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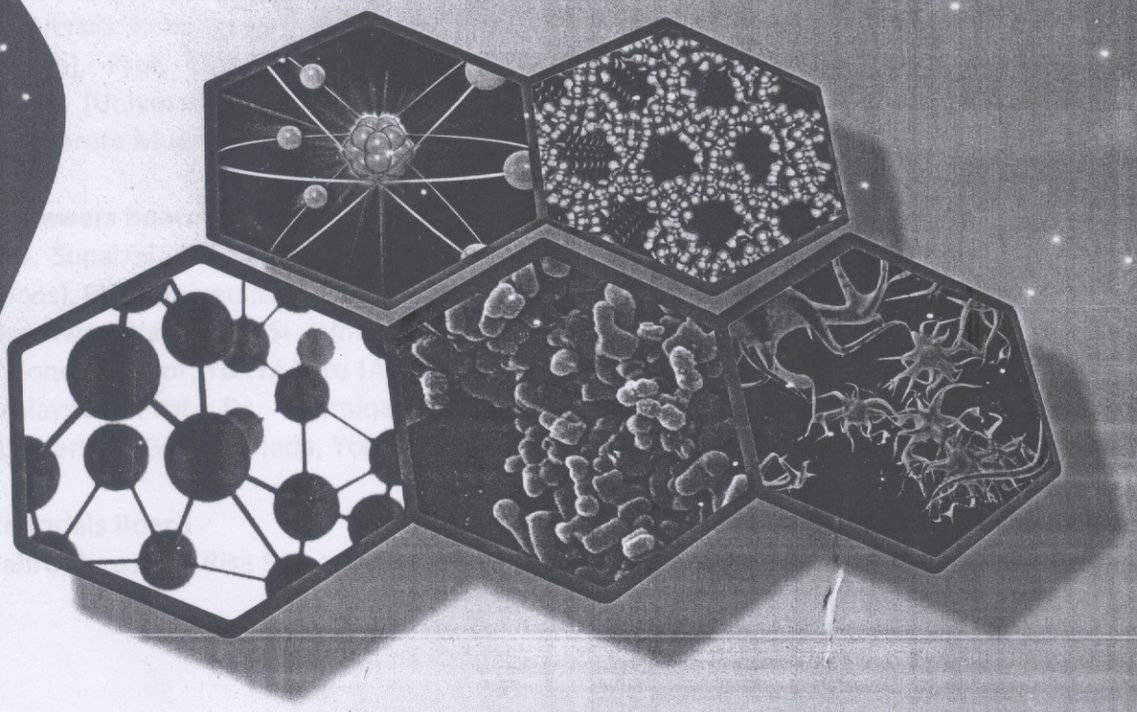
PROCEEDINGS

6th Kentingan Physics Forum
International Conference on Physics and Its Applications (ICOPIA)

The Future of Advance Materials, Nanoscience and Nanotechnology



Solo, October 3, 2012

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Contents

A Review on Particle Surface Charge Determination Instruments

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ABSTRACT

A device being capable of measuring particle surface charge has not been found yet. Therefore, no one is able to measure particle charge directly. Fortunately, there are three instruments capable of determining surface charge indirectly starting from the simplest, Micro-electrophoresis, Laser Doppler Electrophoresis (LDE) to the most sophisticated, Phase Analysis Light Scattering (PALS). Microelectrophoresis determines the surface charge via determination velocity of the moving particles. This was done by setting up a certain distance and measuring the time required by the particles to move across that distance. LDE determines the surface charge by the measurement of the Doppler beat frequency and relates that to the velocity of the particles. Three different designs of LDE instrument are presented and discussed. On the other hand PALS explores the phase shift difference of the scattered light from particles moving across the moving interference pattern results from two crossing beams. A fiber optic PALS instrument is presented and discussed.

