Measurement of zeta potential

LEENA JAIN, R. BHARATI
VIJAY KUMAR, S. BHARATI
S.K. AGGARWAL

ABSTRACT

Zeta potential of a colloidal suspension is an important parameter and is used as an indicator for optimum condition for flocculation. The concept has found applications in numerous areas including increased retention of fibre fines, fillers, chemical additive on a paper sheet during paper making. The article discusses zeta potential and presents a survey of various methods used for its measurement in practice.

INTRODUCTION :

Stability of a colloidal suspension in terms of its flocculation characteristics is dependent on the electrokinetic charges in the suspension. By manipulating these charges, particles in the suspension may be made to coagulate or kept in suspended state. Zeta potential provides a strong indication of these charges and is, therefore, related to flocculation characteristices of a suspension. It has been found that if two systems of different zeta potentials are compared with all other parameters being equal, the one that has higher zeta potential is expected to be more stable with respect to flocculation as compared to the one with lower zeta potential. The fact that zeta potential can be used to optimize flocculation in a number of diverse areas where colloidal suspensions are encountered, several techniques have been used for its practical measurement. Methods based on streaming potential, electrophoresis and sedimentation potential have been conventionally used. The need for the ease and on line measurements of zeta potential has led to several modifications in the above techniques, as well as to the development of a new technique i. e. Electrokinetic sonic amplitude.

ZETA POTENTIAL

A charged particle in a suspension attracts or repels ions or other particles, depending upon their electric charge. A cloud of counter ions (oppositely-charged) is thus formed adjacent to the charged particle, containing a total charge corresponding to the surface charge of the particle under consideration (See-Fig. 1. [1]) . The ionic density of the cloud is maximum close to the particle surface and drops gradually at increasing distance from the particle. The ions closed to the particle are strongly attracted to the particle surface, as compared to the ions away from the surface. The distribution of ions around a charged particle in a suspension and the corresponding potential, gradient near the surface of the particle has been modeled using the theory of double layer. It involves two layers of charges around the particle. The counter ions closed to the particle surface are considered to be immobile. This layer of ions is known as "Fixed" or "Stern" layer. The ions that gather around the Stern layer to compensate for difference in the particle surface charges and charges in the stern layer are called to be in an another layer known as "Diffuse" or "Guoy" layer. The potential of the diffuse layer is known as zeta potential and may be defined as the potential at the surface between the freely mobile liquid and liquid firmly adhering to the particle surface. It is this potential which is responsible for the movement of charged puticles in suspension, when subjected to an externally applied electric field.

Institute of Paper Technology
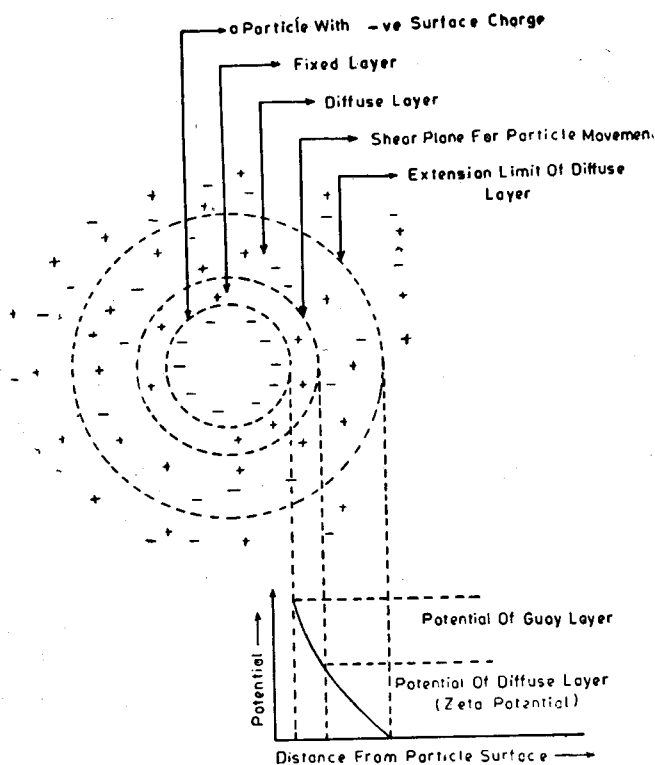(University of Roorkee)
Saharanpur-247001.

Fig. 1. Distribution of charge around a particle in suspension.

MEASUREMENT METHODS :

Most of the methods used for experimental determination of zeta potential are based on electrokinetic phenomena, which involve electricity and tangential movement of two phases along each other. They may arise either from an external electric field directed along the phase boundary and resulting in movement, or from a movement of the phases along each other resulting in transport of electricity. Electroosmosis and electrophoresis are the examples of first kind, while streaming potential and migration potential belong to the other. These methods alongwith electrokinetic sonic amplitude technique are discussed below :

ELECTROOSMOSIS

When an electric field is applied to a suspension in such a way that the particles can not move but the liquid moves with respect to particles, the phenomenon is called as electroosmosis. It can be applied for the measurement of zeta potential either by measuring electroosmotic flow or electroosmotic pressure.

