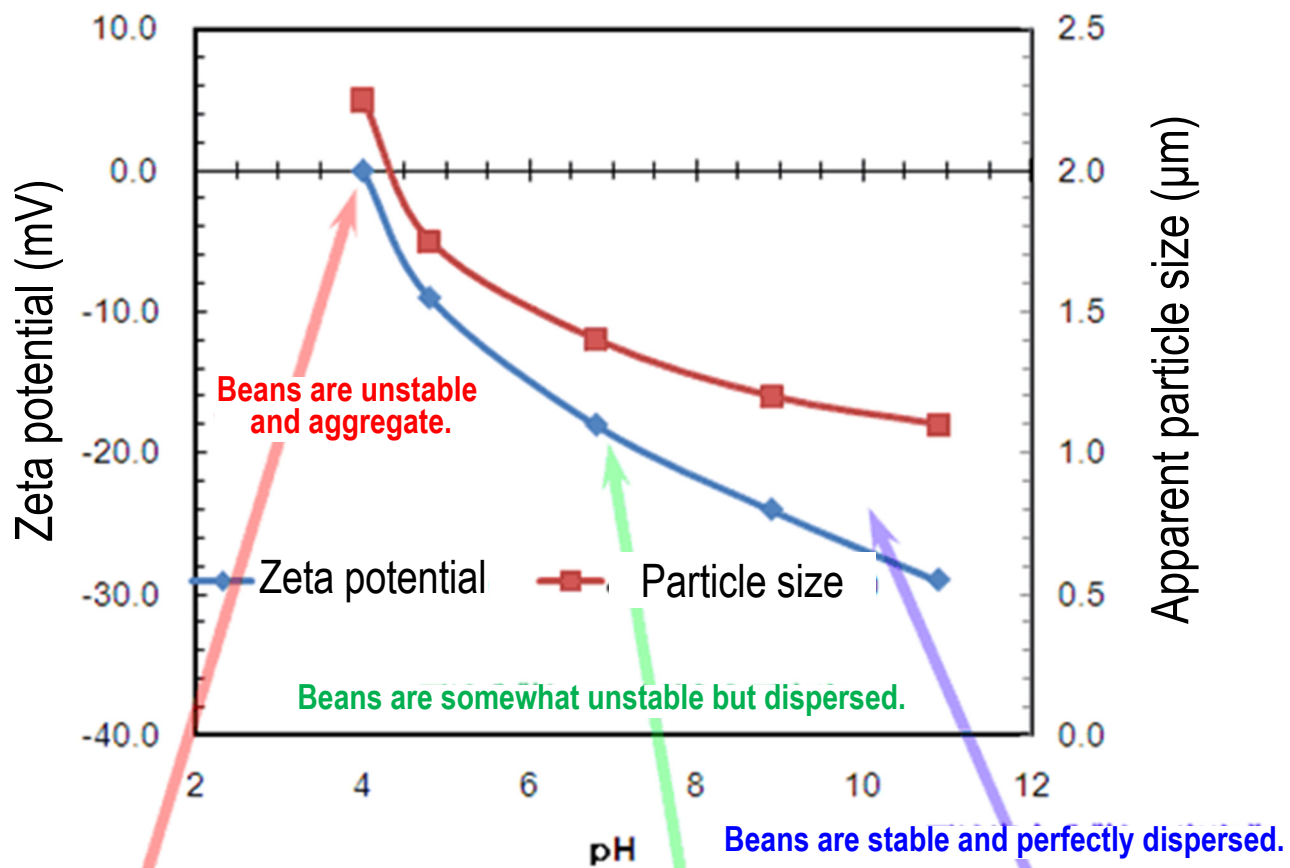
Scattered light of coffee particles

Scattered light from steam particles

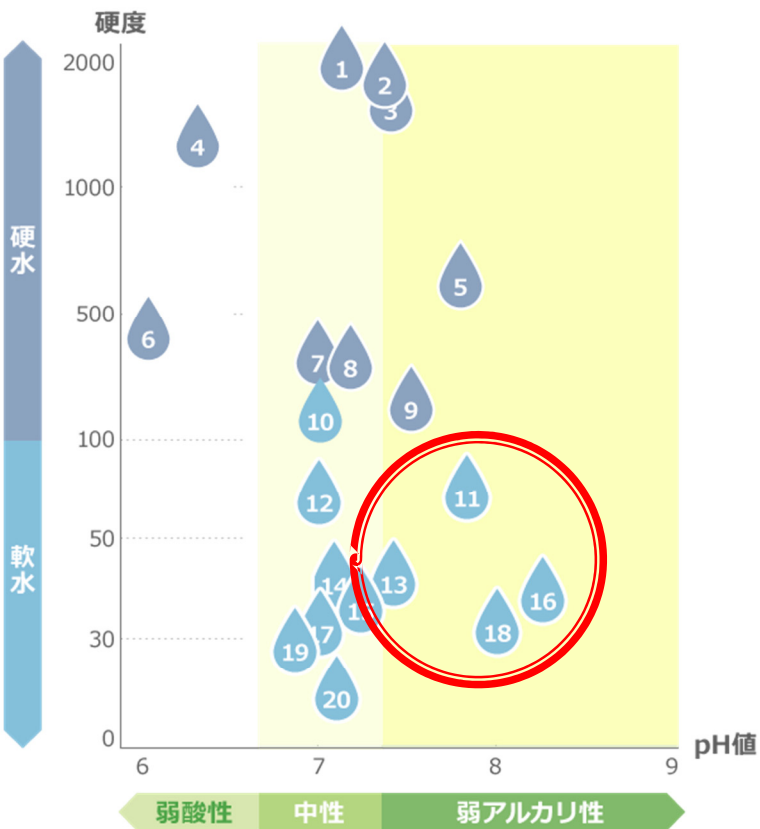
Reflected light from water surface

Tea, black tea, and coffee are colloids.

