Synthetic Chemistry of Fine Particles

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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.

Equilibrium and Kinetics

- Equilibrium and Kinetics
  - In equilibrium, the forward and reverse reaction rates are the same.
  - Processes include irreversible and reversible ones.

Chemical potentials

- They indicate the contribution of the energy change of each components to the Gibbs free energy change of the whole system. Expressed as the following,
- $G = f(T,P,V, n1, n2, n3 \ldots)$
- $dG = (\partial G/\partial T)\, dT + (\partial G/\partial P)\, dP + \Sigma (\partial G/\partial ni)\, d\, ni$

Chemical potentials

- When T,P,nj is to be constant, $(\partial G/\partial ni) = \mu$ is called Chemical potential of component i.
- You can think of it as indicating the degree of Gambari of a component i.

What is the definition of 1 mol?

- Until the 1970s, the definition was 1 mol for 12g of 12C at 0° C and 1 atm. To be changed.
- Definition was revised in 2019.
- Until then, “amount of matter in a system containing as many elementary particles as there are atoms in 0.012 kilograms of C12"
- Furthermore, before that, it was “a system of substances composed of as many elementary particles or assemblages of elementary particles (limited to those with a defined composition) equal to the number of atoms in 0.012 kilograms of C12."

What is the definition of 1 mol?

- $n(\mathrm{X})\mathrm{mol} = N(\mathrm{X}) / N_a$ [X is elementary particles, N is a number]
- 1 mol contains exactly $6.02214076 \times 10^{23}$ elementary particles
- This number is the Avogadro constant NA expressed in units of mol^{-1}, and is called the Avogadro number.
- Unlike the uncertainty up to that point, from 2019 onwards, the Avogadro constant, NA, is assumed to be a value with no uncertainty.

Definition of pH

$$pH = -\log_{10} a_{\mathrm{H}}$$

- a_H is the activity of proton.
- Expanded uncertainty U(k =2) for pH measurement by glass electrode method is 0.025 to 0.030
- ~0.01 if the primary pH standard solution is used and can be considered to have the same composition as this standard solution;
- Expanded uncertainty using differential –potentiometric cell is ~0.004

What is the activity?

- A concept conceived as a bridge between the ideal solution and the actual solution.
- It's the same unit as a concentration, but it's not a correction of a concentration.
- For example, if the protons of 1 mol/L hydrochloric acid had 100% activity, it would have an activity of 1 mol/L, which is not the case in a real solution. At 80% activity, we call it an "activity" of 0.8 mol/L.

What is the activity?

- Compare rattled train with crowded train.
- Volume, pressure, temperature are constant.
- Envision your own and other passengers' range of activities.
- The rattle train allows you to choose where you want to be overwhelmingly more freely.
- This is the activity.
- Born to connect ideal and real solutions.

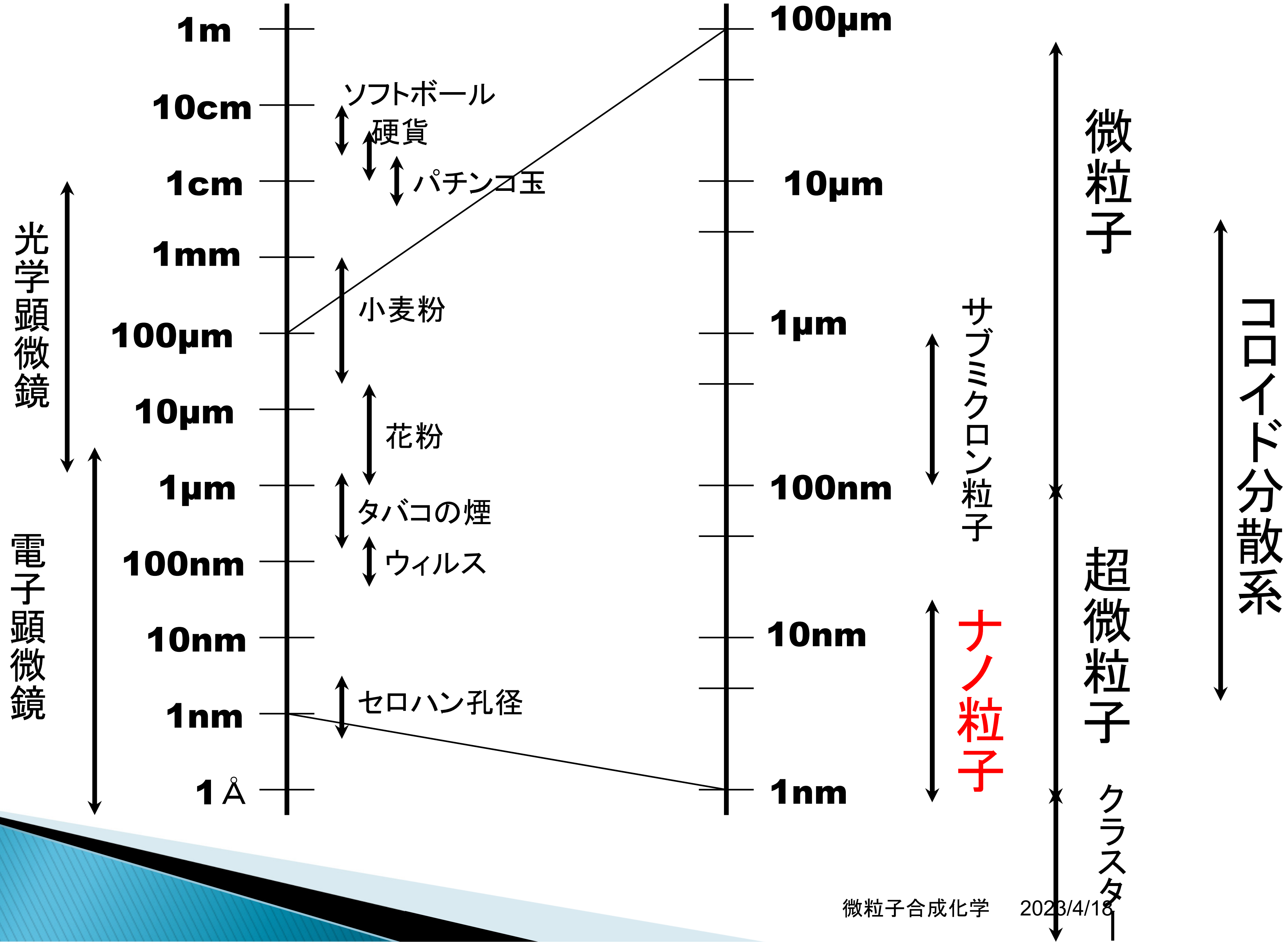
- The concept of fugacity is basically the same.

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?

Particle classification by particle size



COLLOIDS IN LIFE

2023/4/18

Let's take a look at the colloids around us

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 ℃

The red color is caused by oxidation of ferrous ions (Fe(II)), hydrolysis, and then precipitation of solid-phase iron hydroxide $Fe(OH)_3$ 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（℃）	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

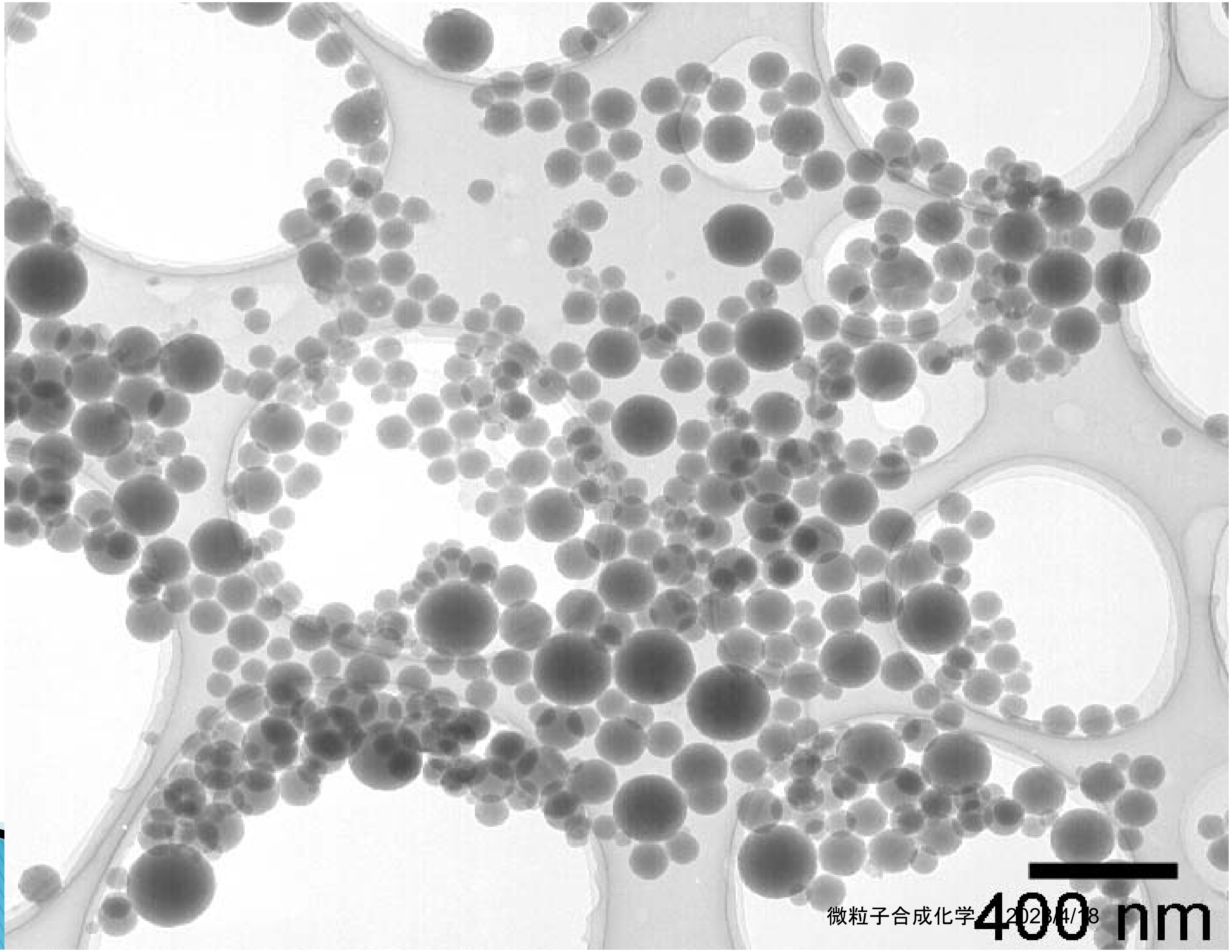
#3　全シリカ

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



SiO_2(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

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

$$\alpha \ll 1 \quad Rayleigh\ scattering$$

$$\alpha \approx 1 \quad Mie\ scattering$$

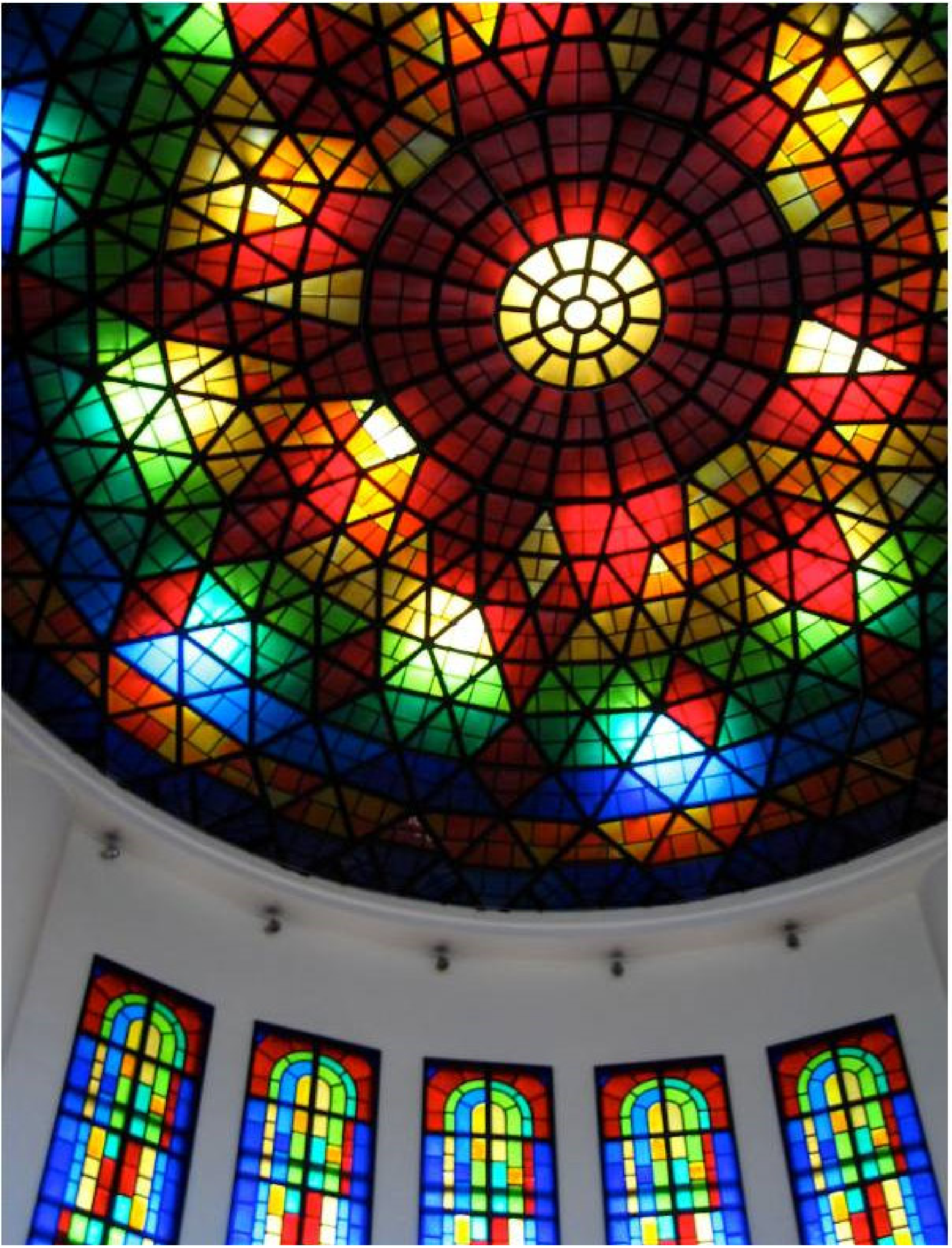
$$\alpha \gg 1 \quad geometric\ optics\ approximation$$

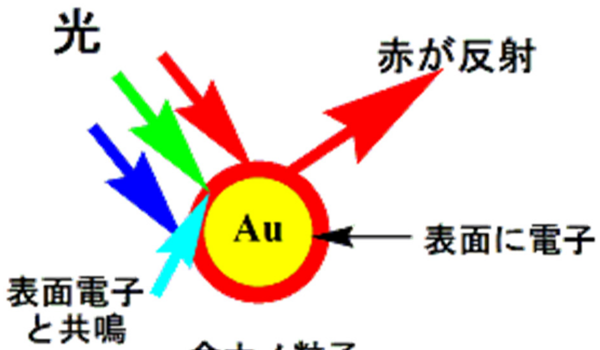
Rayleigh scattering coefficient k_s

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

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...

