Synthetic Chemistry of Fine Particles, 2023

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

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?

Colloids

フリー百科事典『ウィキペディア（Wikipedia）』によると･･･

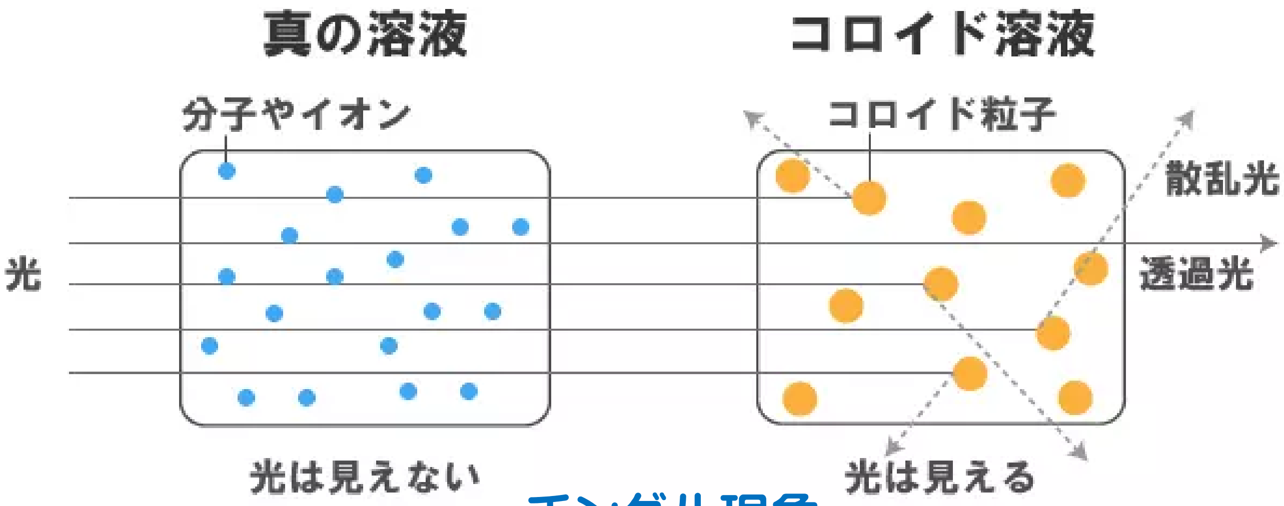
- Colloids exhibit properties common to dispersed systems. For example, colloids develop colors and scatter light by the Tyndall phenomenon.
- Especially when the dispersion medium is a liquid, it is also called a colloidal solution. Specific examples include foams, emulsions, gels, suspensions, and the like.
- Colloids formed from two permanent phases in this way are also called phase colloids. It is used in contrast to molecular colloids, in which the macromolecules themselves become the dispersed phase and are permanently dispersed in the dispersion medium of another phase.

Colloids

フリー百科事典『ウィキペディア（Wikipedia）』によると・・・

- Butter, milk, cream, fog, smog, smoke, asphalt, ink, paint, glue and sea foam are colloids.
- The field was founded by Scottish chemist Thomas Graham in 1861 and is called colloid chemistry. Today, it is developed as surface chemistry.

Yellow means wrong



チンダル現象

Colloids

フリー百科事典『ウィキペディア（Wikipedia）』によると･･･

- In general, dispersoid colloidal particles universally possess interparticle van der Waals attraction, which is the sum of intermolecular forces, synonymous with surface tension. On the other hand, a potential difference exists on the surface of the dispersoid particles due to the difference in composition and polarity of the solvent, and a diffused electric double layer is formed by counterions having the opposite sign to the surface potential. Particles of the same type have the same type of counterion bilayer, so when the particles approach each other, the bilayers overlap, and the entropy effect derived from ion diffusion generates an osmotic repulsive force, preventing particle aggregation and stabilizing the dispersion system. （DLVO theory）。

Colloids

フリー百科事典『ウィキペディア（Wikipedia）』によると･･･

- According to the DLVO theory, when an ionic substance is added to the dispersion system, the ion concentration in the bulk solvent increases, and the ion concentration in the electric double layer decreases (closer to the bulk solvent), resulting in an osmotic pressure (repulsive force) is weakened, and the cohesive force due to the van der Waals force between particles is predominantly expressed. The resulting aggregates are also called coagulations. In general, the stability of colloidal dispersions increases with increasing temperature. As is clear from the definition of osmotic pressure, the higher the temperature, the greater the molecular motion of ions and solvents, and the greater the width of the electric double layer and the greater the potential difference, resulting in an increase in the repulsive force term.

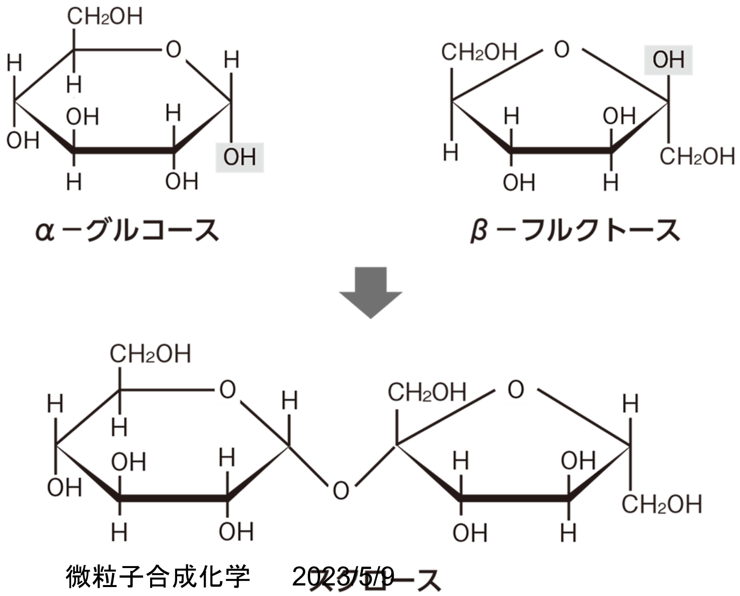
Colloids

フリー百科事典『ウィキペディア（Wikipedia）』によると･･･

- Colloids that use water as a dispersion medium are classified into hydrophobic colloids, which easily precipitate when electrolyte is added, and hydrophilic colloids, which do not easily precipitate. Hydrocolloids, like hydrophobic colloids, have a surface charge and are coordinated by a large number of water molecules due to hydration (solvation). Some hydrocolloids surround hydrophobic colloids to prevent coagulation, and such colloids are called protective colloids. In some cases, the protective colloid is stabilized by adsorption of protein or the like on the surface, changing the surface potential.

The concept of molecular colloid

- The concept of molecular colloids exists when macromolecules are in solution.
- For example, aqueous solutions of salt (NaCl) and sugar (sucrose = sucrose) both become homogeneous solutions and are not molecular colloids at this point.
- When monosaccharides such as glucose undergo polymerization and become macromolecules, they are no longer aqueous solutions but molecular colloids.
- The boundary between the solution and the colloid disappears.



コロイド Colloid

分子が集まって、普通の顕微鏡で見えない程度の粒となって、浮きただようような状態で存するもの

分散と凝集

ただよっている状態が「分散」,
不安定になって固まりになった状態が「凝集」

生活の中のコロイド

身の回りのコロイドを見てみよう

Colloid

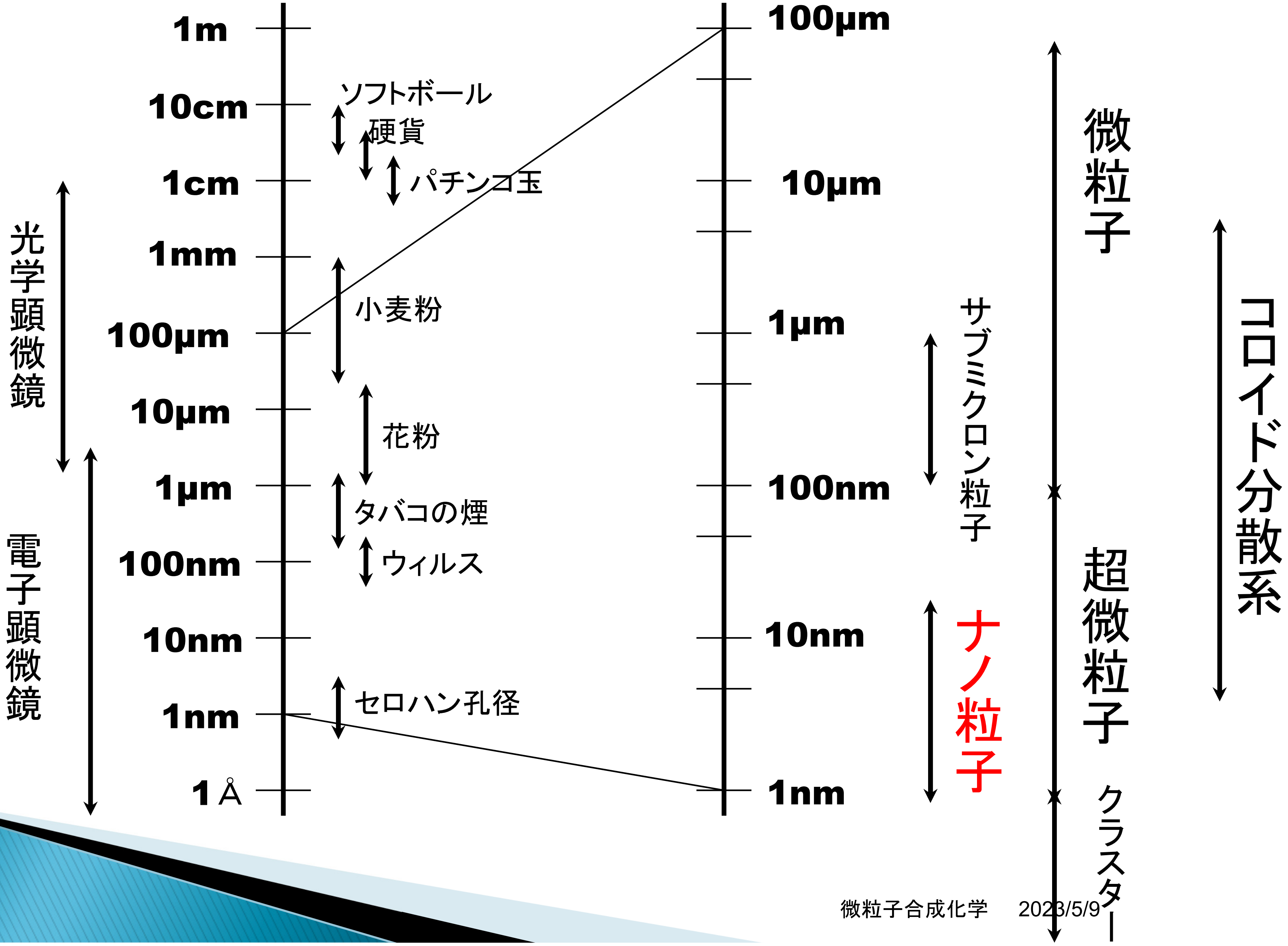
Molecules gather together to form grains that cannot be seen with an ordinary microscope, and exist in a floating state.

Dispersion and Aggregation

The floating state is “dispersed”, and the unstable and clumped state is “aggregation”.

COLLOIDS IN LIFE

Particle classification by particle size



1m
10cm
1cm
1mm
100μm
10μm
1μm
100nm
10nm
1nm
1 Å

ソフトボール
硬貨
パチンコ玉
小麦粉
花粉
タバコの煙
ウィルス
セロハン孔径

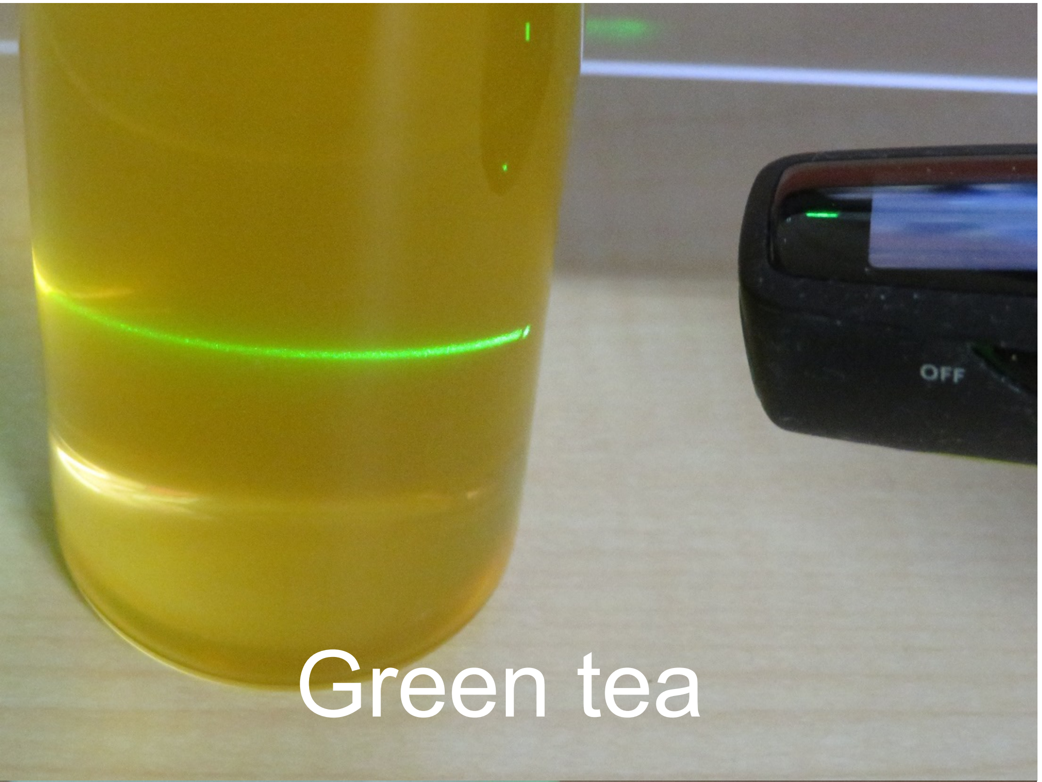
光学顕微鏡
電子顕微鏡

100μm
10μm
1μm
100nm
10nm
1nm

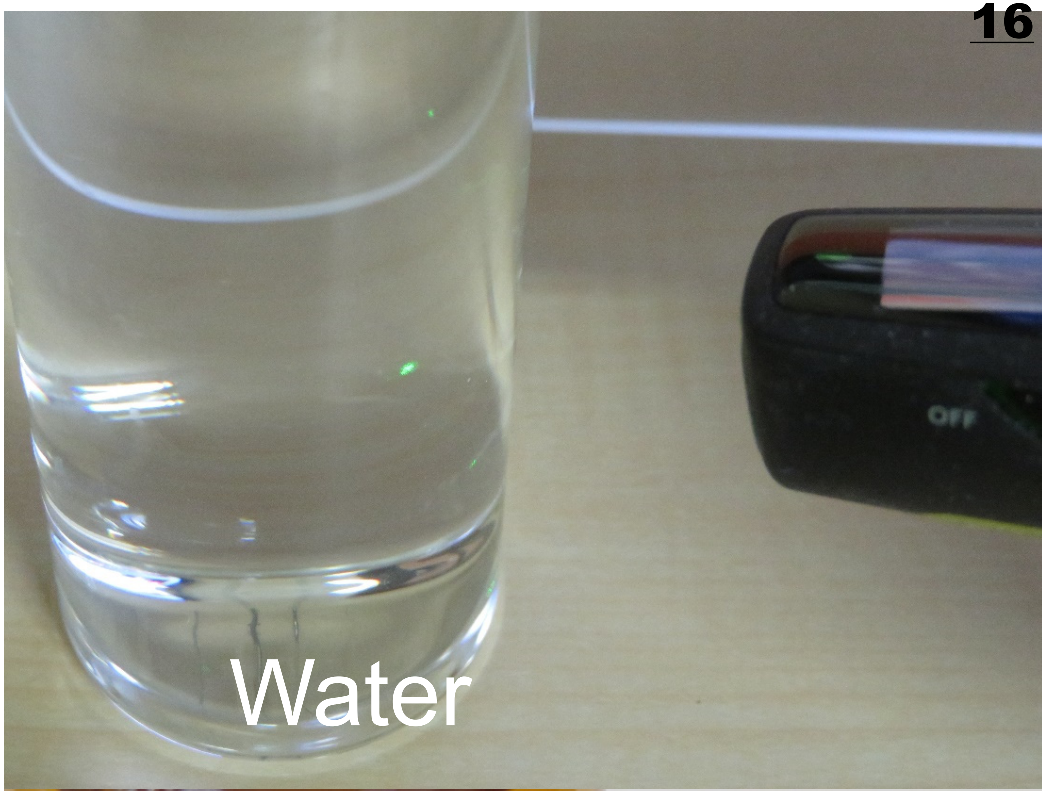
サブミクロン粒子
ナノ粒子
微粒子
超微粒子
クラスター
コロイド分散系

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.



Green tea



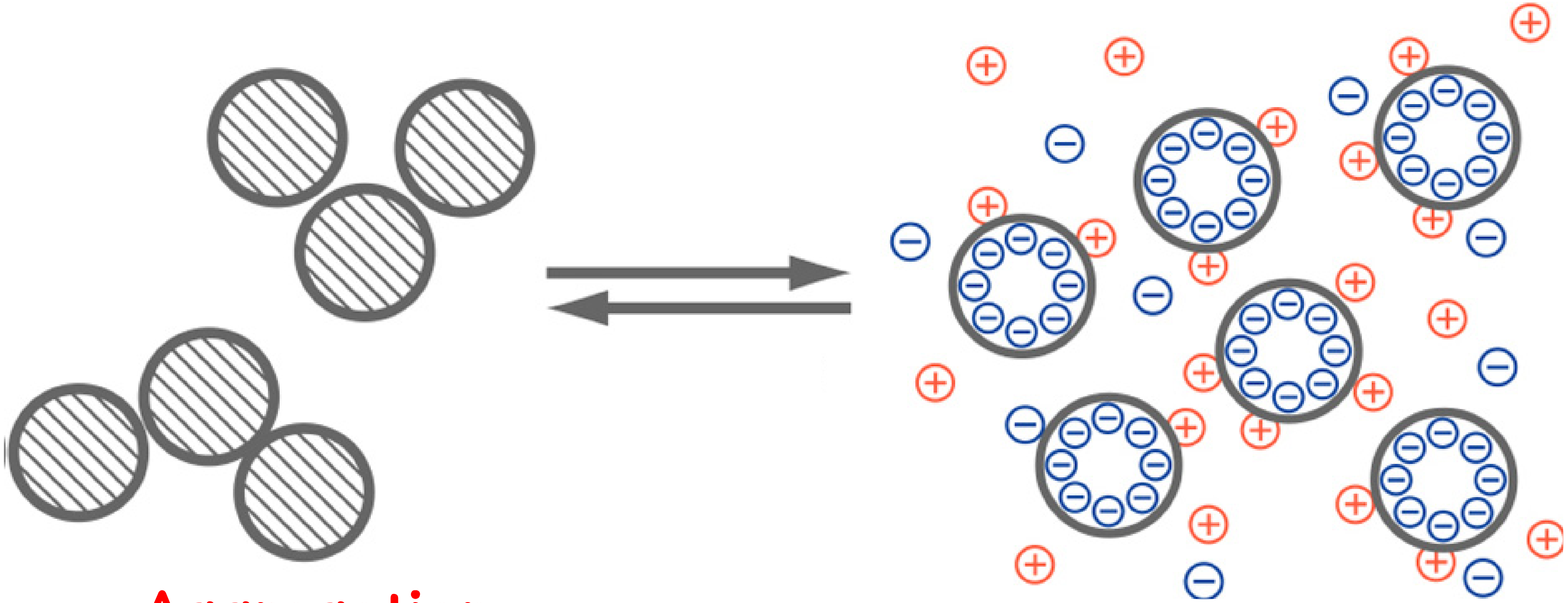
Water

Milk
Diluted

Laser

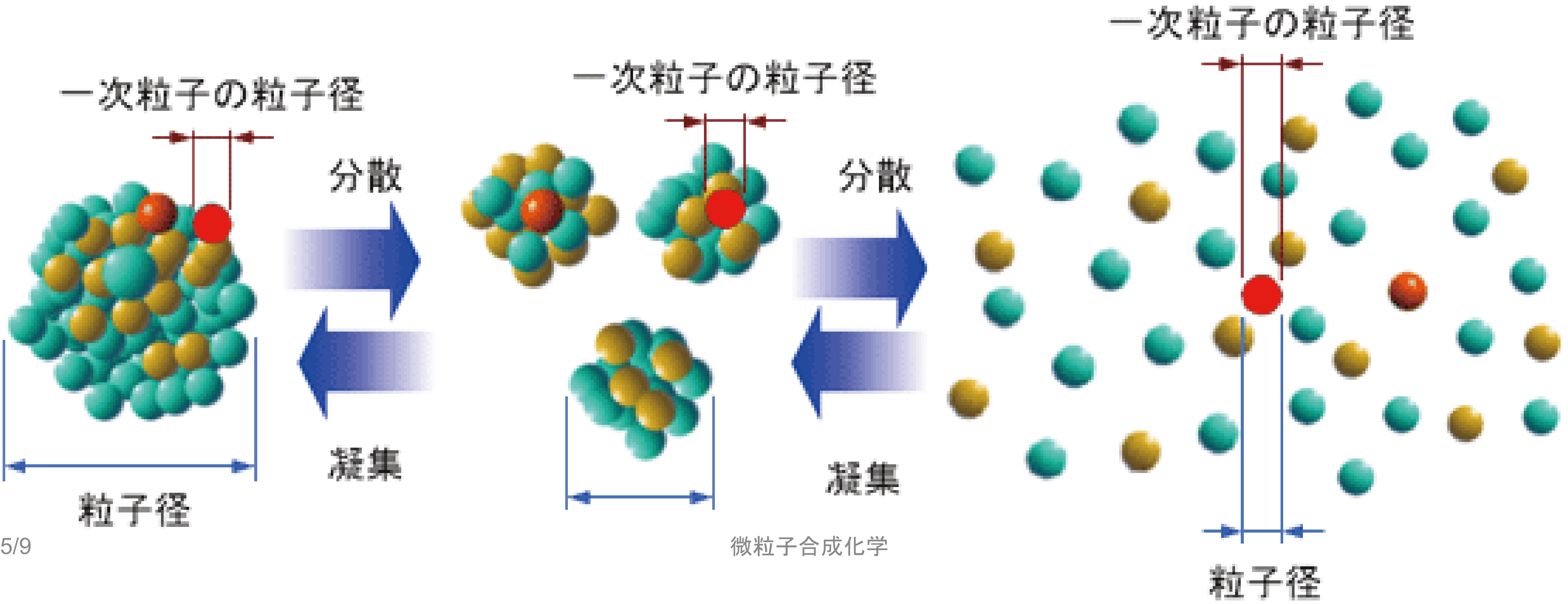
532
nm

Coffee
Diluted



Aggregation

Colloidal dispersion



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

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

↓

- **The key to controlling "dispersion" and "aggregation" is zeta potential!**

There is an electric charge of several tens of mV on the surface of all “matters“

（ ”Surface potential” or ”Zeta potential” ）

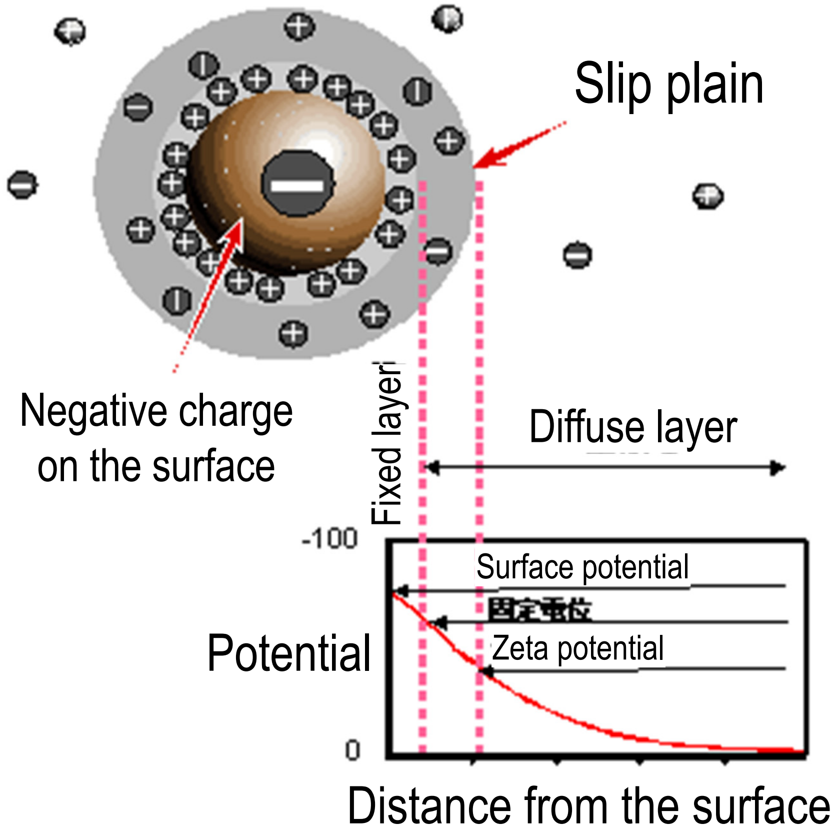
It's on your face, on your desk, on your foam, on everything!