Zeta potential of coffee bean particles



【ミネラルウォーターの比較分布図】



1 エパー (HePAR)
硬度 1,849 pH 7.2

3 コントレックス (Contrex)
硬度 1,468 pH 7.45

5 サンペレグリン
硬度 674 pH 7.8

7 ヴィittel (Vittel)
硬度 315 pH 7.0

9 アイランドチリ (Island Chill)
硬度 117 pH 7.5

2 クールマイヨー
硬度 1,612 pH 7.4

4 ゲロルシュタイナー
硬度 1,302 pH 6.4

6 ペリエ (perrier)
硬度 417 pH 6.0

8 エビアン (evian)
硬度 304 pH 7.2

10 フィジーウォーター
硬度 105 pH 7.0

11 富士山麓の美味しい天然水
硬度 63 pH 7.8

13 クリスタルガイザー
硬度 38 pH 7.4

15 おいしい水 六甲
硬度 32 pH 7.2

17 南アルプスの天然水
硬度 30 pH 7.0

19 い・ろ・は・す
硬度 27.7 pH 6.9

12 ボルビック (Volvic)
硬度 60 pH 7.0

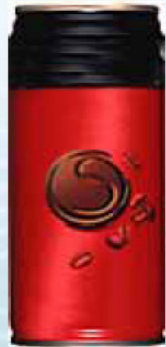
14 森の水だより
硬度 34.6 pH 7.1

16 日田天領水
硬度 32 pH 8.3

18 富士山のバナジウム天然水
硬度 29 pH 8.0

20 熊野古道水
硬度 10 pH 7.1

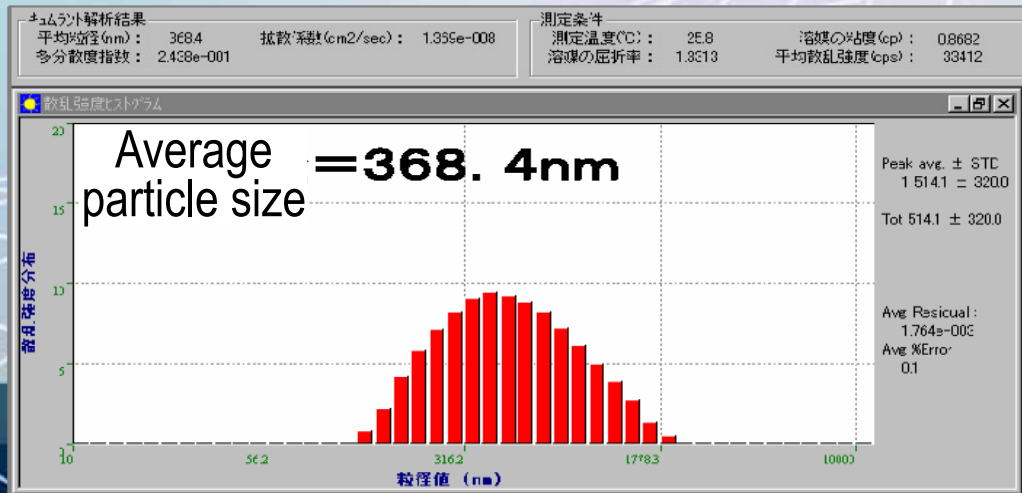
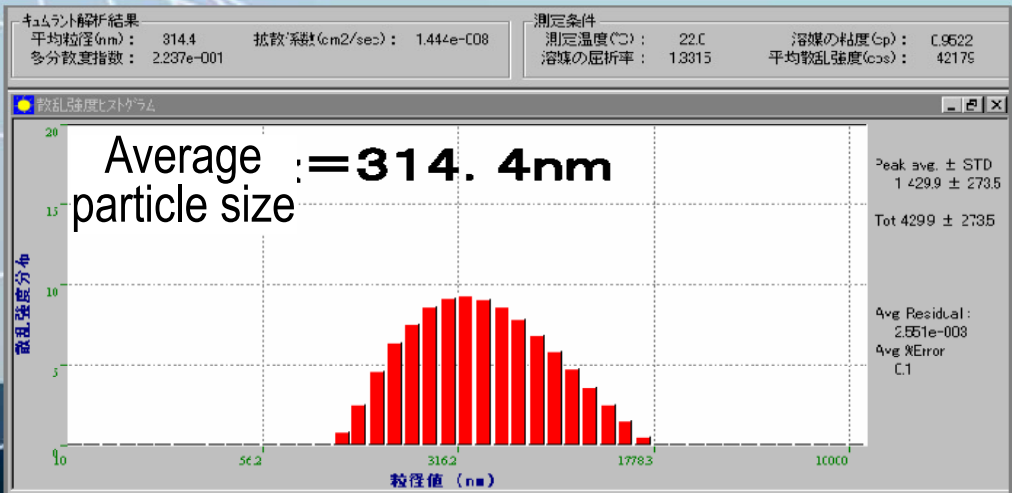
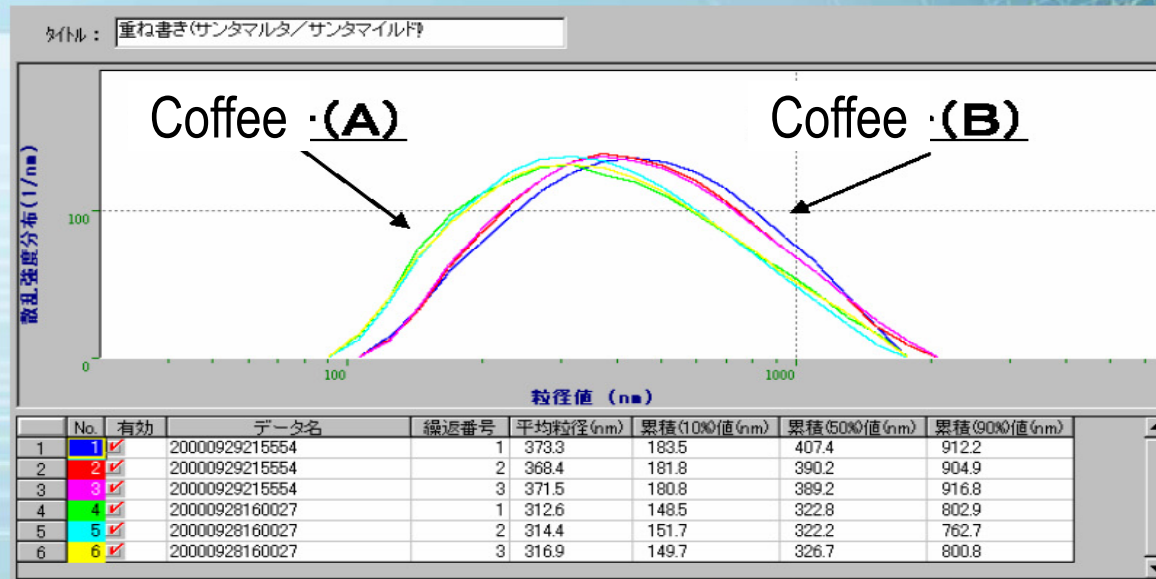
Coffee drinks



A社
= Coffee (A)



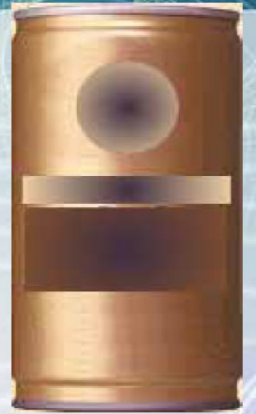
A社
= Coffee (B)



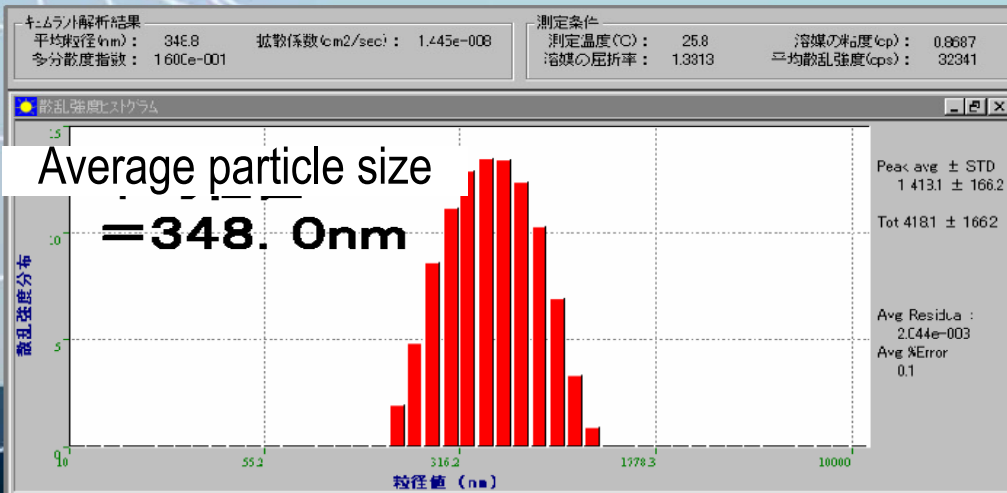
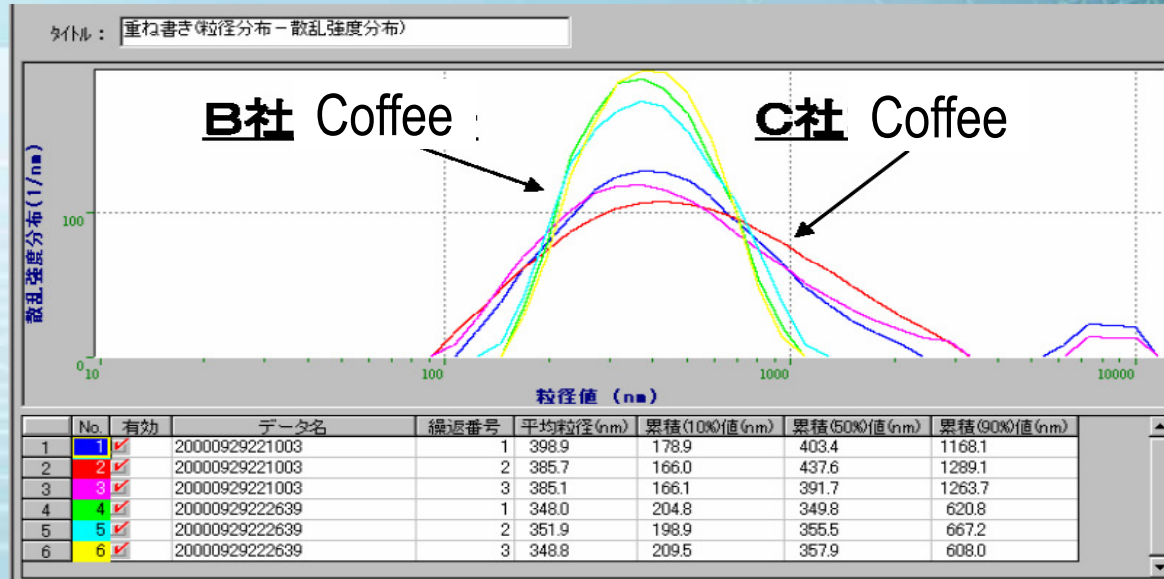
Coffee drink (U社、S社比較)