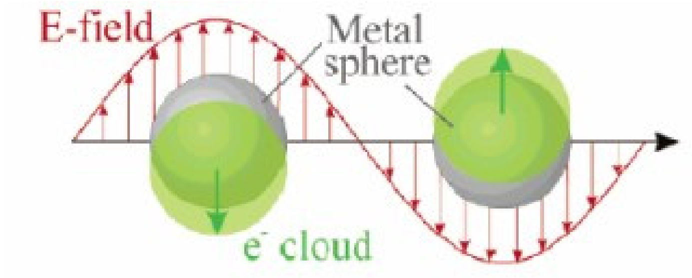


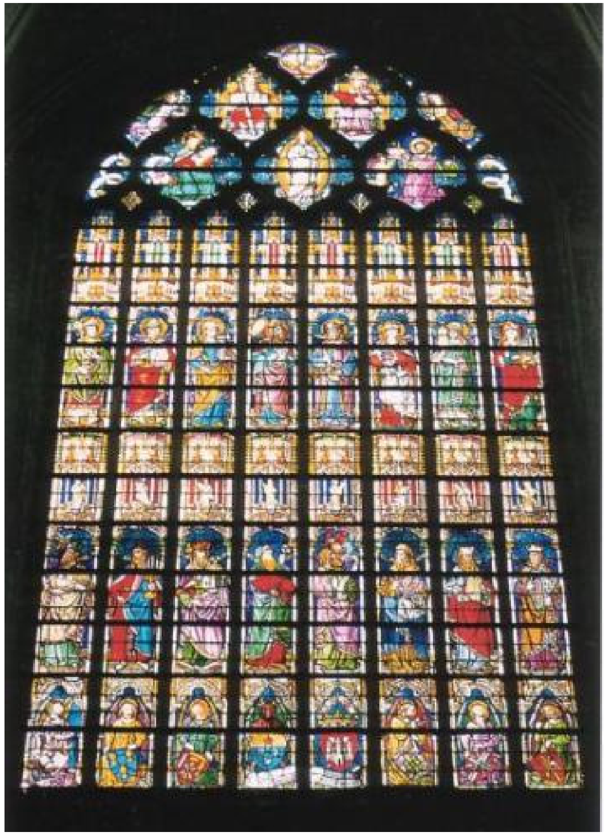


Colored gold nanoparticles

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





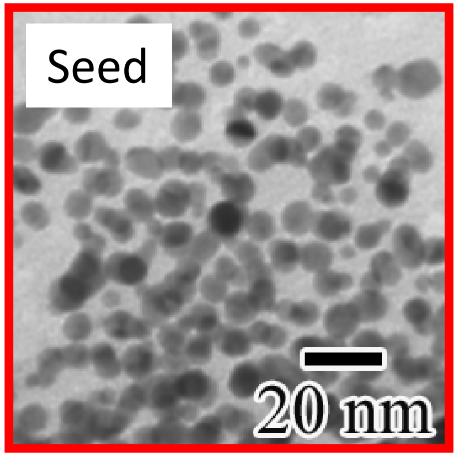
church stained glass

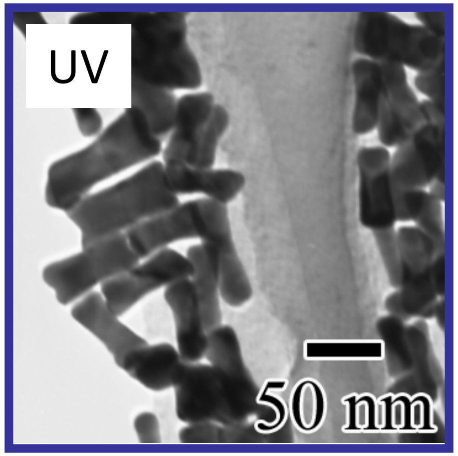
Late Roman Lycurgus Cup

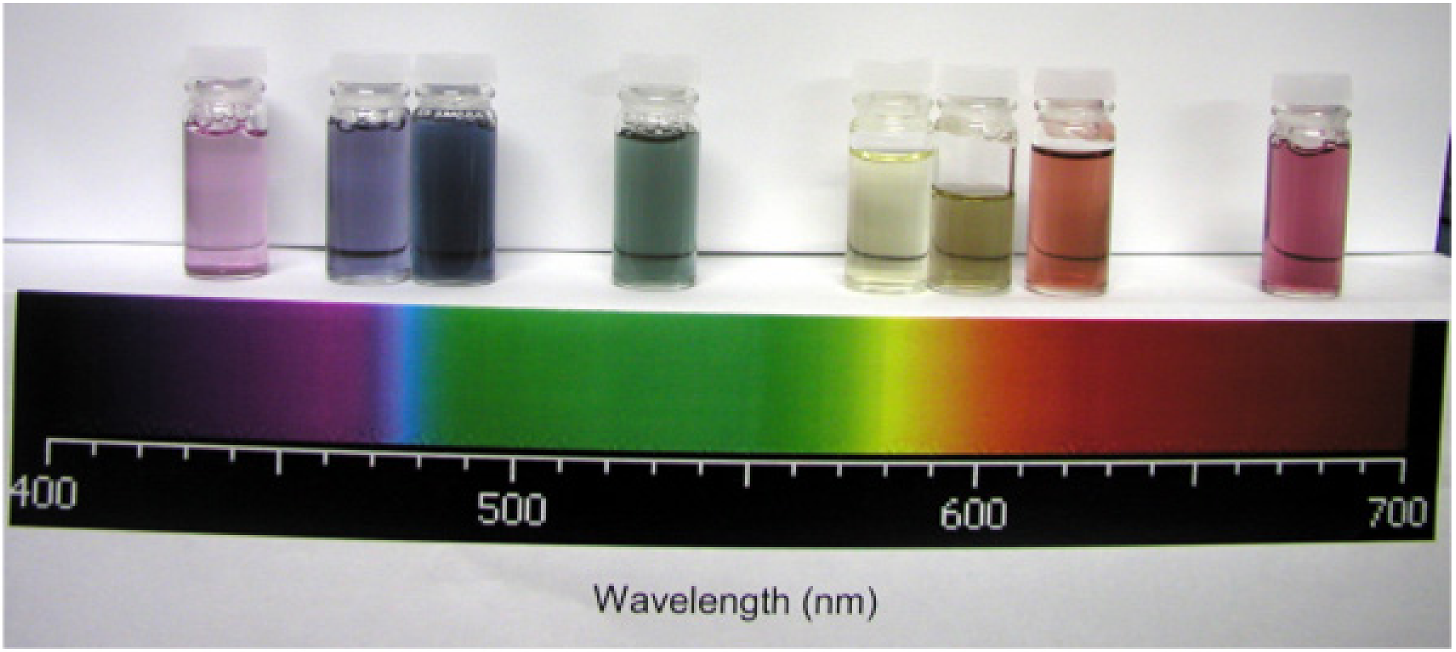
Baroque Ruby Glass

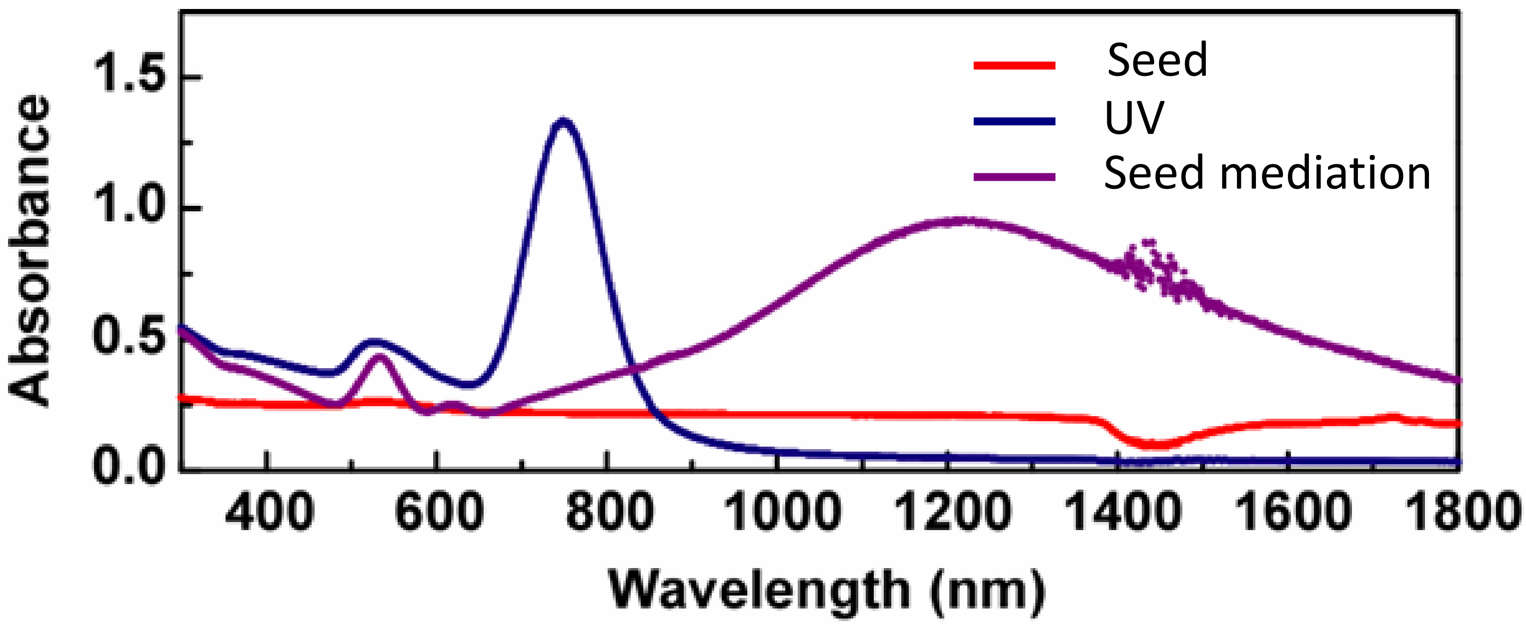
Colloidal dispersion of gold nanoparticles