Keywords : electrophoresis, particle surface charge, microelectrophoresis, Laser Doppler Electrophoresis (LDE), Phase Analysis Light Scattering (PALS)

INTRODUCTION

The stability of colloidal dispersions is extremely important to produce the best quality of various products such as printing ink, dye, and painting and coating solution. The existence of van der Waals attractive force causes the interacting particles to coagulate and grow to become larger coagulant. Inevitable, sedimentation processes of the coagulants would follow suit. Coagulation and sedimentation must be avoided to produce a stable solution.

In general the stability of the colloidal dispersion may be achieved by the adsorption of charges on the surface of the suspended particles.[1] Certain amount of charge on the surface of each particle is required in order for dispersion to be stable. However, there is no instrument capable of measuring particle surface charge directly. Therefore, indirect determination of particle surface charge has to be done.

A few techniques were developed by different researchers and the related instrumentations are presented in this paper. Starting from the simplest instrument, microelectrophoresis, which is capable of determining electrophoretic mobility of particles moving in aqueous solutions.[2] The value of mobility is then converted into particle surface charge. The instrument was not able to determine the surface charge of particle suspended in nonpolar solution due to particle slow motion. It is hard to human eyes to observe particles moving at the speed of 100micrometers per second and it is impossible to determine particle's velocity accurately due to the contributions of the comparable speed of Brownian motion. A more sensitive instrument is needed to observe the motion of particle in nonpolar liquid.

The answer to the problem is Laser Doppler Electrophoresis instrument. It is based on the fact that the frequency of the scattered light is slightly shifted compared to the original one. [3-5] The interference between this scattered light and the original light results in Doppler's effect. The beat frequency of the Doppler's effect may be related to the velocity and the charge of the particles.

The LDE was then developed by Miller [3, 6-8]to become PALS by taking advantage the fact that besides shifting in frequency the scattered light also undergo phase shift. Miller and his coworkers were able to relate the phase shift change in time

to the velocity of the particles and finally to the surface charge of the particles.

MICRO-ELECTROPHORESIS INSTRUMENTATION

When a charged particle moves under influence of electric field, the electrostatic force $F_e = qE$, and the viscous force, $F_v = 6\pi\eta Rv$ will soon be in balance. At this stage the charge of the particle is given by

$$q = \frac{6\pi\eta Rv}{E}$$

Equation 1

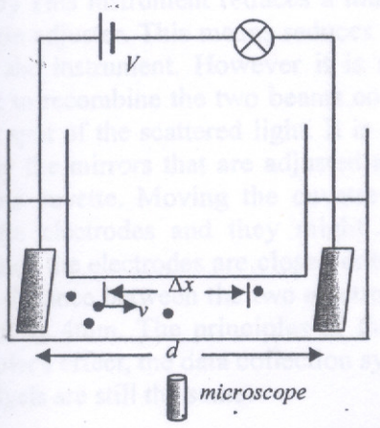

Figure 1. Diagram of micro-electrophoresis instrument

The viscosity of the solution and the radius of the particle are known parameters. Therefore the charge of the particle may be found by determining the velocity of the particle and the electric field strength.

The velocity of the particle, v (where $v=\Delta x/\Delta t$) is determined by setting a certain distance Δx and observing the interval time Δt needed by the particle to move across this distance. (see Figure 1) The electric field strength, E (where $E=V/d$) is determined by measuring the potential difference across the electrodes, V and the distance between the two electrodes.

The micro-electrophoresis instrument capable of determining the surface charge is given in Figure 1. The instrument contains a U tube glass, a pair of electrodes, a DC power supply and a simple microscope. The U tube glass is basically a solution container. A clean and transparent glass is essential in order to observe the motion of the particle in the solution. A pair of electrodes and a DC power supply are used to produce an electric field. It is extremely important to have a very stable DC power supply in order to avoid the decrease in electric field strength during the measurement. A simple microscope with 500x magnification is sufficient to be used in this experiment. A particle with 1 micrometer in diameter may be seen as 0,5mm under this microscope.