B社
Coffee



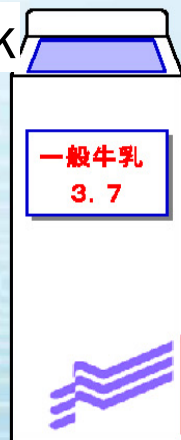
C社
Coffee



Comparison of particle size distribution of various types of milk

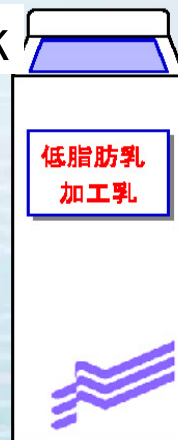
① Common milk

一般的な牛乳で、ホモジナイザーで乳脂肪を細かく粉砕して安定化して保存性を良くしたものの。



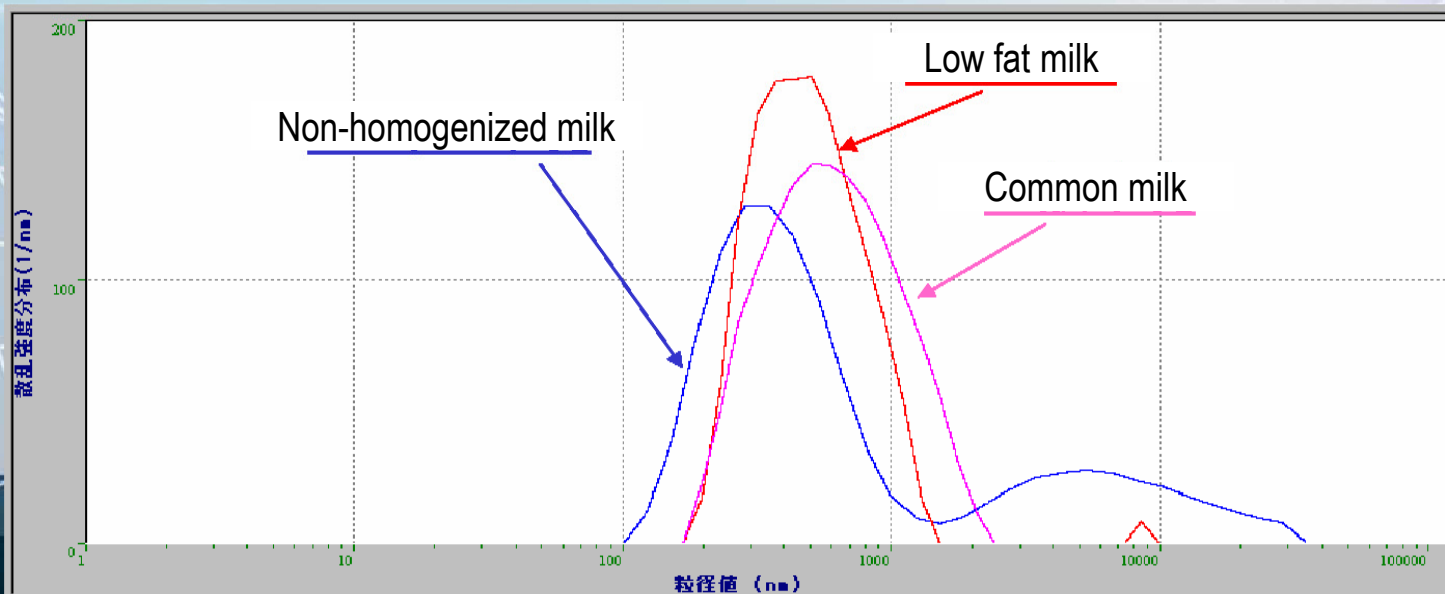
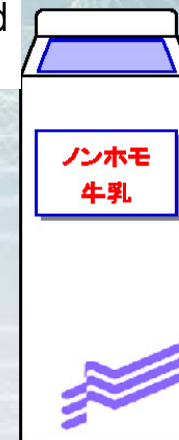
② Low fat milk

脱脂粉乳を還元して牛乳と同じように加工したもの。脂肪分が少ない。



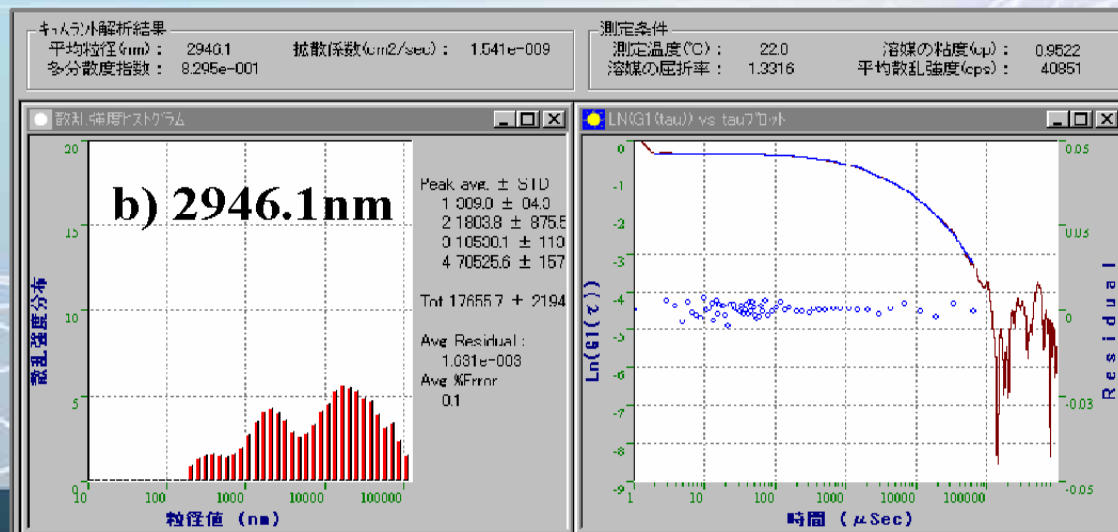
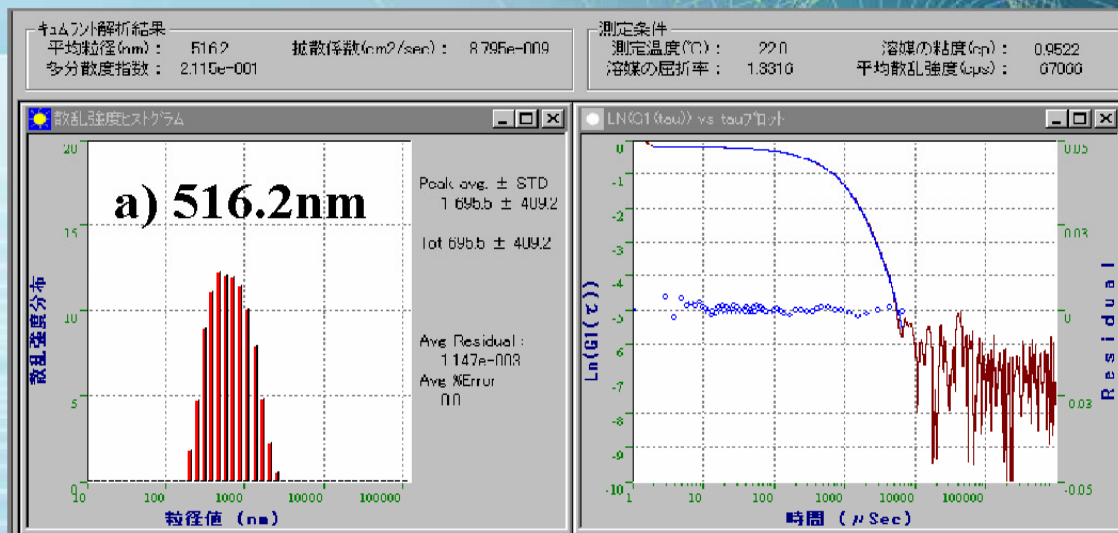
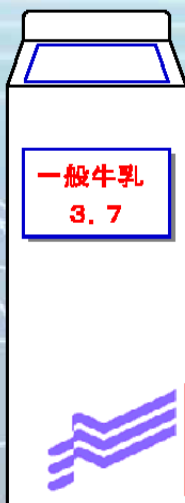
③ Non-homogenized milk