Electroosmotic Flow

With particles stationary in a suspension, the flow of liquid under the influence of an applied electric field is known as electroosmotic flow. The mobile portion of the diffuse layer around the suspended particles will flow with the liquid and a constant flow rate will be reached when the force exerted by the external field on the counter ions (hence, on the liquid as a whole) is exactly balanced by the frictional forces arising from the viscosity of the liquid. The electroosmotic velocity thus achieved is a function of the applied external electric field, the potential of the diffuse layer (i. e Zeta potential), and the viscosity of the liquid.

Assuming laminar flow for the liquid and using Poisson 's equation, it can be shown that electroosmotic velocity Ve, can be given by the following expression [2] :

$$Ve = \frac{D E \zeta}{4\pi \eta} \qquad \ldots\ldots \qquad (1)$$

where E is the external applied electric field, D is dielectric constant, ζ is the zeta potential and η is the viscosity of the liquid.

For electroosmotic flow in a capillary of uniform cross sectional area A, volume flow rate Ve of the liquid may be written as

$$Ve = AVe = \frac{ADE\zeta}{4\pi\eta} \qquad \ldots\ldots\ldots (2)$$

assuming that all the liquid moves with the same velocity Ve. For a capillary, it is true only when the thickness of the double layer is much smaller than the capillary diameter. In practice, the thickness of double layer seldom exceeds 0.1 μm, which is small compared to normal capillary dimensions

Application of electric field E causes current i to flow through the liquid. The relationship between E and i may be written as.

$$E = \frac{i}{A\lambda + S\lambda s} \qquad \ldots\ldots (3)$$

where λ represents the specific conductivity of the liquid, and λs represents the excess conductance along the surface of the capillary as a consequence of accumulation of ions in the double layer. For dilute solutions, λs may be of the order of same magnitude as the conductance through the bulk of the liquid. S represents the circumference of the capillary.

Substituting E in Eqn. (2) and by re-arranging the terms, we obtain

$$\zeta = \frac{4\pi\eta \, Ve \, (\lambda + S\lambda S/A)}{Di} \quad \dots \quad (4)$$

For zero surface conductance, the above expression reduces to

$$\zeta = \frac{4\pi\eta \, \lambda \, Ve}{Di} \quad \dots \dots \quad (5)$$

For an incompressible liquid, the above equation may be applied to capillary of arbitrary and non uniform cross sectional area [2]. As a porous plug can be represented by a parallel combination of capillaries each of non uniform cross section, the above equation is valid for porous plugs also, provided the pore diameters are large compared to double layer thickneses.

Schematic diagram of an apparatus [2] for the measurement of electroosmotic flow is as shown in Fig.2 (a). Electric field is applied across a porous plug placed in the tube. In order to avoid gas being discharged at the electrodes, it may be necessary to use reversible electrodes such as Ag-AgCl. Because of the electric field, the liquid moves while the particles are stopped due to the presence of porous plug. Rate of movement of liquid is measured by measuring the movement of a small bubble in the capillary and converting it into flow rate.
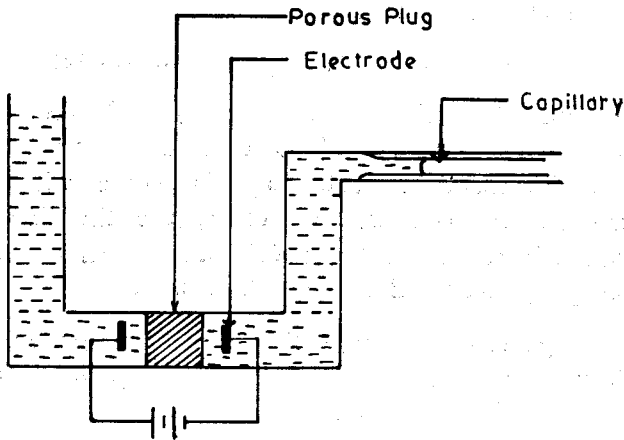

Fig.2 (a) Apparatus for measuring electro-osmotic flow.

Electro-Osmotic Pressure :

Electro-osmotic pressure is defined as the counter pressure required to obtain zero flow rate of liquid through a capillary or porous plug for a given externally applied electric field. By comparing the back flow due to electroosmotic pressure with flow rate as given in Eqn. (2), expression for zeta potential in terms of electroosmotic pressure may be obtained.