Apart from the above a voltmeter, a ruler and a stopwatch are needed to measure potential difference between the electrodes, distance and interval time respectively. A voltmeter which is capable of measuring a voltage from 100μV to several mV is required. A 10cm length ruler is sufficient to measure the distance between electrodes and the traveling distance of the particles.

Since the measurements of the interval time needed by the particles to move across the preset distance are done manually, the standard deviation is expected to be reasonably large. Therefore many repeated measurements of interval time should be done. It is usually done 10-20 times on 10-20 different particles and the final interval time is the average of the above 10-20 measurements.

LASER DOPPLER ELECTROPHORESIS INSTRUMENT

The measurement of the Doppler beat frequency is done by using a spectrum analyzer. The creation of Doppler's effect is achieved by making interference between the scattered light and the original light. A beam of laser light from a 20mW HeNe laser is split into two. One is directed toward the sample so that the scattered light is frequency shifted. The other bypasses the sample by the use of two pairs of mirror. The latter beam is then combined with the scattered one to produce the Doppler's effect.

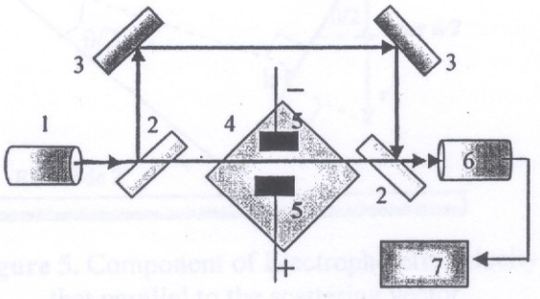

Figure 2. Diagram of LDE instrumently by Cummins et al [9-10]: 1. Laser, 2. Semi transparent mirror, 3. Mirror, 4. Cuvette, 5. Electrodes, 6. Detector, 7. Spectrum analyzer

LDE Instrument designed by Cummins et al in 60's uses a semi transparent mirror to recombine these two beams. (see Figure 2) Alignment of the double prism, the two mirrors, and the semi transparent mirror is very critical to produce a proper interference that results in the Doppler's effect. Some five angle adjusters should be employed to ease the alignment.

Ware and his coworkers in early 70's used a different approach to recombine the two beams of light. They used exit spot of the scattered light on the cuvette wall to recombine the beams. (see Figure 3) This instrument reduces a mirror and a five angle adjuster. This means reduces the initial cost of the instrument. However it is somewhat difficult to recombine the two beams correctly on the exit spot of the scattered light. It is suggested that only the mirrors that are adjusted and not to touch the cuvette. Moving the cuvette will also move the electrodes and they might block the light, since the electrodes are closed one to another. The distance between the two electrodes is approximately 4mm. The principles of the creation of Doppler's effect, the data collection system, and the analysis are still the same.

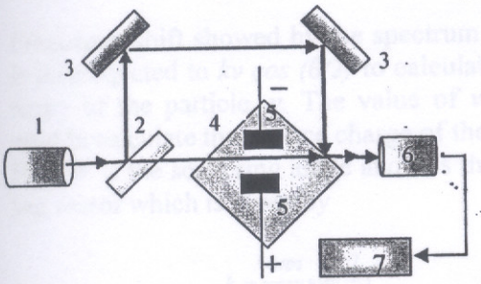

Figure 3. Diagram of LDE instrument by Ware et al[11-12]: 1. Laser, 2. Semi transparent mirror, 3. Mirror, 4. Cuvette, 5. Electrodes. 6. Detector. 7. Spectrum analyzer

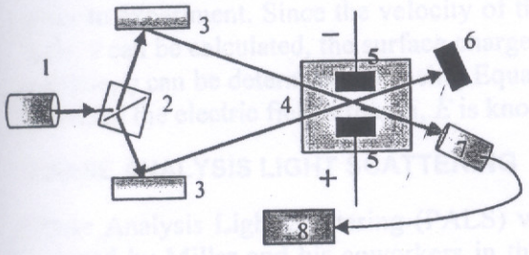

Figure 4. LDE instrument by Yoshimura et al[13] : 1. Laser, 2. Double prism, 3. Mirroes, 4. Cuvette, 5. Electrodes, 6. Beam Stopper, 7. Detector, 8. Spectrum analyser

On the other hand Yoshimura in 1972 used two crossing beams to produce the interference that results in the Doppler's effect. Figure 4 shows the crossed beam LDE developed by Yoshimura et al. In the case of Yoshimura's design the position of the detector is not critical.