Color change due to change in morphology of gold nanoparticles







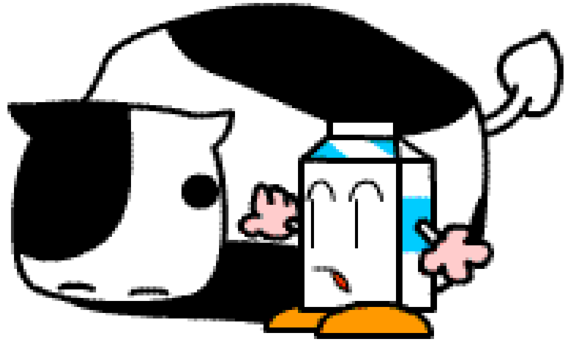


Absorption wavelength shifts to longer as aspect ratio increases

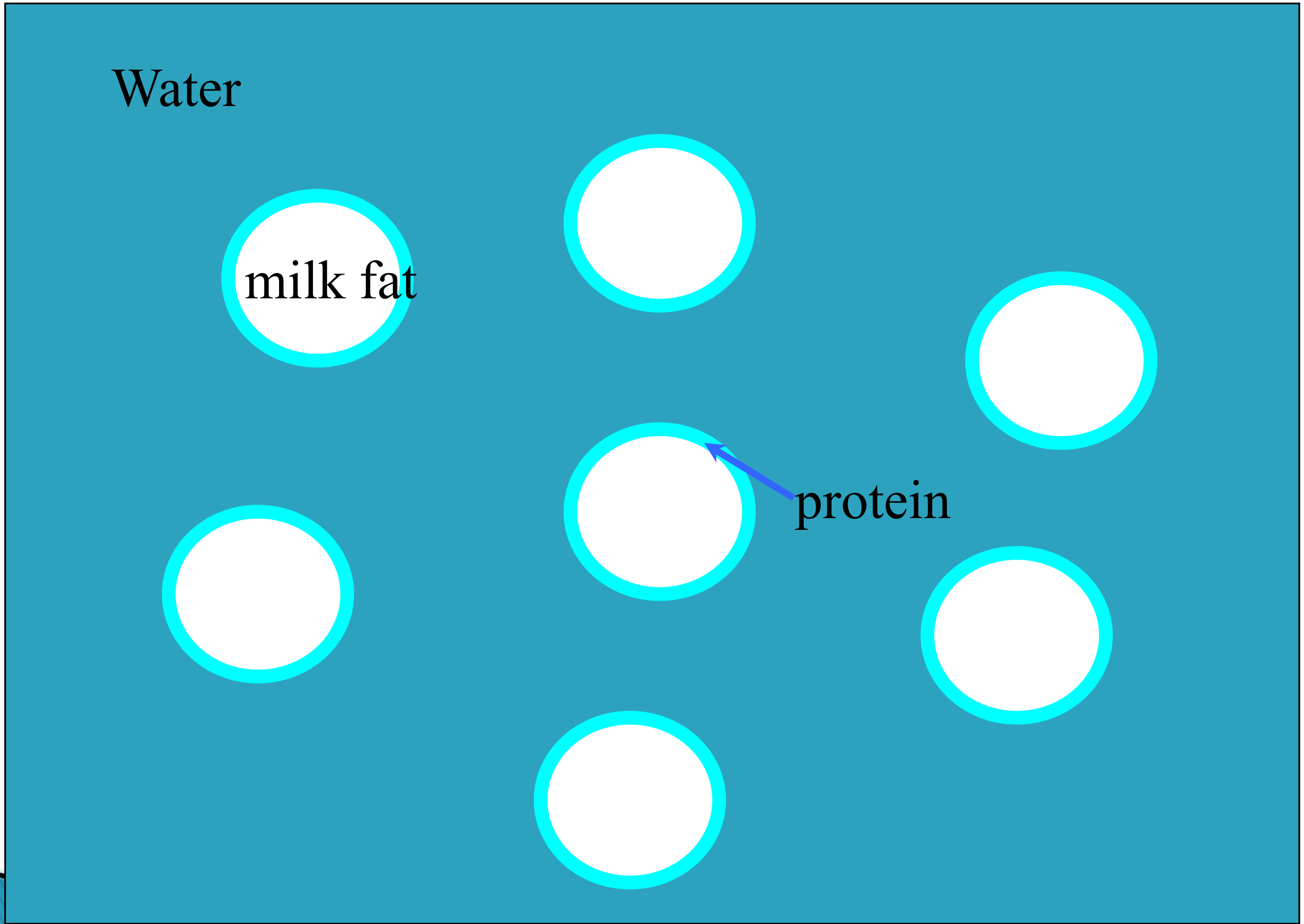
Colloids around us

Milk

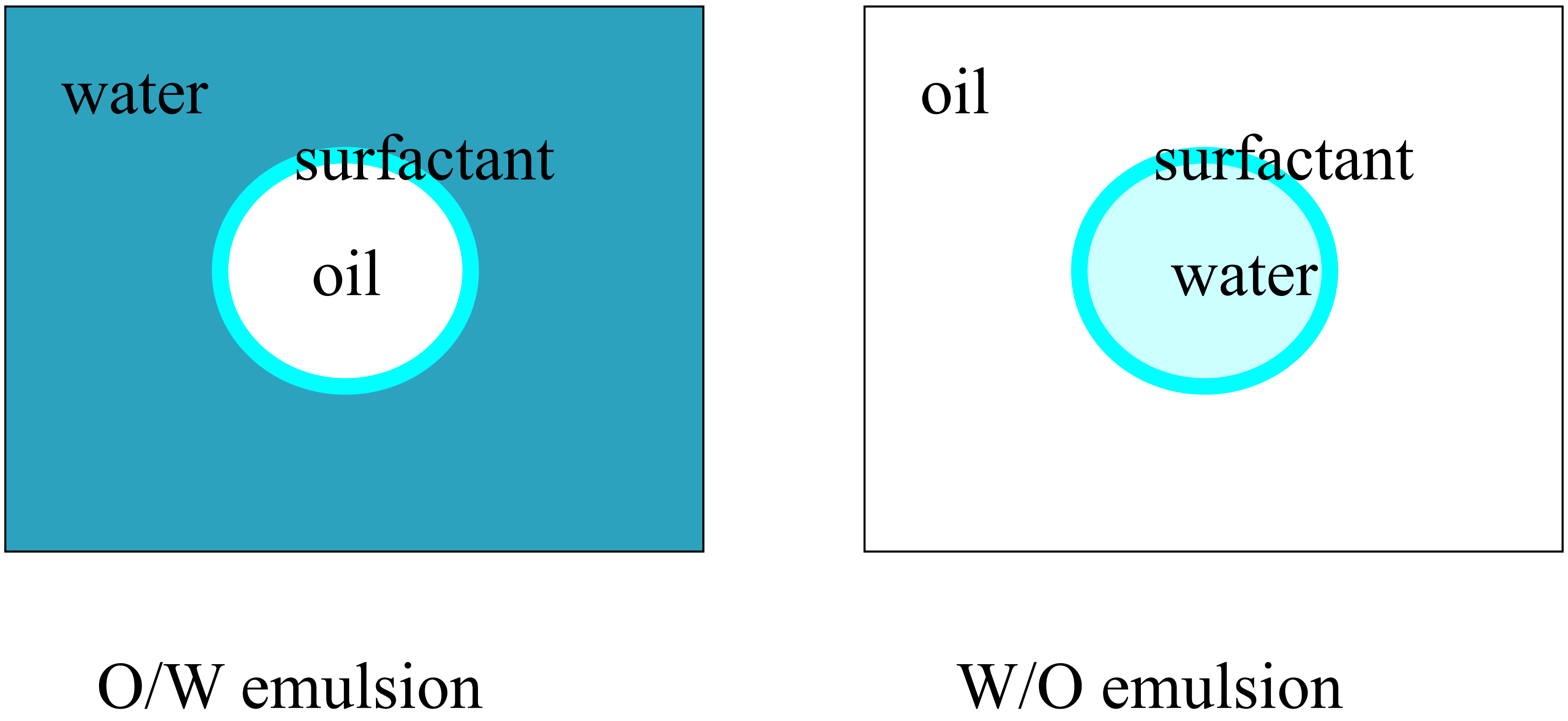
Milk



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

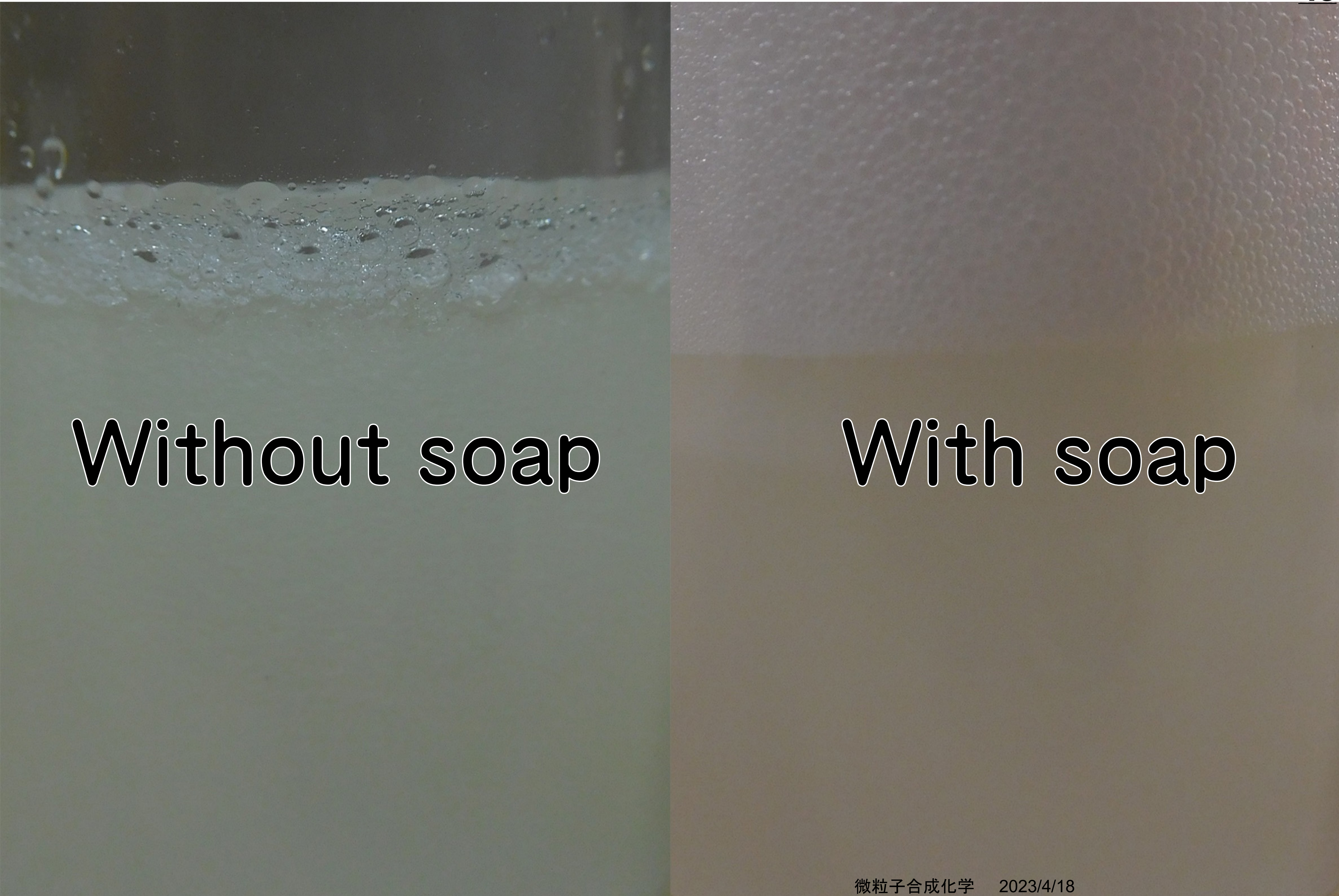



water

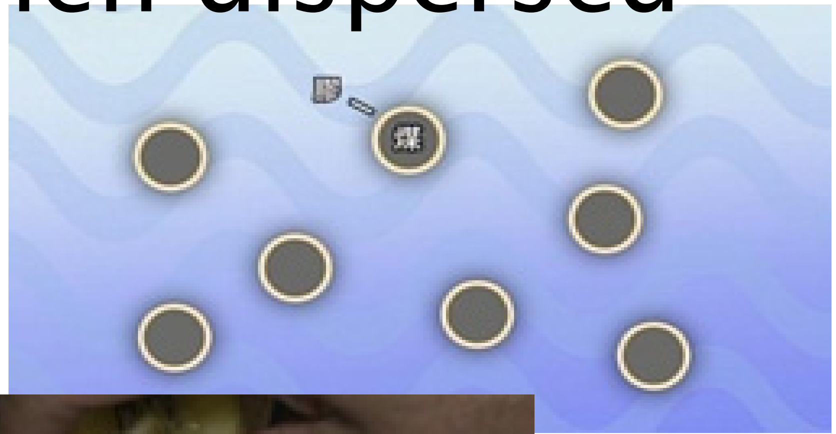

Salad oil

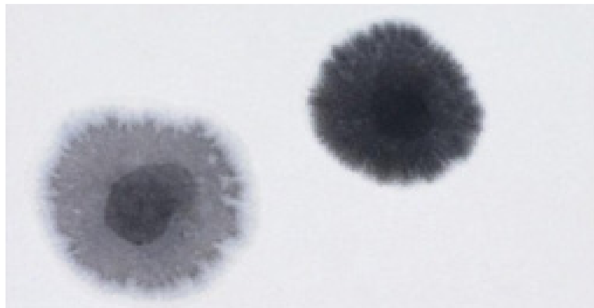

Water
Soap
Salad oil


Salad oil
Water


Without soap
With soap

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





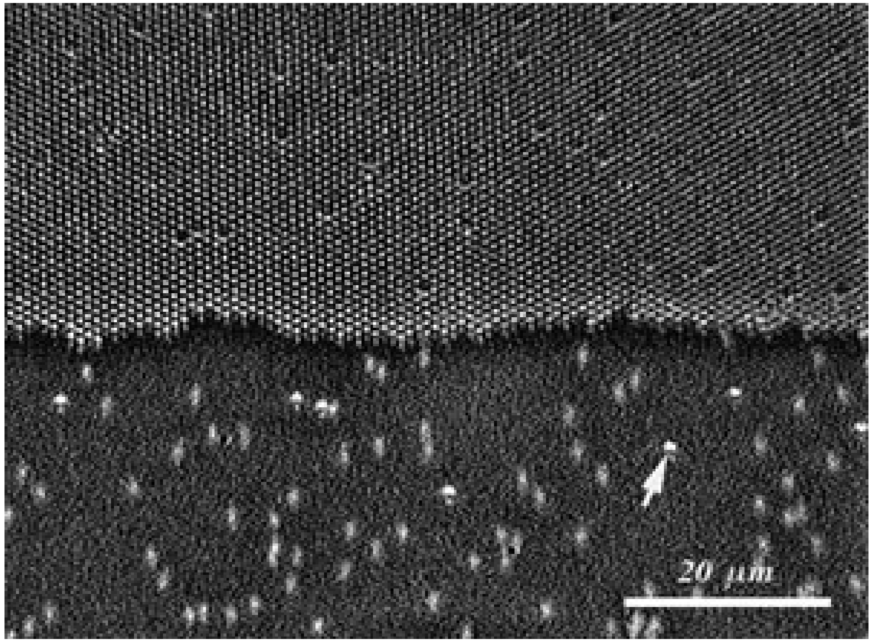
NHK高校講座「芸術（美術Ⅰ／書道Ⅰ）」第12回 漢字の書(2) ～さまざまな表現～

Colloids around us

Beer

beer foam

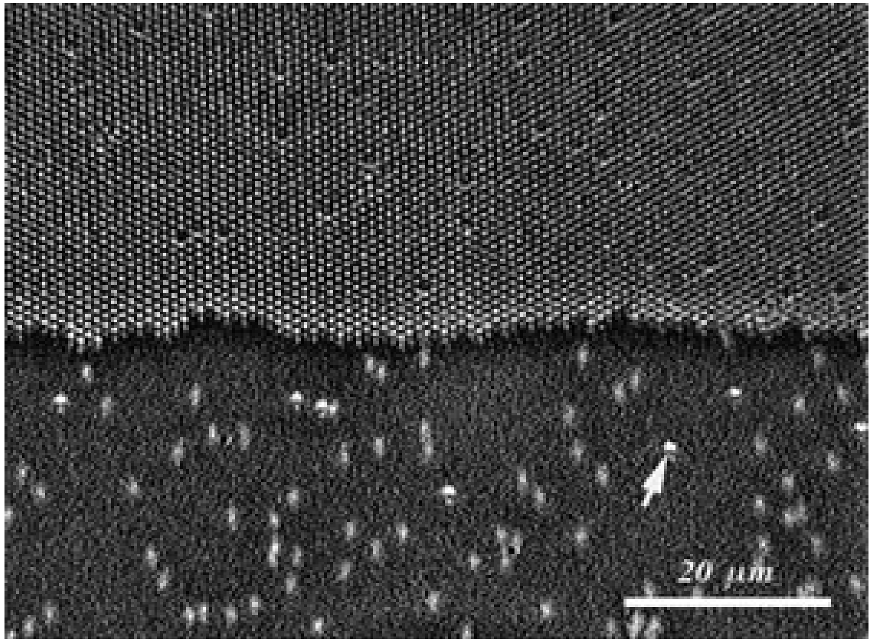
Nagayama Project Beer



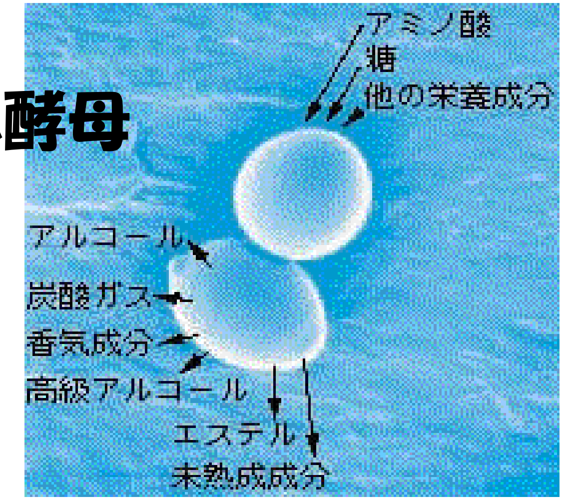
Colloids that are transported from bottom to top by advective accumulation to form a two-dimensional crystal structure. The lower colloid is blurred because it is moving.

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、分散剤的な働きをしている



ビール酵母



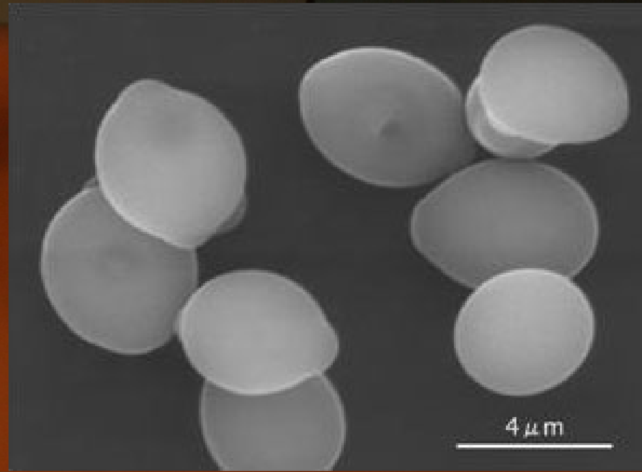
How to pour beer properly

Pour slowly and gently without foaming


サッポロビール
SINCE 1876
NEW
SUNTORY
Homogeneous nucleation:
Bubbles come out of the solution

Heterogeneous nucleation:

Bubbles come out of disposable chopsticks when inserted

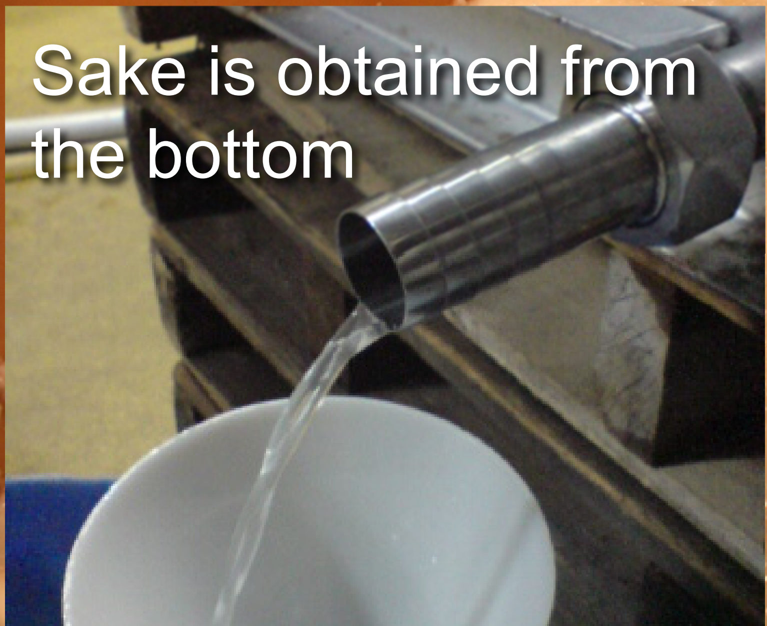


Japanese sake fermentation

The zeta potential of yeast is positively charged.