For a capillary of uniform cross section, length l and radius r, the black flow due to electroosmotic pressure P_e is given by Poisenille's equation [3].

$$V_e = \frac{\pi P_e \, r^4}{\eta 8 l} \quad \dots \dots \dots \quad (6)$$

Comparing the above equation with Eqn. (2) and by rearranging the terms, we obtain

$$\zeta = \frac{\pi P_e \, r^4}{2DEl} \quad \dots \dots \dots \quad (7)$$

where El represents the voltage applied across the capillary.

For a diaphram of area A and length l, the back flow is given by the following equation [3].

$$V_e = \frac{KPA}{\eta l} \quad \dots \dots \dots \quad (8)$$

In the above equation, K represents a constant, which has to be determined experimentally by measuring flow rate through the diaphram as a function of pressure with zero applied electric field.

From Eqns. (8) and (2), we obtain

$$\zeta = \frac{P_e \, 4\pi K}{DEl} \quad \dots \dots \dots \quad (9)$$

Fig. 2. (b) shows an apparatus for measuring electroosmotic pressure. When an electric field is applied, liquid rises in one of the arms to some equilibrium level. Electroosmotic pressure may be calculated by measuring the height of liquid rise.
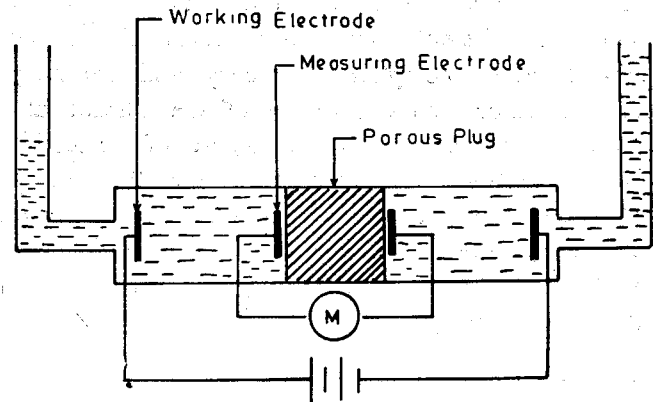

Fig.2 (b) Apparatus for Measuring electroosmotic pressure.

Dispersions of quartz in KCl solutions [4], aqueous dispersions of Kaolinite, calcite and bentomite in solutions of various salts have been examined using electroosmosis [3].

STREAMING POTENTIAL :

A voltage difference is developed between the ends of a capillary tube or a porous diaphram, when liquid in a suspension is forced to flow through it by an externally applied pressure. The flowing liquid carries with it the mobile part of the double layer and its contained charge, and therefore a voltage difference is established in the direction of liquid flow, which is known as streaming potential. The phenomenon is opposite to that of the electro-osmotic pressure.

For a capillary of uniform diameter the rate of charge transported through it, as a result of the movement of diffuse layer under an applied pressure difference P, can be given as follows [3].

$$i = \frac{PDr^2\zeta}{4\eta l} \qquad \qquad (10)$$

The expression is valid for laminar flow and deviation may occur at pressures causing turbulent flow In addition, the thickness of the double layer must be much smaller than the diameter of the capilarly.

Current conducted through the capillary due to streaming potential E_s may be given by the following equation :

$$i = \frac{E_s (\lambda A + S \lambda s)}{l} \qquad \qquad (11)$$

or

$$= \frac{E_R (\lambda \pi r^2 + 2 \pi r \lambda s)}{l} \qquad \qquad (12)$$

At steady state, the charges transported by the moving double layer will be balanced by the current conducted through the liquid. Therefore, comparing Eqns (10) and (12) and by rearranging the terms, we obtain

$$\zeta = \frac{4\pi\eta E_s (\lambda + \frac{2\lambda s}{r})}{PD} \qquad \qquad (13)$$

For zero surface conductance λs, Eqn. (13) reduces to

$$\zeta = \frac{4\pi\eta E_s \lambda}{PD} \qquad \qquad (14)$$

The above expression is valid for porous diaphrams also :

Streaming potential for a suspension can be experimentally measured by using the apparatus as shown in Fig. 3 [2] The suspension is forced through a capillary with a constant externally applied pressure.

Electrodes are used on either side of the capillary to measure the streaming potential. Electrodes used for measurement should behave reversibly, but bright electrodes may be used provided the measurement circuit is designed in such a way so that it practically draws no current from the electrodes (5). If the values of conductivity, viscosity and dielectric constant of the liquid are known, Eqn. (14) may be used to calculate the zeta potential.
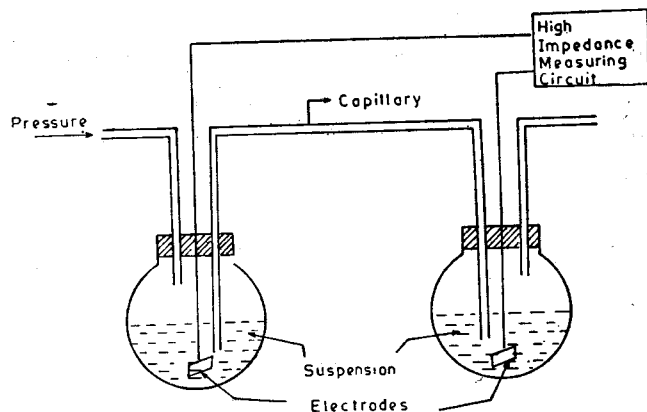

Fig. 3. Apparatus for Measuring Streaming potential.