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

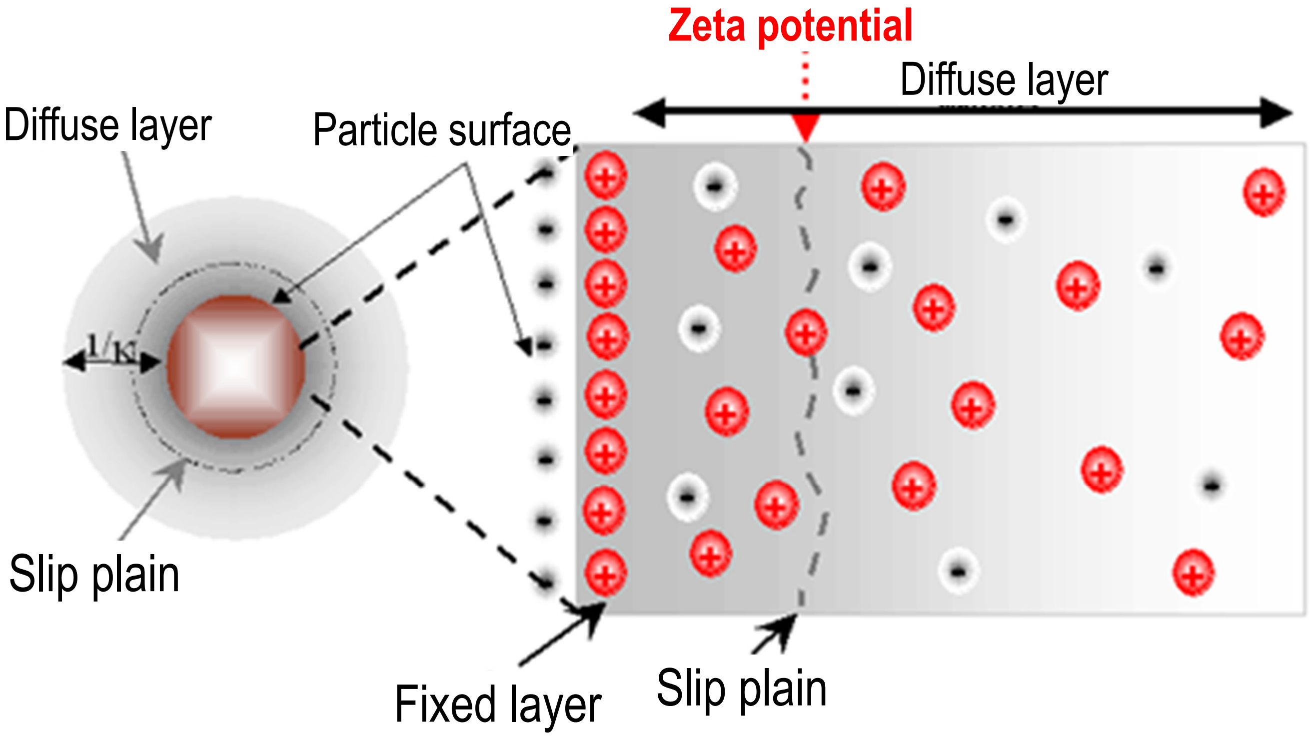
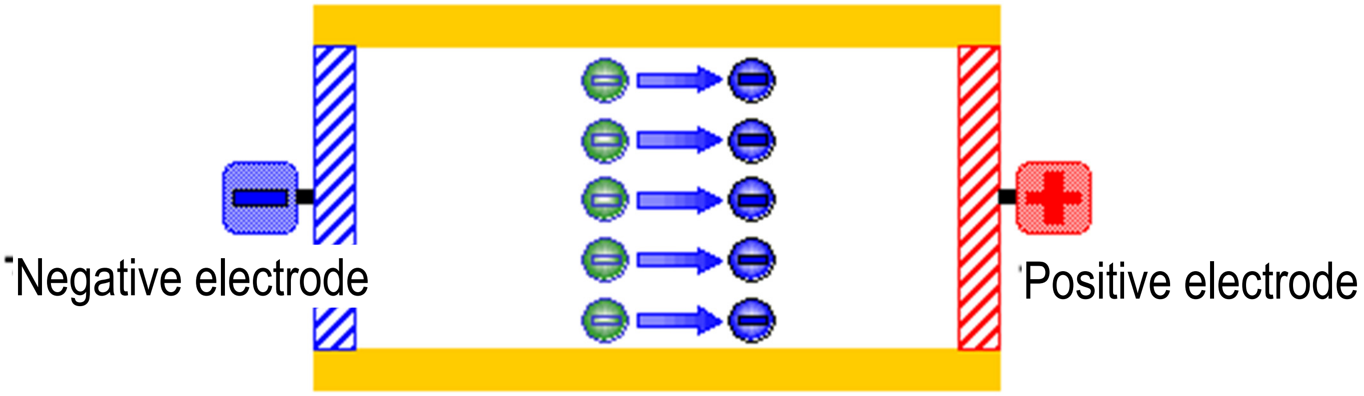
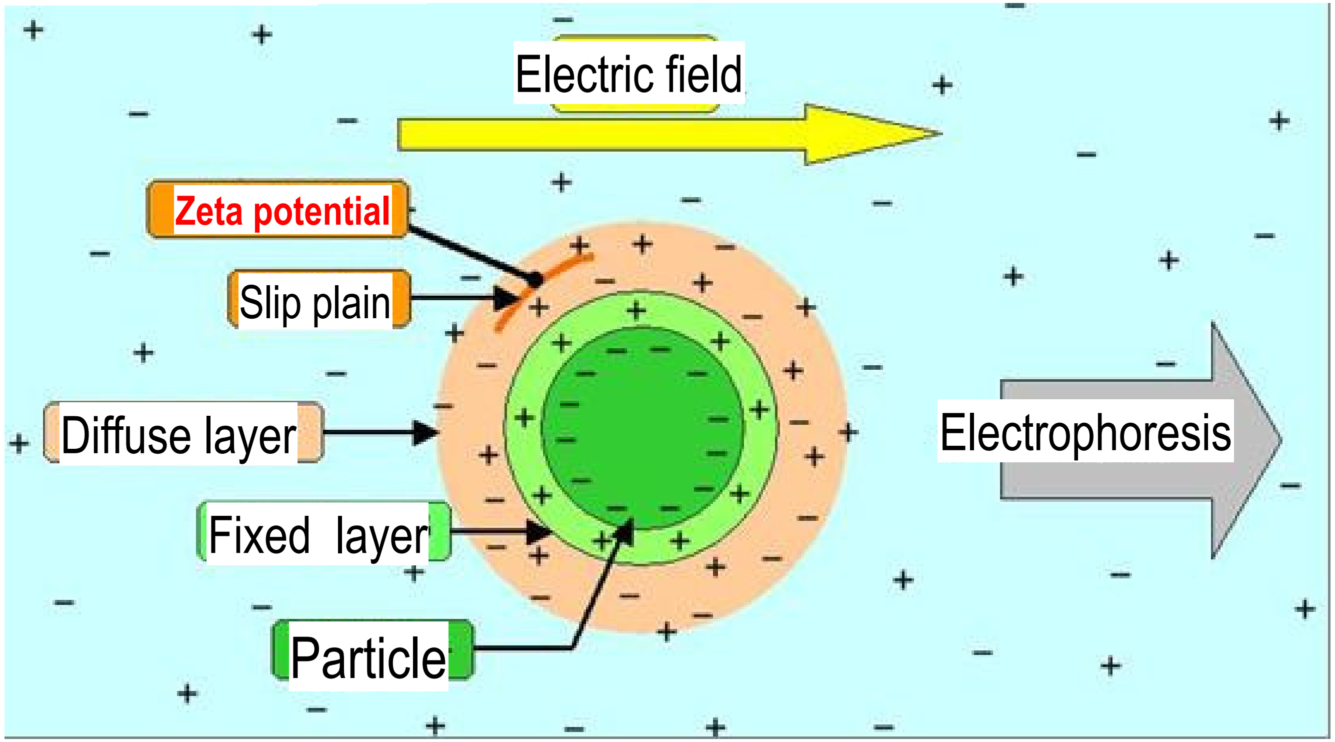


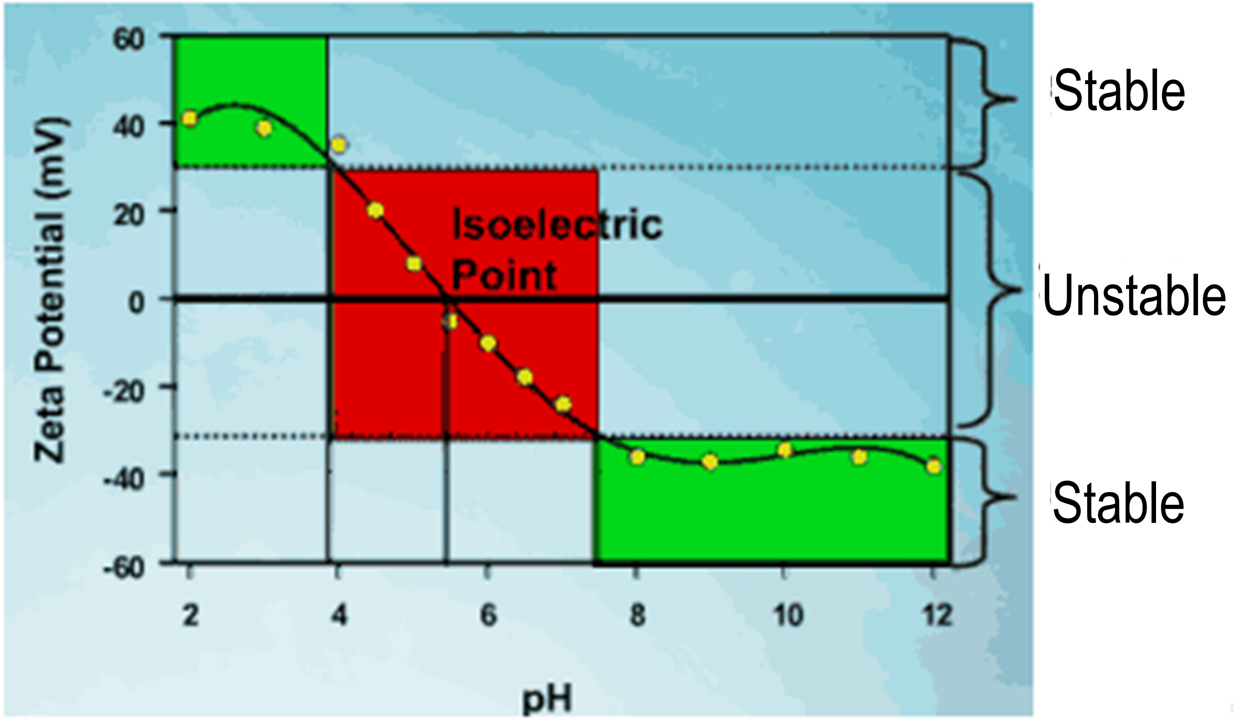
図6 Electrophoresis



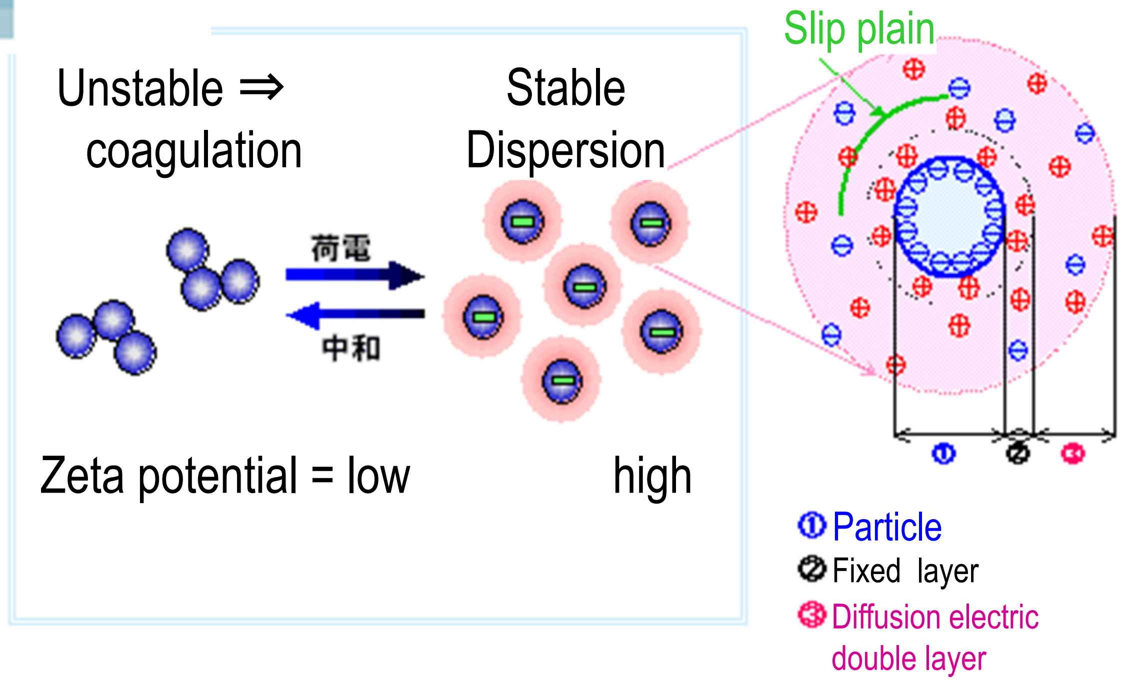
Particles with the same negative charge are moving to the positive electrode.



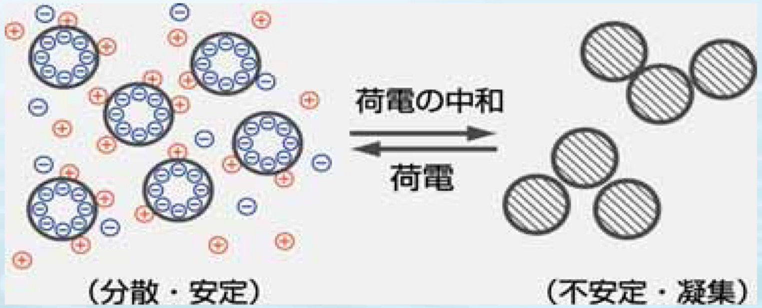
Zeta potential as a function of pH



Zeta potential and dispersion



What can we learn from zeta potential?

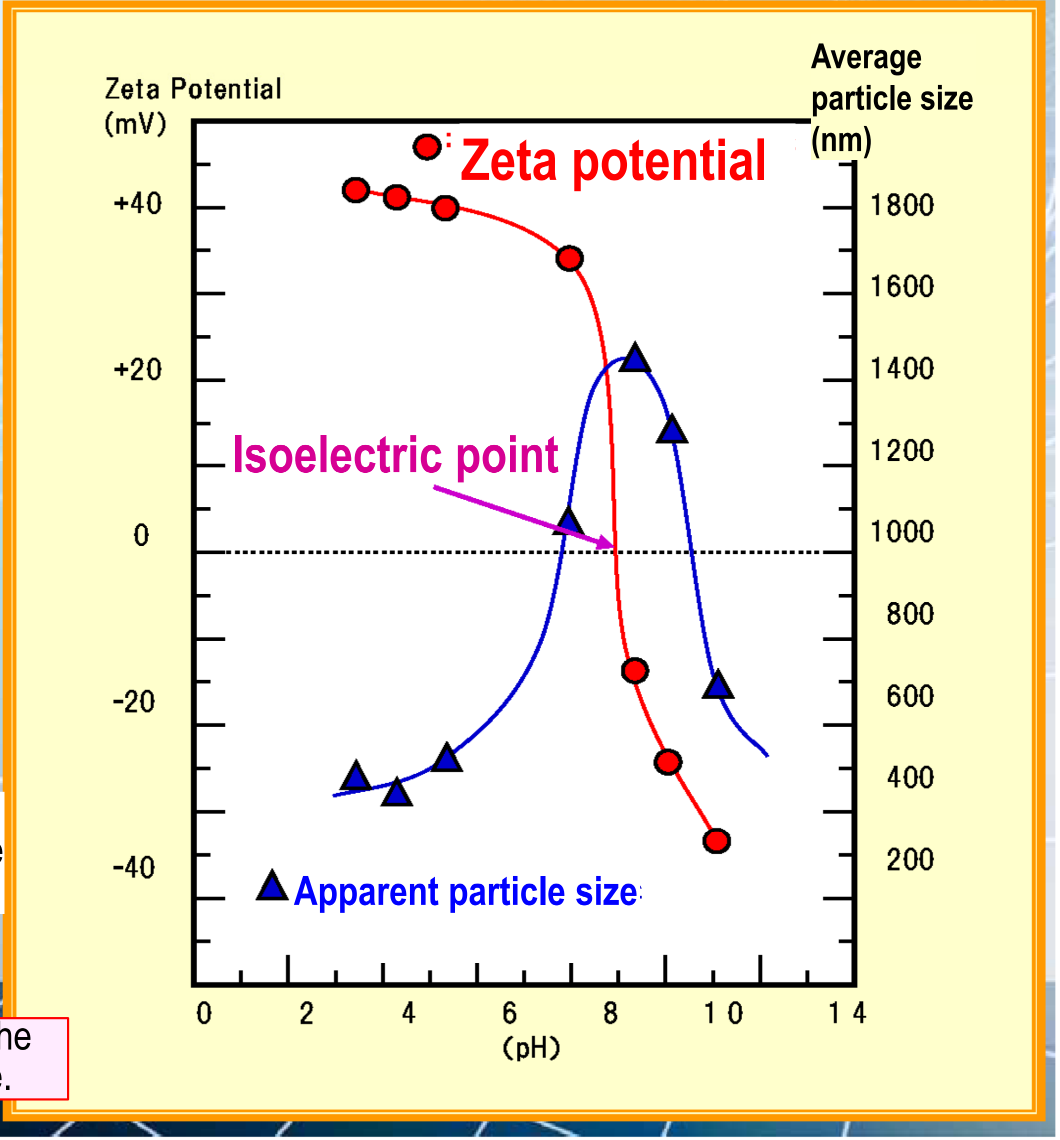


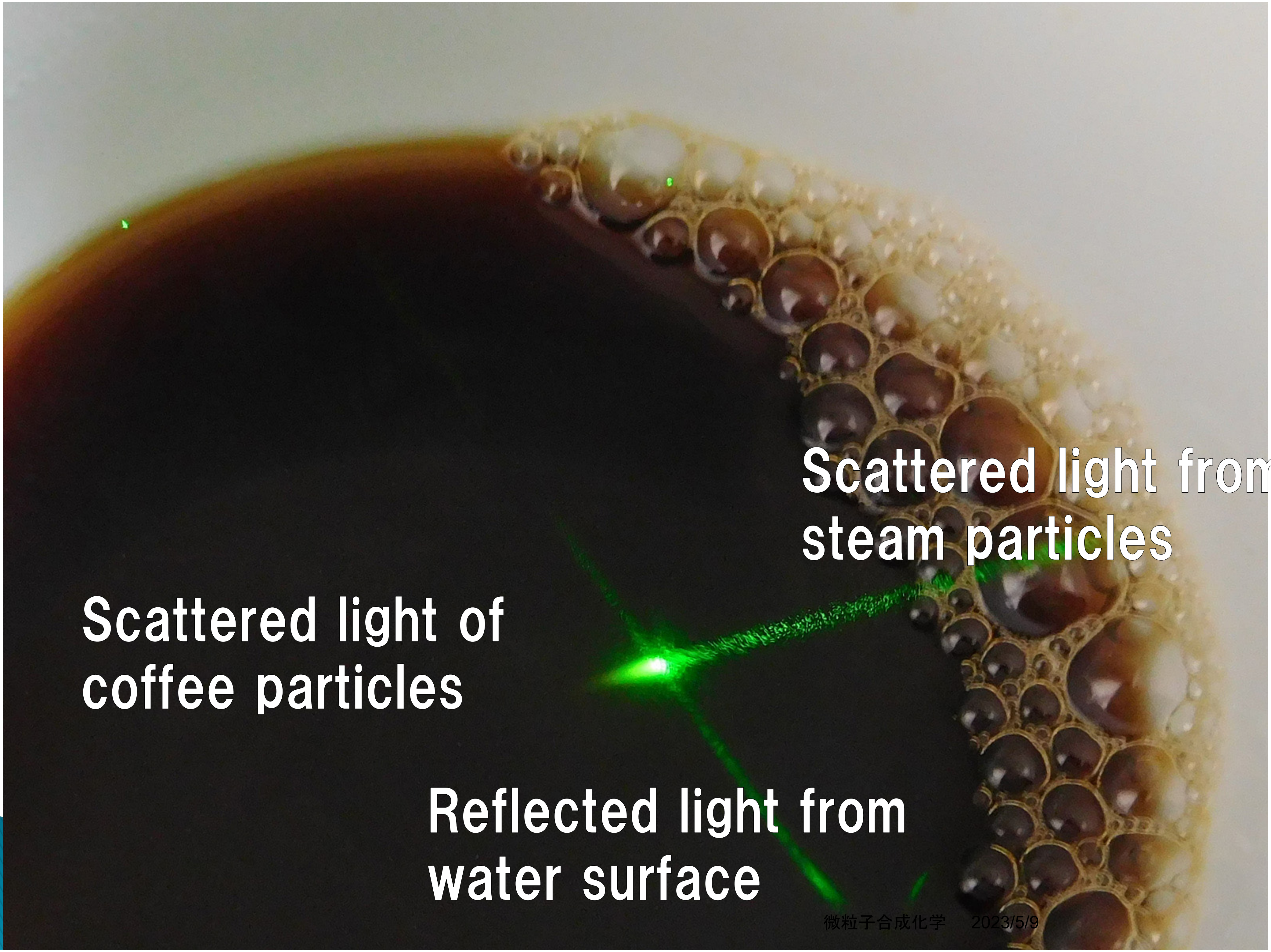
The larger the absolute value of the zeta potential, the better the dispersibility. However, if it is small, it is unstable and tends to aggregate.

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.





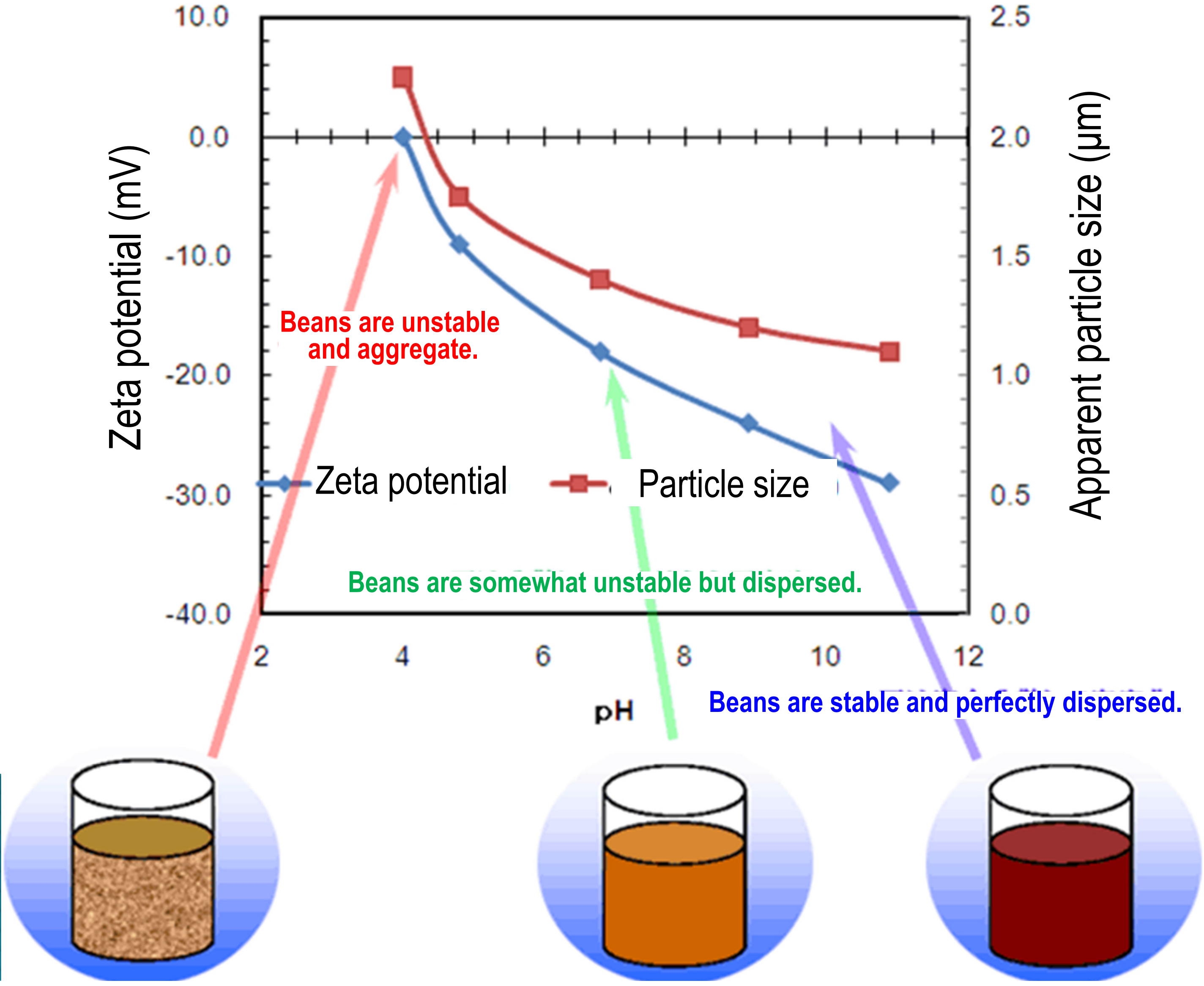
Scattered light from steam particles

Scattered light of coffee particles

Reflected light from water surface

Tea, black tea, and coffee are colloids.