Go up with negatively charged bubbles along with CO_2 generated by fermentation

Same as top-fermenting yeast in beer



Sake is obtained from the bottom

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

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

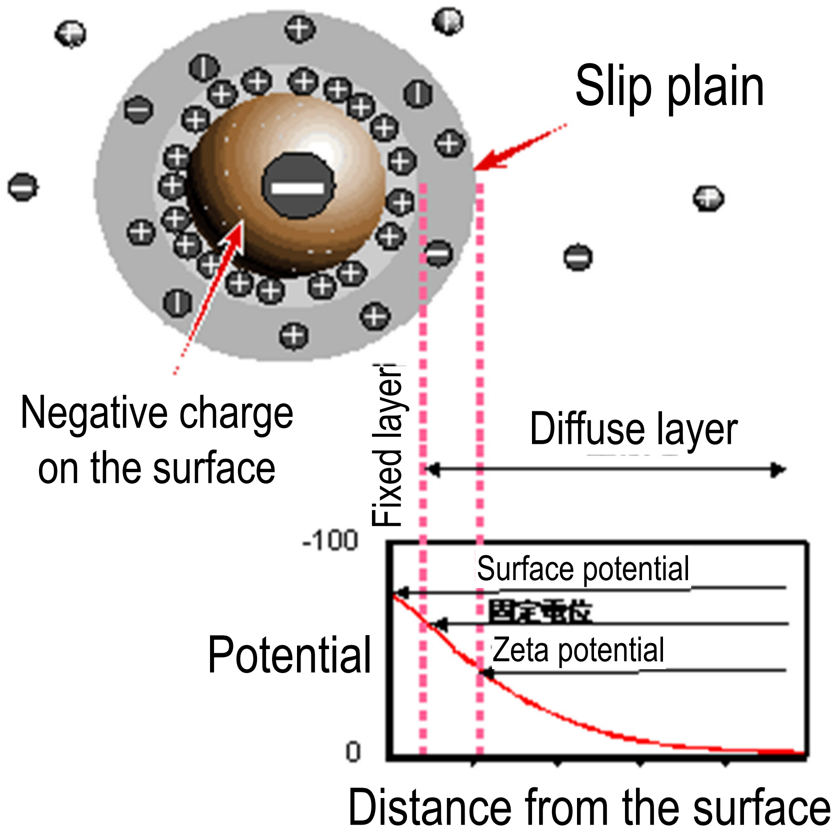
n:粒子数, *d*:粒子径, *m*:反射係数, λ:波長

WHAT IS THE THEORY BEHIND？

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

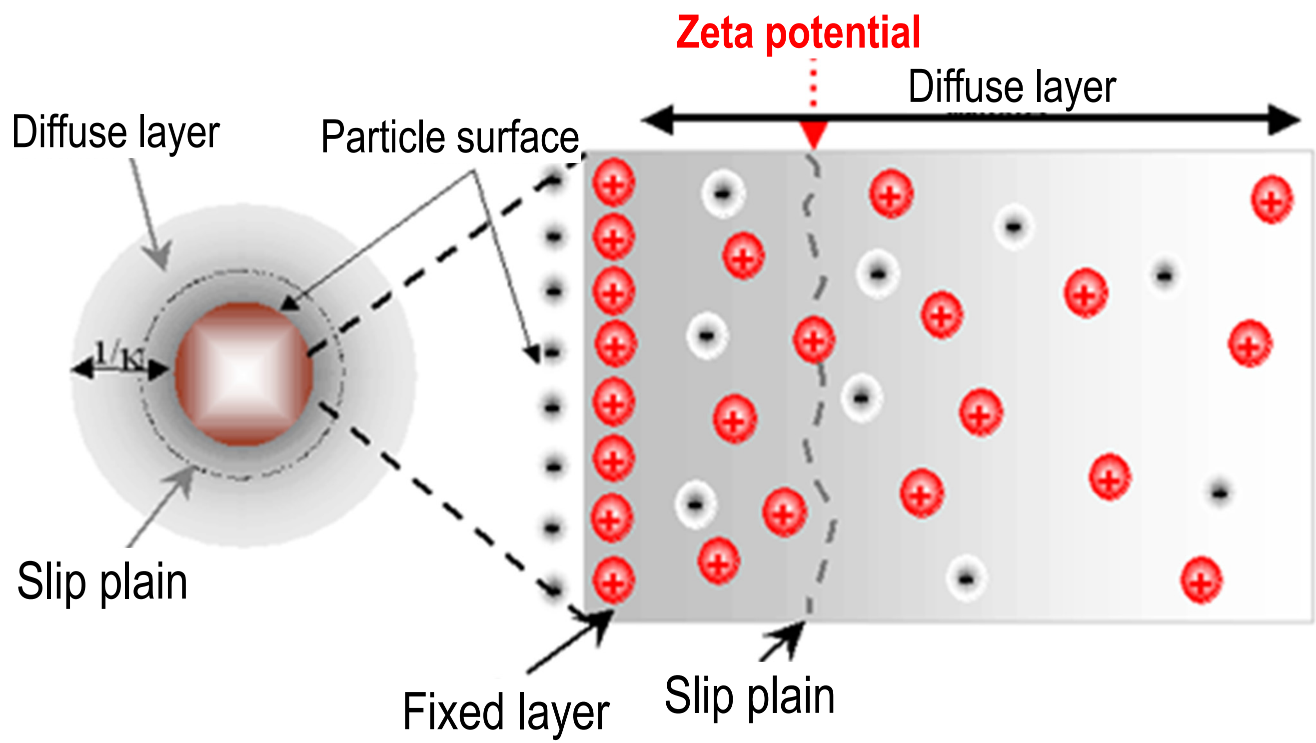
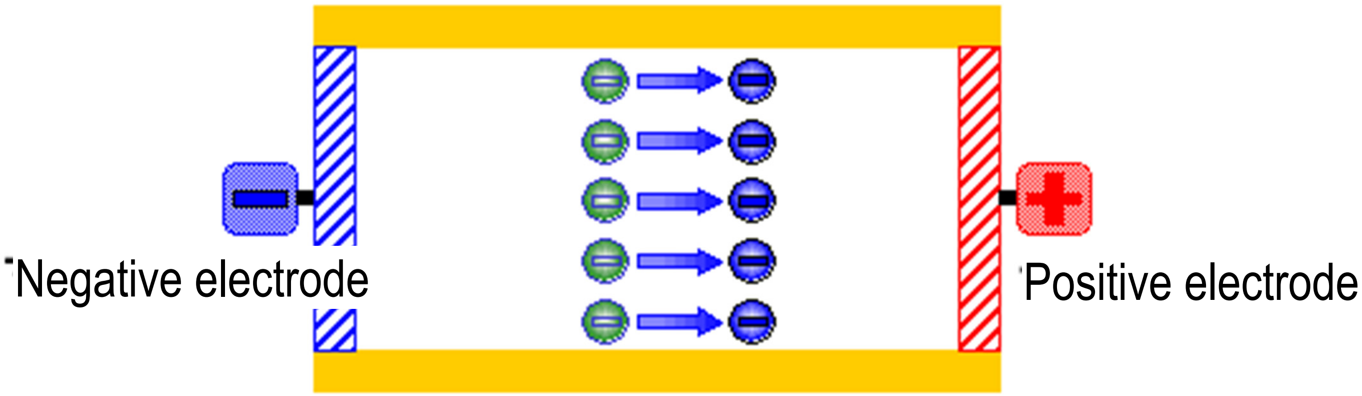
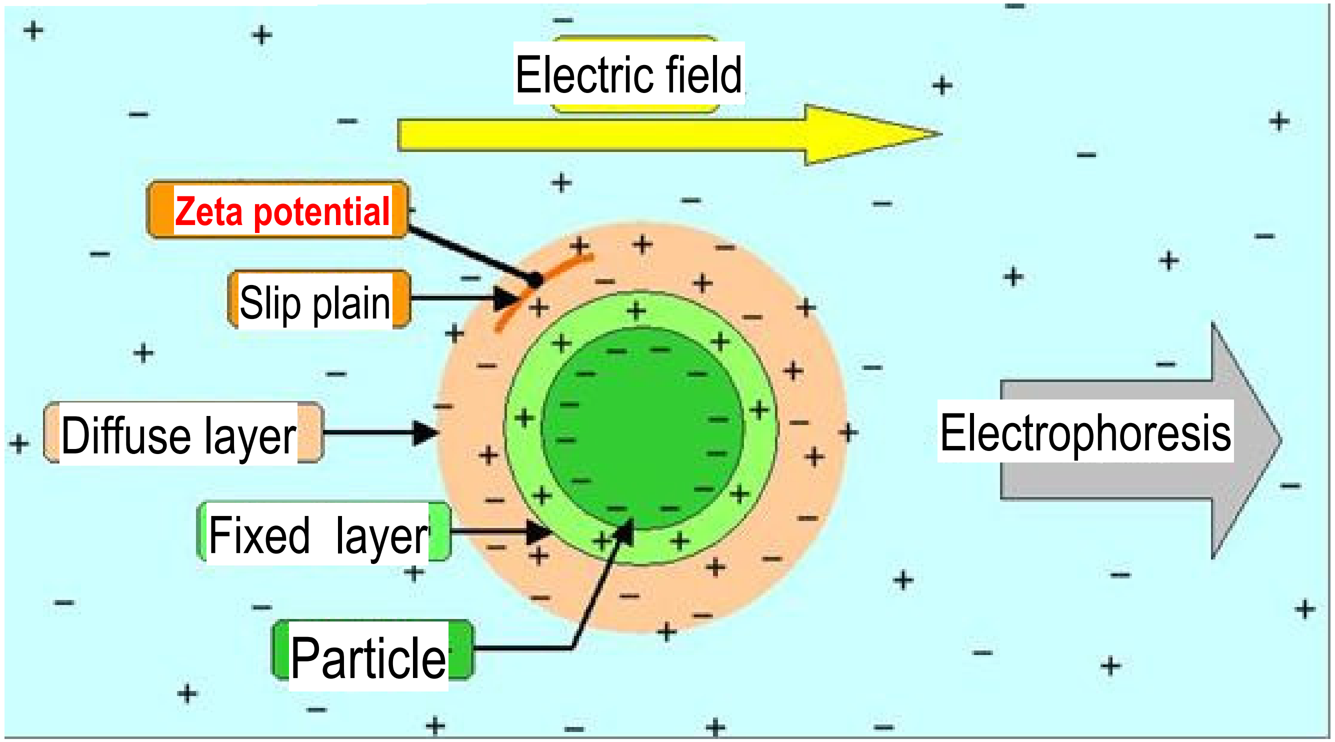


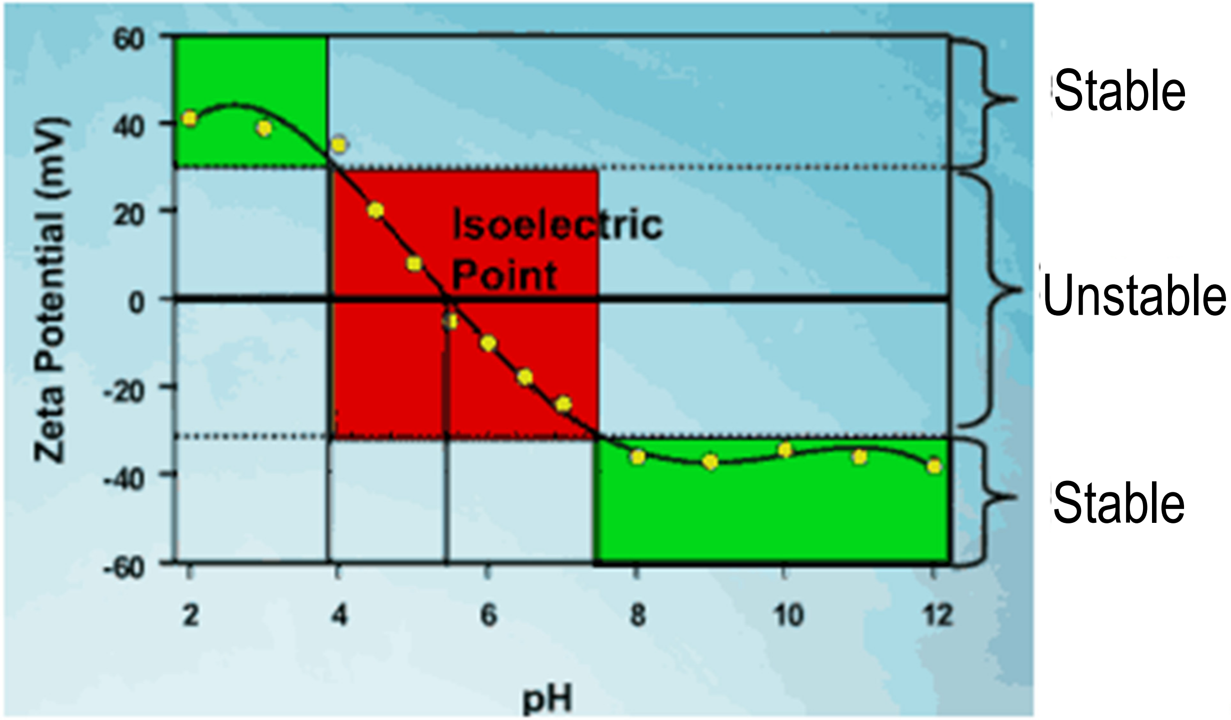
図6 Electrophoresis



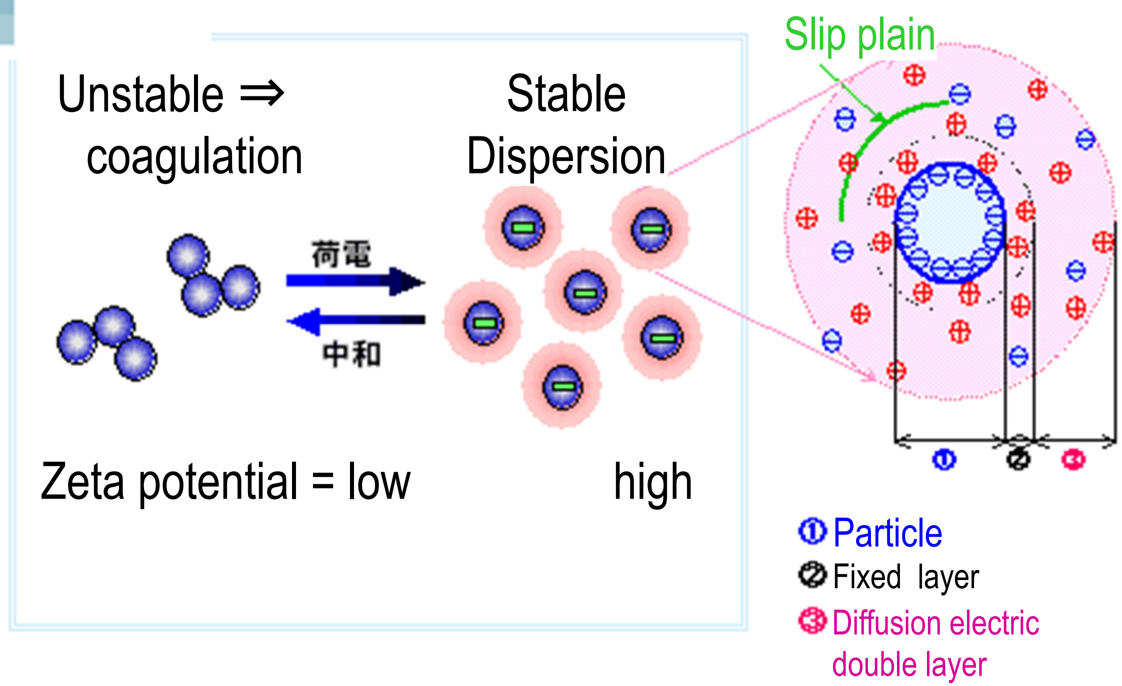
Particles with the same negative charge are 、
moving to the positive electrode.



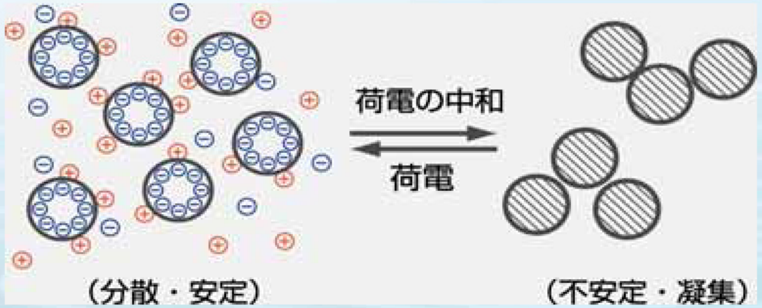
Zeta potential as a function of pH



Zeta potential and dispersion



What can we learn from zeta potential?