The particles move due to diffusion and electrophoresis. The diffusion causes the power spectrum to be broadened and the electrophoresis causes the peak frequency to be shifted. The Fick's II Law[14] of the concentration fluctuation due these motion is given by:

$$\frac{\delta C(x,t)}{\delta t} = D\frac{\delta^2 C(x,t)}{\delta x^2} + v\frac{\delta C(x,t)}{\delta x}$$

Equation 2

where v is the electrophoretic velocity of the particles. This causes the intensity time autocorrelation function to become

$$g^1(k,\tau) = epx(-ikv\tau)\exp(-Dk^2\tau)$$

Equation 3

Fourier transformation of Equation 12 from time domain to frequency domain results in [3-5]

$$I(\omega) = \frac{2Dk^2}{(\omega + kv)^2 + (Dk^2)^2}$$

Equation 4

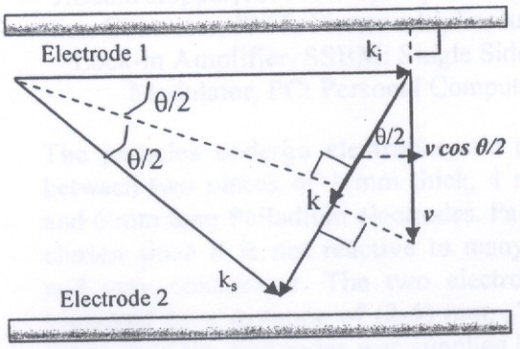

Figure 5. Component of Electrophoretic velocity that parallel to the scattering vector

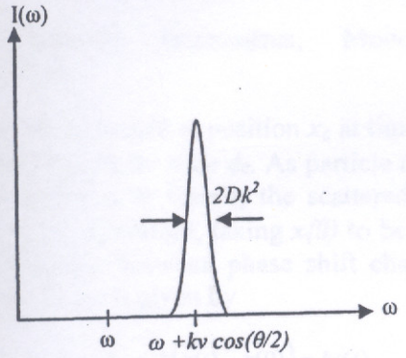

Figure 6. Frequency shift from to ω to $\omega + kv \cos(\theta/2)$ due to electrophoresis.

Equation 4 shows that the power spectrum broadening is given by Dk^2 and the peak frequency shifting is given by kv, which is from ω to $\omega + kv$. (see Figure 6) However, the direction of the electrophoretic velocity of the particles is usually normal to the electrodes. So that it is not parallel to the scattering vector, k. Therefore, the component of velocity contributing to the frequency shift should be the one that is parallel to k. (see Figure 5) which is $v \cos(\theta/2)$.[4-5] Therefore, the frequency shift measured by the spectrum analyzer becomes $kv \cos(\theta/2)$.

Frequency shift showed by the spectrum analyzer is then equated to $kv \cos(\theta/2)$ to calculate the velocity of the particle, v. The value of v is then used to calculate the surface charge of the particle. Here θ is the scattering angle and k is the scattering vector which is given by

$$k = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right)$$

Equation 5

Refractive index of the solvent, n, wavelength of light, λ, and scattering angle, θ, are determined prior to experiment. Since the velocity of the particle, v can be calculated, the surface charge of the particle, q can be determined by using Equation 1, provided the electric field strength, E is known.