搾り立ての牛乳に近く、乳脂肪が固まりやすく、放置するとバターが分離します。



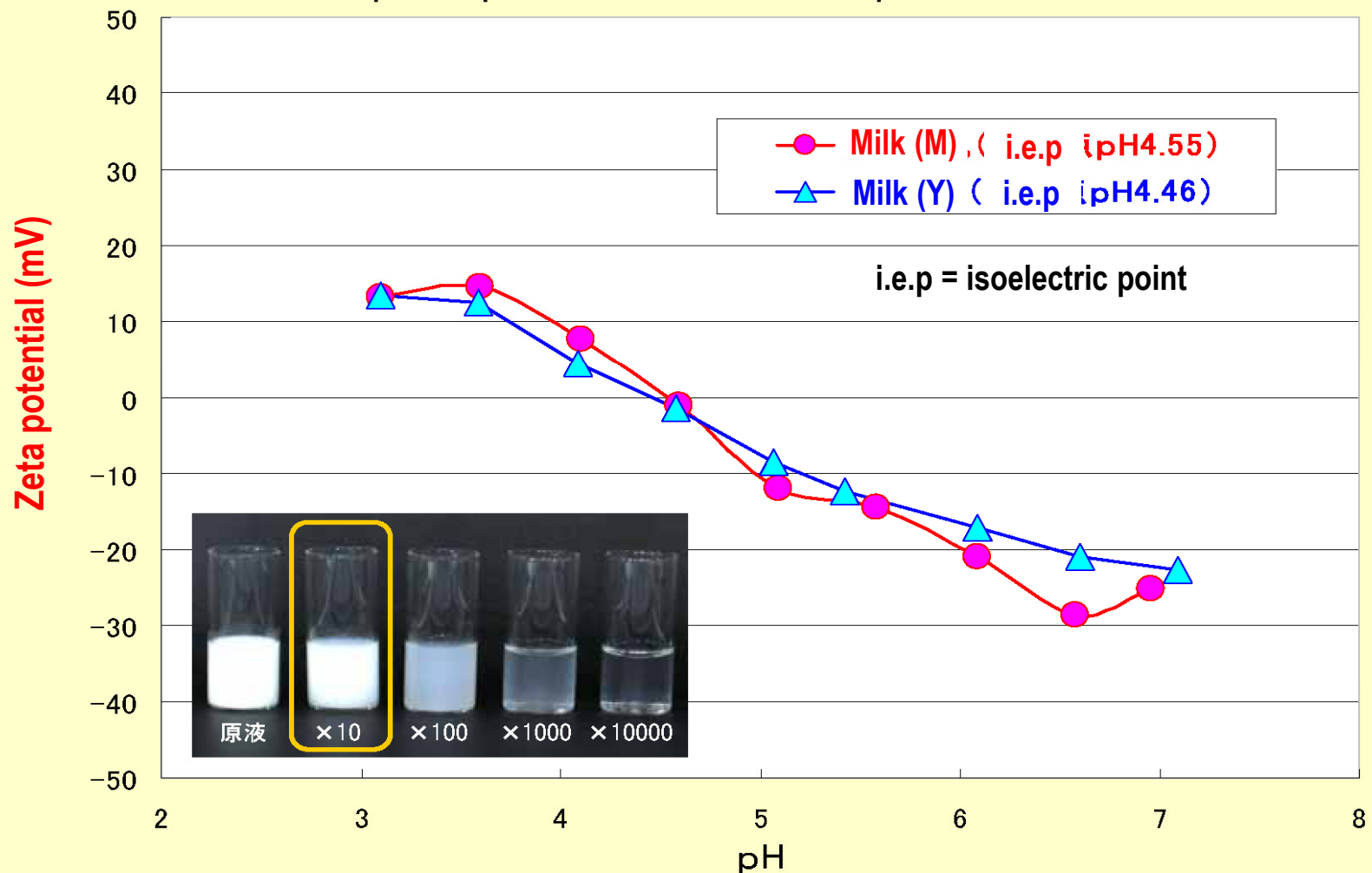
Changes in creaming of regular milk

- a) Fresh regular milk
- b) Milk left indoors was changed as creaming.