Zeta potential of coffee bean particles

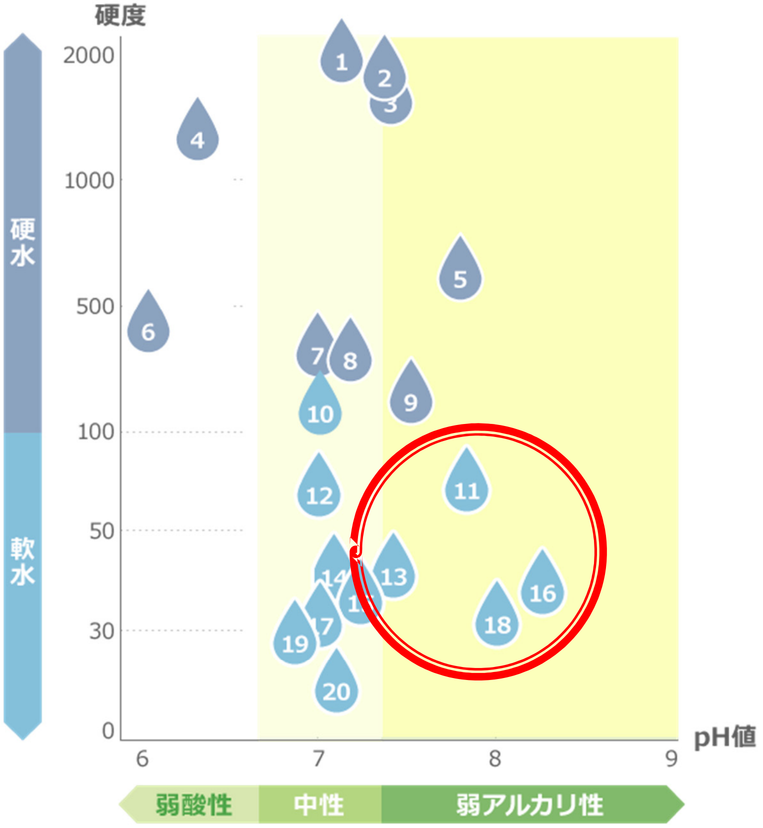


Beans are unstable and aggregate.

Beans are somewhat unstable but dispersed.

Beans are stable and perfectly dispersed.

【ミネラルウォーターの比較分布図】



		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	29	8.0
19	い・ろ・は・す	27.7	6.9
20	熊野古道水	10	7.1

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.**

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

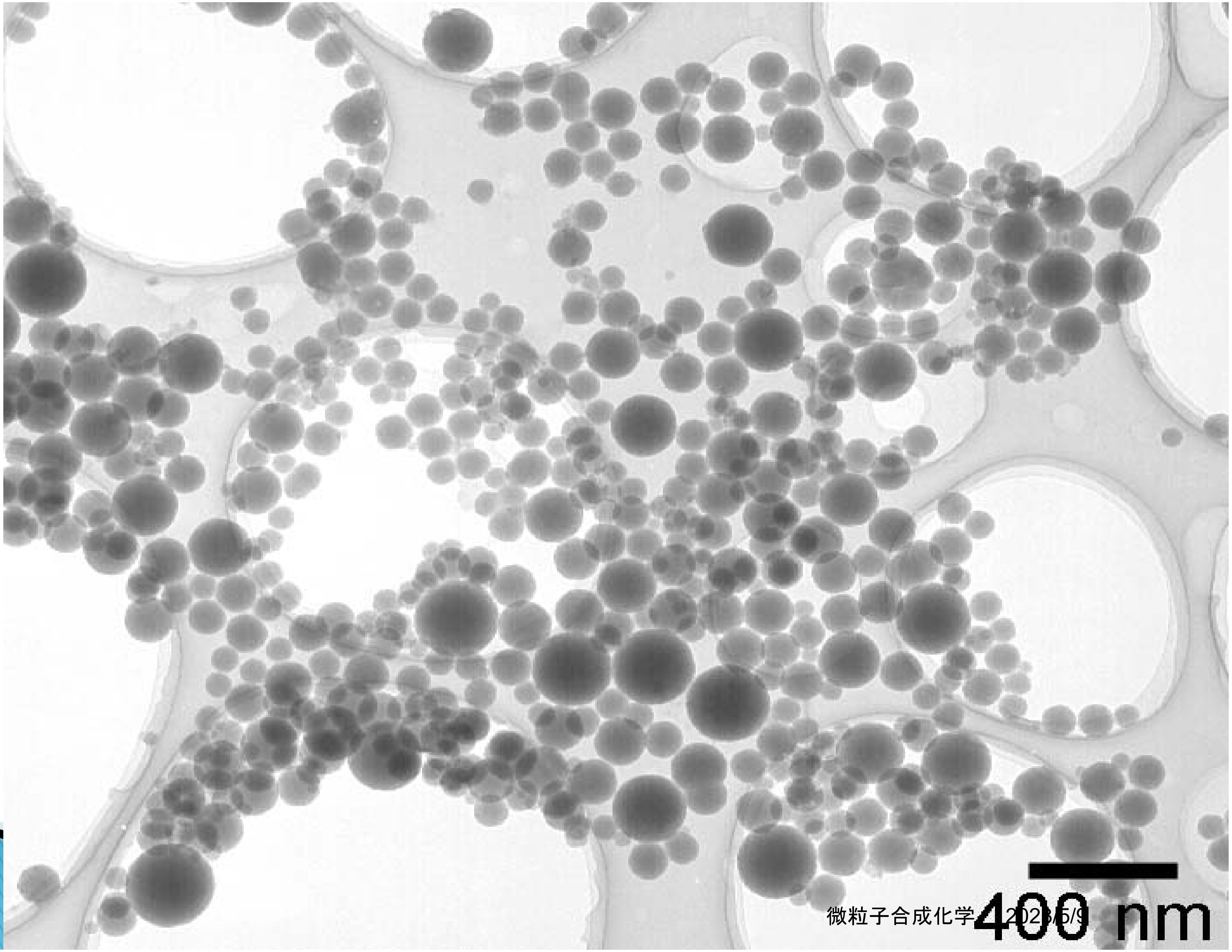
分析者：大沢信二・川村隆夫

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

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

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

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

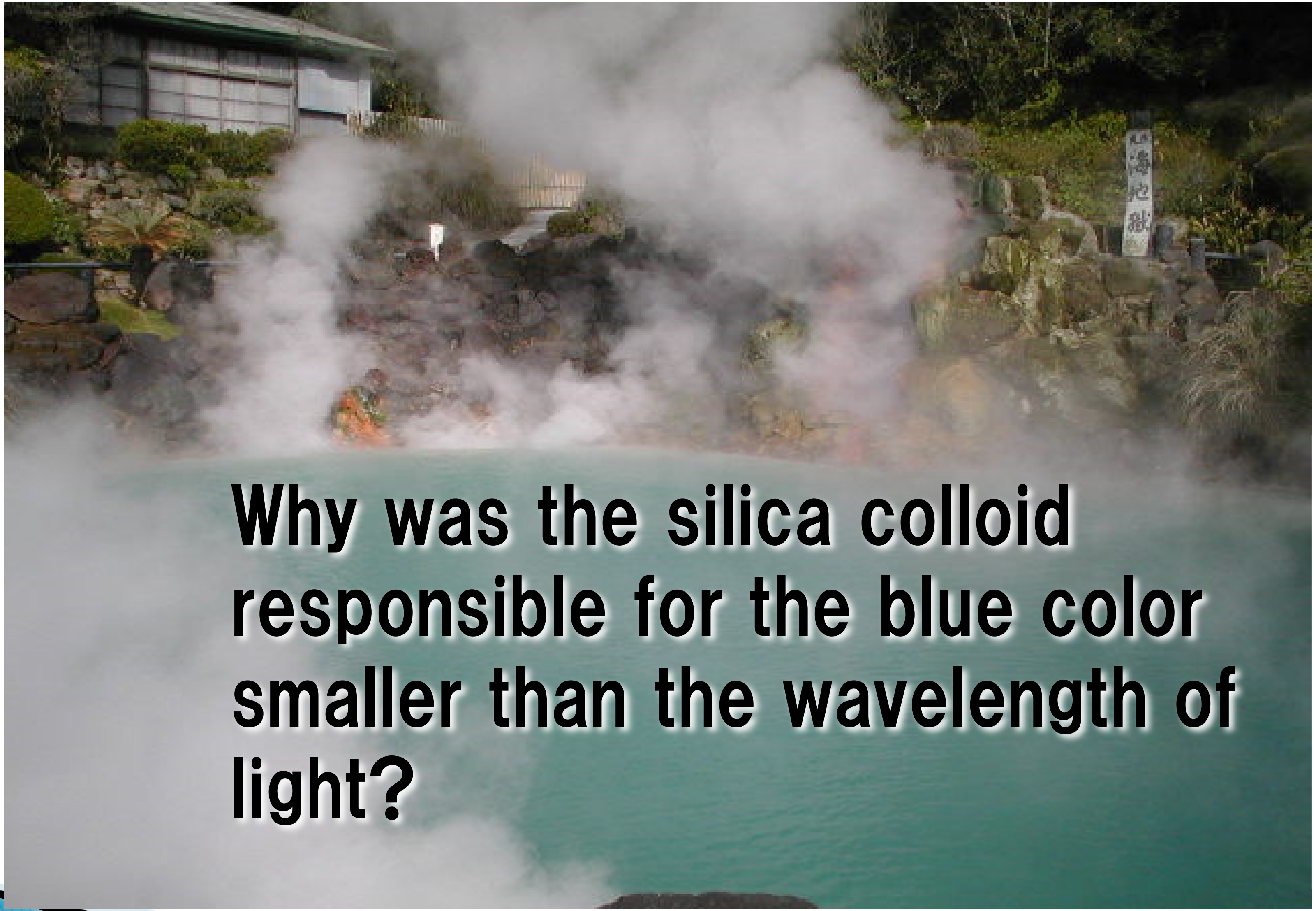
$$\alpha \gg 1 \quad geometric\ optics\ approximation$$

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

Silica colloids in Beppu sea hell



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

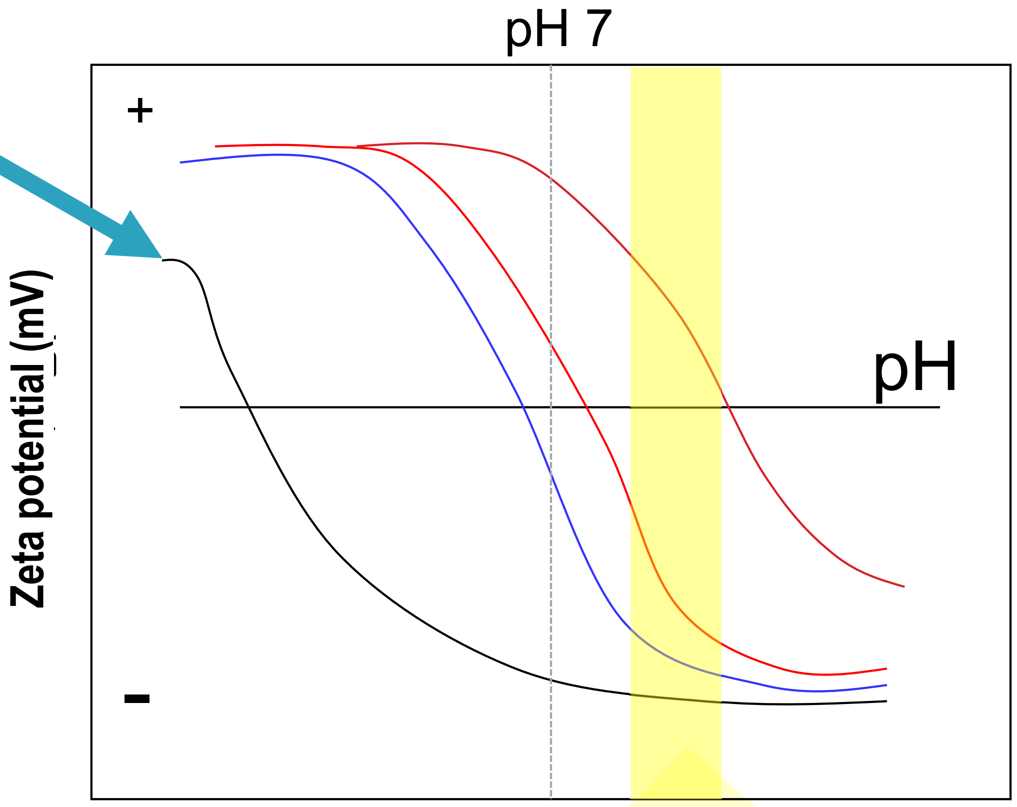
Why were the silica particles smaller than the wavelength?
That's because it didn't aggregate and was stably dispersed in water!

Isoelectric point of oxides

depending on crystal plane, structure, etc.

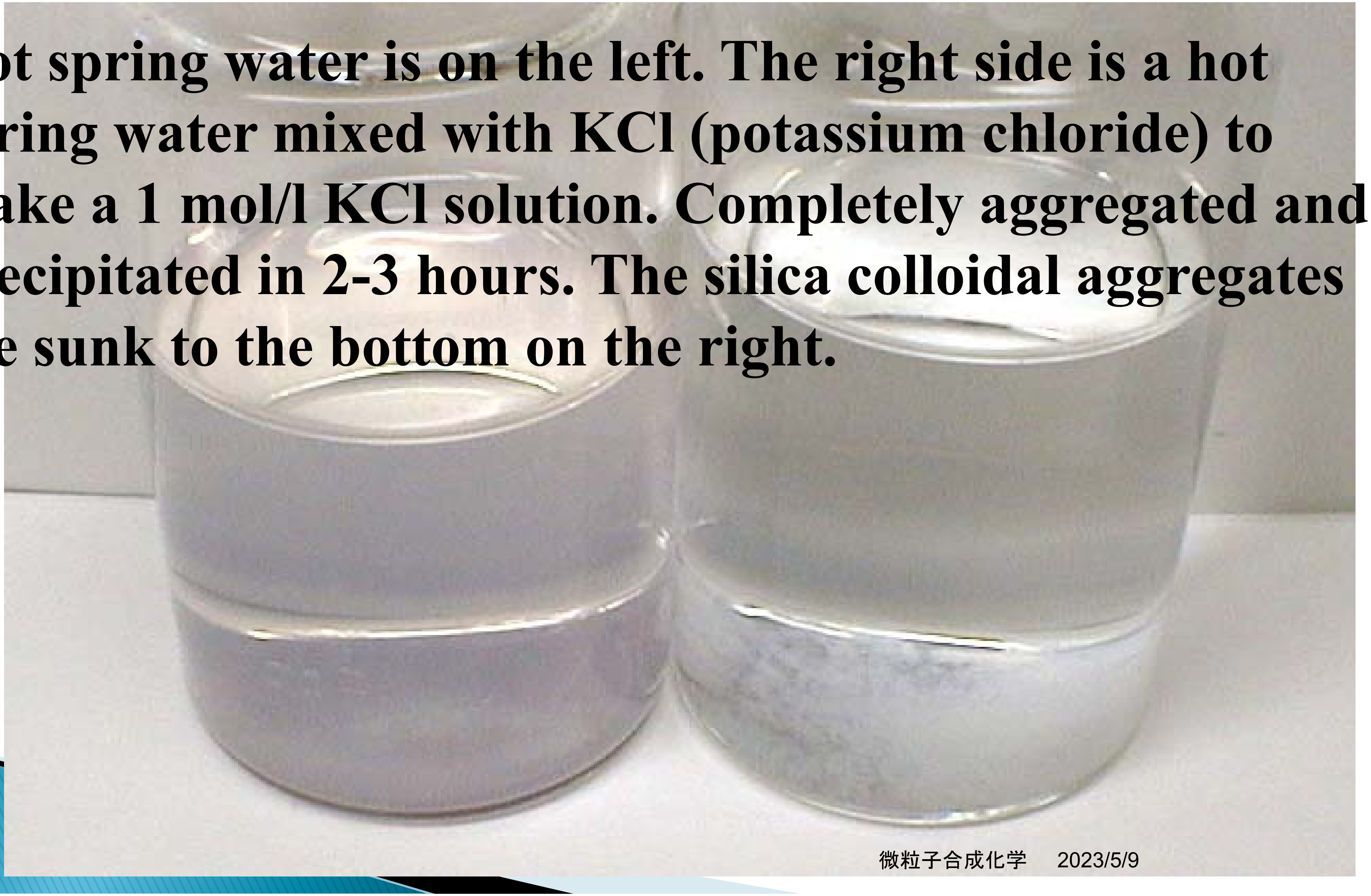
SiO_2	2〜3
TiO_2	6〜8
Fe_2O_3	6〜8
ZrO_2	7〜9
Al_2O_3	7〜9
MgO	9〜11

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



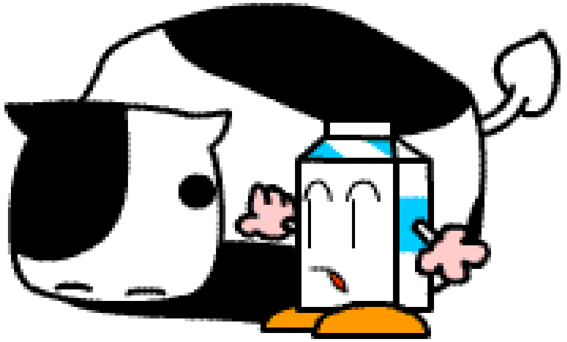
pH of Umi Jigoku hot spring water： 8〜9

Aggregation and precipitation of silica colloid

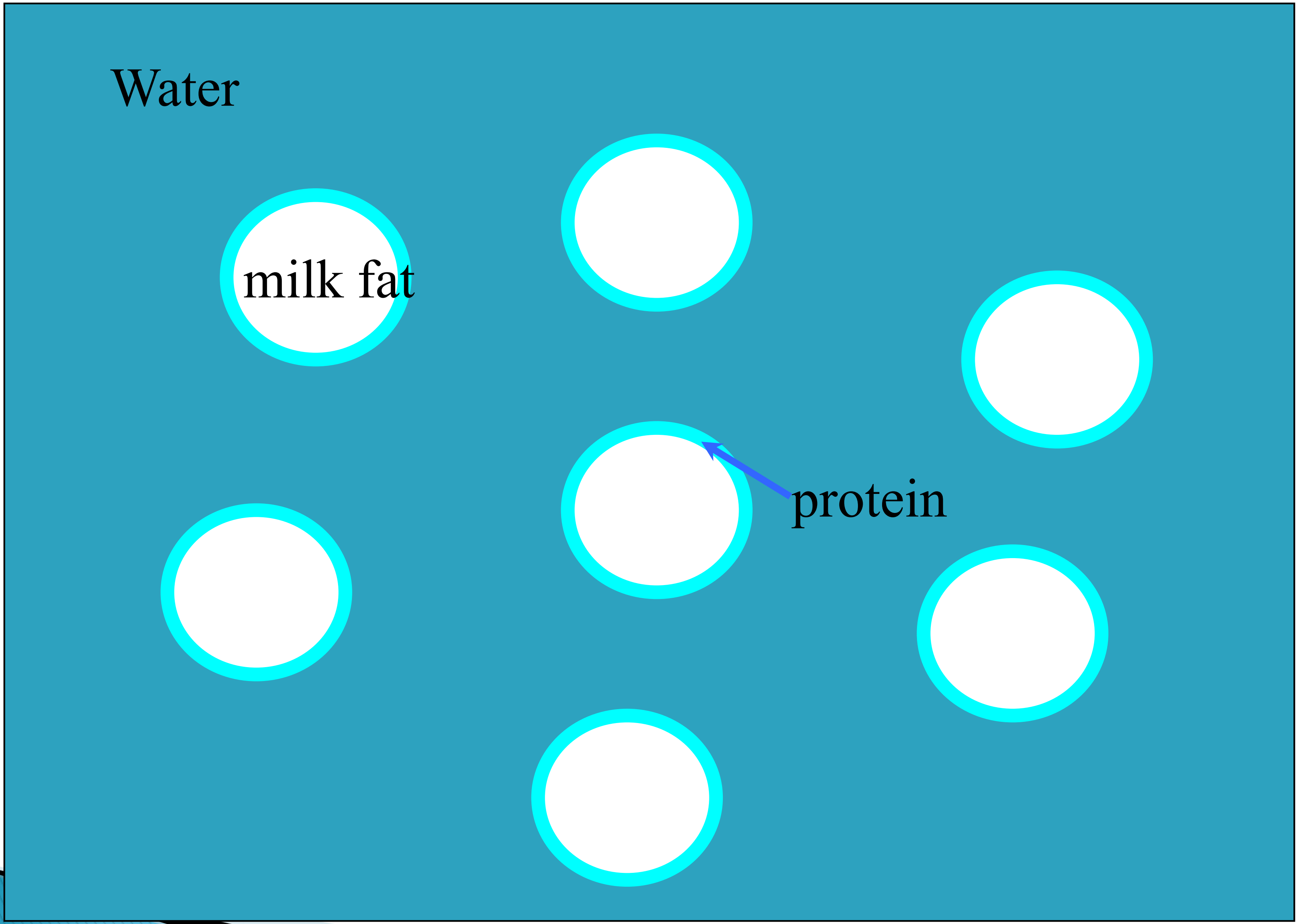


Hot spring water is on the left. The right side is a hot spring water mixed with KCl (potassium chloride) to make a 1 mol/l KCl solution. Completely aggregated and precipitated in 2-3 hours. The silica colloidal aggregates are sunk to the bottom on the right.