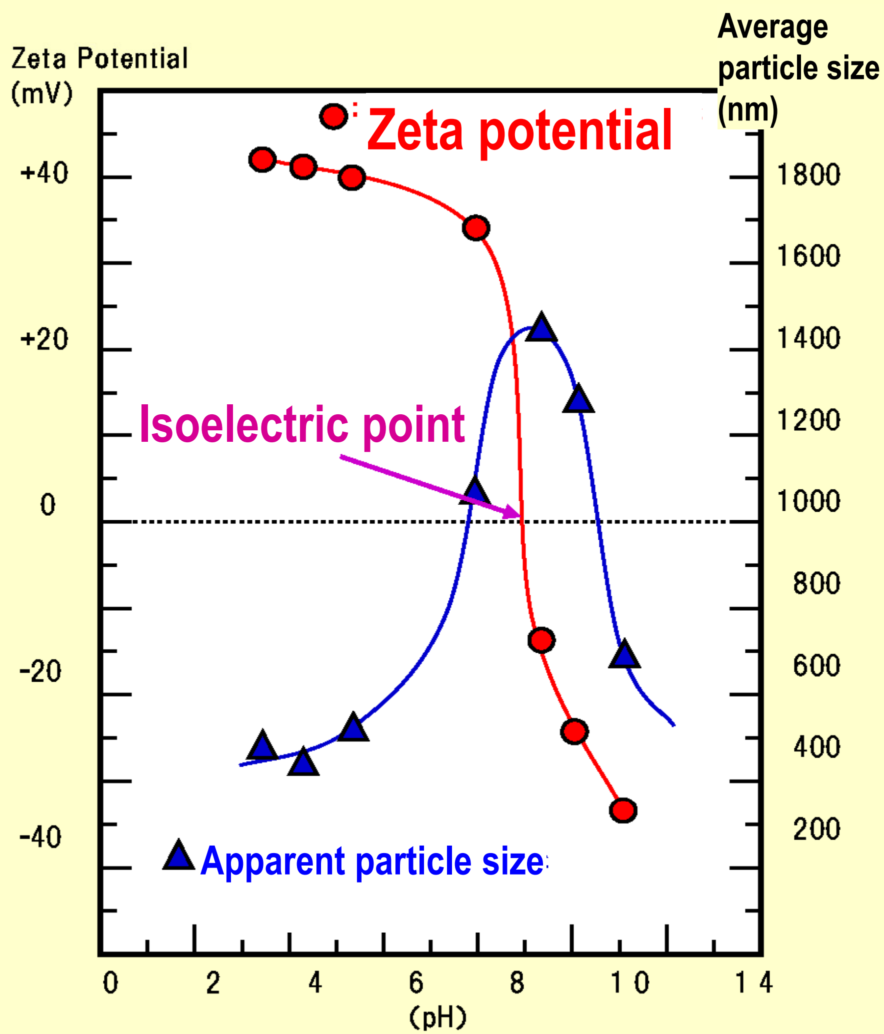


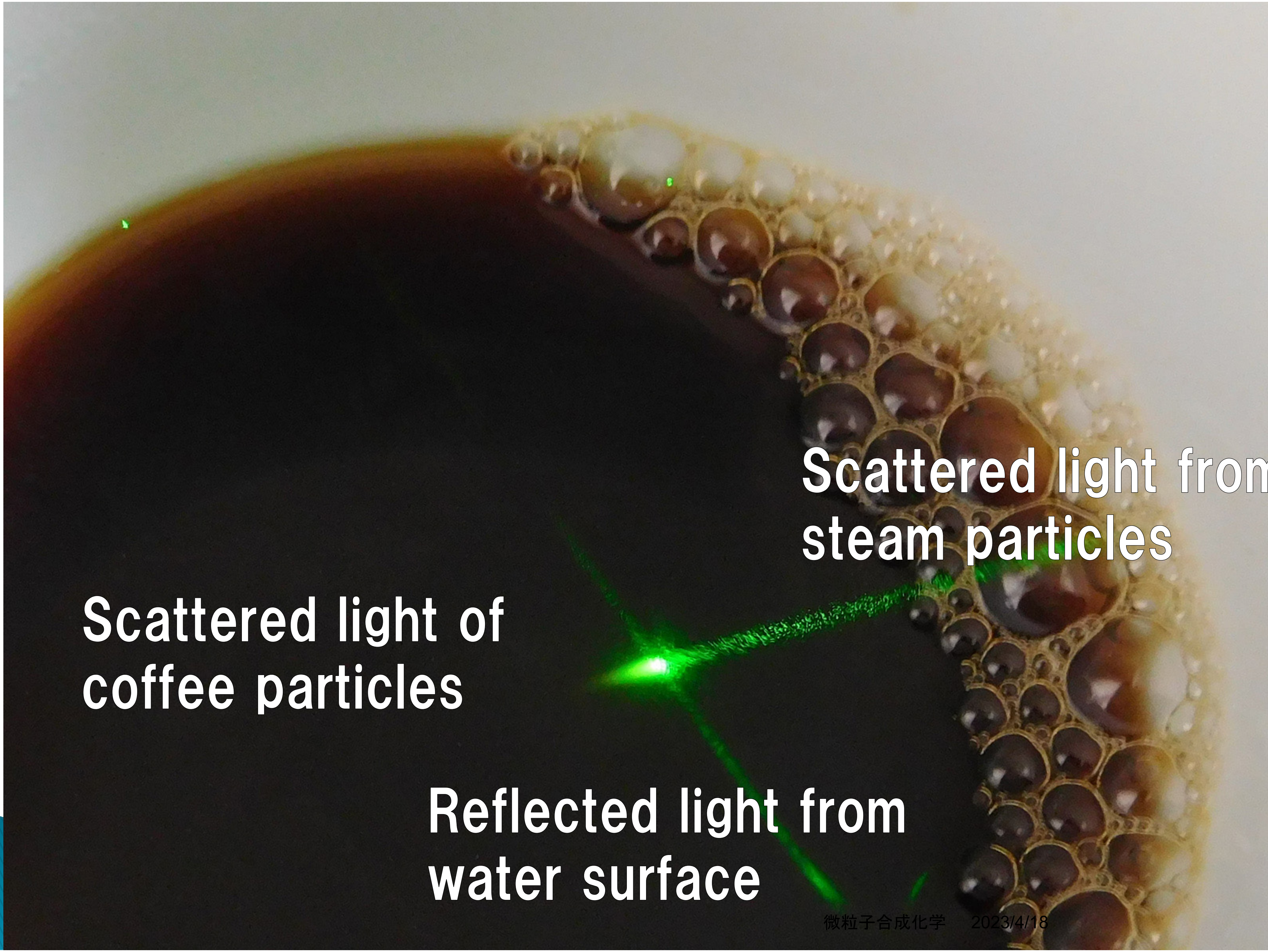
The larger the absolute value of the zeta potential, the better the dispersibility. However, if it is small, it is unstable and tends to aggregate.

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.

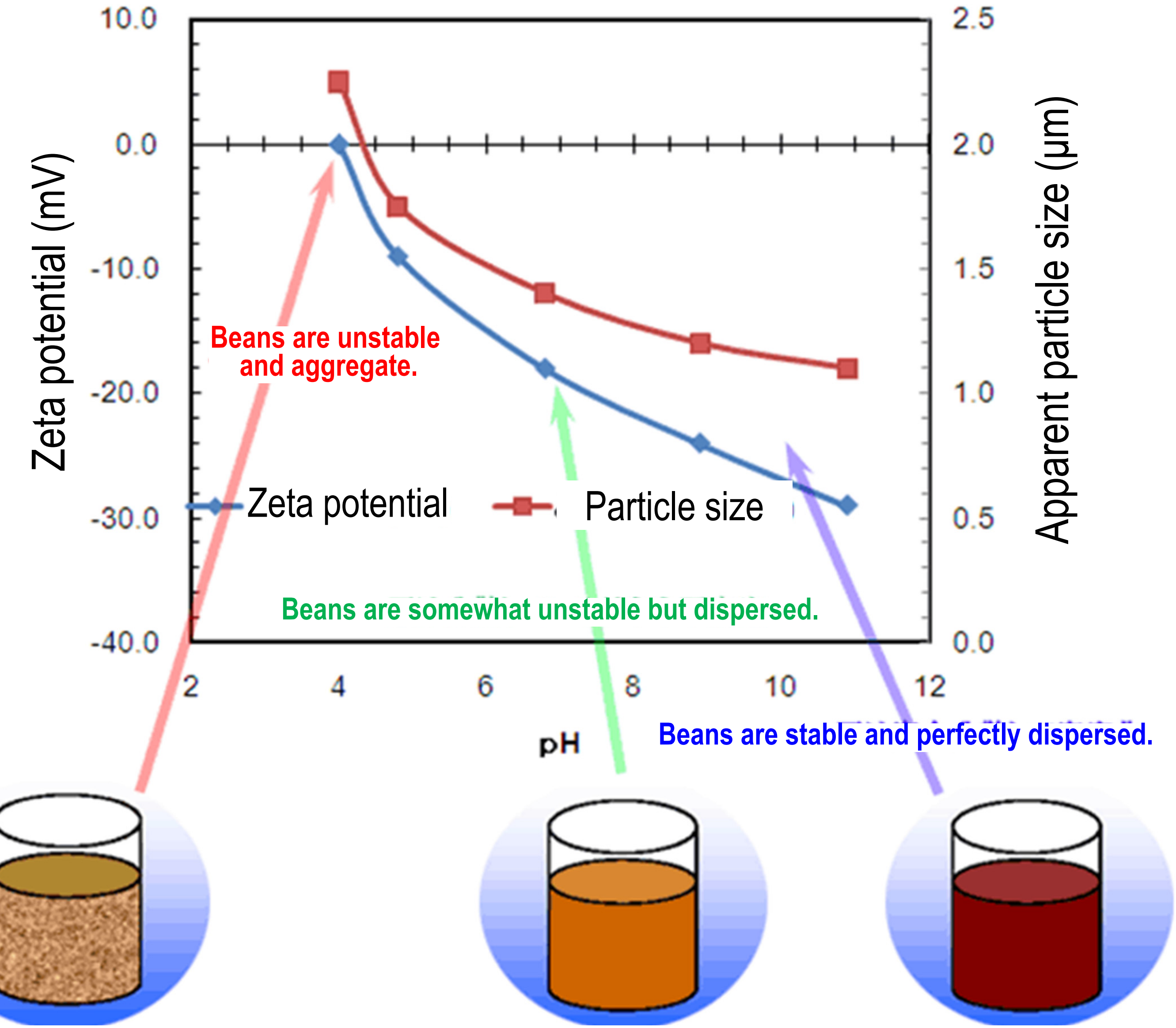
The larger the absolute value of the zeta potential, the better the dispersibility. If it is small, it is unstable and tends to aggregate.



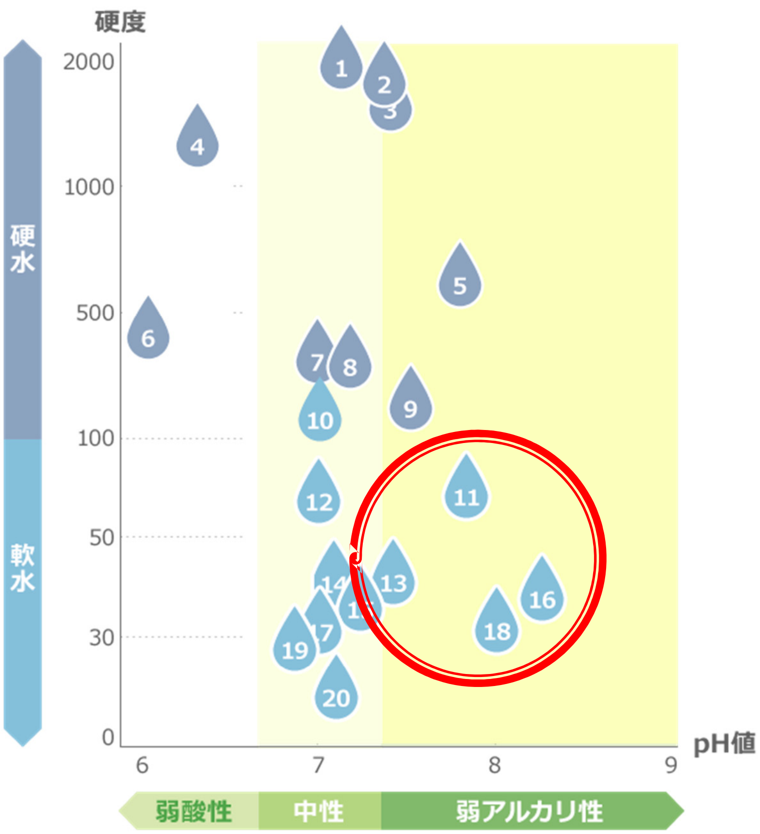

Scattered light from
steam particles
Scattered light of
coffee particles
Reflected light from
water surface

Tea, black tea, and coffee are colloids.

Zeta potential of coffee bean particles



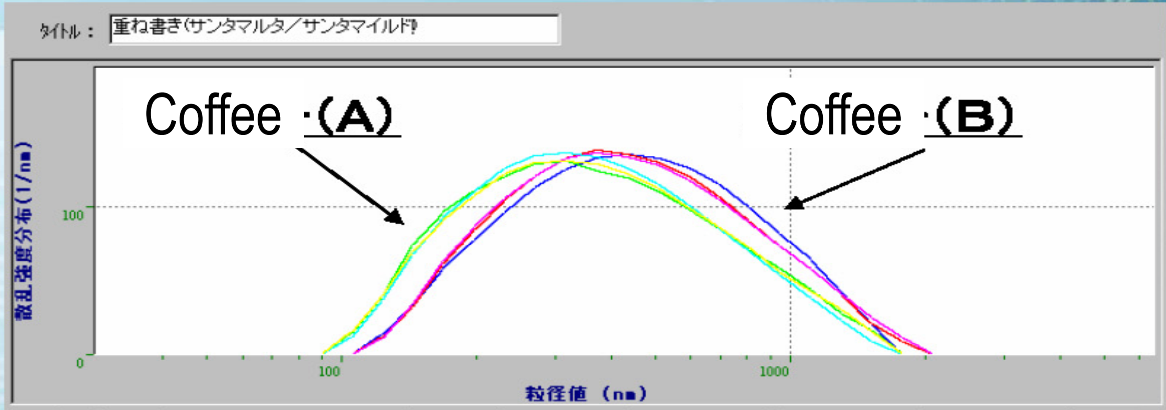
【ミネラルウォーターの比較分布図】



No.	名称	硬度	pH
1	エパー（HePAR）	1,849	7.2
2	クールマイヨー	1,612	7.4
3	コントレックス（Contrex）	1,468	7.45
4	ゲロルシュタイナー	1,302	6.4
5	サンペレグリノ	674	7.8
6	ペリエ（perrier）	417	6.0
7	ヴィッテル（Vittel）	315	7.0
8	エビアン（evian）	304	7.2
9	アイランドチリ（Island Chill）	117	7.5
10	フィジーウォーター	105	7.0
11	富士山麓のおいしい天然水	63	7.8
12	ボルビック（Volvic）	60	7.0
13	クリスタルガイザー	38	7.4
14	森の水だより	34.6	7.1
15	おいしい水　六甲	32	7.2
16	日田天領水	32	8.3
17	南アルプスの天然水	30	7.0
18	富士山のバナジウム天然水	29	8.0
19	い・ろ・は・す	27.7	6.9
20	熊野古道水	10	7.1