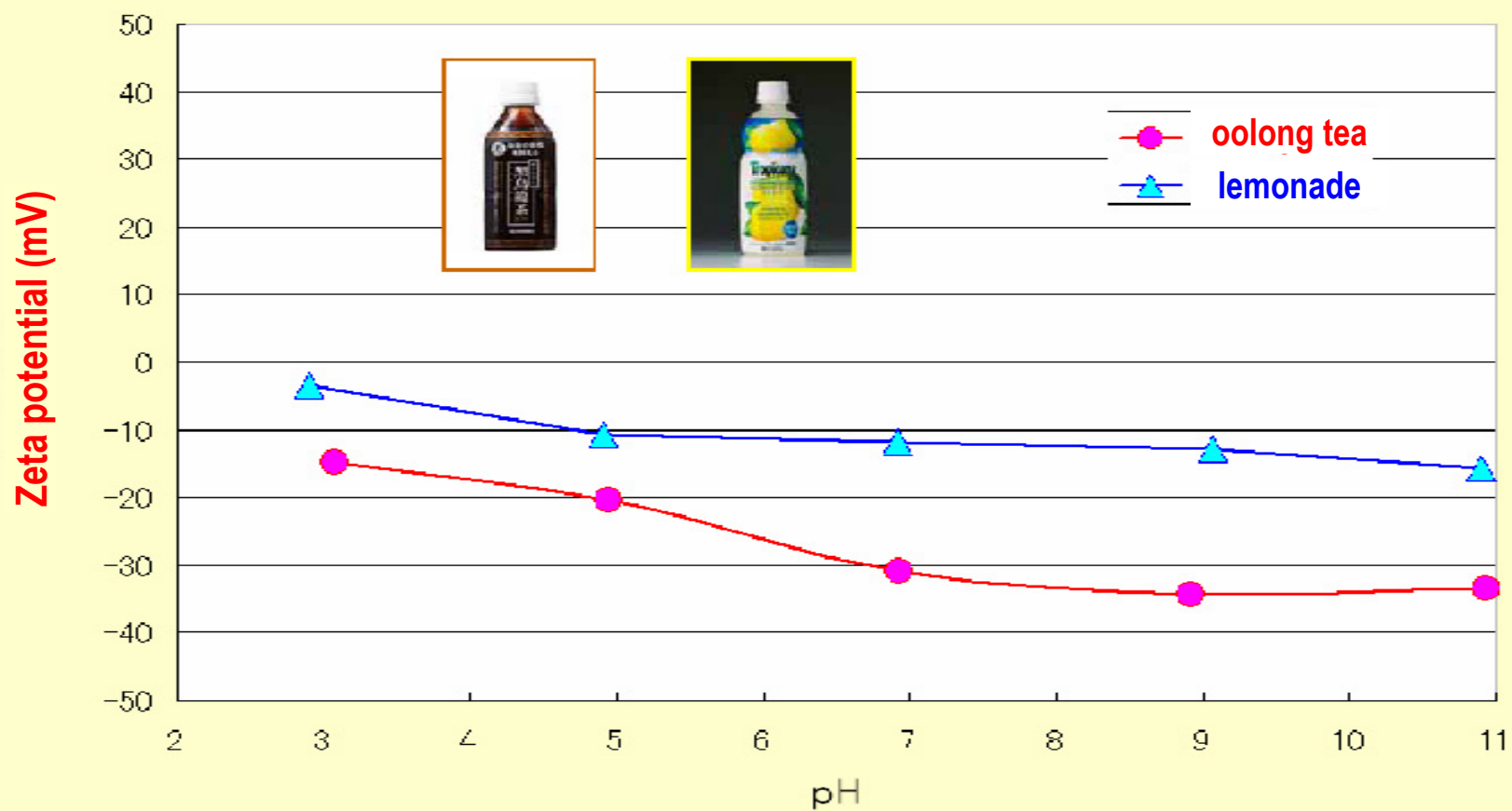
pH titration of 10-fold diluted milk

pH dependence of the zeta potential of milk



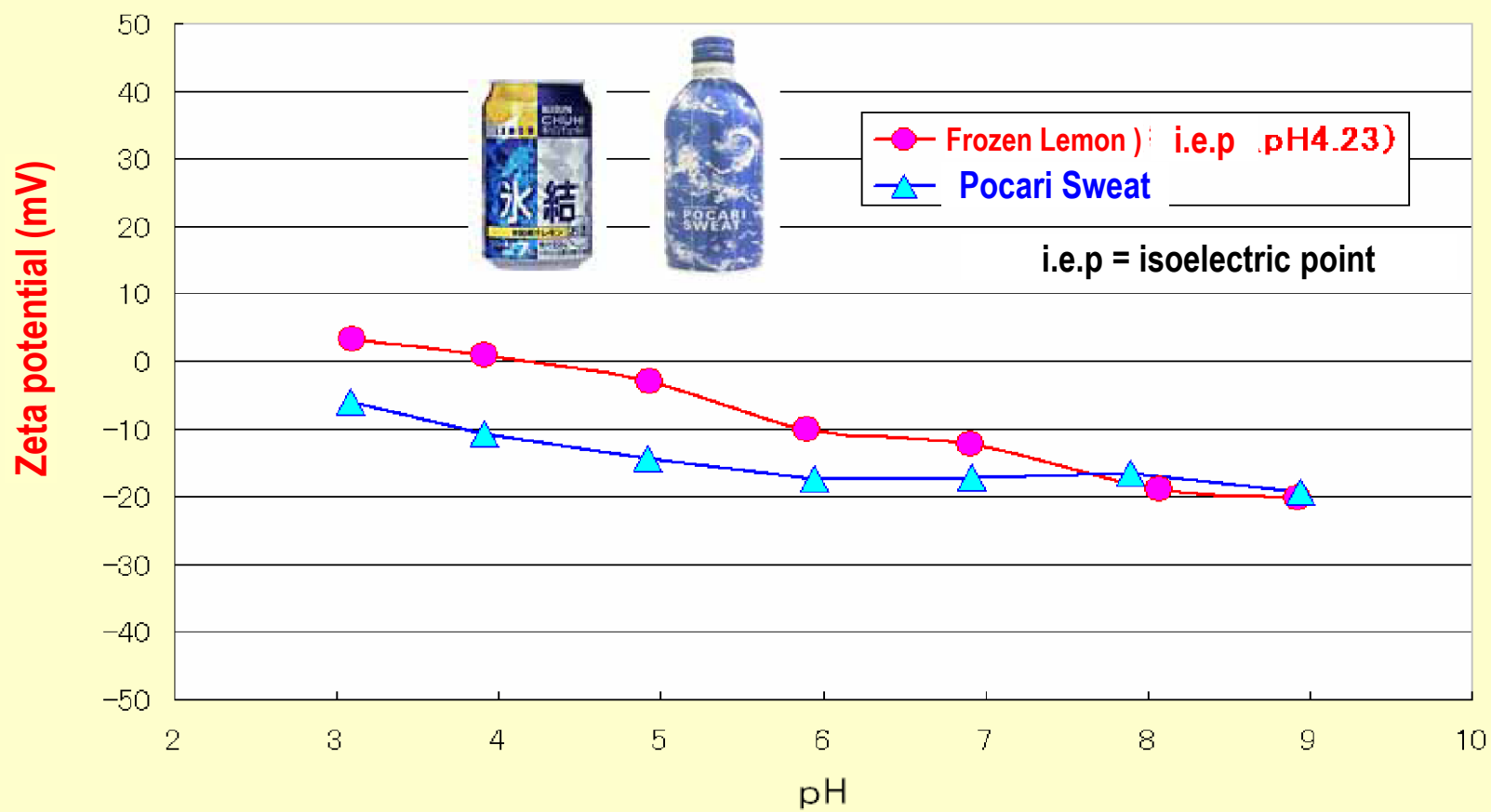
pH titration of oolong tea and lemonade

pH dependence of the zeta potential of oolong tea and lemonade

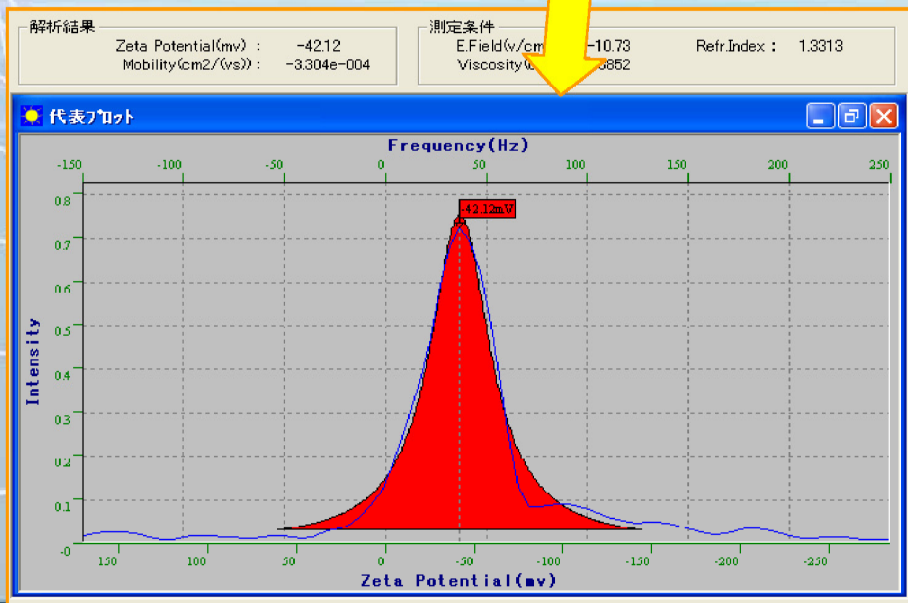


pH titration of Frozen Lemon and Pocari Sweat

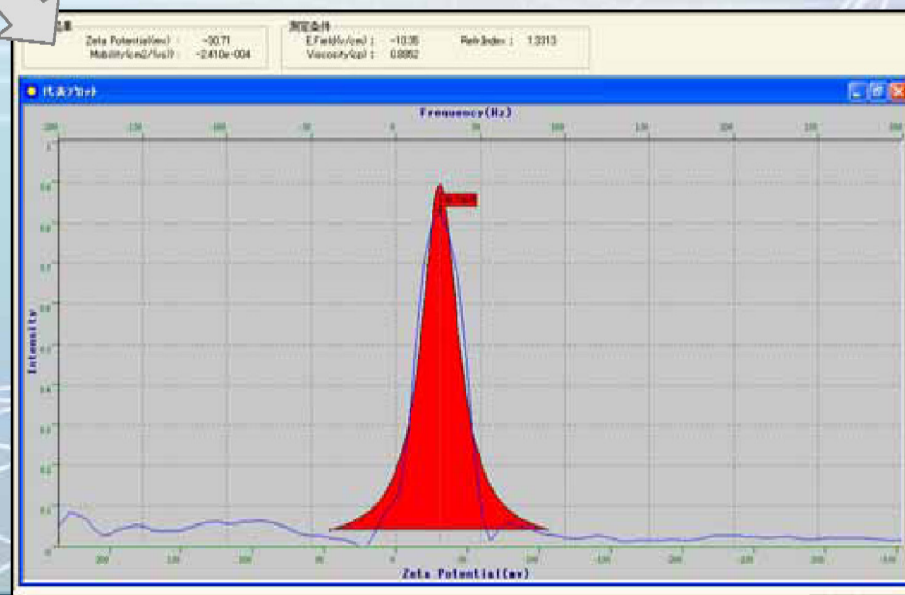
pH dependence of the zeta potential of Frozen Lemon and Pocari Sweat



Zeta potential of color ink for printer



■ Zeta potential of yellow ink for printers



■ Zeta potential of black ink for printers

Zeta potential of color ink for printer

Zeta potential measurement of printer ink

Zeta potential measurement of printer ink

1) Each color has a different zeta potential.



It is important to stabilize each color.

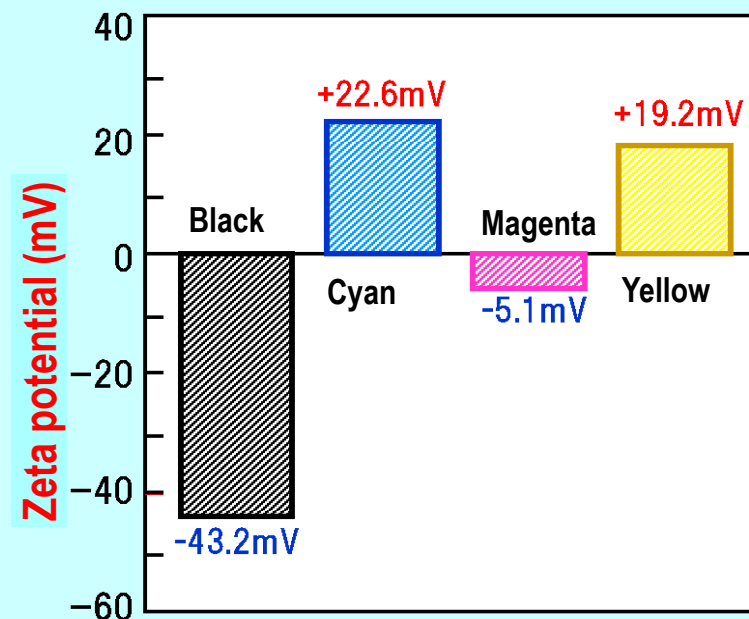
2) It is important to keep the dispersion state.