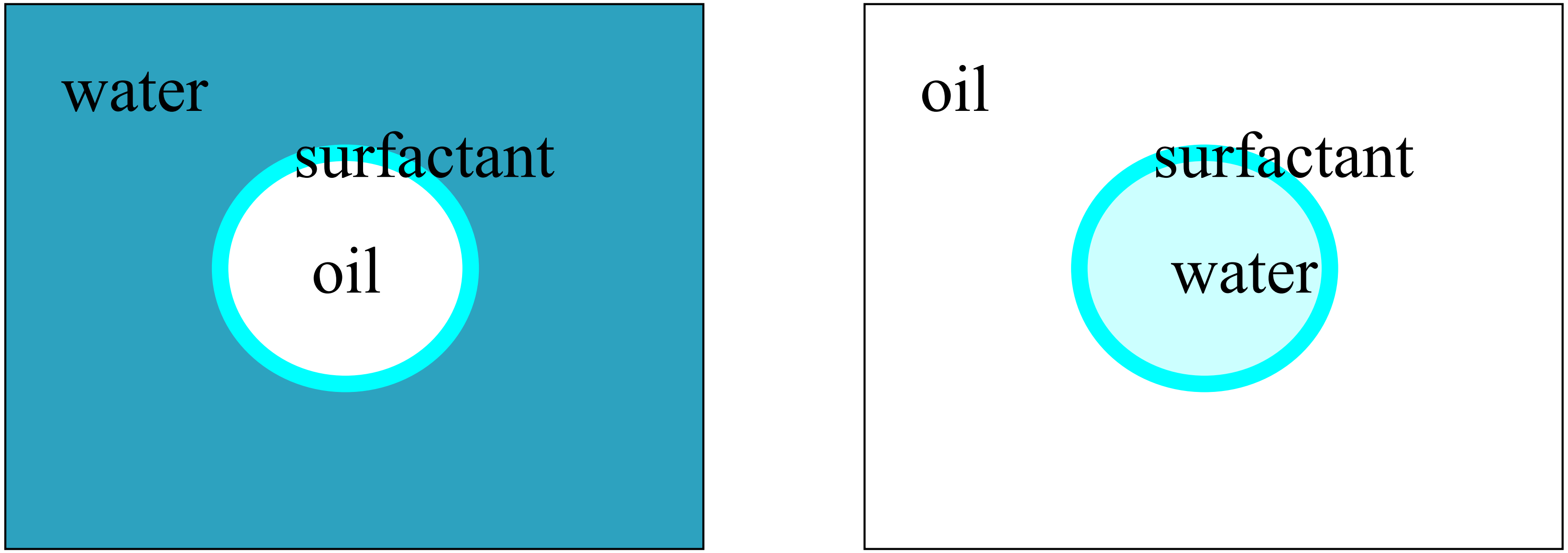
Milk



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

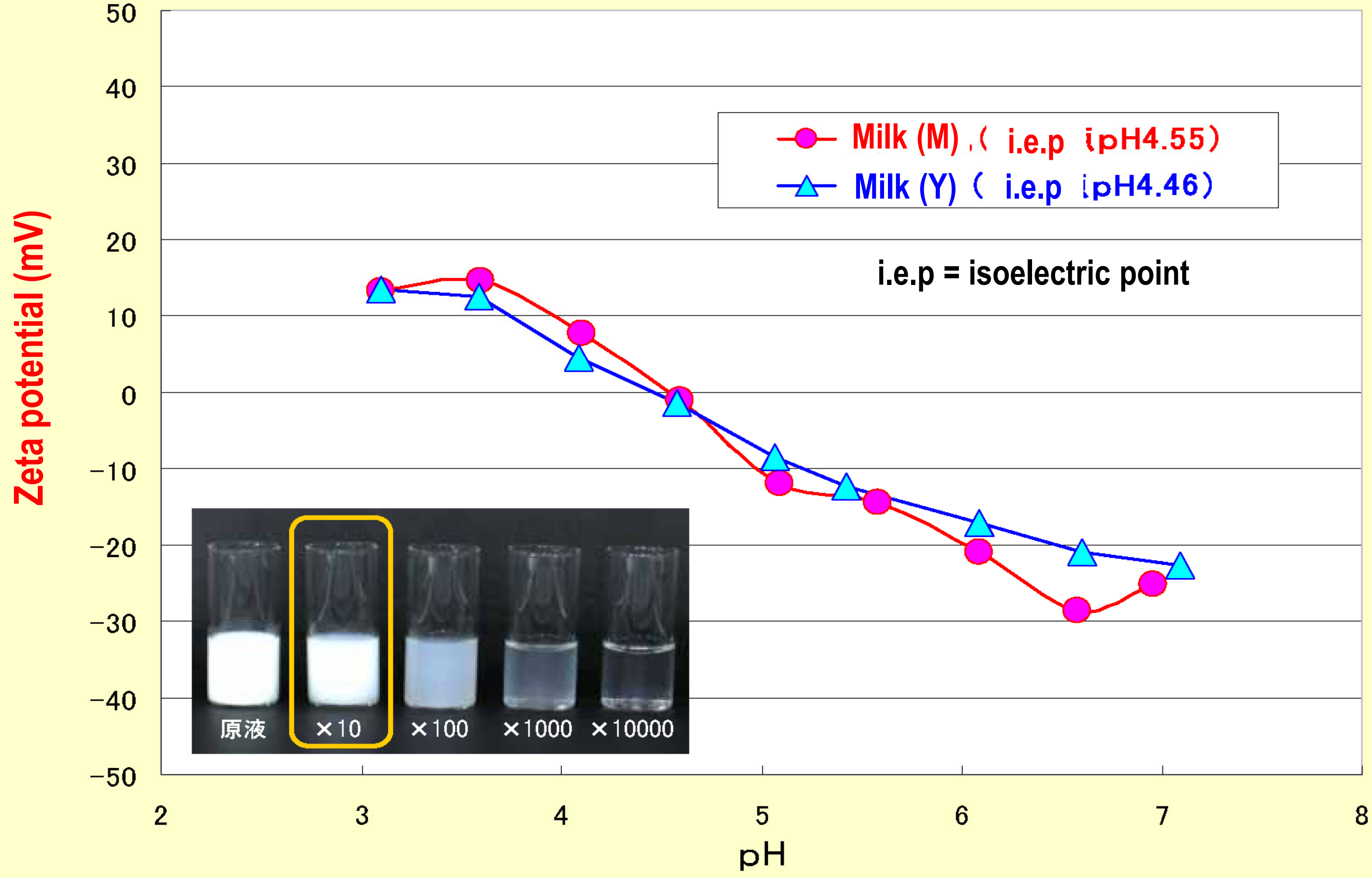


O/W emulsion

W/O emulsion

pH titration of 10-fold diluted milk

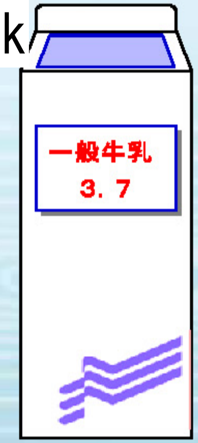
pH dependence of the zeta potential of milk



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。

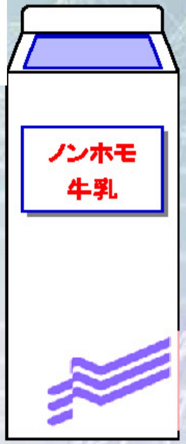


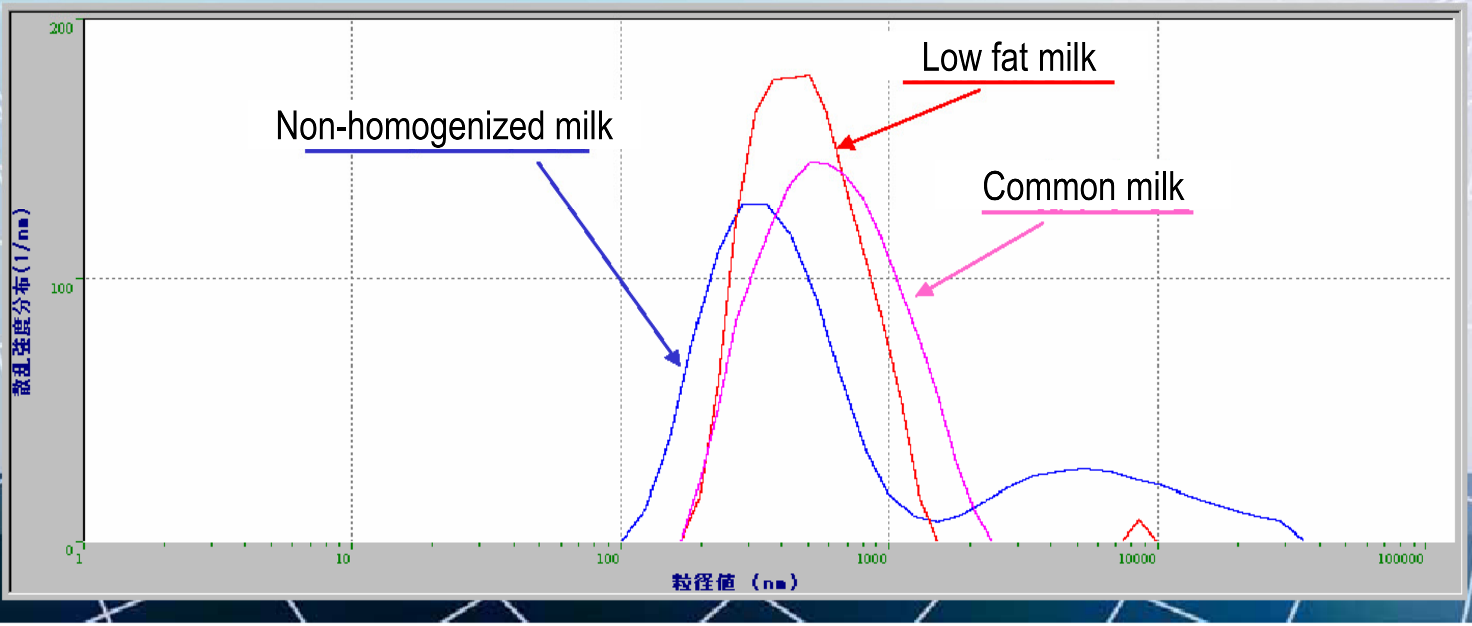
② Low fat milk

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。

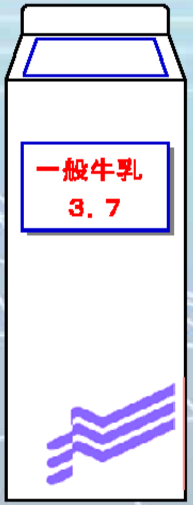


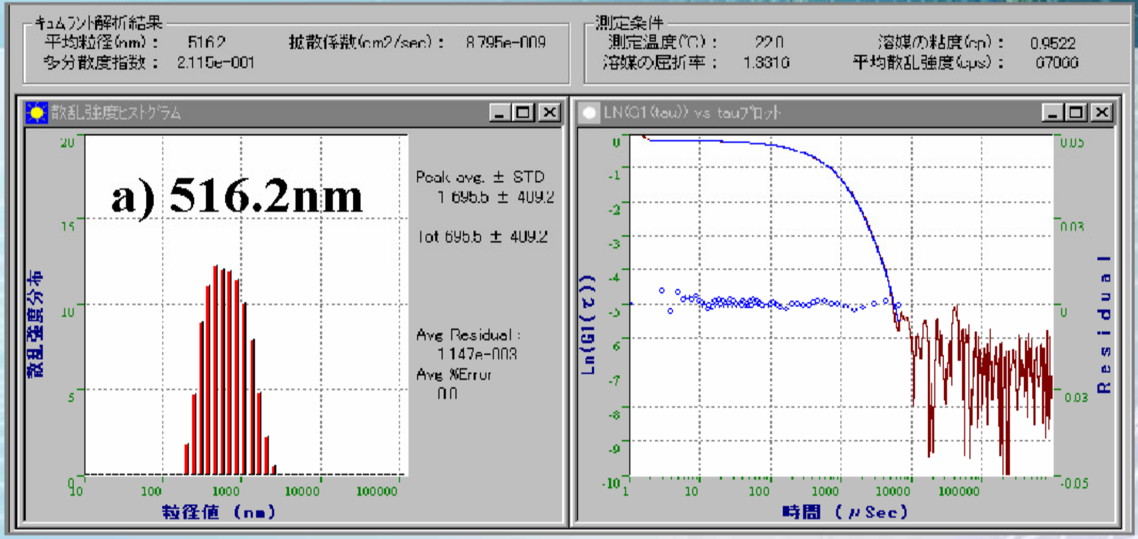


Changes in creaming of regular milk

a) Fresh regular milk

b) Milk left indoors was changed as creaming.





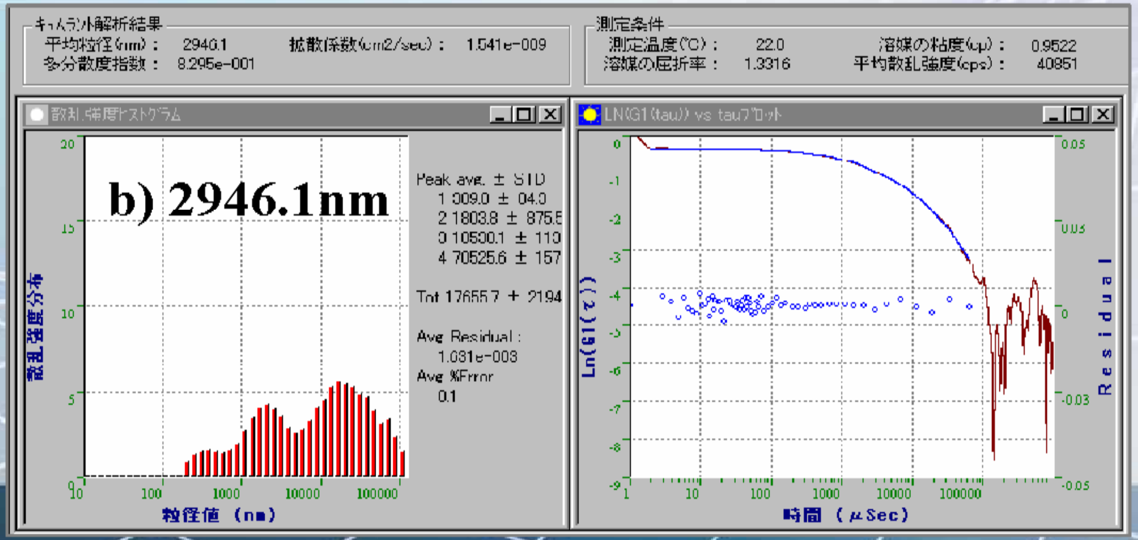
キュムラント解析結果
平均粒径(nm)： 516.2　拡散係数(cm2/sec)： 8.795e-009
多分散度指数： 2.115e-001

測定条件
測定温度(℃)： 22.0　溶媒の粘度(cp)： 0.9522
溶媒の屈折率： 1.3310　平均散乱強度(cps)： 07000

Peak ave. ± STD
1 695.5 ± 409.2

Tot 695.5 ± 409.2

Ave Residual :
1.147e-003
Ave %Error
0.0



キュムラント解析結果
平均粒径(nm)： 2940.1　拡散係数(cm2/sec)： 1.541e-009
多分散度指数： 8.295e-001

測定条件
測定温度(℃)： 22.0　溶媒の粘度(cp)： 0.9522
溶媒の屈折率： 1.3316　平均散乱強度(cps)： 40851

Peak ave. ± STD
1 309.0 ± 04.0
2 1803.8 ± 875.5
3 10500.1 ± 110
4 70525.6 ± 157

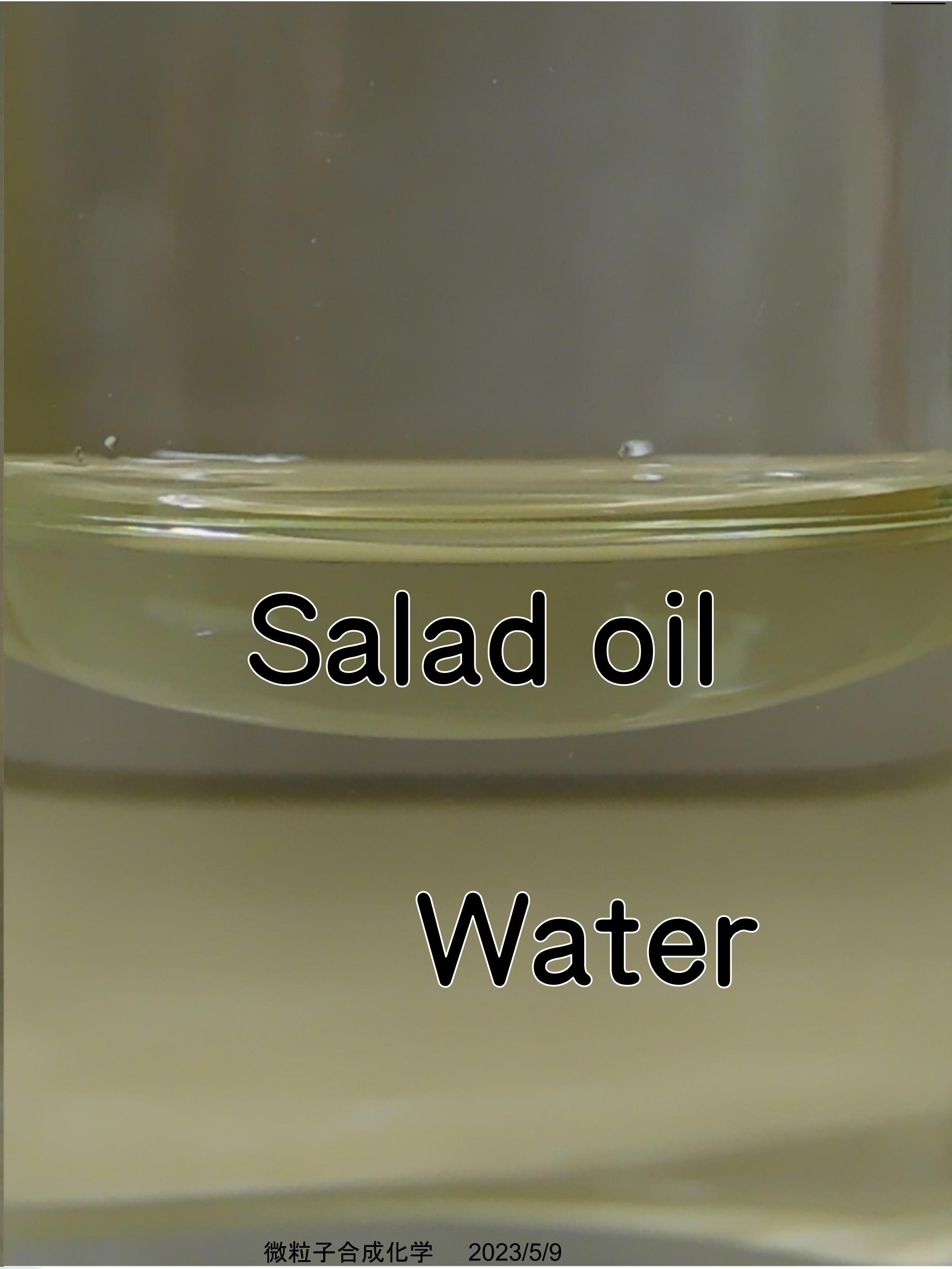
Tot 17655.7 ± 2194

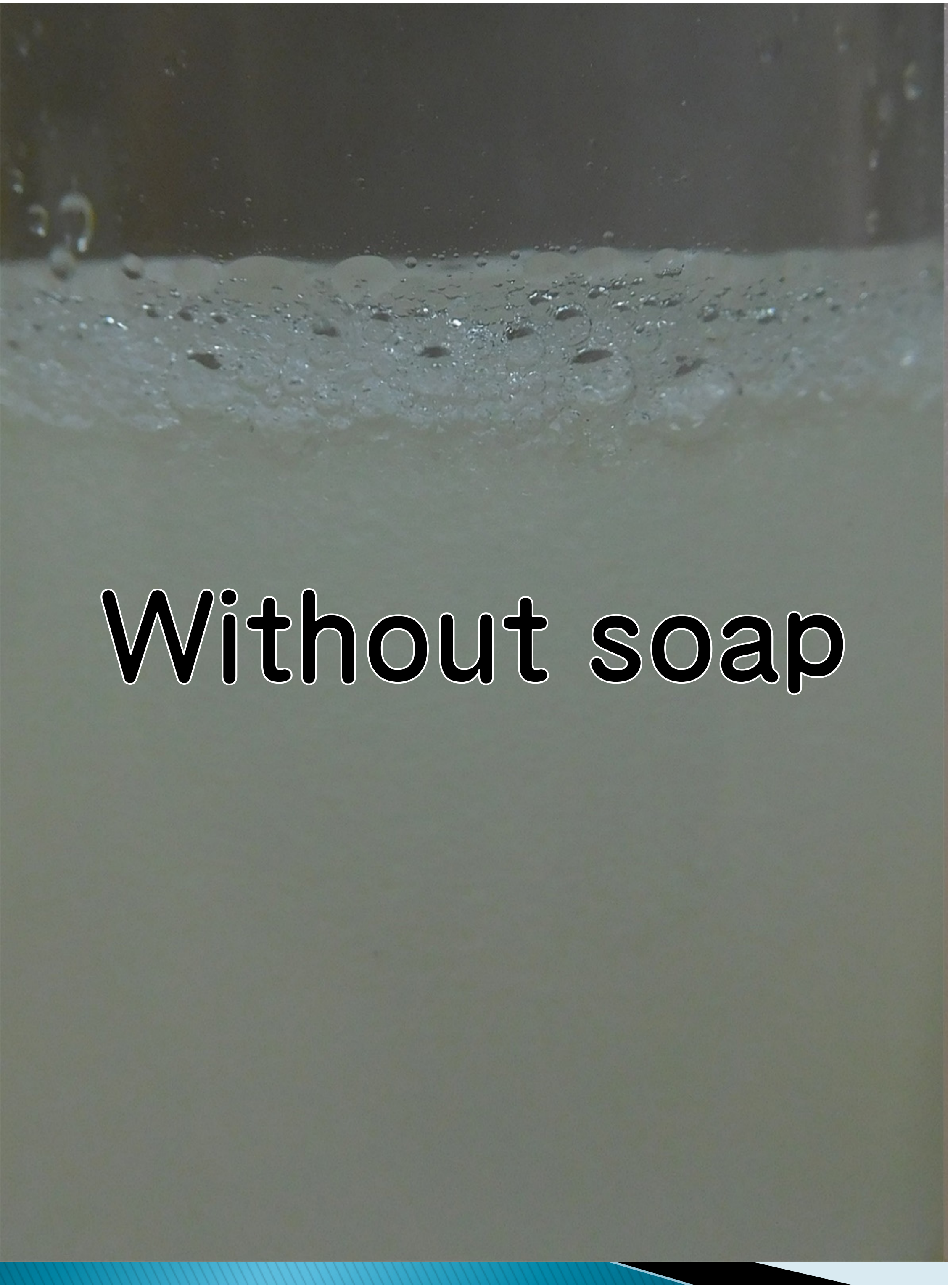
Ave Residual :
1.031e-003
Ave %Error
0.1


water

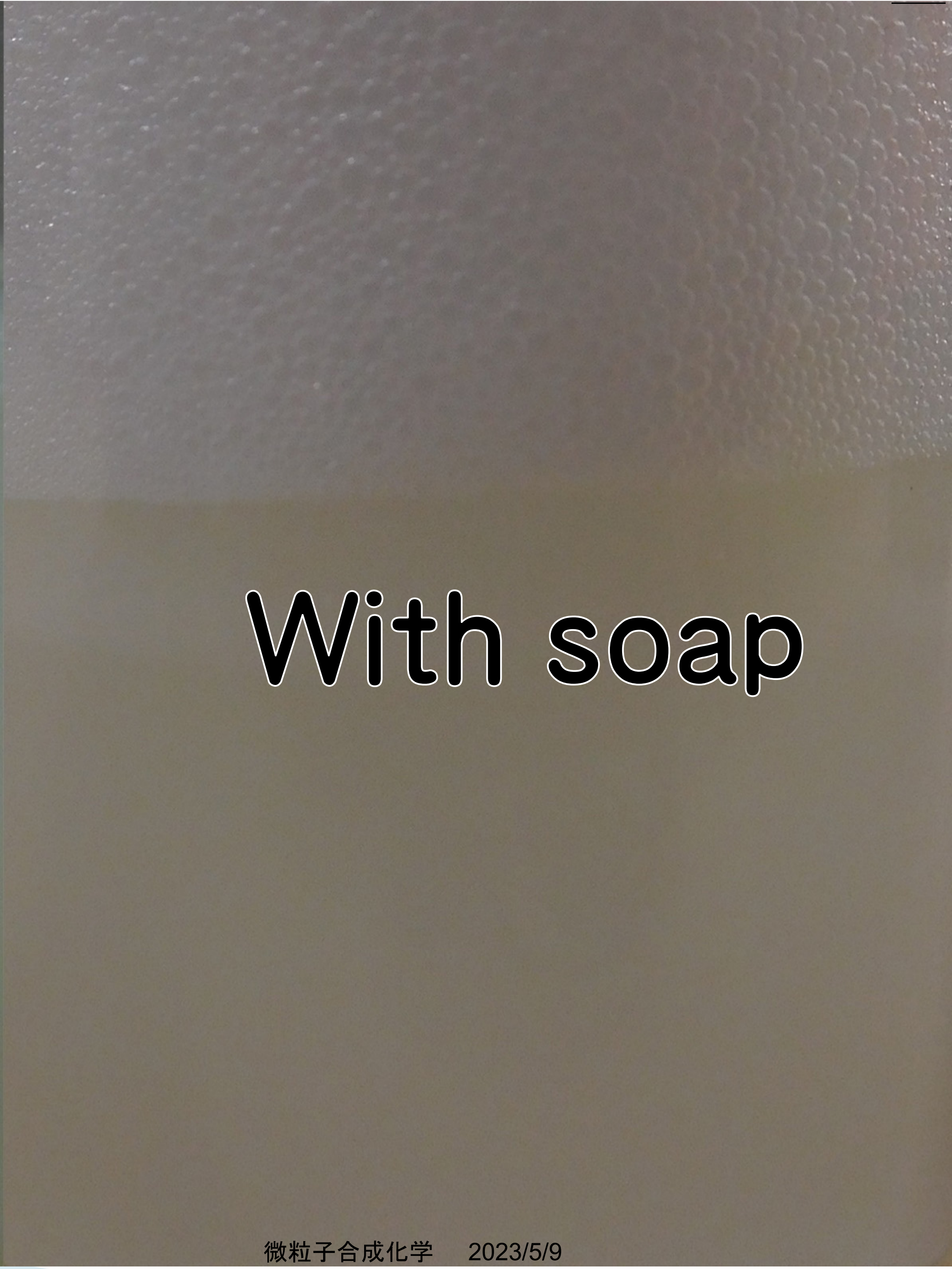

Salad oil


Water
Soap
Salad oil


Salad oil
Water



Without soap



With soap

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 prime example of a “aggregated" product!**

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

Ureshino specialty! Hot spring tofu

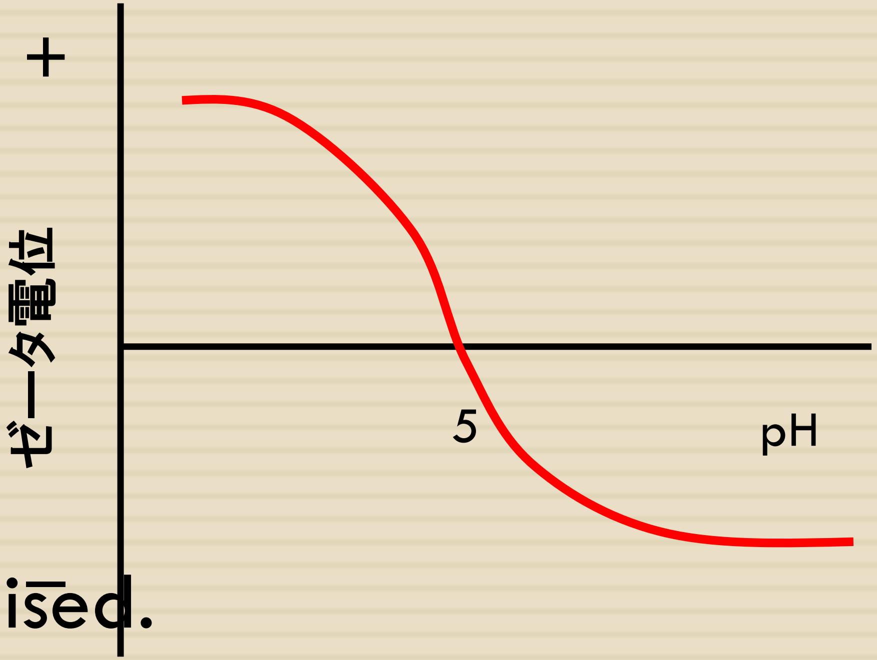
The secret of Ureshino Onsen tofu

- 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.