PHASE ANALYSIS LIGHT SCATTERING

Phase Analysis Light Scattering (PALS) was developed by Miller and his coworkers in the early 90's.[3] It explores the phase shift change in time of the scattered light to determine the velocity of the particle and finally the surface charge.[15-17] PALS instrument employed a fiber optic probe is shown in Figure 7.[4-5] An 850mm focal length lens was used to focus a 10mW HeNe laser running at 632.8nm into the scattering area inside a 10mm path length rectangular cuvette. The beam was split using a double prism into two. Both of them were then crossed correlated in the scattering region using two mirrors after passing two Bragg cells. This PALS instrument employs two Bragg cells to shift the frequencies of both laser split beams. One beam was shifted by 80MHz and the other was shifted by 80MHz and 2 kHz. The beams were then crossed at the scattering area to produce moving interference fringes. The Bragg cell (Isomet AOM, Model 1205C-2) was driven by an acousto-optic driver (Brimrose, Model FFA-80).

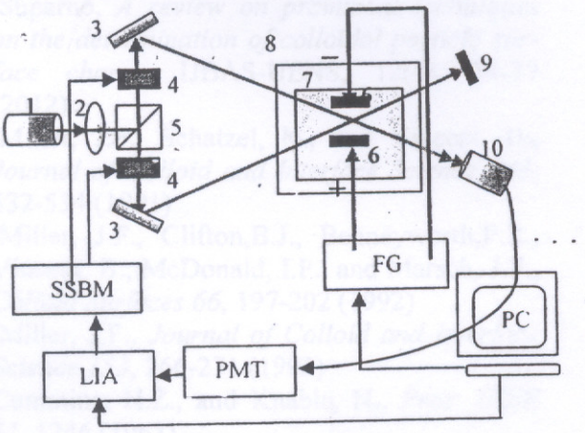

Figure 7. Diagram of PALS instrument: 1. Laser, 2. Lens 3. mirror, 4. Bragg cell, 5.Double prism, 6.Electrodes, 7.Cuvette, 8. Temperature control, 9.Beam stopper,10. Fiber optic probe, FG: Function Generator, PMT: Photomultiplier tube, LIA: Lock-in Amplifier, SSBM: Single Side Band Modulator, PC: Personal Computer

The particles undergo electrophoretic motion in between two pieces of 1 mm thick, 4 mm wide, and 6 mm long Palladium electrodes. Palladium is chosen since it is not reactive to many solvents and very conductive. The two electrodes were separated by a distance of (2-4) mm. The wave function of the electrodes was supplied by a function generator (Stanford research System, Model DS335) A fiber optic probe made of a single mode fiber optic and 2 ST Connectors was used to catch the scattered light and sent to the detector. A Lock-In Amplifier (LIA) was used to supply a reference frequency for Single Side Band modulator to drive the Bragg cells and to analyze signal from PMT (photomultiplier tube). This device was controlled by a PC through a GPIB controller

card (National Instruments, Model AT-GPIB/TNT).

In principle a particle at position x_0 at time t_0 scatters light with phase shift ϕ_0. As particle moves to other position x_1 at time t_1 the scattered light is shifted to ϕ_1. Therefore, taking $x(0)$ to be original the relationship between phase shift change and position change is given by

$$\phi_1 - \phi_0 = k\big(x(t) - x(0)\big) = kx(t)$$

Equation 6

where k is scattering vector. The time derivation of both sides of Equation 6 gives

$$\frac{d\phi(t)}{dt} = k\frac{dx(t)}{dt}. = kv(t)$$

Equation 7

Equation 7 shows that the phase shift change of the scattered light in time is directly related to the velocity of the particle. Therefore, by detecting the phase shift change in time of the scattered light the electrophoretic velocity can be determined. Using the same treatment as above the surface charge of the particles can be calculated. A more thorough treatment may be found in International Journal of Basic and Applied Science-International Journals of Engineering and Sciences. [3-5].

CONCLUSION

The three instruments capable of determining particle surface charged have been reviewed in a simple yet understandable method. Firstly, micro-electrophoresis is suitable for the measurement of surface charge of polar solutions. Then, the more sensitive LDE and PALS are suitable for any solutions including nonpolar solutions. Understanding the work of the above instruments enables us, in one hand to appreciate other people innovations. On the other hand it enables us to develop our own instrument in the future.

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