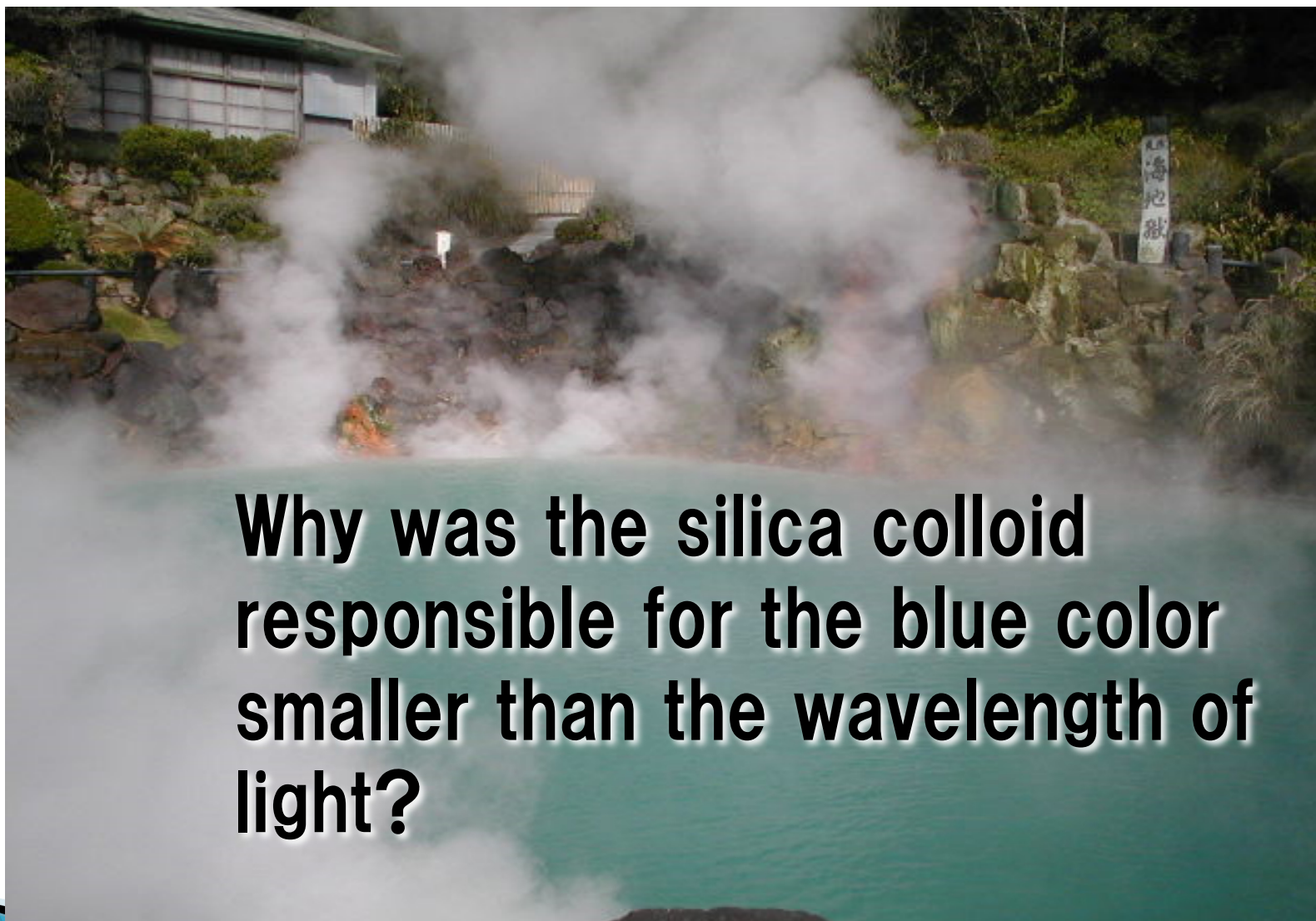
If it aggregates and hardens, it becomes impossible to ink-jet. This leads to uneven coloring.

製品寿命、品質向上のための条件検討

Zeta potential of organic pigments



Go back to Beppu sea hell



Why was the silica colloid responsible for the blue color smaller than the wavelength of light?

Why were the silica particles smaller than the wavelength?

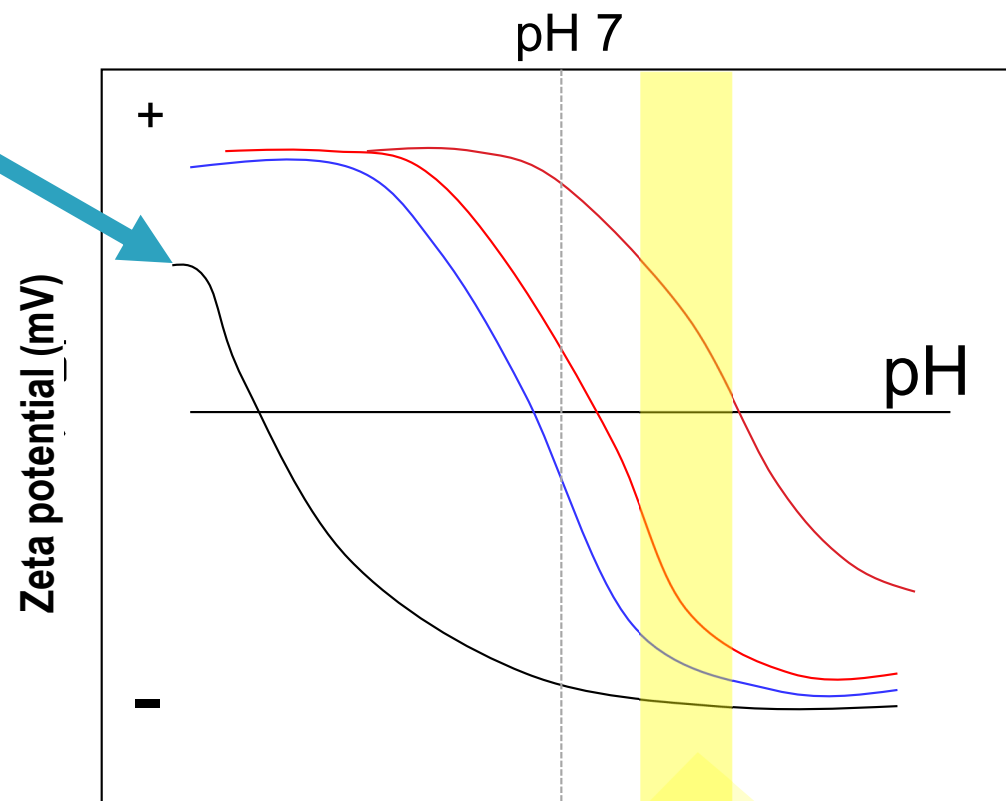
That's because it didn't aggregate and was stably dispersed in water!

Isoelectric point of oxides

depending on crystal plane, structure, etc.

The isoelectric point is the pH at which the zeta potential becomes 0 (zero).

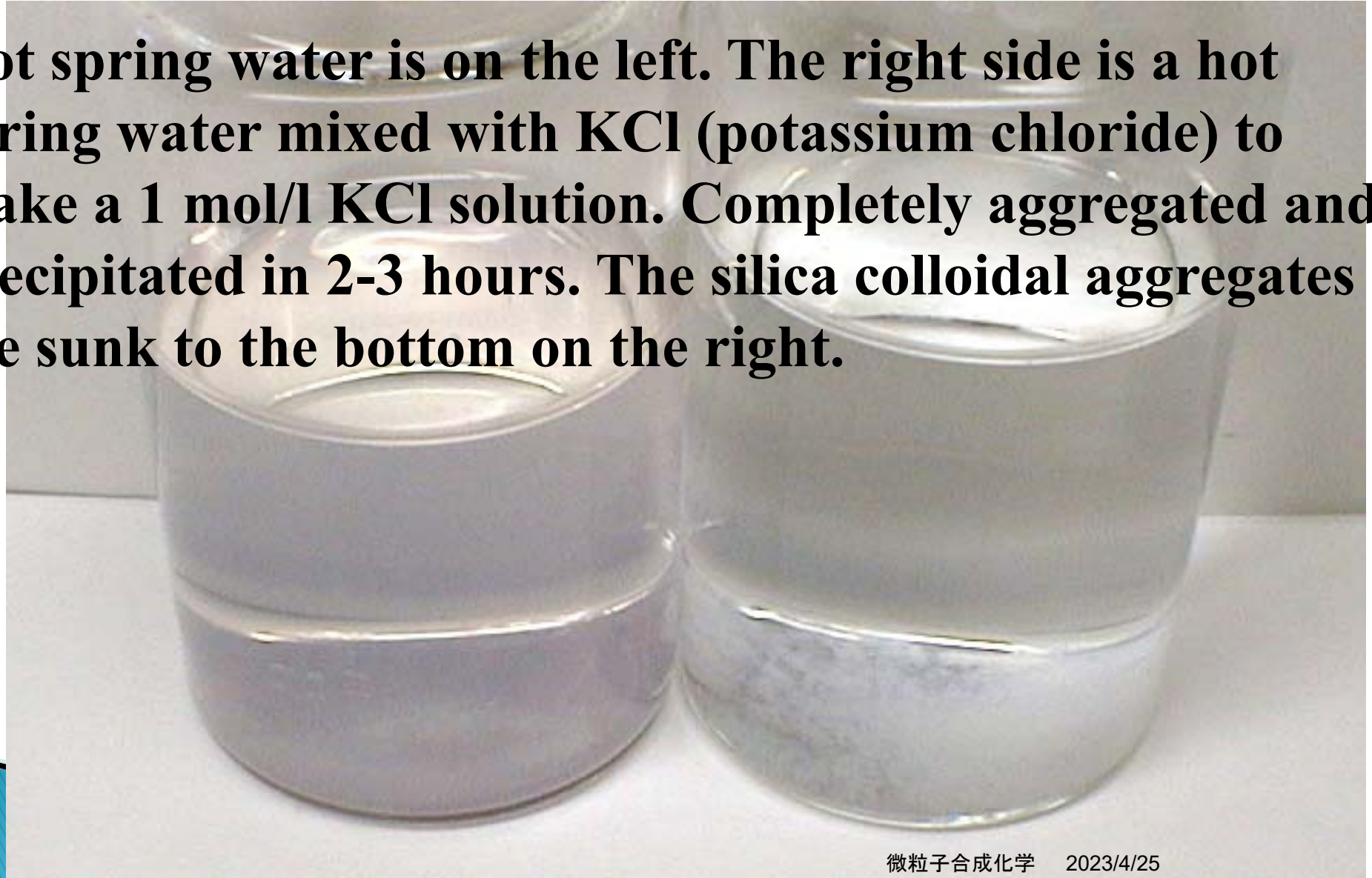
- ▶ SiO_2 2~3
- ▶ TiO_2 6~8
- ▶ Fe_2O_3 6~8
- ▶ ZrO_2 7~9
- ▶ Al_2O_3 7~9
- ▶ MgO 9~11