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

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

↓

- **Next is whiskey.**
- **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。

テイスティングノート

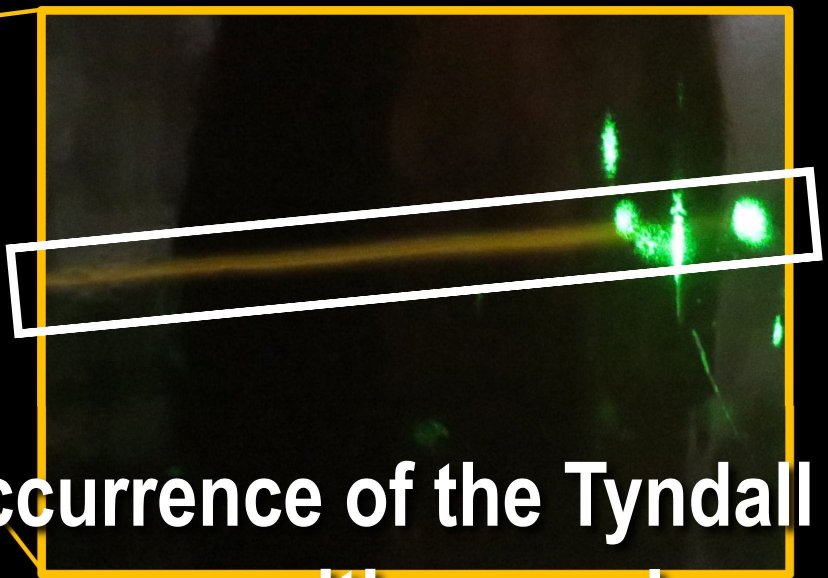
シェリー樽熟成由来の甘美な芳香が馥郁と立ちのぼる。年月を誇る長期熟成原酒の甘味と苦みが織り成す複雑で重厚な香味。陶然とした余韻は長く、深い。

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


THE YAMAZAKI
SINGLE MALT
WHISKY
AGED 12 YEARS
山崎
THE YAMAZAKI
SINGLE MALT
WHISKY
AGED 18 YEARS
山崎
THE YAMAZAKI
SINGLE MALT
WHISKY
AGED 25 YEARS
山崎
ウイスキー

The Tyndall phenomenon also occurs in green tea with a green laser. Same as this!



The occurrence of the Tyndall phenomenon with green lasers indicates the existence of nanoparticles of the order of 100-300 nm or something of that size.

What is the cause of "mellowness"?

We hypothesized that the increase in the mellowness of whiskey with aging 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, it was thought that the reason why it takes time for aging is that it takes time for the formed structure to stabilize.

This was explicated at SPring-8

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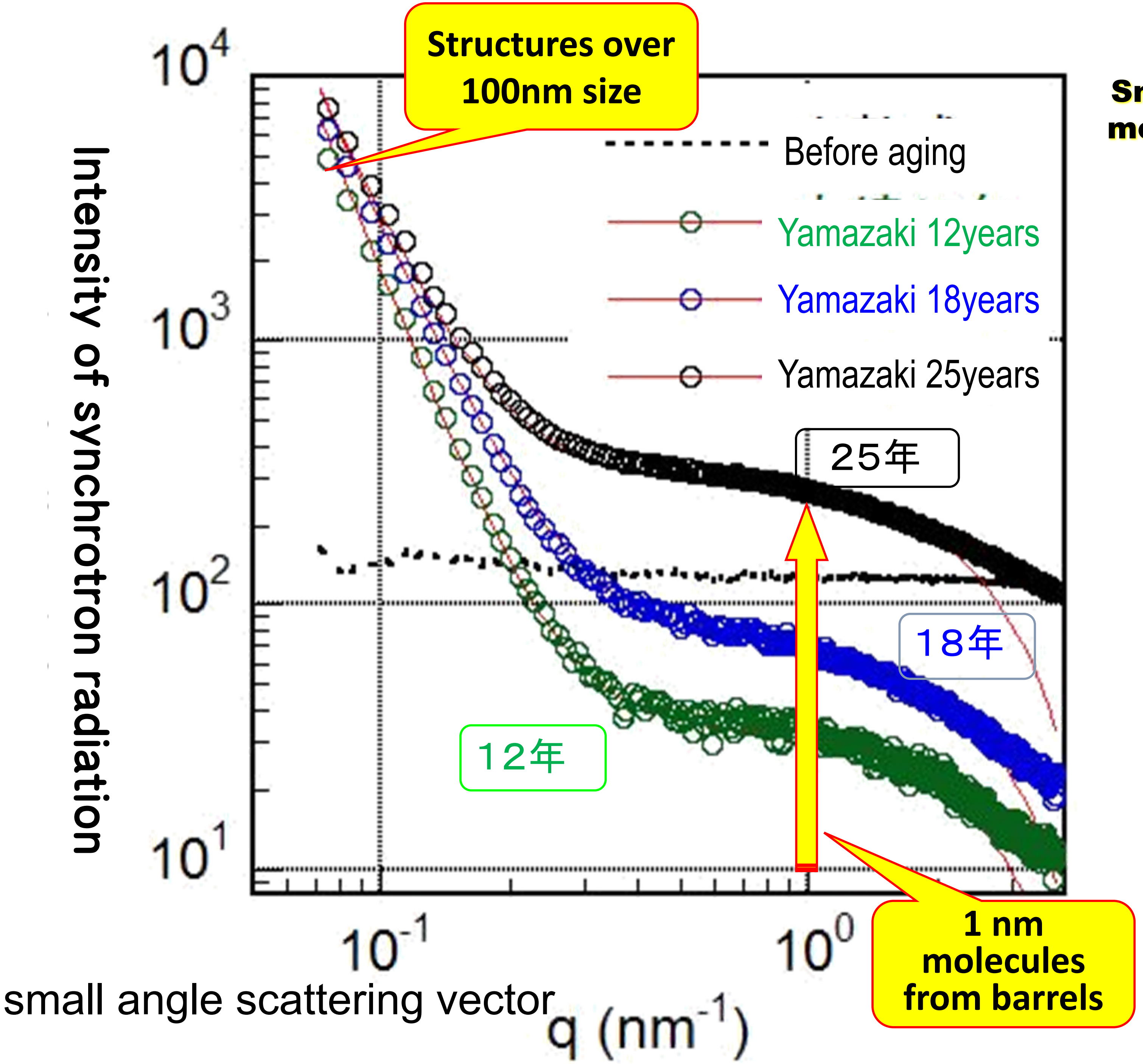
SPring-8

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



Structures over 100nm size

1 nm molecules from barrels

Aging process:

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

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!"

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Micelle formation:

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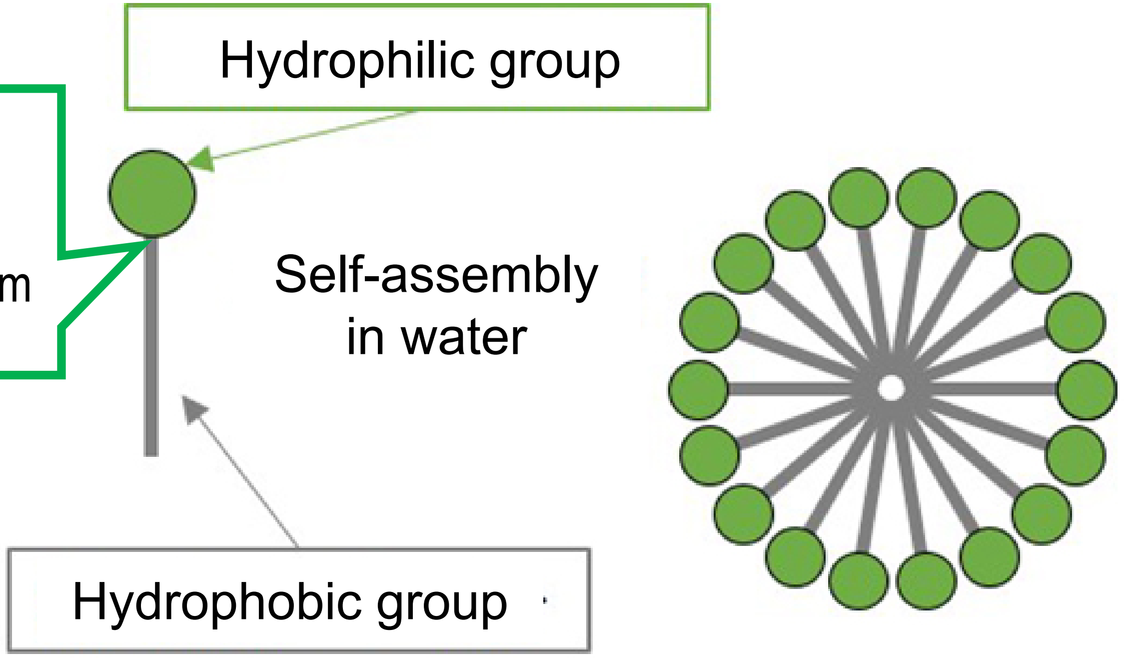
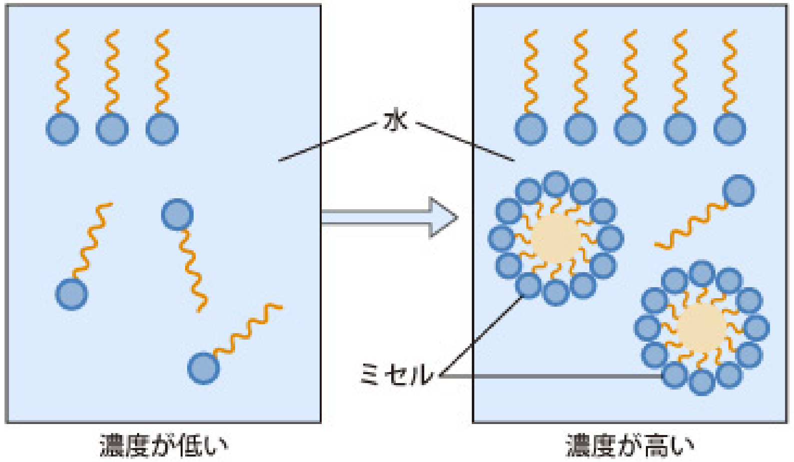
"The cause of the mellowness!"



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



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
- 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！

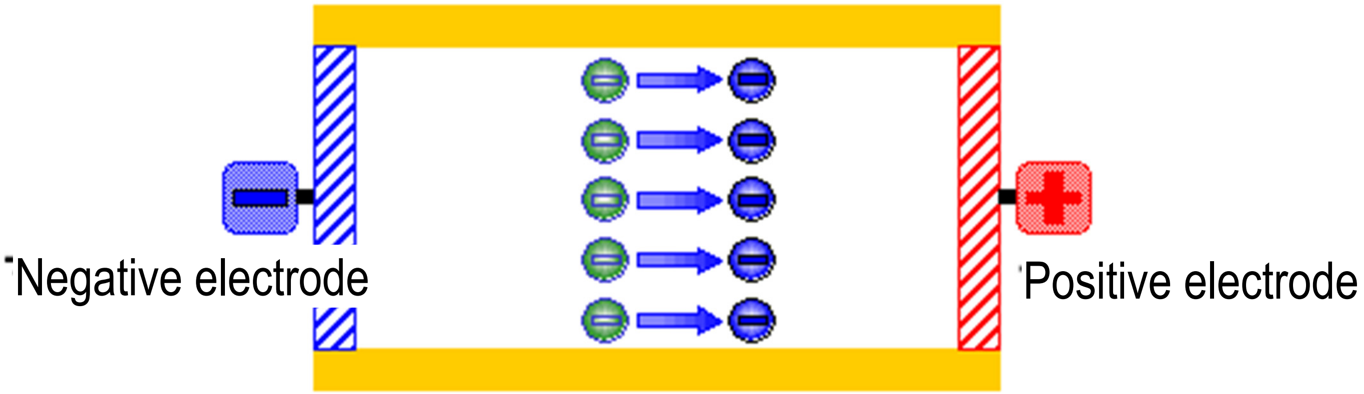
- Focus on colloidal dispersion and aggregation!
- What is "dispersion"?
- What is "aggregation"?
- The keyword to controlling "dispersion" and "aggregation" is the zeta potential!

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

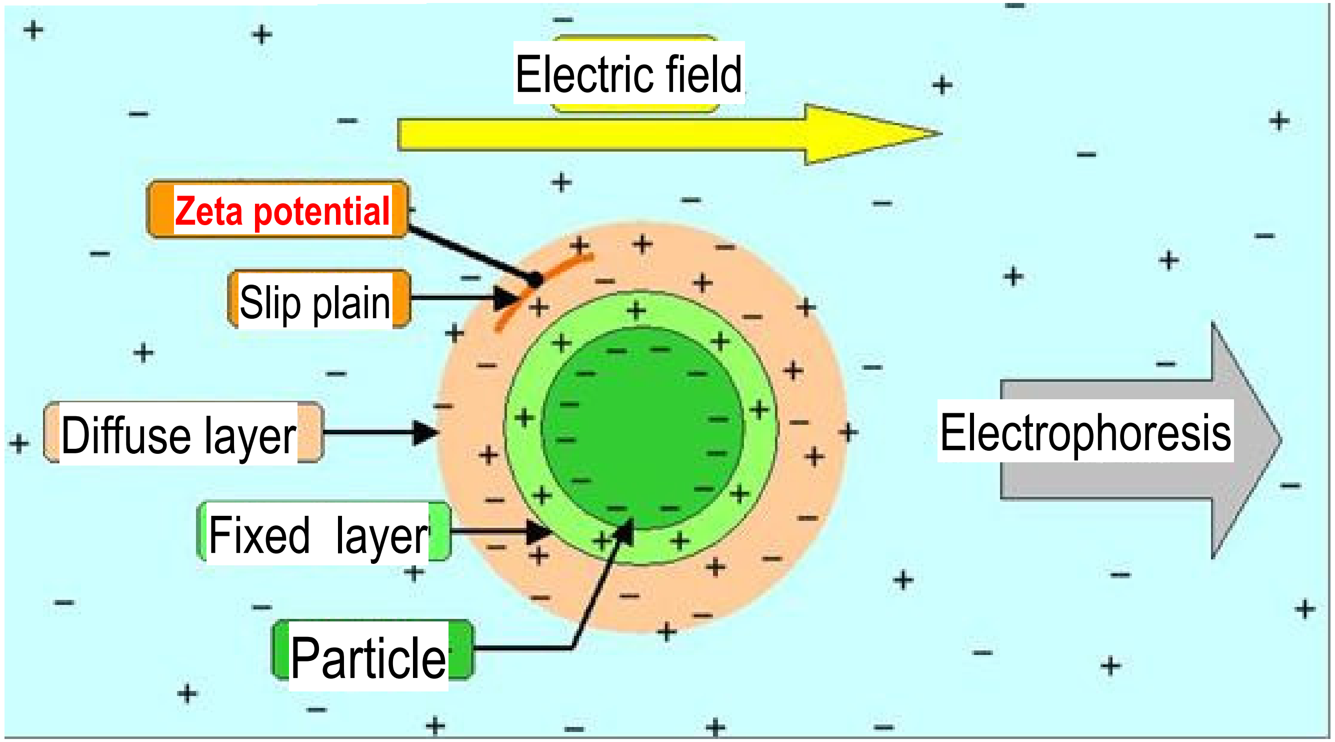
It's on your face, on your desk, on your foam, on everything!

What is the theory behind this?

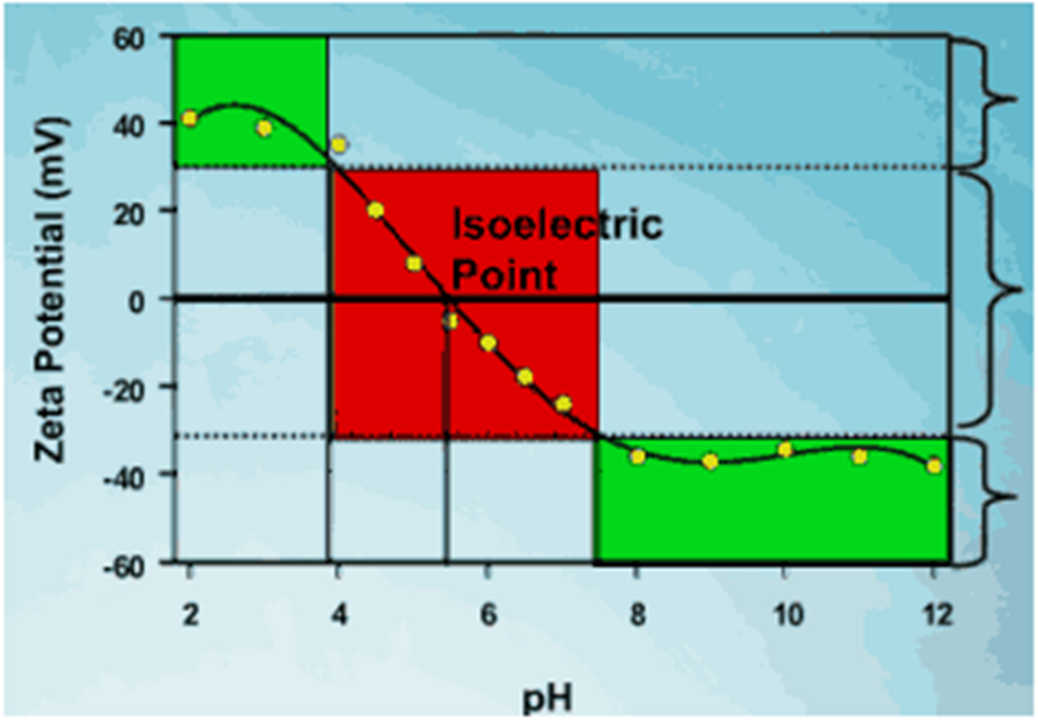
図６ Electrophoresis



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



Zeta potential as a function of pH

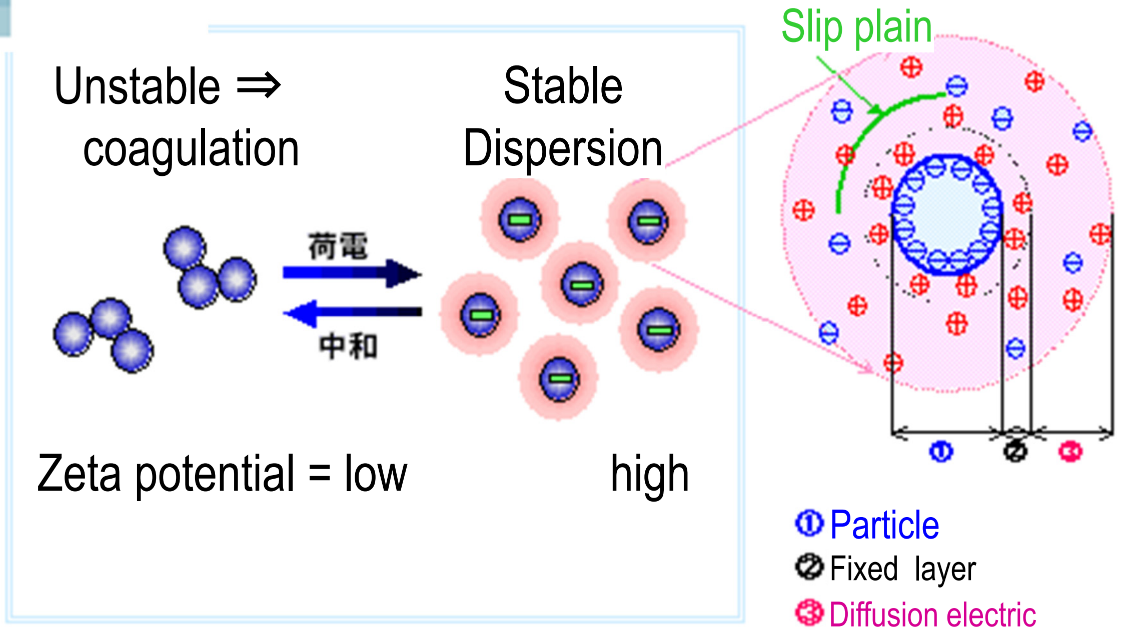


Stable

Unstable

Stable

Zeta potential and dispersion



Slip plain

Unstable ⇒ coagulation

Stable Dispersion

Zeta potential = low

high

① Particle

② Fixed layer

③ Diffusion electric double layer

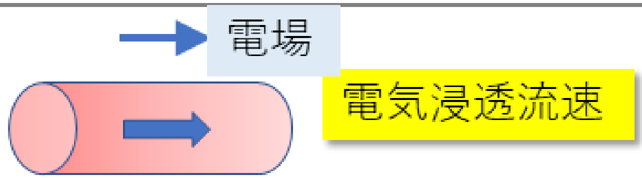
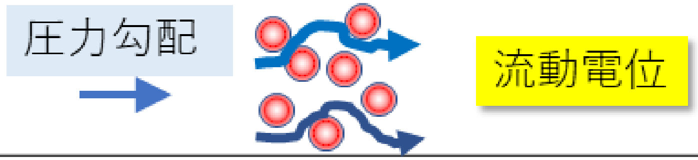
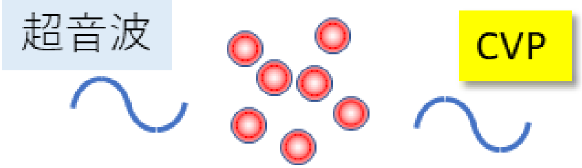
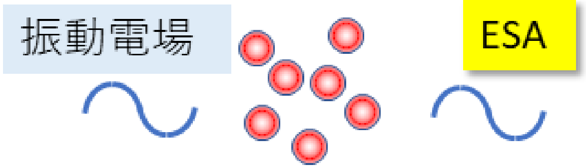
What is electrokinetic phenomenon?

A so-called electric double layer is formed at the phase interface of substances in the liquid phase.
An electric double layer is approximately represented by two electric layers with different signs, like a capacitor.
However, since one layer has the property of being diffusively movable (diffusion layer), only one layer has the property of deforming when subjected to external mechanical stimulation.
Due to this property, the motion of the electric double layer is always accompanied by electrical strain. The phenomenon caused by this electrical strain is the electrokinetic phenomenon (Electrokinetic Phenomena).
The following electrokinetic phenomena are generally known.