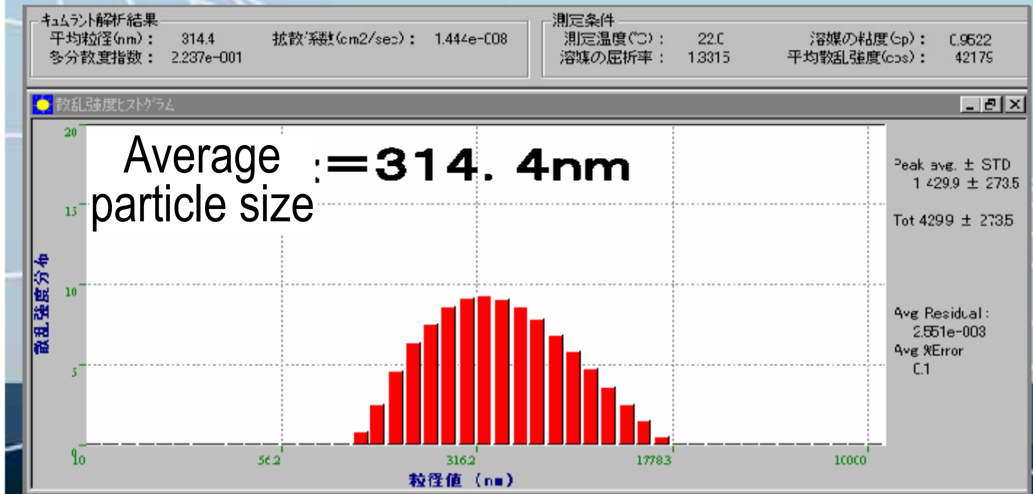
Coffee drinks

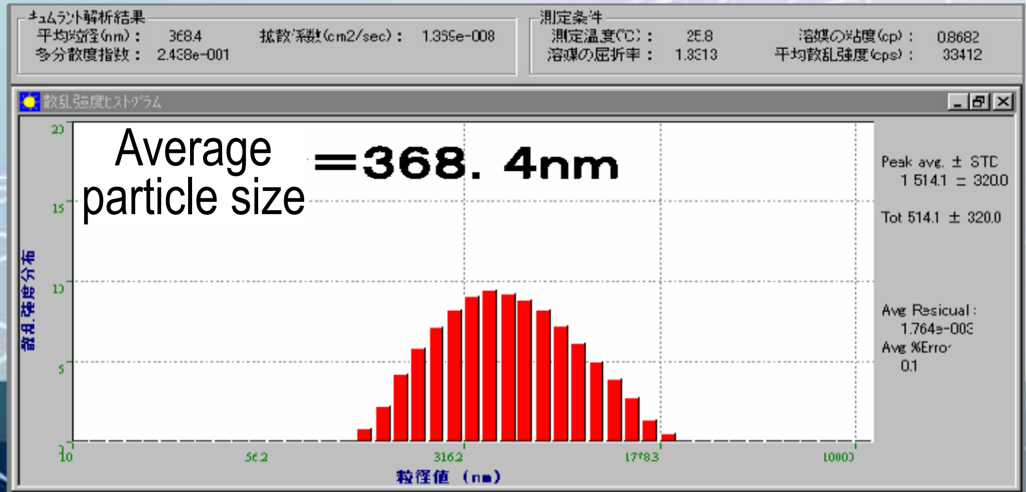
A社
: Coffee ·(A)

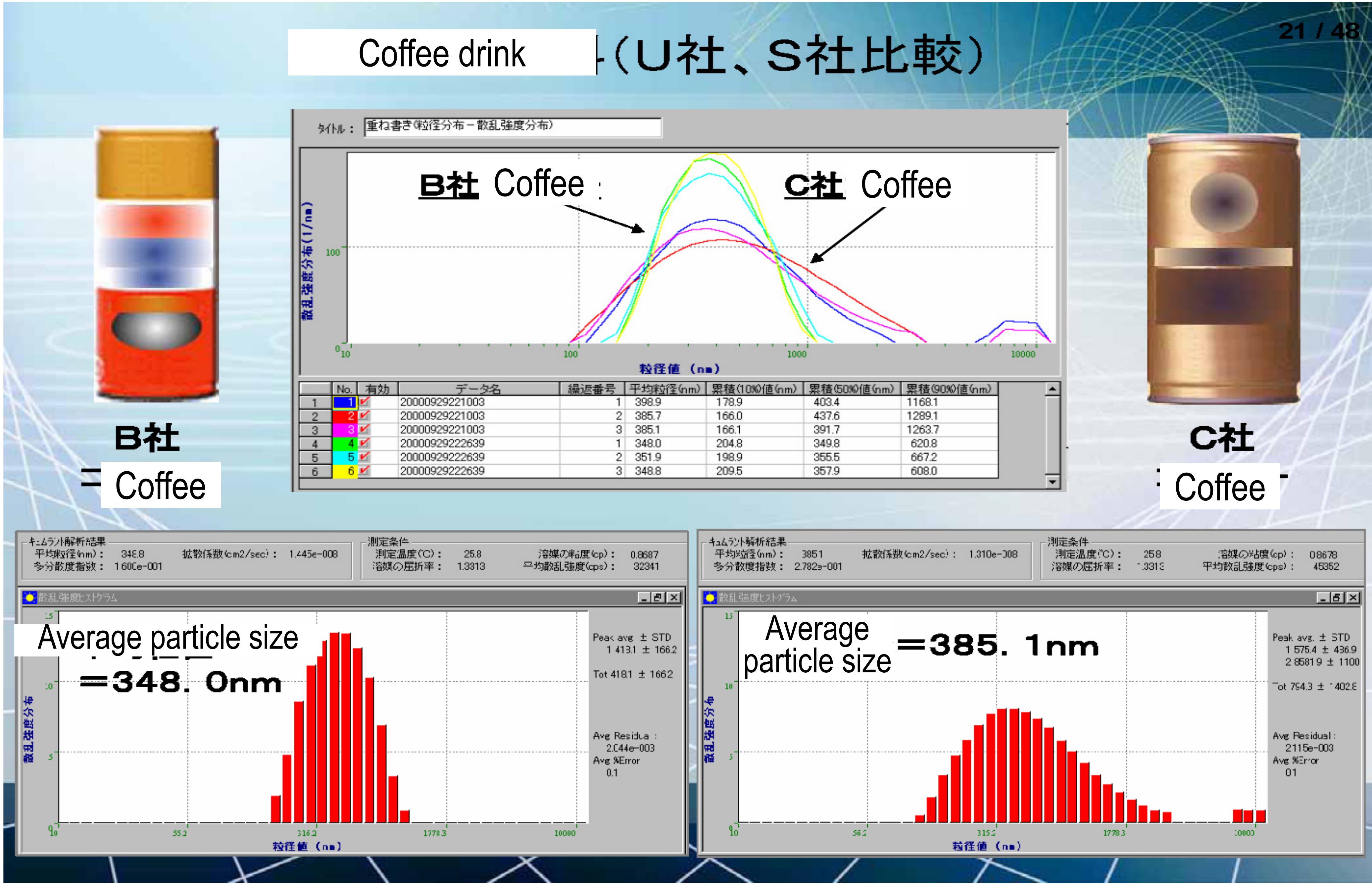


	No.	有効	データ名	繰返番号	平均粒径(nm)	累積(10%値(nm)	累積(50%値(nm)	累積(90%値(nm)
1	1	✓	20000929215554	1	373.3	183.5	407.4	912.2
2	2	✓	20000929215554	2	368.4	181.8	390.2	904.9
3	3	✓	20000929215554	3	371.5	180.8	389.2	916.8
4	4	✓	20000928160027	1	312.6	148.5	322.8	802.9
5	5	✓	20000928160027	2	314.4	151.7	322.2	762.7
6	6	✓	20000928160027	3	316.9	149.7	326.7	800.8

A社
: Coffee ·(B)





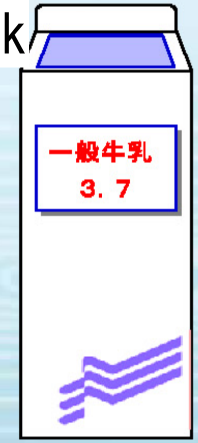


	No.	有効	データ名	繰返番号	平均粒径(nm)	累積(10%)値(nm)	累積(50%)値(nm)	累積(90%)値(nm)
1	1	✔	20000929221003	1	398.9	178.9	403.4	1168.1
2	2	✔	20000929221003	2	385.7	166.0	437.6	1289.1
3	3	✔	20000929221003	3	385.1	166.1	391.7	1263.7
4	4	✔	20000929222639	1	348.0	204.8	349.8	620.8
5	5	✔	20000929222639	2	351.9	198.9	355.5	667.2
6	6	✔	20000929222639	3	348.8	209.5	357.9	608.0

Comparison of particle size distribution of various types of milk

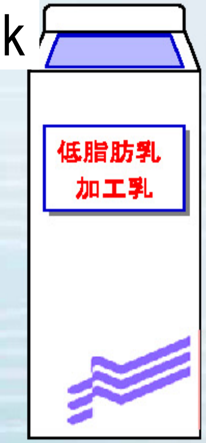
① Common milk

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。



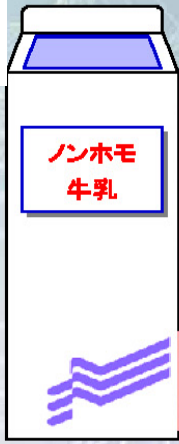
② Low fat milk

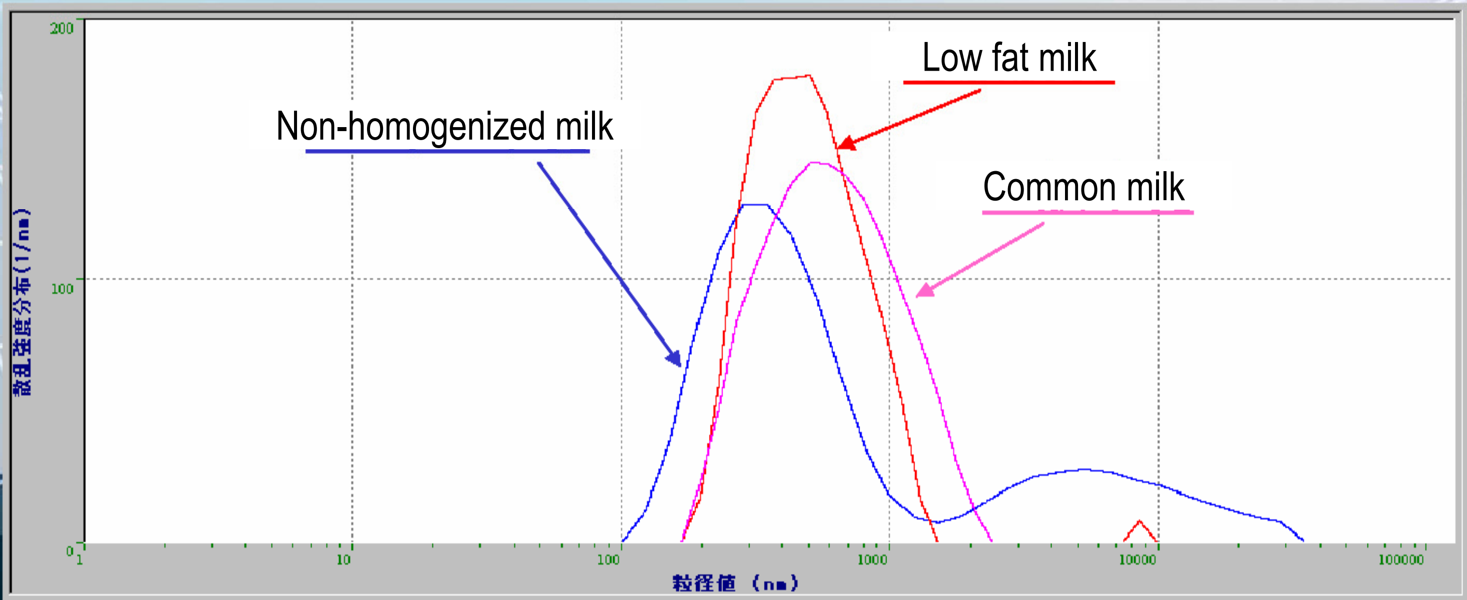
脱脂粉乳を還元して牛乳と同じように加工したもの。脂肪分が少ない。



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。

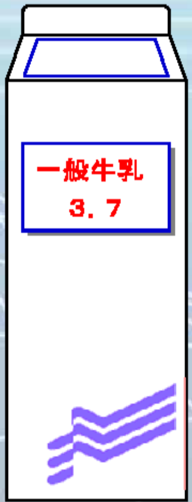


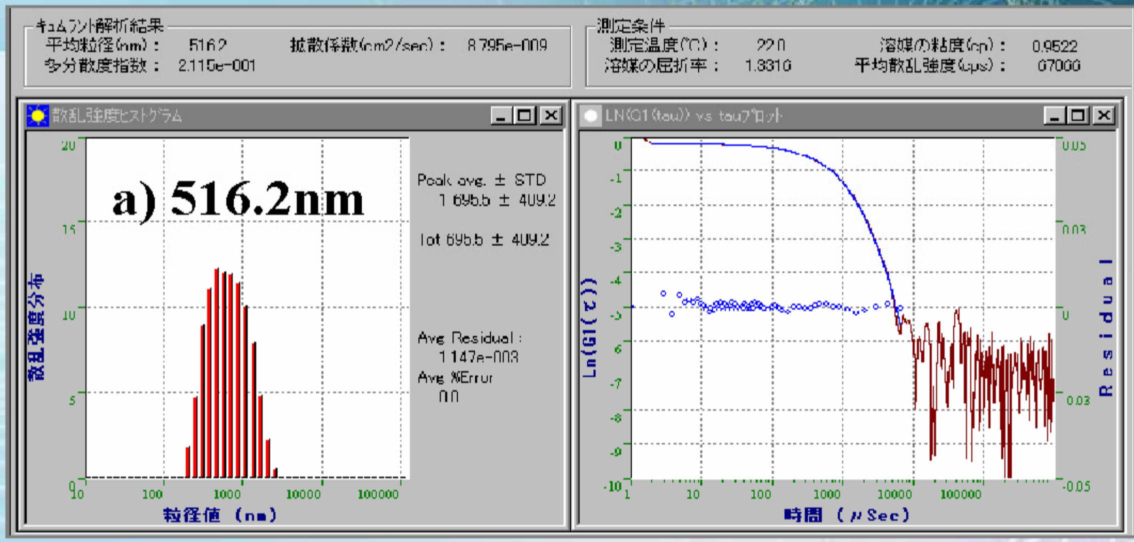


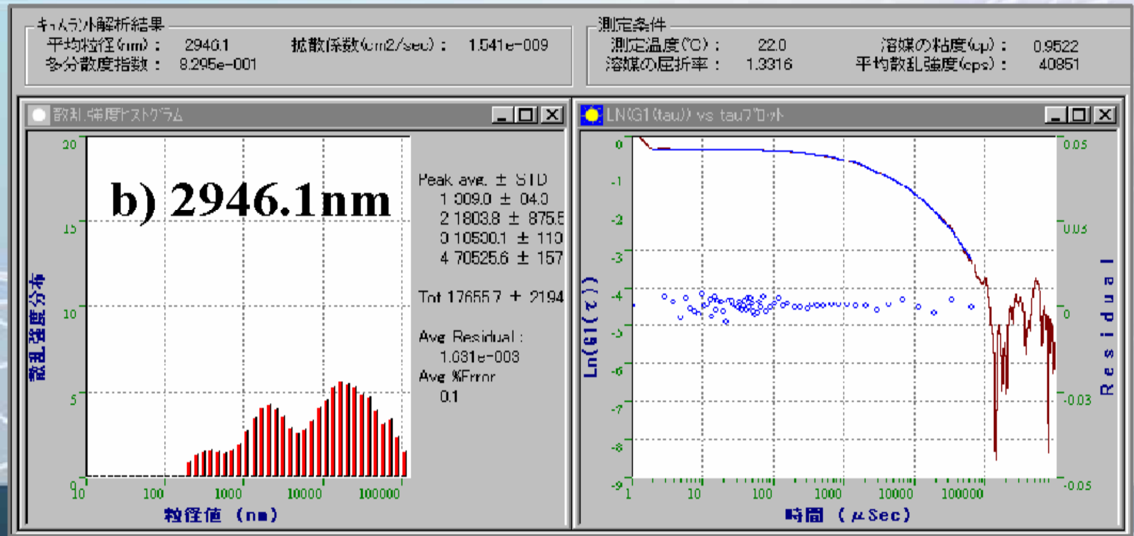
Changes in creaming of regular milk

a) Fresh regular milk

b) Milk left indoors was changed as creaming.