pH of Umi Jigoku hot spring water : 8~9

Aggregation and precipitation of silica colloid

Hot spring water is on the left. The right side is a hot spring water mixed with KCl (potassium chloride) to make a 1 mol/l KCl solution. Completely aggregated and precipitated in 2-3 hours. The silica colloidal aggregates are sunk to the bottom on the right.



Let's take a look at the colloids around us !

- ▶ **Focus on colloidal dispersion and aggregation!**
- ▶ **What is "dispersion"?**
- ▶ **What is "aggregation"?**
- ▶ **Tofu is a typical example of a "aggregation" product!**

Ureshino specialty! Hot spring tofu



The secret of Ureshino Onsen tofu

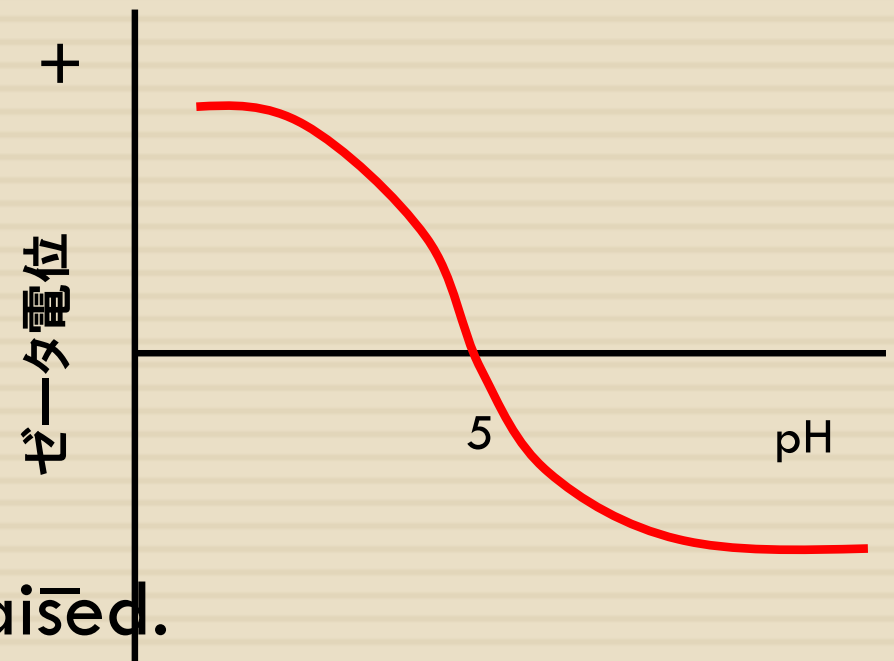
- ▣ The relationship between Ureshino Onsen and



Why does boiled tofu dissolved in Ureshino Onsen water?

Tofu

- The isoelectric point of normal soybean protein is about 4.5 to 5.0.
 - ▣ Over pH 5: —
 - ▣ Below pH 4.5 : +
- pH of household water
 - ▣ 5.0 ~ 6.0
- Homoaggregation near the isoelectric point
- They disperse when the pH is raised.



Tofu is a product of rapid aggregation.

- The main ingredient of nigari, which is used to harden tofu, is magnesium chloride with a small amount of magnesium sulfate.
- Magnesium and calcium dissolve as divalent cations.
- The sulfate ion of magnesium sulfate is a divalent anion.
- In general, when substances aggregate, there is a certain trigger. This is called rapid aggregation, and the trigger is electrolyte ions, that is, salts.
- When you make butter from milk, you use salt, and it's the same.

Tofu is a product of rapid aggregation.

- In aggregative sedimentation, divalent and trivalent ions are overwhelmingly more advantageous than monovalent ions for obtaining the same aggregates. The effect is inversely proportional to the sixth power of the ion valence.
- In other words, magnesium ions have the power to aggregate 6 times, that is, 64 times more than sodium ions even at the same concentration.

Ingredients of Ureshino Onsen

- Ureshino Onsen is a sodium-bicarbonate-chloride spring. It is a weakly alkaline spring (pH7.5-8.5), and the sodium ion content is about 400-500mg in 1kg of sample.
- Since the amount of calcium and magnesium that coagulates tofu is small, the tofu is dispersed due to the pH effect.
- This is not the decomposition of proteins, as is generally said, but a physicochemical phenomenon called "dispersion".



2023/4/25

Colloids in life

□ Udon

The concept of colloidal surface chemistry is also included in "Udon"!

The amount of salt used for Sanuki udon is 3% or more of the flour.



Sanuki Udon

The fabric is stable and does not sag too much.

- Wheat flour can be kneaded in fresh water to form gluten, but salt water produces stronger gluten.
- This is called the astringent effect of salt, and it becomes the base of the udon noodles.
- The salt helps keep the dough from getting mushy if it's ripened for the right amount of time.

Let's take a look at the colloids around us !

- ▶ Focus on colloidal dispersion and aggregation!
- ▶ What is "dispersion"?
- ▶ What is "aggregation"?
- ▶ Whiskey is the next.
- ▶ It's distilled, so it shouldn't be a colloid!
- ▶ But scattered! Why!



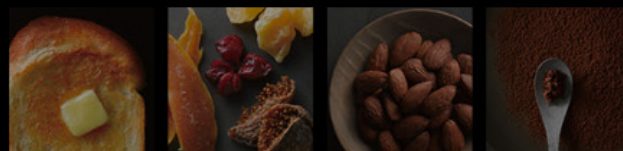
山崎25年

複雑かつ重厚、円熟の深い余韻。

酒齢25年を超える長期熟成シェリー樽原酒を厳選。丁寧にヴァッティングしたスーパープレミアムウイスキー。年間生産本数千数百本の限定品です。

テイastingノート

シェリー樽熟成由来の甘美な芳香が馥郁と立ちのぼる。年月を誇る長期熟成原酒の甘味と苦みが織り成す複雑で重厚な香味。陶然とした余韻は長く、深い。

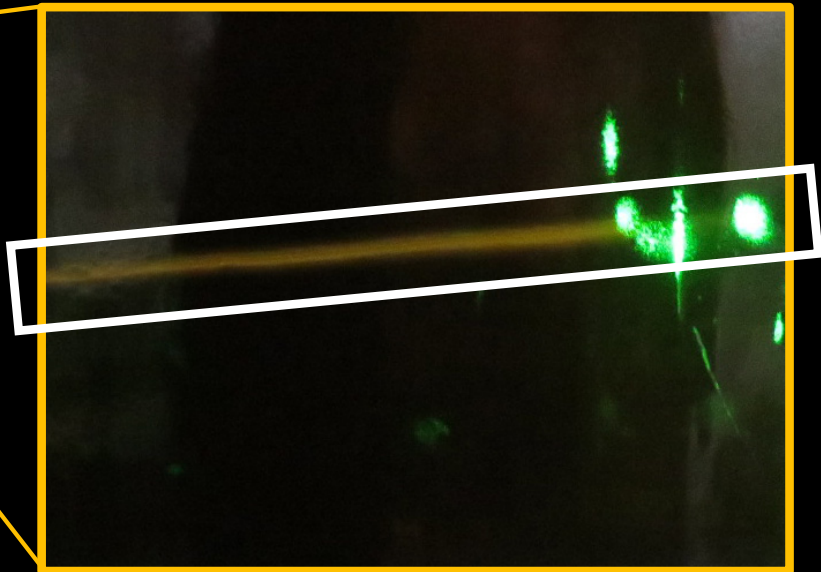


色	濃い赤褐色
香り	レーズン、イチゴジャム、ビターチョコレート
味	しっかりとした酸味、ほろ苦さ、厚み
フィニッシュ	ドライフルーツ、樽香、酸味、苦味、長く深い余韻

700ml・43度



Even green tea is Tyndall phenomenon with green laser. Same as this!