Electrophoresis, electroosmosis, streaming potential, zeta potential electrorheological effect, oscillating potential

界面動電現象

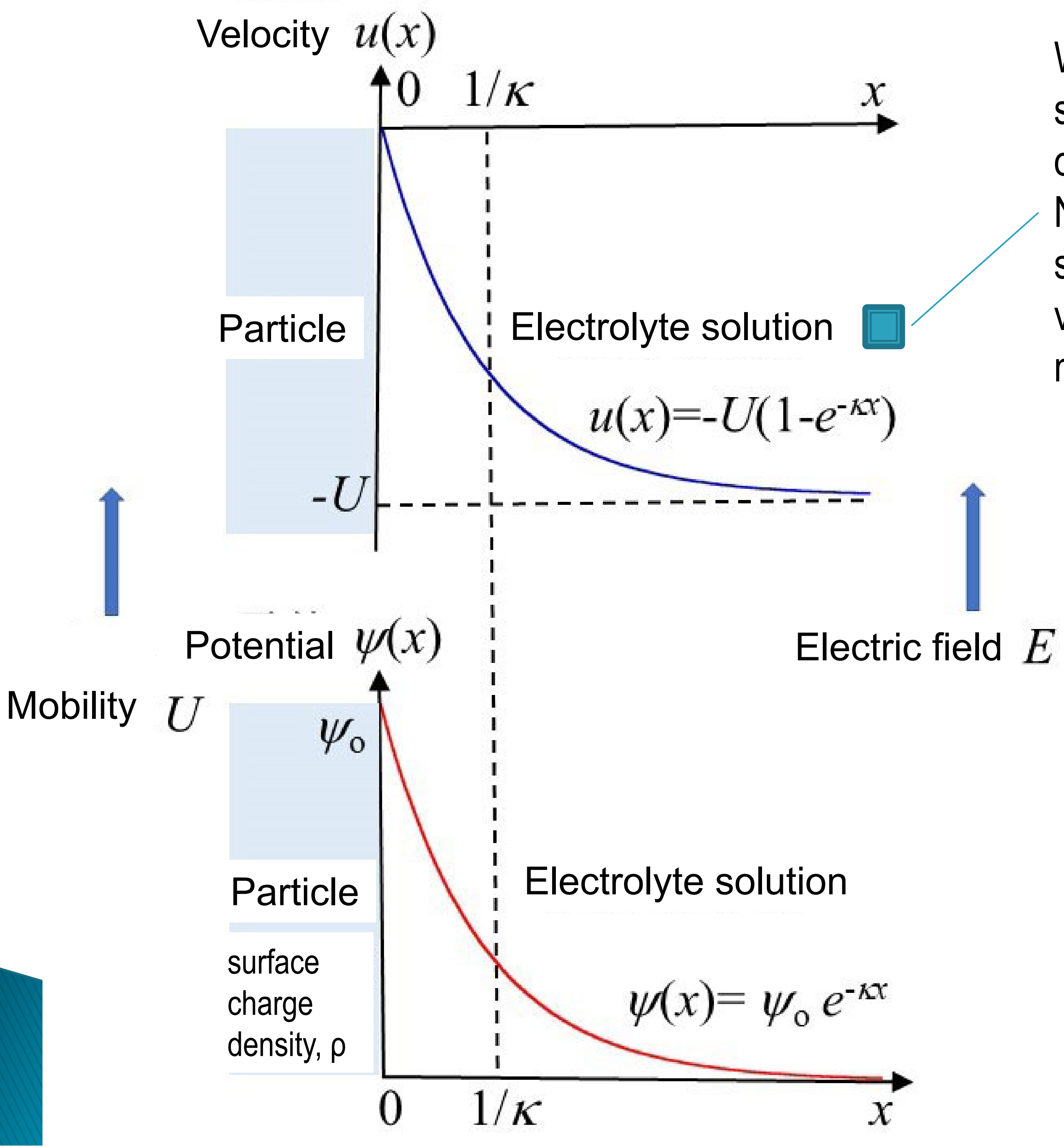
武田コロイドテクノ・コンサルティング株式会社

界面動電現象	外場	流れ	測定量
電気泳動	静電場	粒子	電場 電気泳動移動度
電気浸透	静電場	液体	電場 電気浸透流速
沈降電位	重力	粒子	重力 沈降速度・沈降電位
流動電位	圧力勾配	液体	圧力勾配 流動電位
コロイド振動電位(CVP)	超音波	粒子	超音波 CVP
電気音響超音波振幅(ESA)	振動電場	粒子	振動電場 ESA

Electrokinetic Phenomenon ~Electrophoresis~

- Suppose that a DC electric field E is applied from the outside parallel to the solid-liquid interface with an electric double layer on the solution side. Since the solid surface is stationary, a laminar flow on the solution side causes a distribution of velocities along the interface. Now, assuming a microcube in the solution, the electric force and the viscous force acting on the cube must balance in the steady state. If the average charge density in the cube is ρ, the electric force is ρE, which is balanced with the viscous force ($\eta d^2u/dx^2$) in the steady state (SI unit system) (equation 6).

$$\rho E = \eta \frac{\mathrm{d}^2 u}{\mathrm{d}x^2} \cdots\cdots\cdots\cdots\cdots\cdots (6)$$



When laminar flow occurs on the solution side, a velocity distribution occurs along the interface.

Now, assuming a microcube in the solution, the electric force and the viscous force acting on the cube must balance in the steady state.

$$\rho E = \eta \frac{d^2 u}{dx^2}$$

Electrokinetic Phenomenon ~Electrophoresis~

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$$\rho E = \eta \frac{\mathrm{d}^2 u}{\mathrm{d}x^2} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (6)$$

Electrophoresis and zeta potential

- u (u = V/E) is the relative velocity of the interface or particle and solution, i.e. the electrophoretic mobility. After substituting Poisson's formula into this relation and rearranging it, the following formula is obtained by integrating both sides twice.

$$V = (\varepsilon_0 \varepsilon_\mathrm{r} / \eta)\, \phi_0 E \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (\,7\,)$$

The potential in the diffusion layer is obtained based on Poisson's equation.

$$\Delta\psi = \mathrm{div}\ (\mathrm{grad}\ \psi) = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = -\frac{\rho}{\varepsilon_r \varepsilon_0}$$

ε_r: Dielectric constant of solution

ε_0: Dielectric constant in vacuum

ρ: Charge density

Smoluchowski formula

- Electrophoretic mobility, $u = V/E$ is represented by

$$u = (\varepsilon_0 \varepsilon_r / \eta)\zeta \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (8)$$

- where η indicates viscosity. Also, in equation (8), the surface potential ψ_0 is replaced with the zeta potential ζ. This equation is called the Smoluchowski equation and is the most widely used electrophoretic equation. Although this formula was derived for flat plates, it can be applied to spherical particles where the particle radius (*a*) is larger than the thickness of the electric double layer ($1/\kappa$) ($a \gg 1/\kappa$, or $\kappa a \gg 1$). It can also be used for cylindrical particles with large radii. Furthermore, it can be said that it is a very useful formula because it can be applied to large particles of any shape.
- In particular, in water at 25℃ (ε_r = 78.5, η = 0.89mPa), it can be expressed as follows. $\zeta = 12.8\, u$ (mV)

Hückel formula

- The second method is to think of the external electric field as “acting on a point charge”, which is the opposite limit of the Smoluchowski equation, i.e., the limit of small particle radius a or thick double layer ($a \ll 1$), which is called Hückel's formula.

$$u = \frac{2\varepsilon_0 \varepsilon_r \zeta}{3\eta} \quad \cdots\cdots\cdots\cdots (10)$$

- Like Smoluchowski's equation (8), Hückel's equation does not depend on the particle radius, a, but differs in that it has a factor of 2/3.

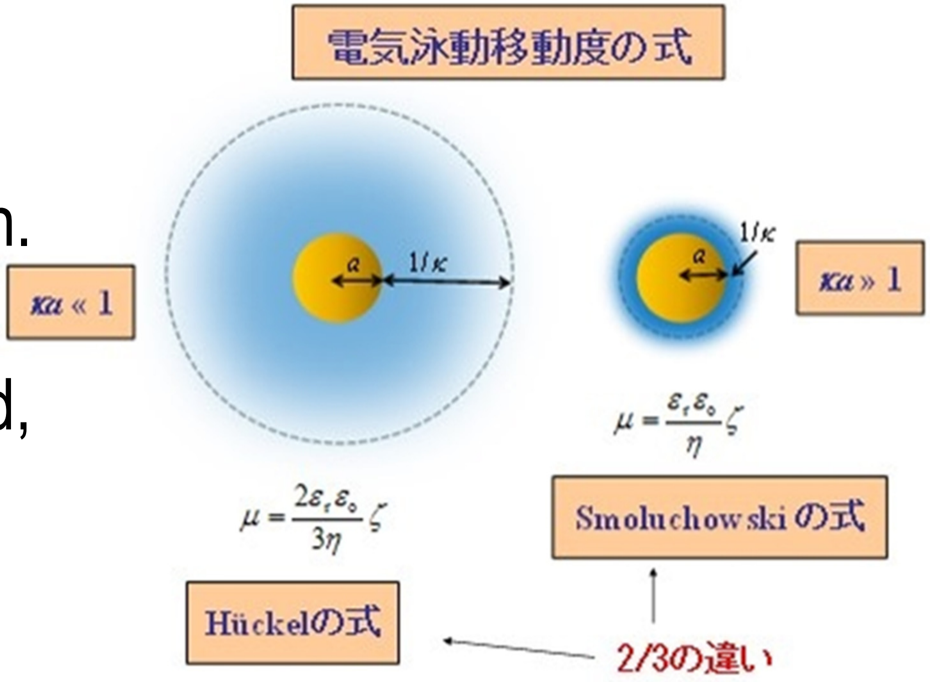
Henry formula

- Henry thought about this contradiction as follows. The Smoluchowski equation takes into account the distortion of the electric field due to the presence of particles (the electric field acts parallel to the interface), whereas the Hückel equation ignores the distortion of the external electric field due to the presence of very small particles. . This distortion of the electric field is strictly treated as a function of *κa*, and the effect (retarding effect) due to the movement of counterions in the liquid flowing in the opposite direction, rather than the particles migrating in the stationary liquid, is also considered. and derived the following equation.

$$u = (\varepsilon_0 \varepsilon_r / \eta) \zeta \cdot f(\kappa a) \quad \cdots\cdots\cdots\cdots\cdots\cdots (12)$$

Henry coefficient

- The function $f(\kappa a)$ is called Henry's coefficient and expresses the degree of distortion of the external electric field due to the presence of particles. Here, when $\kappa a \to 0$, $f = 2/3$ and the Henry equation becomes the Hückel equation.
- Conversely, when $\kappa a \to \infty$, $f = 1$ and the Smoluchowski equation is obtained, and in this limit the external electric field is completely distorted. The intermediate values of κa are shown in the figure on the next slide.



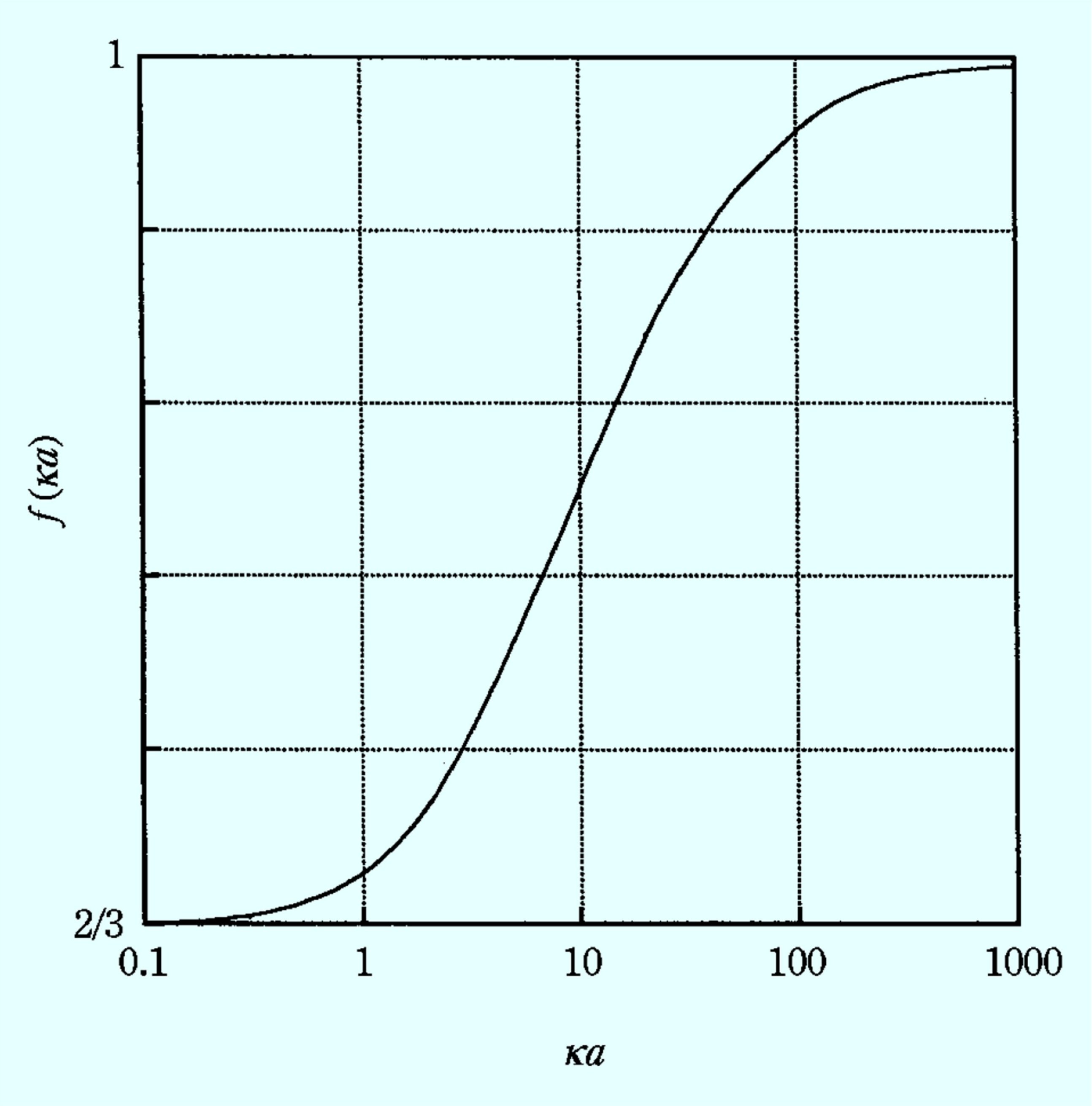


図 2　Henry 係数 f の κa による変化

Relaxation effect

- One problem still remains in the relationship between electrophoretic mobility and ζ potential. It is a well-known relaxation effect in the theory of electrical conduction in strong electrolytes. It is the effect that the opposite electric force acts on the particles because the double layer is deformed by an external electric field and becomes asymmetric.
- a) In colloidal electrophoresis with a ζ potential of 50 mV or less, the relaxation effect is negligible.
- b) In colloidal systems satisfying $\kappa a \gg 1$ or $\kappa a \ll 1$, the effect of the relaxation effect is small.
- c) In colloidal systems with $1 < \kappa a < 100$ and a ζ potential of 75 mV or more, u is greatly affected by the relaxation effect, making it difficult to estimate the ζ potential from the value of u.

Electrophoresis measurement

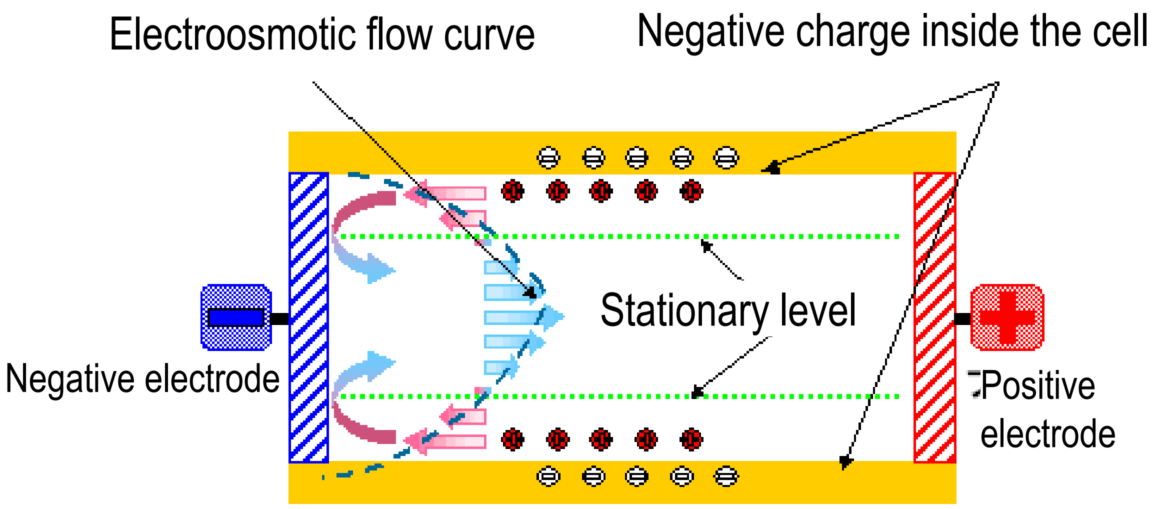
- A major problem with performing electrophoretic measurements in thin glass cells is the electroosmotic effect that occurs on the glass walls. Since the glass wall is negatively charged with respect to the aqueous solution, the solution flows due to the electroosmotic effect when an electric field is applied, and this flow u_{osm} is superimposed on the true electrophoretic mobility, *u*, of the colloidal particles. That is, the apparent particle migration mobility, u_{app}, observed under a microscope and *u* are related as follows.

$$u_{\mathrm{app}} = u + u_{\mathrm{osm}} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (14)$$

- u_{app} varies parabolically with cell depth *h* and is given by the following equation when *k* = (cell width/cell depth)>>1.

$$u_{\mathrm{osm}} = \frac{u_0}{2}\left(\frac{3h^2}{b^2} - 1\right) \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (15)$$

- *b* : 1/2 of the cell thickness, u_0 is the electrophoretic mobility at the wall surface ($h = \pm b$)



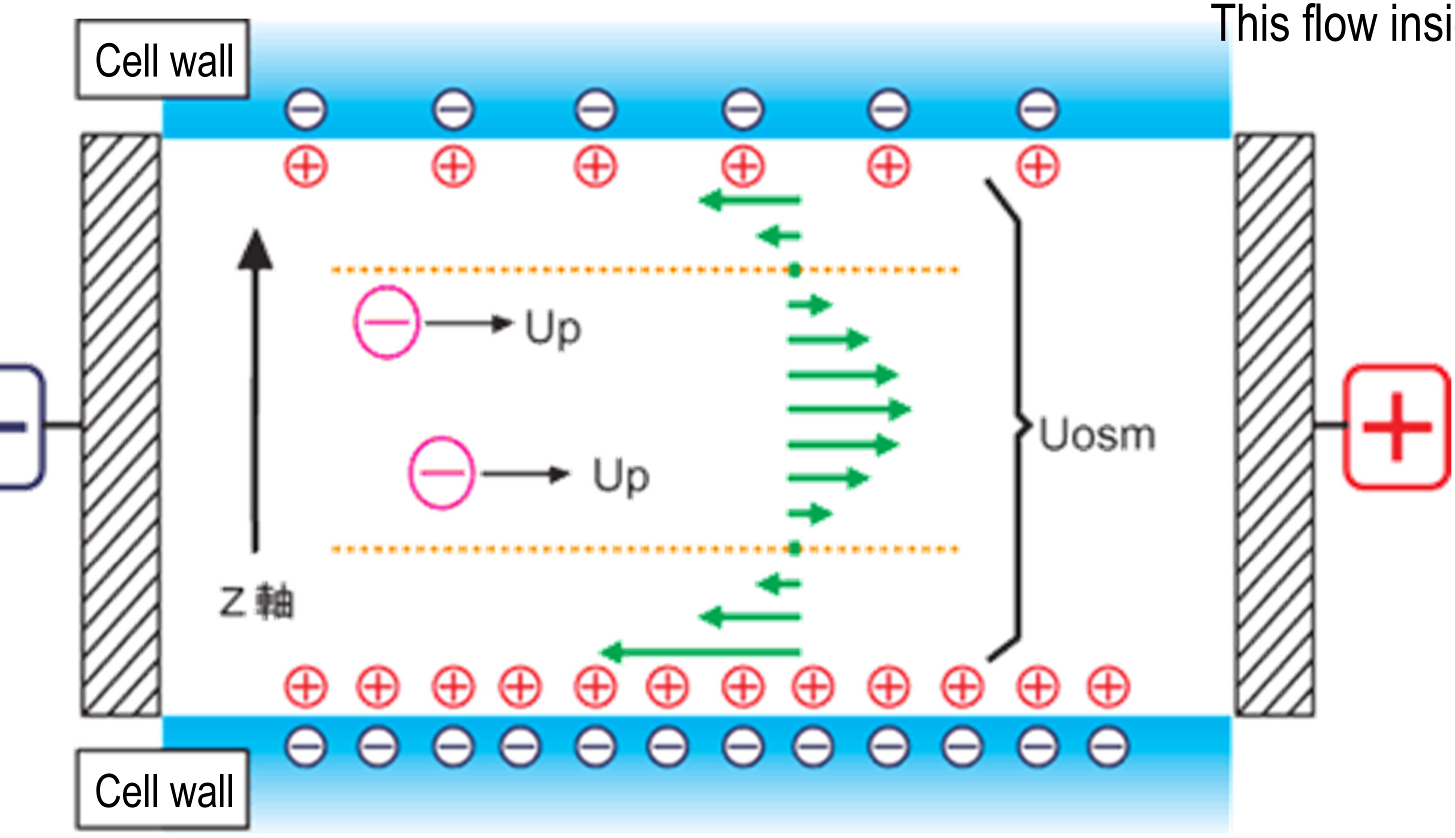
Electroosmotic flow

Quartz cells are generally used as measurement cells. The isoelectric point of quartz is 2 ～ 3, and the surface of the cell is usually negatively charged.

There are many ions.

When a voltage is applied to the cell, the positive ions near the cell wall are pulled toward the cathode and move, creating a flow. Since the cell is normally a closed system, the flow in the vicinity of the cell wall is circulated, and the flow in the opposite direction occurs in the vicinity of the cell center.

This flow inside the cell is called electroosmotic flow.