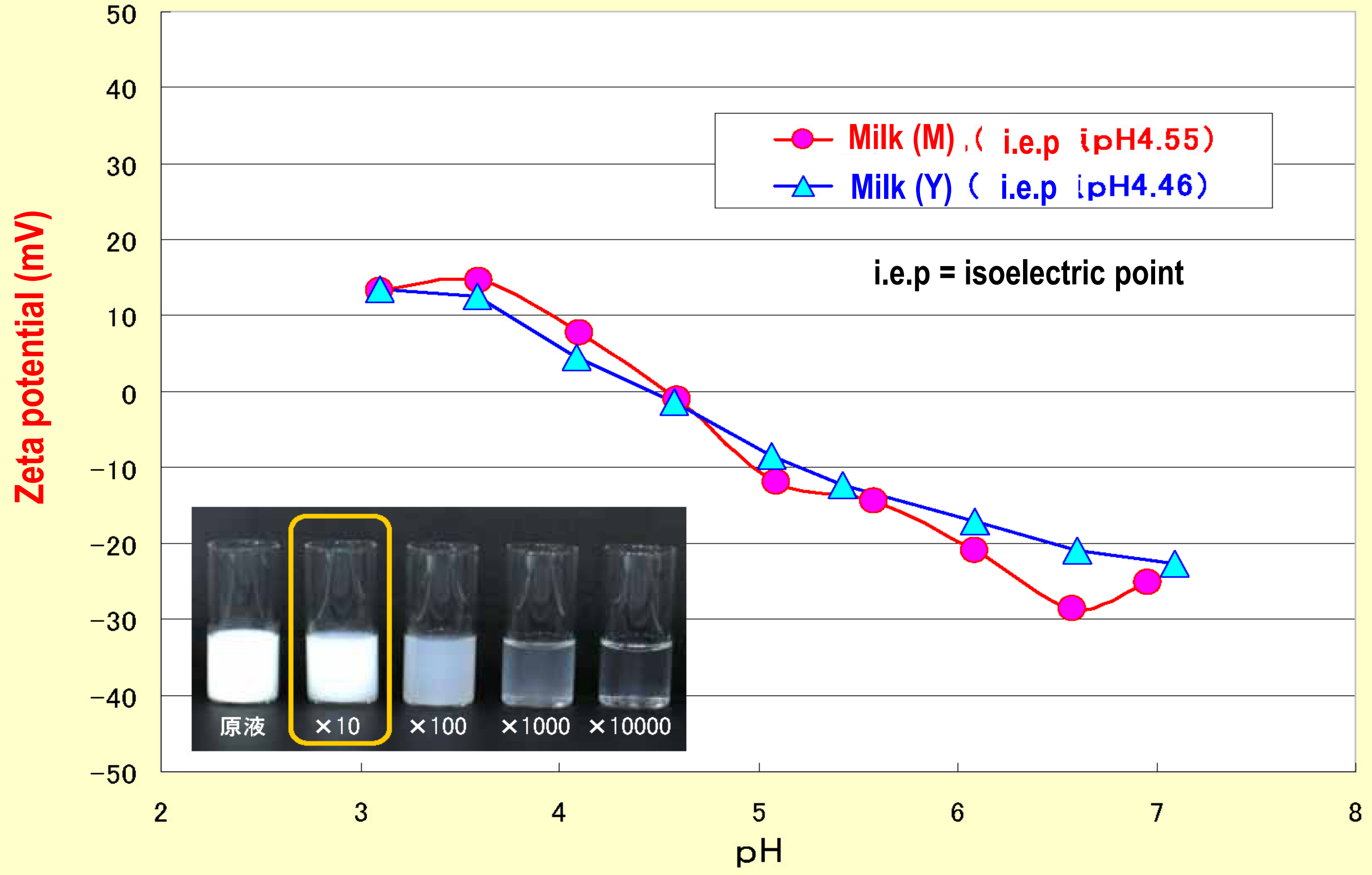




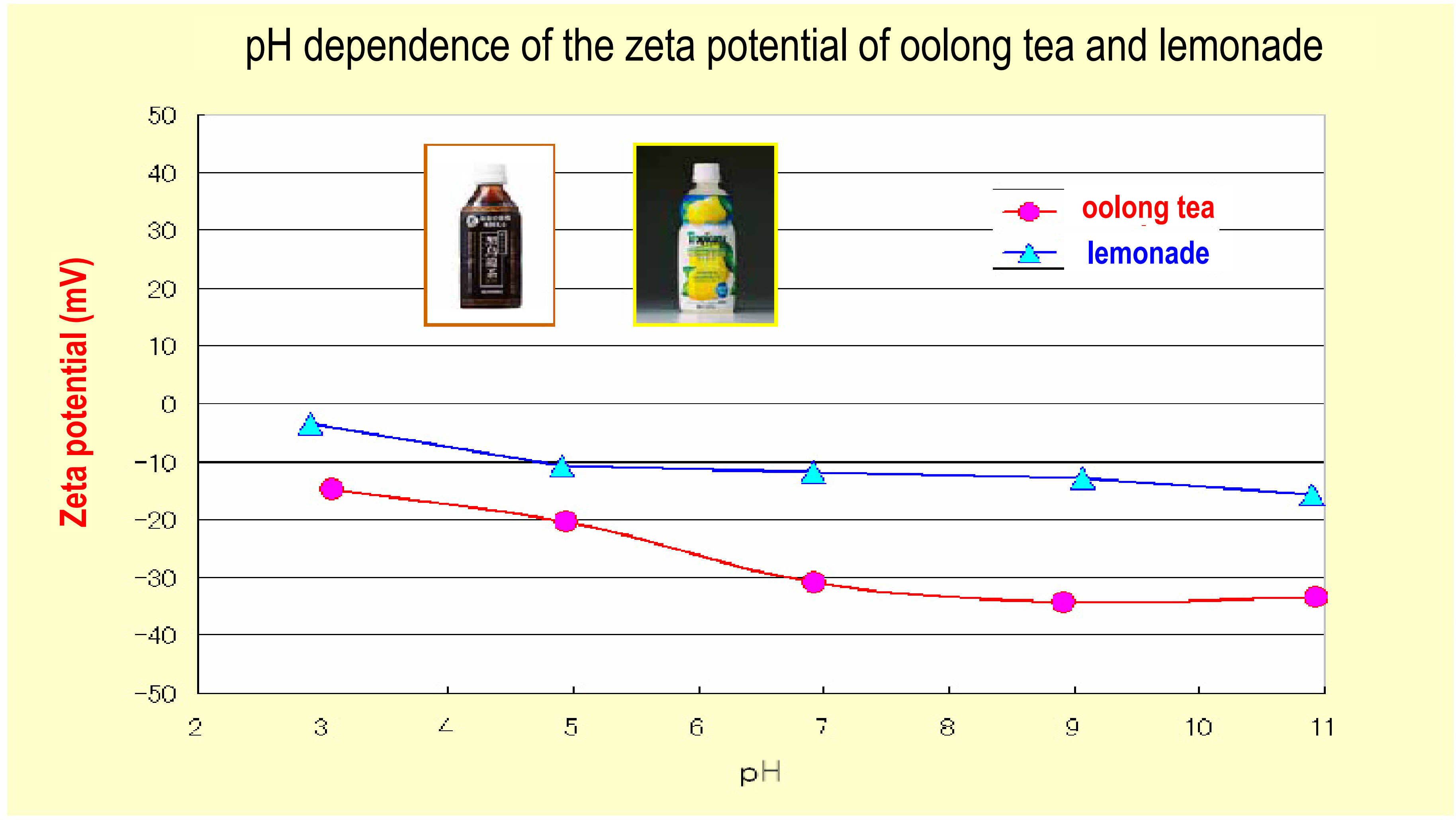


pH titration of 10-fold diluted milk

pH dependence of the zeta potential of milk

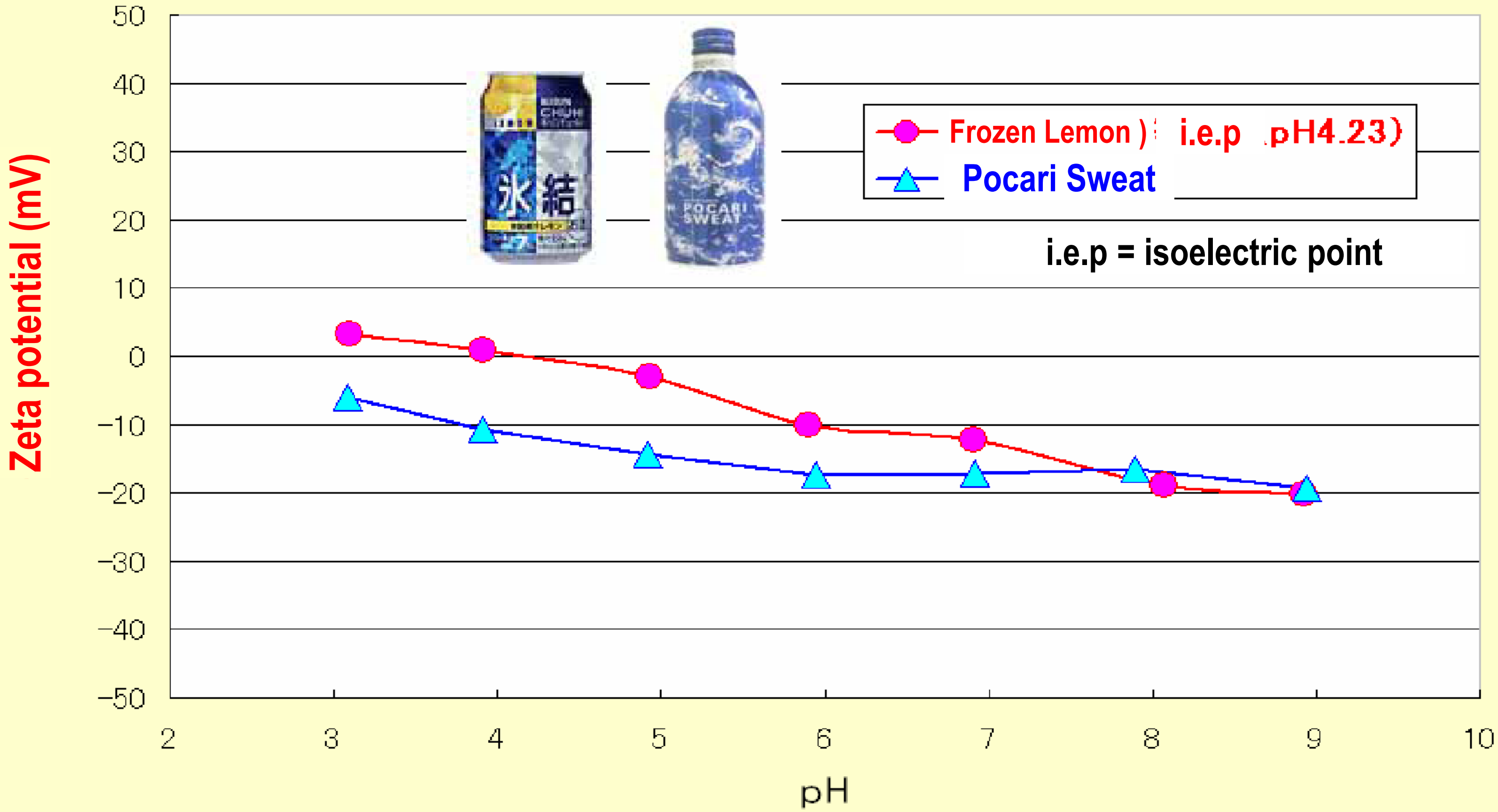


pH titration of oolong tea and lemonade

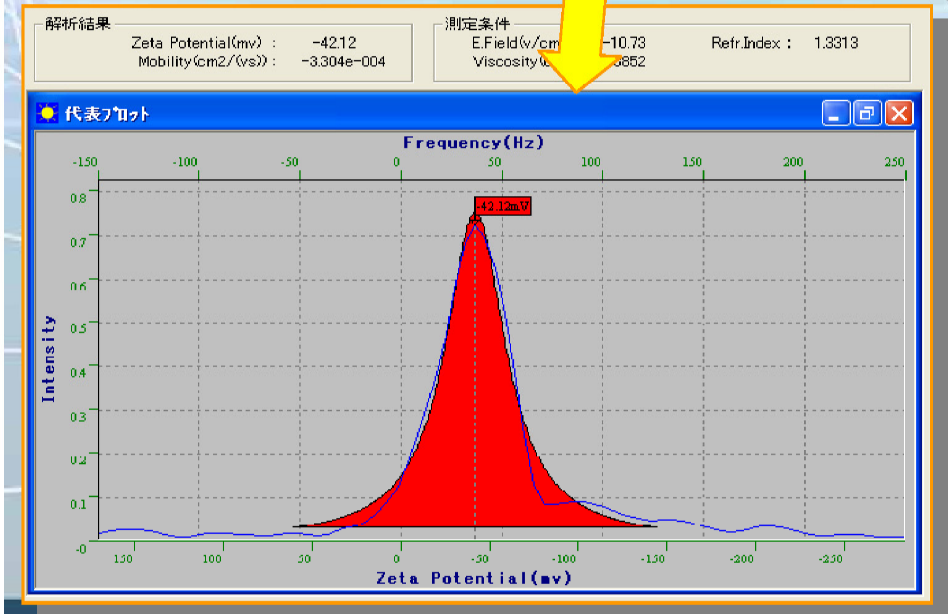


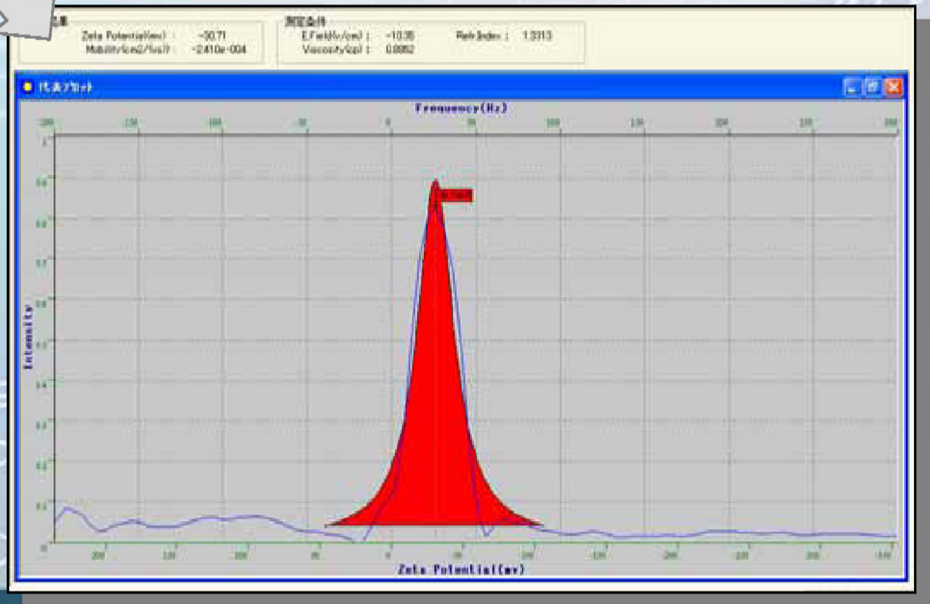
pH titration of Frozen Lemon and Pocari Sweat

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 blak 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.