Tyndall effect with green laser
⇒ Nanoparticles of about 100 to 300 nm and
Indicates the existence of something of that
size . . .

微粒子合成化学

What is the cause of "mellowness"?

We hypothesized that the increase in the mellowness of whiskey over time might result in the masking of ethanol due to the formation of a three-element structure consisting of water, ethanol, and barrel-derived components, thereby reducing alcohol stimulation.

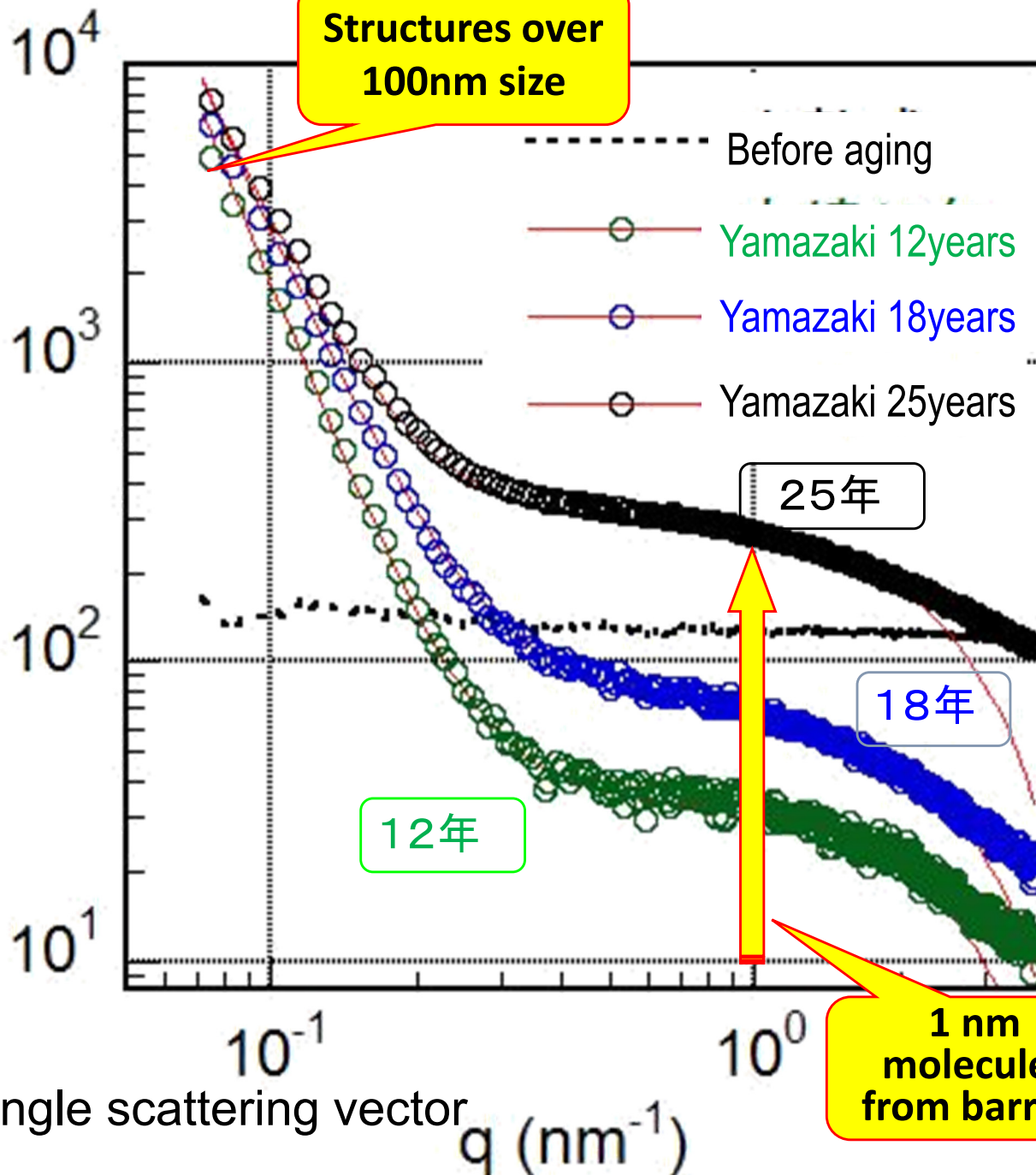
In addition, we thought that the reason why it takes time for aging is that it takes time for the formed structure to stabilize.

This was elucidated at SPring-8

SPring-8

Small-angle X-ray scattering measurement method(SAXS)

Intensity of synchrotron radiation



Aging process:

- Time elapsed \Rightarrow Ingredients derived from barrels \Rightarrow Elution into whiskey
- Ingredients derived from barrels \Rightarrow Low molecular weight, about 1 nm

Micelle formation:

- Some of the low molecular components \Rightarrow Forms micelles with the hydrophobic portion on the inside and the hydrophilic portion on the outside >100 nm size
- Incorporation of many ethanol molecules and hydrophobic components \Rightarrow It is possible to suppress stimulation as a taste "The cause of the mellowness!"

Micelle formation:

Some of the low molecular components

⇒ Forms micelles with the hydrophobic portion on the inside and the hydrophilic portion on the outside

>100 nm size

• Incorporation of many ethanol molecules and hydrophobic components

⇒ It is possible to suppress stimulation as a taste

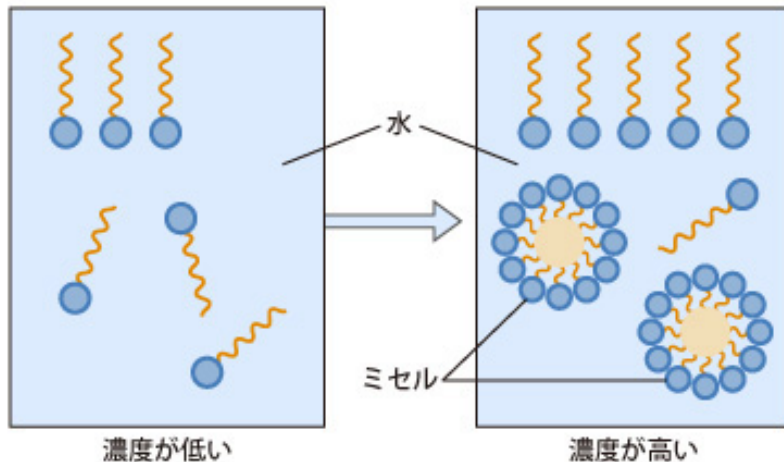
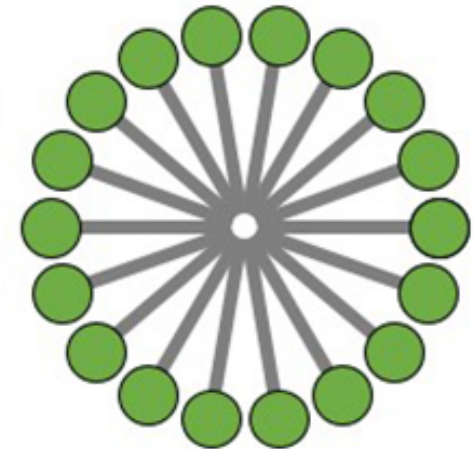
"The cause of the mellowness!"

Ingredients derived from barrels
⇒ Elution into whiskey
⇒ Low molecular weight, about 1 nm

Hydrophilic group

Self-assembly
in water

Hydrophobic group



Regarding the number of associations, there is no particularly preferred value, which is determined by the balance between hydrophobic and hydrophilic groups.

・親水基を外側に向けて安定化する
2023/11/25 ミセルの中に油性成分が可溶化する (とりこむ)

Let's take a look at the colloids around us !

- ▶ Focus on colloidal dispersion and aggregation!
- ▶ What is "dispersion"?
- ▶ What is "aggregation"?

- ▶ Let's enter the world of theory of "dispersion" and "aggregation"!