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$$u_{\mathrm{osm}} = \frac{u_0}{2}\left(\frac{3h^2}{b^2} - 1\right) \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (15)$$

- b : 1/2 of the cell thickness, u_0 is the electrophoretic mobility at the wall surface ($h = \pm b$)

Electrophoresis measurement

- u_{app} at level h_s, giving u_{osm}=0, gives the true electrophoretic mobility *u*. This h_s is called the stationary level and given by the following equation.

$$h_s = \pm\frac{b}{\sqrt{3}} = \pm 0.577b$$

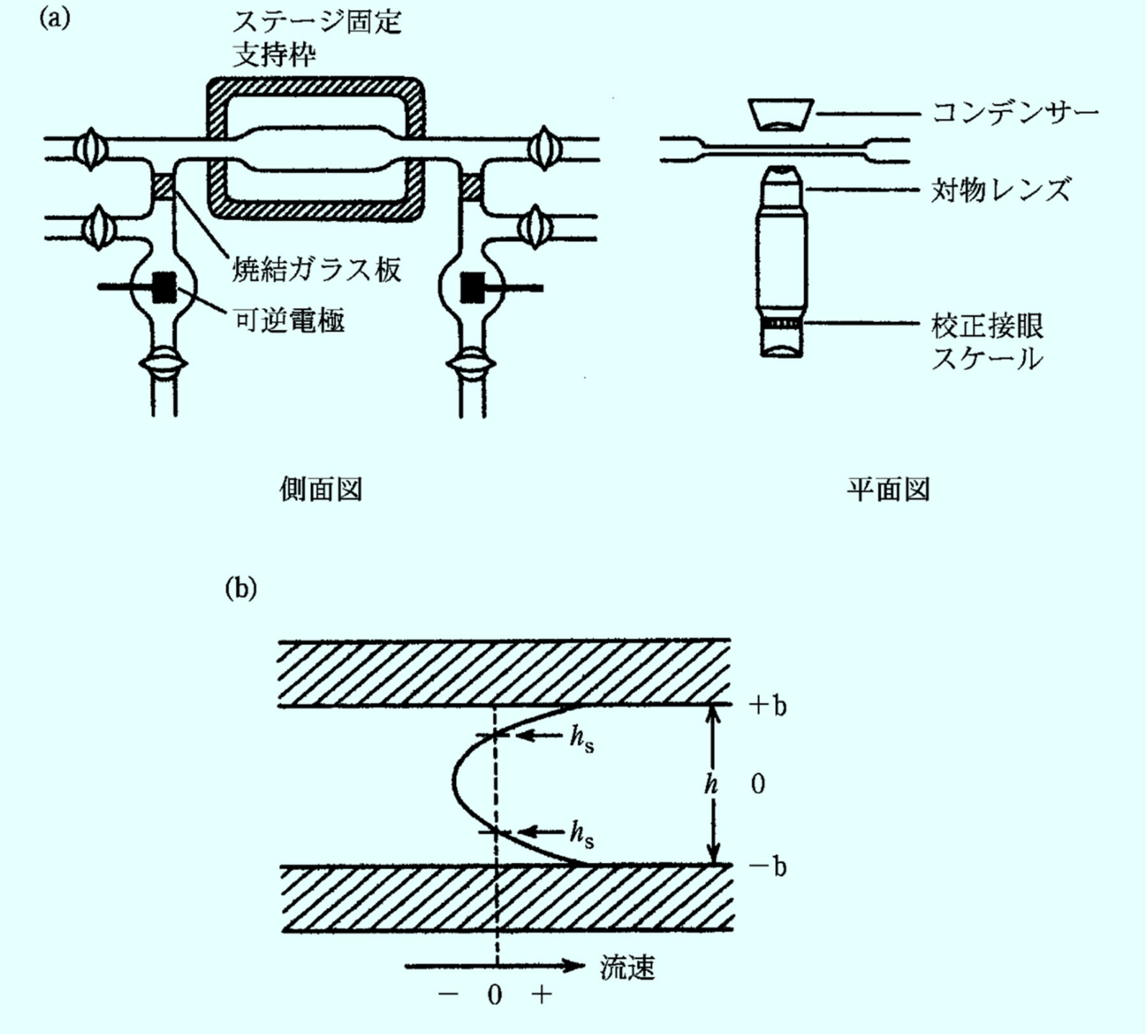
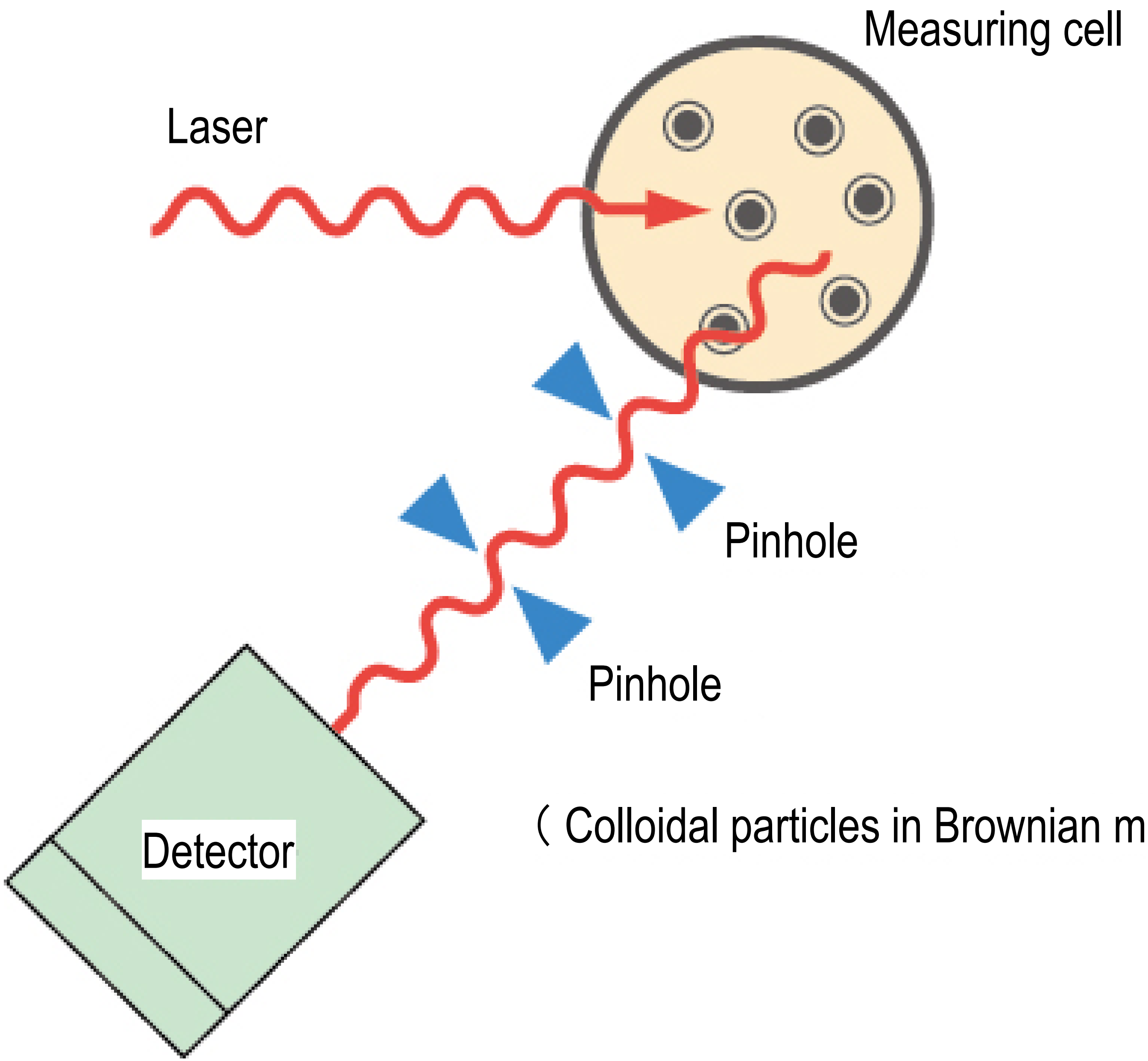


図 4　顕微鏡電気泳動測定装置(a)とセル中の流速の分布と座標の取り方(b)

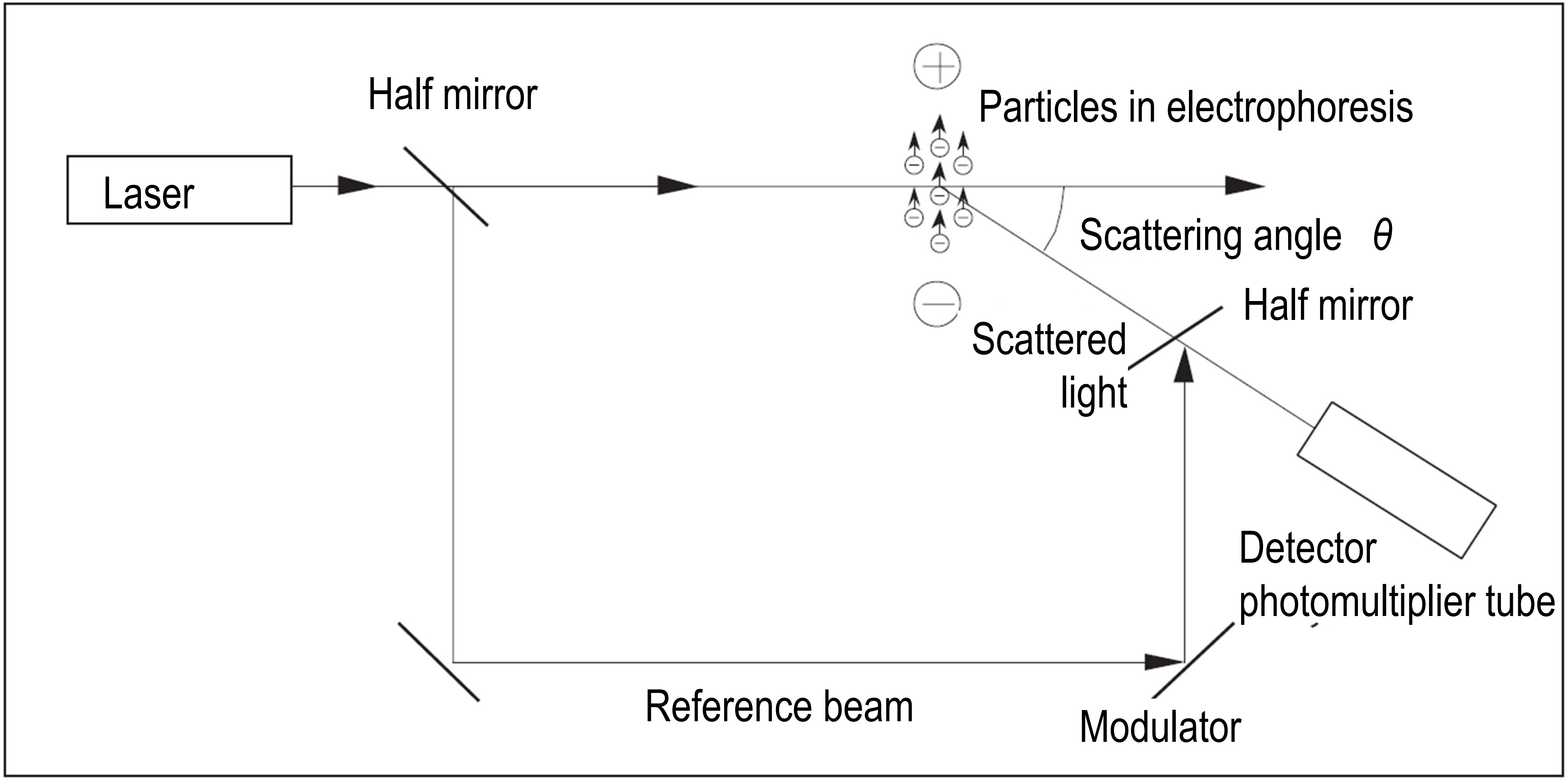
Electrophoretic light scattering measurement method

- The electrophoretic light scattering measurement method is also called the laser Doppler method. This is a method that uses the “Doppler effect” to give the migration velocity of particles. The Doppler effect is the phenomenon that when light or sound waves strike a moving object and are reflected or scattered, the frequency of the light or sound wave changes in proportion to the speed of the object. When electrophoretic particles are irradiated with laser light, the scattered light from the particles undergoes a frequency shift due to the Doppler effect. We can see the migration speed of the particles.



（ Colloidal particles in Brownian motion ）

Electrophoretic light scattering measurement method



ヘテロダイン法による電気泳動光散乱光度計の光学系

Electrophoretic light scattering measurement method

- In general, particles migrate at a slow speed, so their Doppler shift amount (~100 Hz) is significantly smaller than the frequency of incident light (5 × 10 12 Hz). The Heterodyne method is a technique for detecting such small frequency differences. It mixes part of the incident light (reference light) and scattered light in the optical system. Doppler-shifted scattered light from migrating particles and reference light corresponding to non-migrating particles are simultaneously observed.). It is expressed as an autocorrelation function of scattering intensity by a photon correlator. Since the observed particles are in Brownian motion, this autocorrelation function becomes a decaying cosine wave. That frequency corresponds to the amount of Doppler shift.

Electrophoretic light scattering measurement method

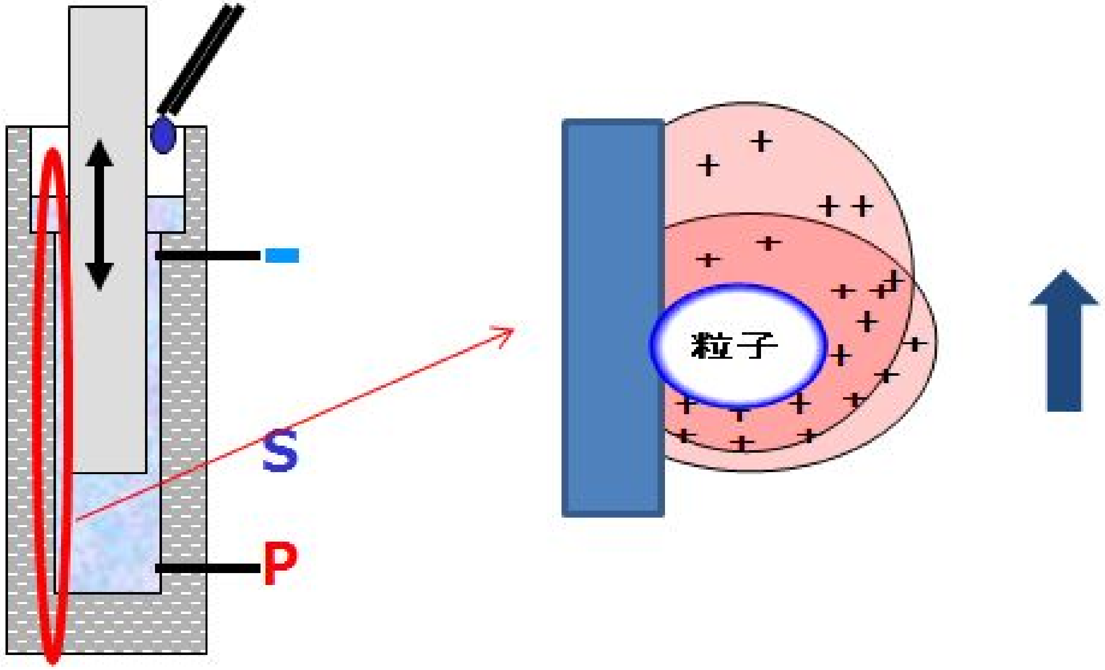
- By performing FFT analysis on the obtained autocorrelation function, the distribution of frequency components can be obtained. Furthermore, the distribution of electrophoretic mobility is required. Actually, a sample dispersed in a solvent with a refractive index (n) is irradiated with a laser beam of a wavelength (λ), and the mobility (U) and the Doppler shift (Δv) when detected at the scattering angle (θ) The relationship is expressed by the following equation.

$$\Delta\nu = \frac{2V n \sin(\theta/2)}{\lambda}$$

$$U = V / E$$

Streaming potential zeta potential measurement

Focus on the particles attached to the two walls of the Teflon cell. When the piston vibrates up and down, the particles attached to the wall do not move, and the liquid around the particles moves up and down according to the movement of the piston. At this time, a potential difference is generated in the solution between the bottom of the Teflon cell, which does not move vertically, and the top of the cell, which is close to the liquid surface. This is called streaming potential. This streaming potential is measured with two electrodes. The relationship between the zeta potential, ζ, and the streaming potential is given by the following equation.



$$\text{Streaming Potential} = \frac{k \times v_0 \times \varepsilon \times \zeta}{\eta}$$

k —— 定数
v_0 —— 流速
η —— 粘度
ε —— 誘電率
ζ —— ζ電位

Dorn potential （ bubble zeta potential ）

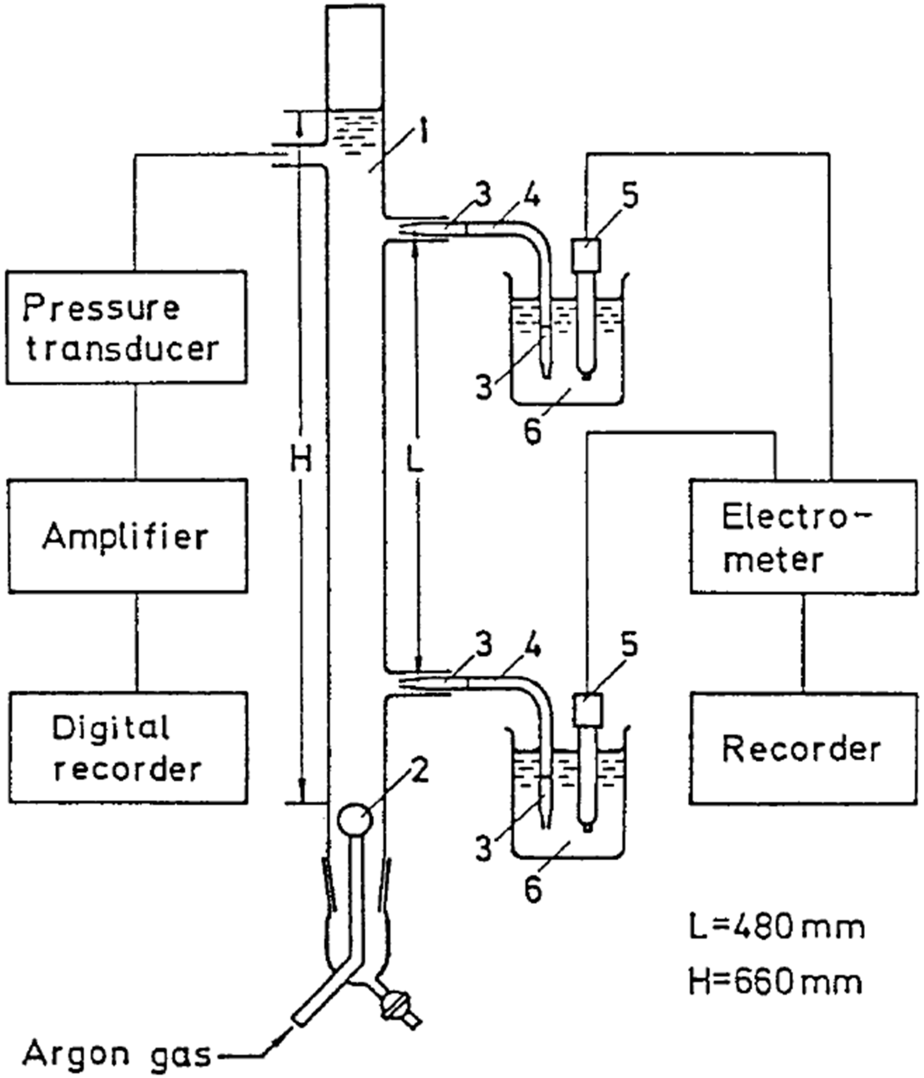


Fig.6 Schematic drawing of apparatus for measuring the Dorn effect of bubbles[15, 16]: 1) Pyrex glass tube; 2) gas disperser; 3) 0.1 M KCl–agar bridge; 4) vinyl tube filled with 0.1 M KCl solution; 5) saturated calomel electrode; 6) 0.1 M KCl solution.

Dorn potential （ bubble zeta potential ）

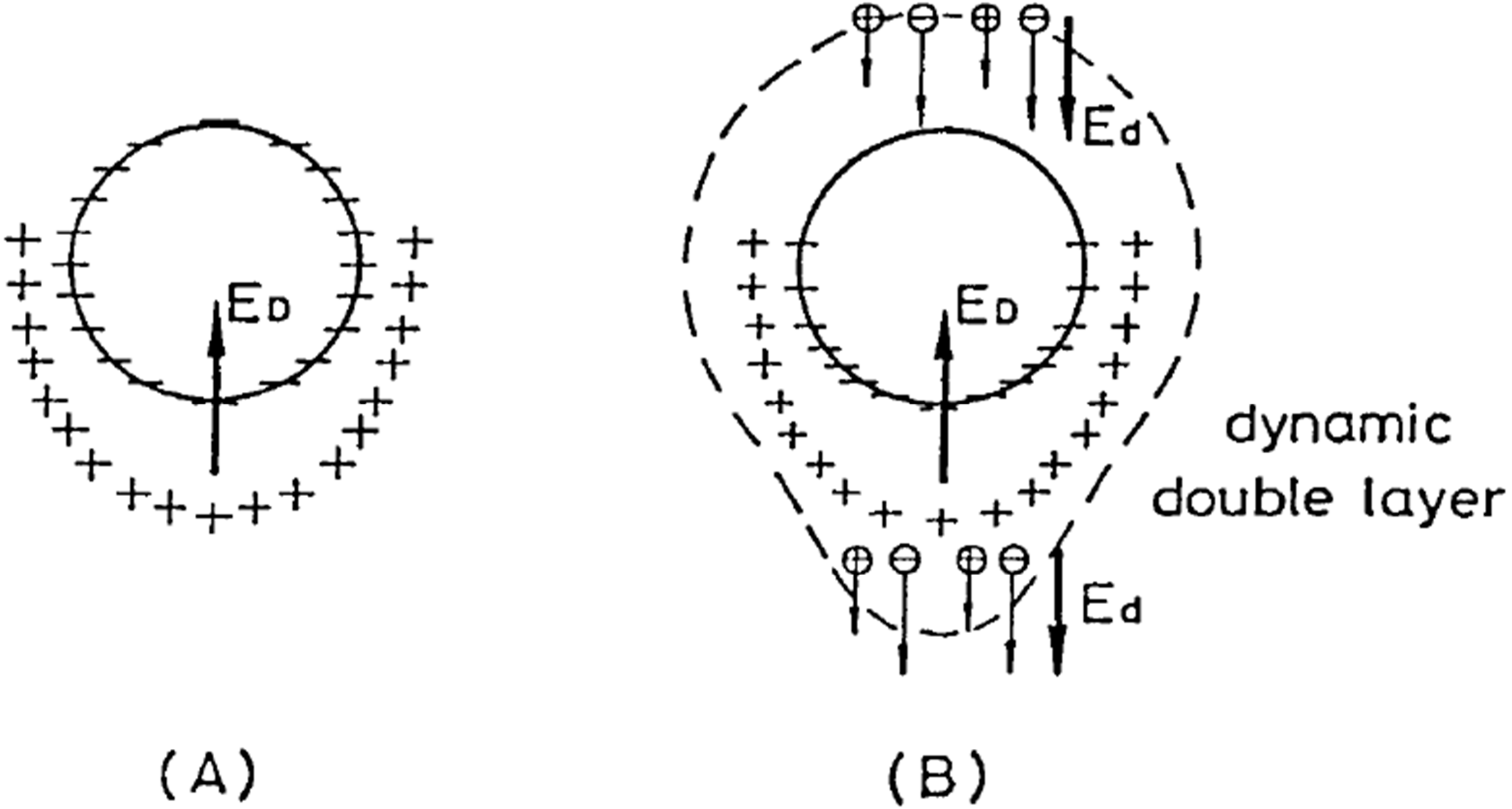


Fig.14 Schematic representation of the equilibrium (A) and the dynamic double layer of a rising bubble (B) where $D_- > D_+$. E_D :diffusion potential.

Dorn potential （ bubble zeta potential ）

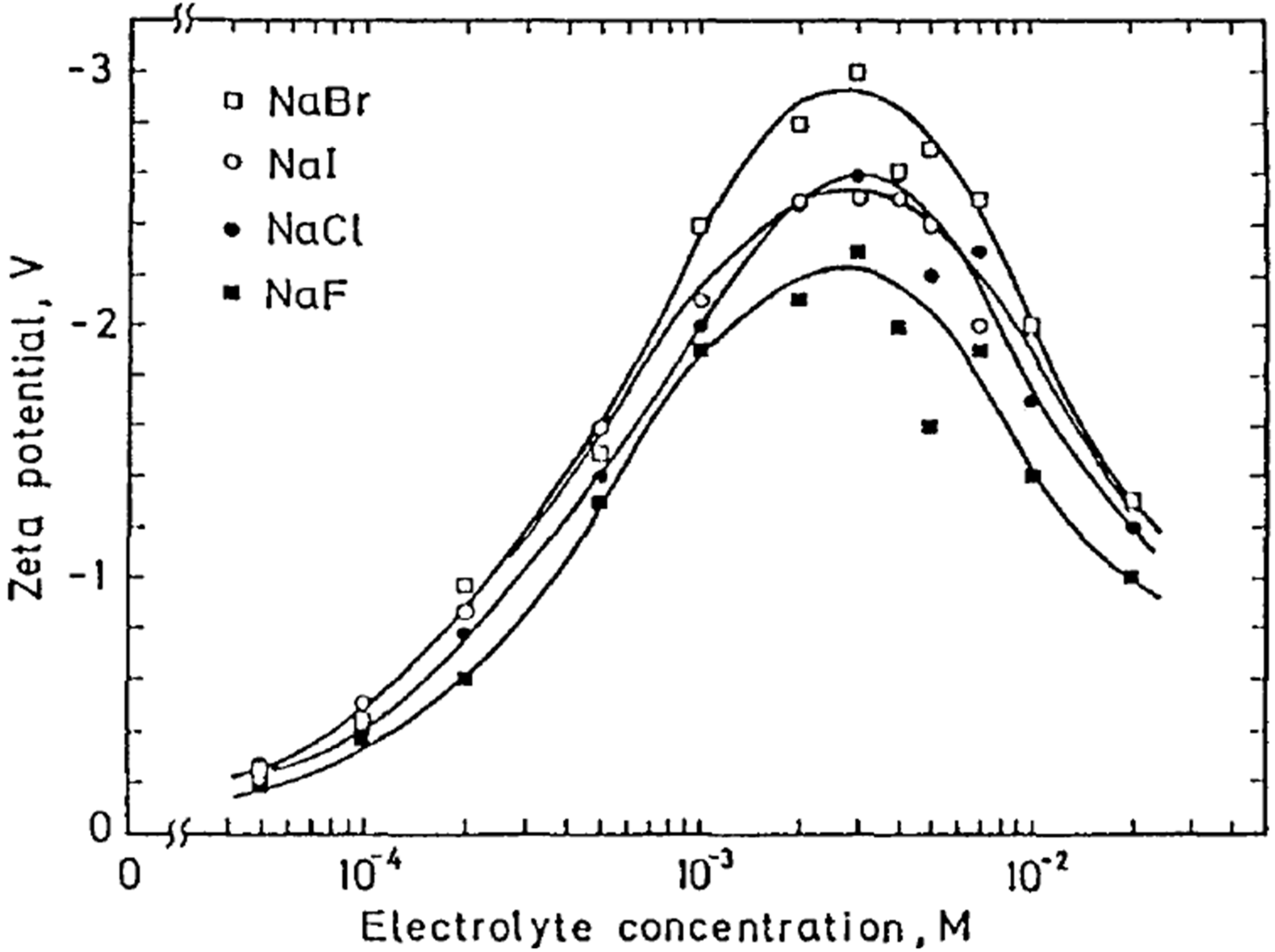


Fig.11 Zeta potential of argon bubbles as a function of sodium halide concentration. Ethanol: 4.2×10^{-2} M.