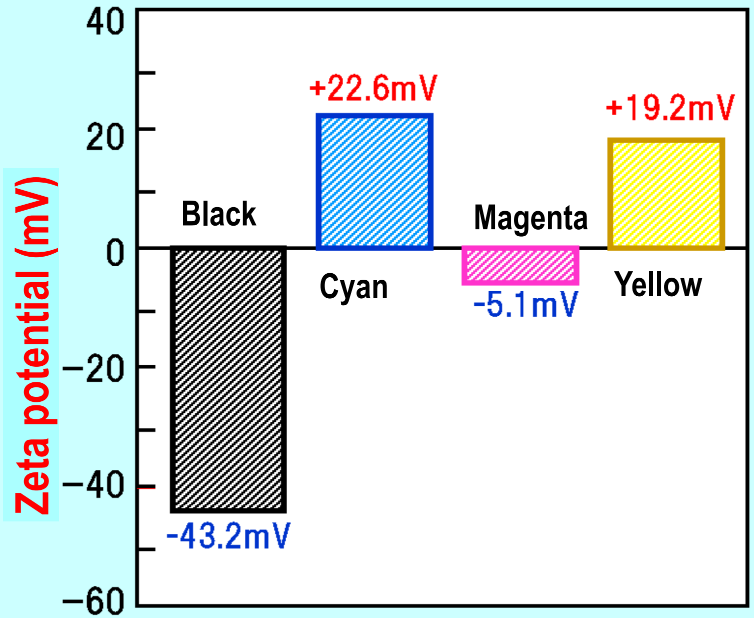
2)It is important to keep the dispersion state.

↓

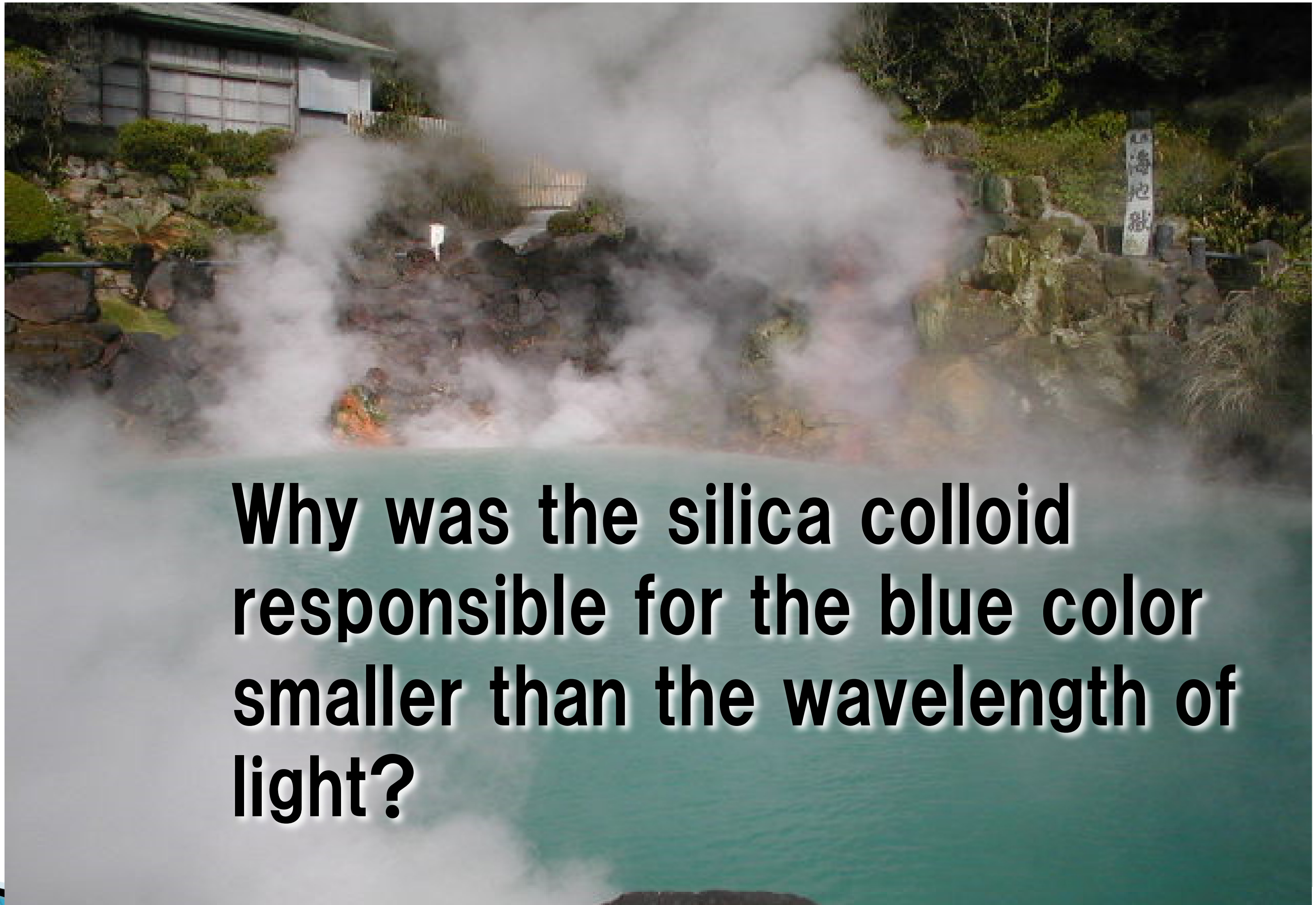
If it aggregates and hardens, it becomes impossible to ink-jet. This leads to uneven coloring.

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?

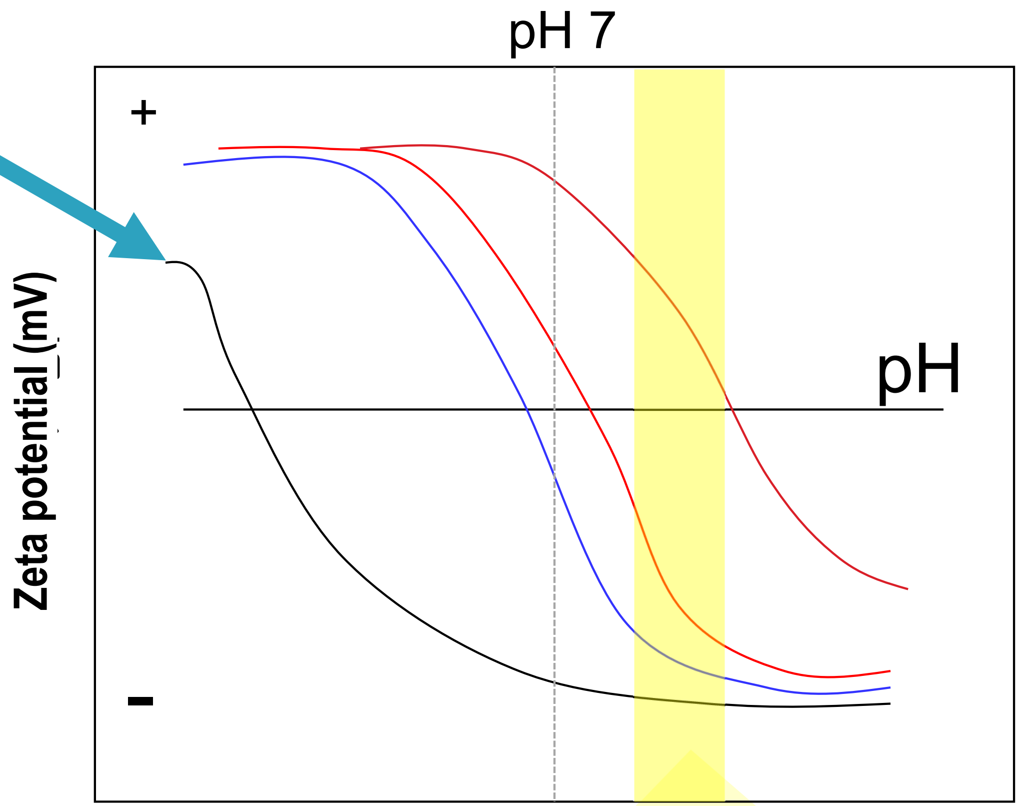
Why were the silica particles smaller than the wavelength?
That's because it didn't aggregate and was stably dispersed in water!

Isoelectric point of oxides

depending on crystal plane, structure, etc.

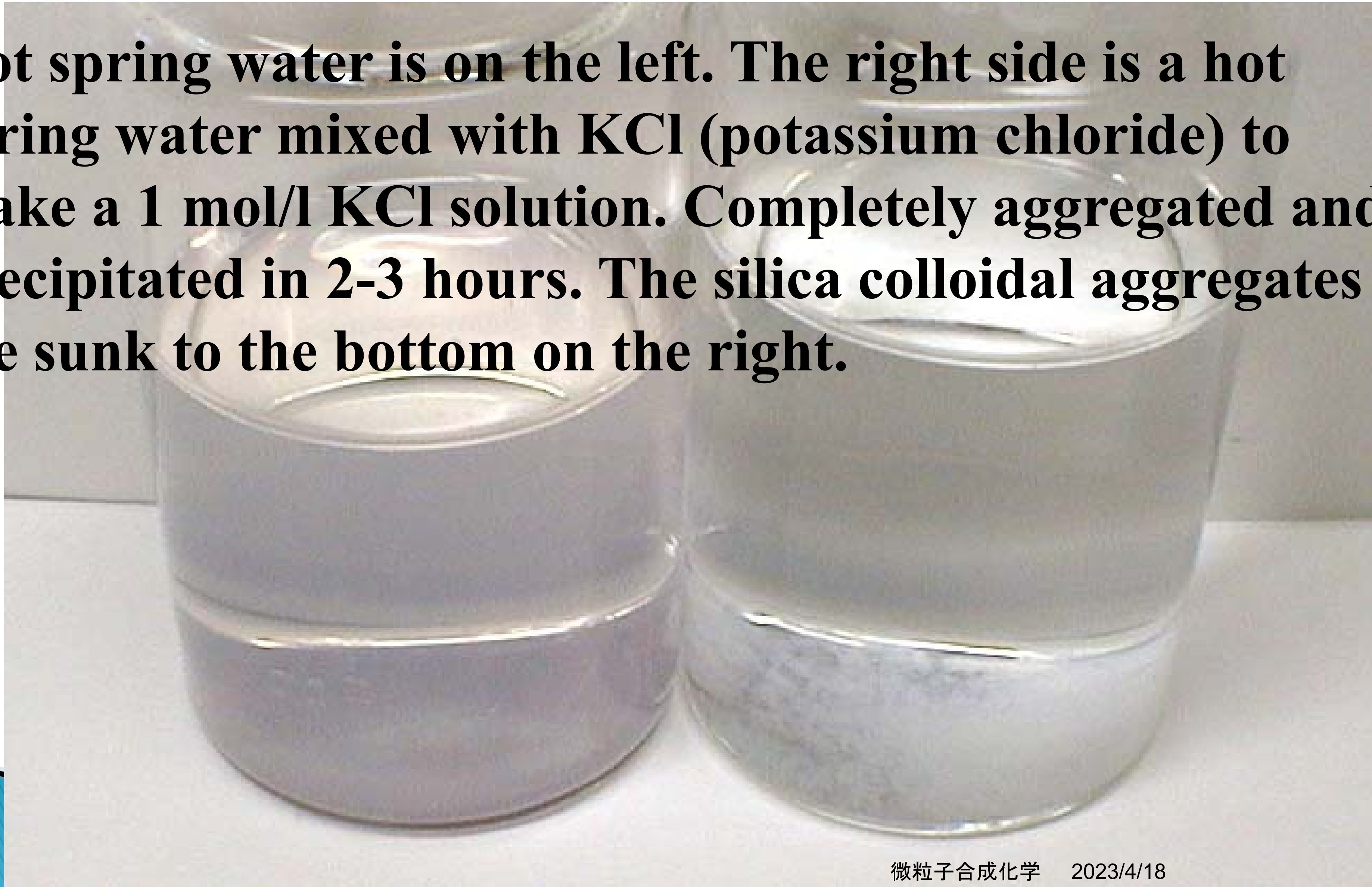
- SiO_2 2〜3
- TiO_2 6〜8
- Fe_2O_3 6〜8
- ZrO_2 7〜9
- Al_2O_3 7〜9
- MgO 9〜11

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



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.

嬉野温泉環境協会のWeb http://www.spa-u.net/shopping.html?cate=3

Ureshino specialty! Hot spring tofu

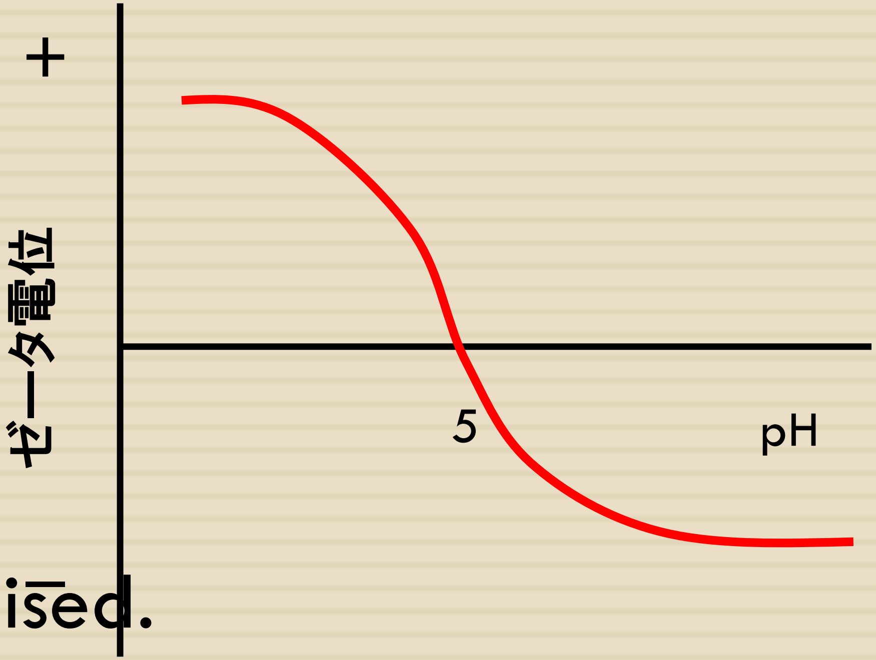
The secret of Ureshino Onsen tofu

- 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.

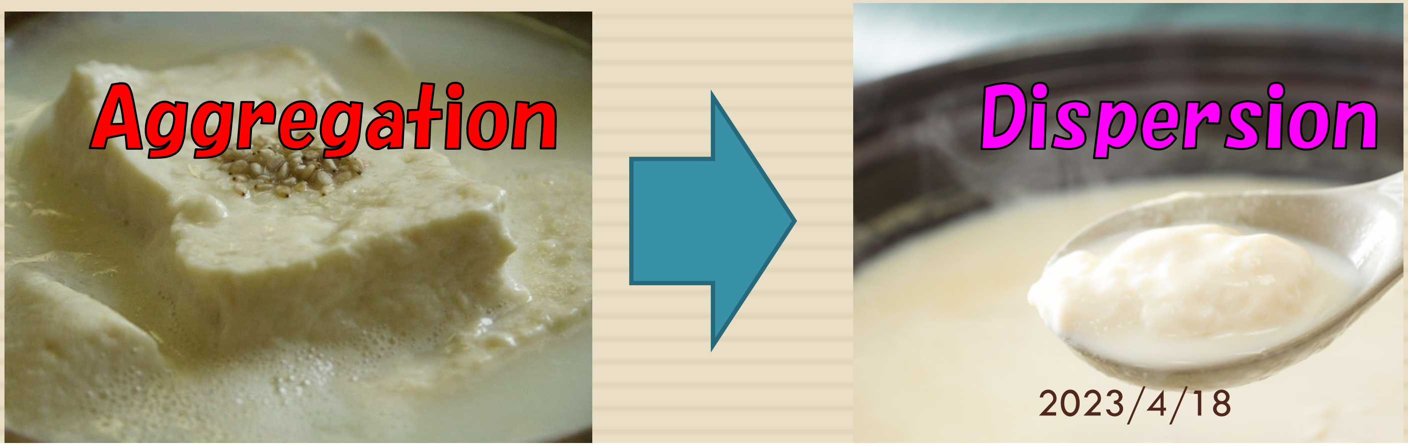
- The main ingredient of nigari, which is used to harden tofu, is magnesium chloride with a small amount of magnesium sulfate.
- Magnesium and calcium dissolve as divalent cations.
- The sulfate ion of magnesium sulfate is a divalent anion.
- In general, when substances aggregate, there is a certain 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″.



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.