Dorn potential （ bubble zeta potential ）

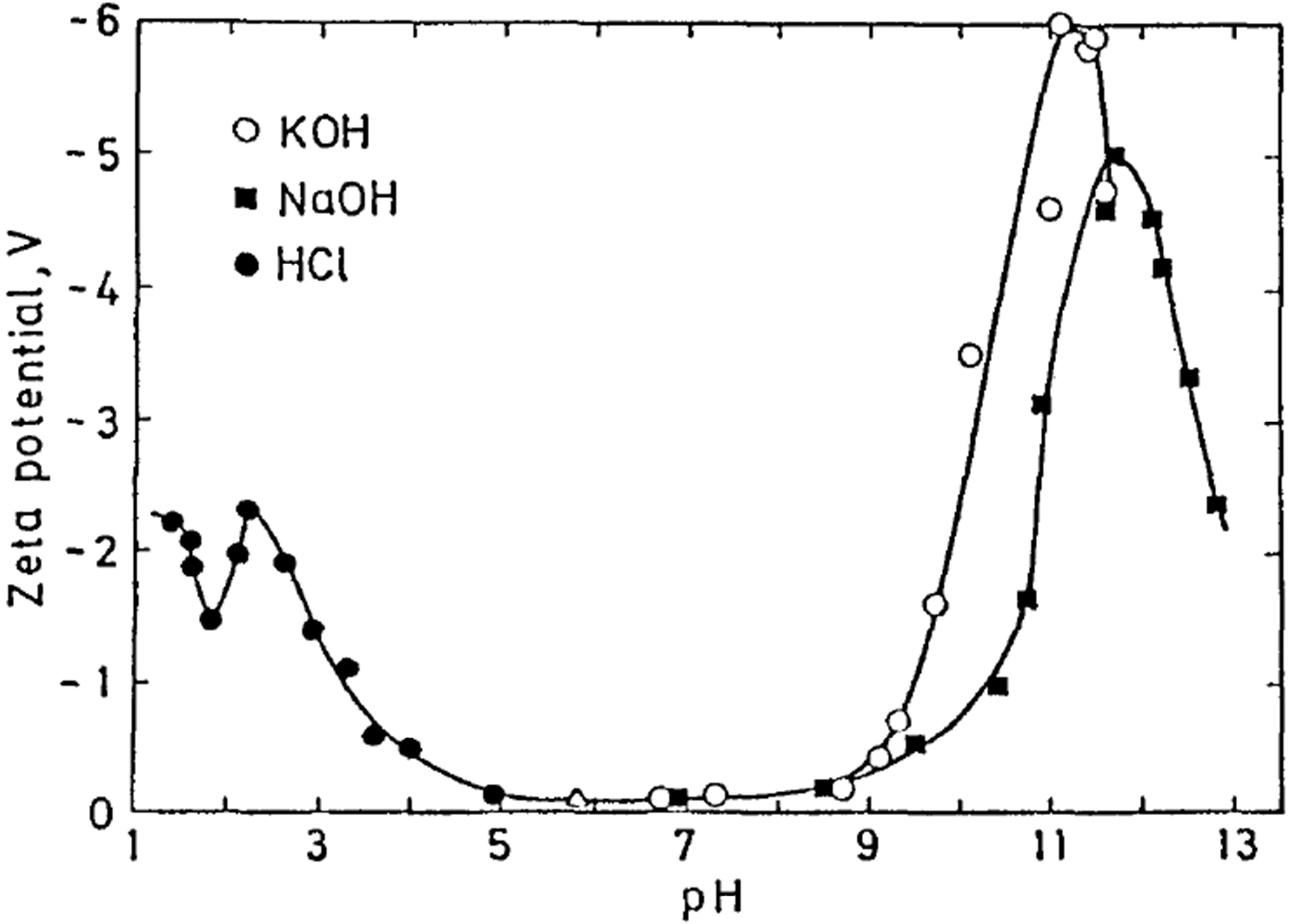


Fig.12 Zeta potential of argon bubbles as a function of pH. Ethanol: 4.2×10^{-2} M.

Plane Interface Technique

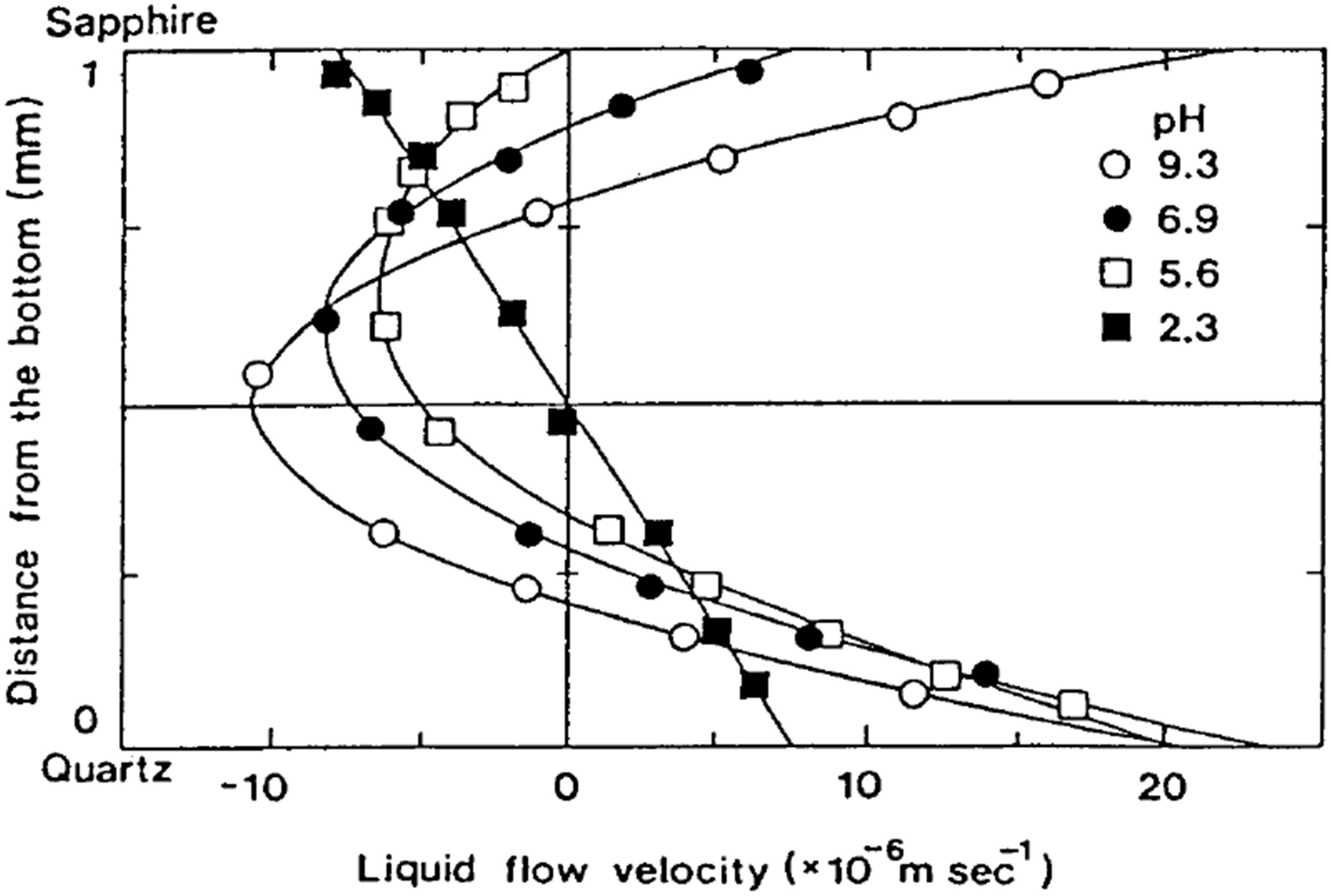
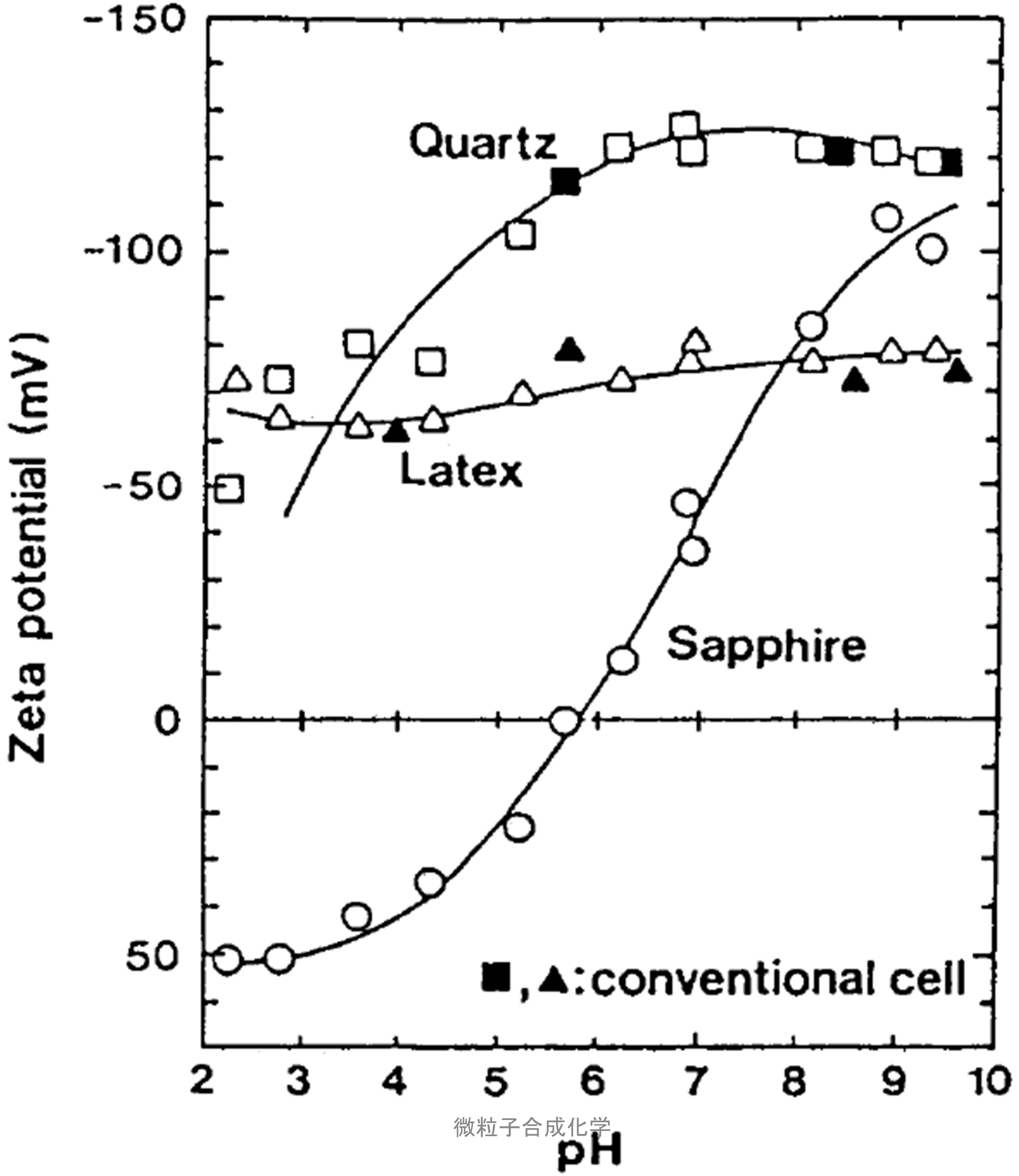


Fig. 5 Liquid flow velocity – depth profile in an asymmetric cell in solutions of various pH.

Plane Interface Technique



Plane Interface Technique（ gas-liquid interface ）

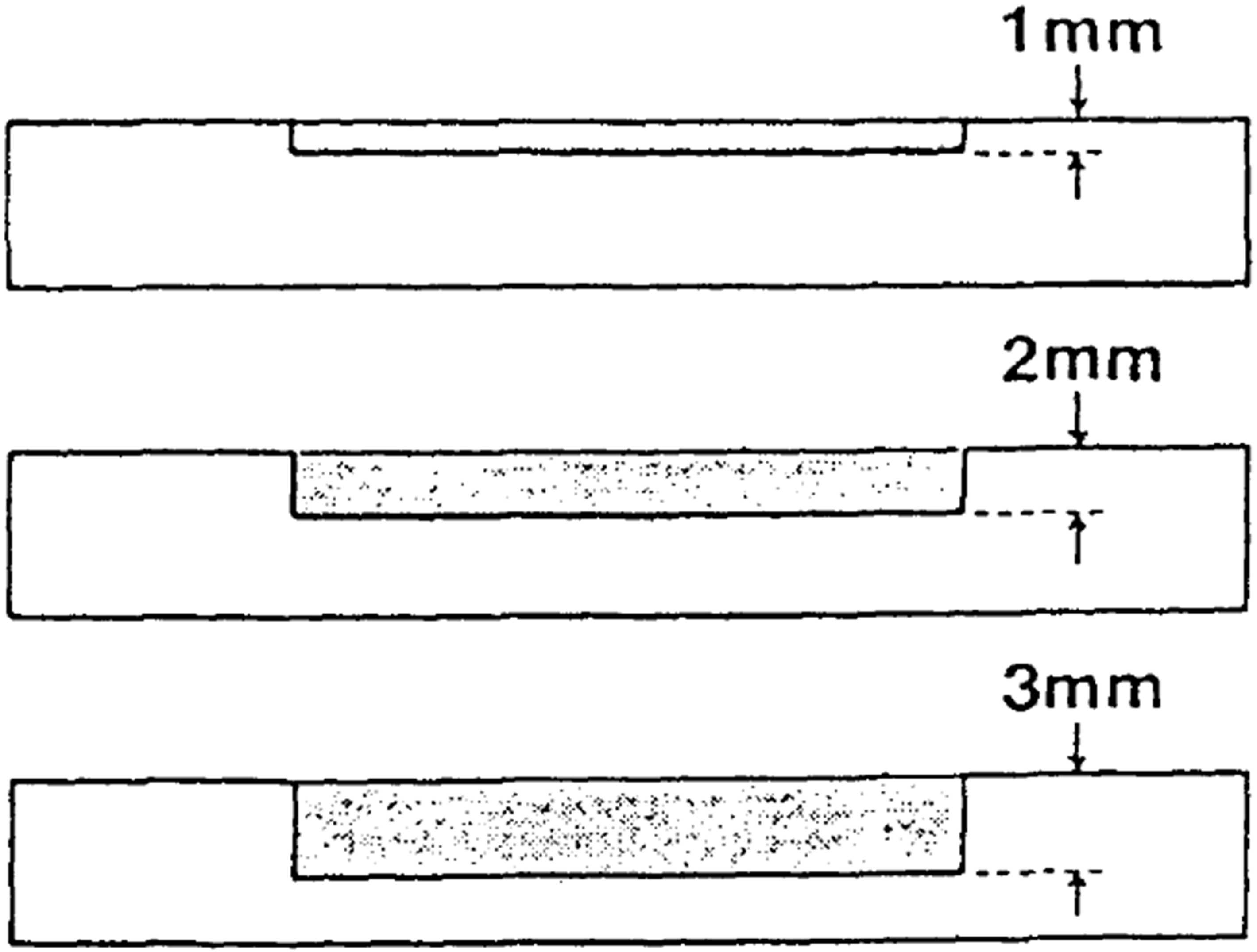
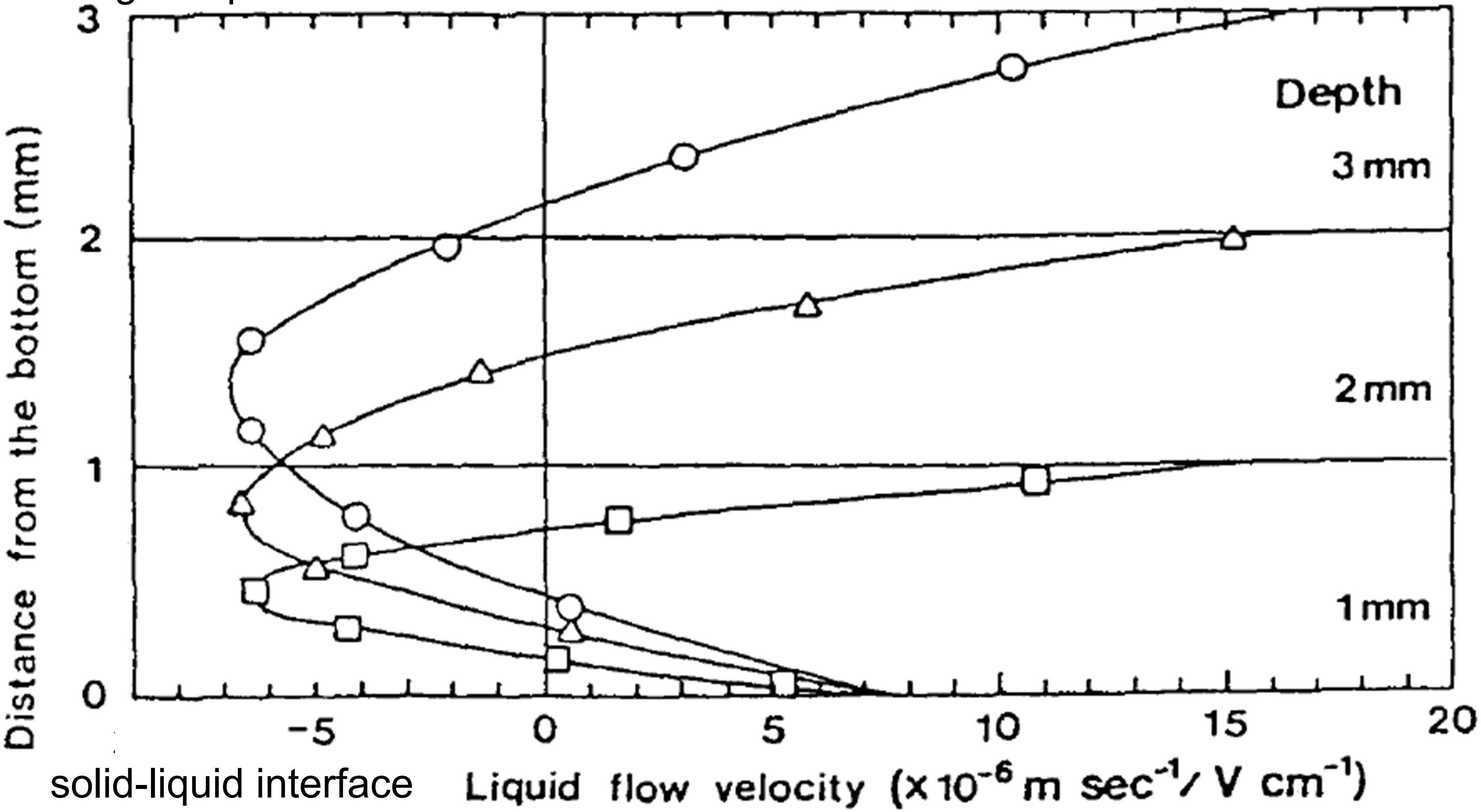


Fig.13 Side views of new open cells filled with latex suspensions differing in inside depth.

Plane Interface Technique（ gas-liquid interface ）

gas-liquid interface



solid-liquid interface

Fig.14 Liquid flow velocity – depth profile in the open cell, SHS : 0.1m mole dm^{-3}.

Plane Interface Technique（ gas-liquid interface ）

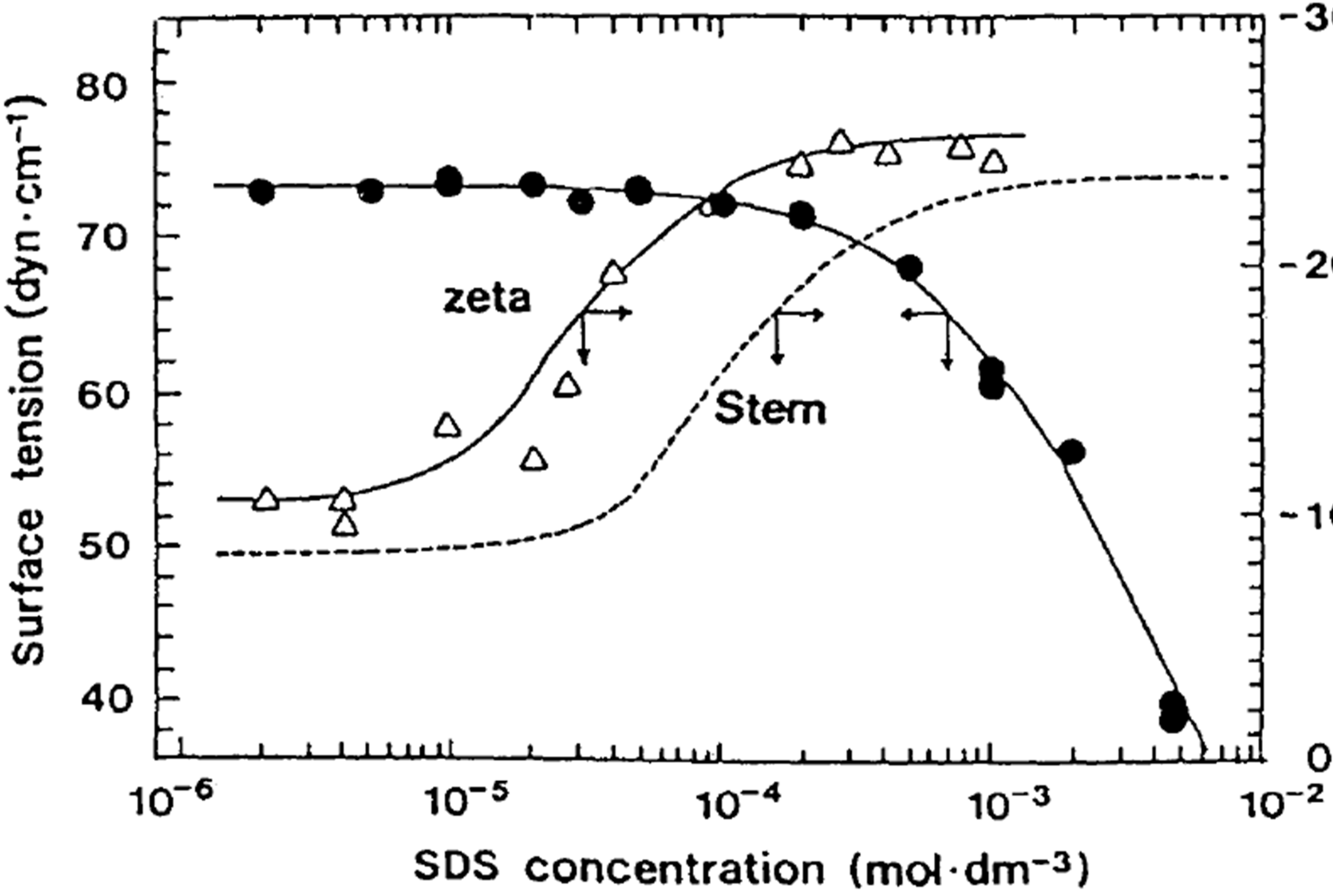


Fig.15 Comparison between zeta potential obtained by plane interface technique and the Stern potential calculated from surface tention vs. concentration data.

Isoelectric point, i.e.p.

- Normally, the isoelectric point is the pH at which the ζ potential becomes zero under the condition where specific adsorption (chemisorption) does not occur.
- In oxide particles, the isoelectric point is on the acidic side for acidic oxides and on the alkaline side for basic oxides.
- When specific adsorption occurs, the isoelectric point changes even for the same material.
- On the other hand, the pH at which the true surface potential becomes 0 is called the point of zero charge. When chemisorption of sign ions occurs, the isoelectric point changes even though the surface potential is zero.