$BaSO_4$, Al_2SO_3, SnO_2, Fe_2O_3 TiO_2 in various electrolytes, stainless steel in acids, quartz in acetate solutions have been examined using streaming potential determinations (3,6).

ELECTROPHORESIS :

The phenomenon of migration of particles in a colloidal suspension in response to an applied electric field is known as electrophoresis. Electrophoretic mobility of colloidal particles is defined as the distance travelled by them per unit time, and is in every respect comparable to electroosmotic flow, since in both cases forces acting on the double layer as a result of an applied electric field produce a relative movement. Eqn. (1), therefore, provides an expression for electrophoretic mobility also, which is repeated as follows :

$$V_E = \frac{DE\zeta}{4\pi\eta} \qquad \qquad (15)$$

If the diffuse layer is thin compared to the dimension of the particle, the shape and size of the particle has no effect on its electrophoretic mobility. However, this condition is difficult to meet in case of finely divided colloidal dispersions.

Under the influence of an externally applied electric field, the counter ions in the liquid move in a direction opposite to that of the particle. They impart

their movement to the liquid surrounding them, and in this way cause a flow of liquid in the opposite direction. The .electrophoretic mobility is therefore decreased, because the particles do not move in a stationary liquid but in a moving liquid. To account for the above effect, Eqn. (15) may be modified as :

$$V_E = \frac{f_H DE\zeta}{4\pi\eta} \qquad \ldots\ldots \quad (16)$$

where f_H is known as retardation factor. It is equal to 1 for cylindrical particles with their axis in the direction of the field, between 1 and $\frac{1}{2}$ for cylinders perpendicular to the field, and between 1 and 2/3 for spherical particles [2].

Rearranging the above expression, zeta potential may be given as

$$\zeta = \frac{4\pi\eta V_E}{f_H DE} \qquad \ldots\ldots\ldots \quad (17)$$

Electrophoretic measurements may be made as detailed below :

Microelectrophoresis

In microelectrophoresis, velocity of individual particles is measured under the influence of an applied electric field. The apparatus is as shown in Fig.4 (a). It consists of a microscope with a calibrated reticule for the observation of individual particles and a thin transparent cell equipped with electrodes that contains the speciman. Cylindrical as well as flat cells of rectangular cross section have been used and are available commercially. Electric field in the cell is best established by means of reversible electrodes such as Ag-AgCl, Cu-CuSO$_4$ or Zn - ZnSO4. Care must be taken to prevent the electrolyte of the electrodes from conta-

Fig.4 (a) Microelectrophoresis.

minating the dispersion. Platinized electrodes behave reversibly with low currents, but gas evalution causes trouble at high currents [2].

Irrespective of the cell geometry, the electrical double layer at the cell wall also imparts a motion to the zeta potential of cell wall-liquid interface, the suspension moves rapidly in one direction at the centre of the cell. At some point in the cell, there is no net motion applied to liquid phase. It is at this point that the observed velocity of particles in the system is equal to their electrophoretic velocity. Calculations have shown that this stationary level is located at a distance equal to 21.13% of the total cell thickness from the top (or bottom) of a wide flat cell and at a distance equal to 14.64% of the diameter from the wall of a cylindrical cell [2] . To detemine the position of stationary level in microelectrophoretic measurements, an optical correction must be applied owing to the differing refractive indices of air, glass and water [5].

For measuring electrophoretic mobility, microscope is focussed at the stationary level and the time for a particle to move a known distance in the suspension is measured. When particles of several kind are presents (each kind having its own characteristic mobility,) a number of particles may be traced so that the distribution and average of mobility is obtained. Averaging also helps in eliminating the effect of Browinian motion (being a random effect) superimposed on electrophoretic migrations.

The technique can only be applied to dilute suspensions so that the individual particles may be distinguished and traced. The particles must be small enough or have a density close enough to that of the suspending medium, so that they neither rise nor fall out of the stationary level under the influence of gravity, while they are being observed. However, corrections for any sedimentation effect may be made by observing with and without any applied electric field. Heating effect on electrophoretic mobility may be minimized by effective thermosetting. The particles have to be large enough to be seen in the microscope. Commercial instruments use ultramicroscope and dark field illumination to extend the method to finer particles. The electrophoretic mobility may be converted to zeta potential using Eqn. (17).
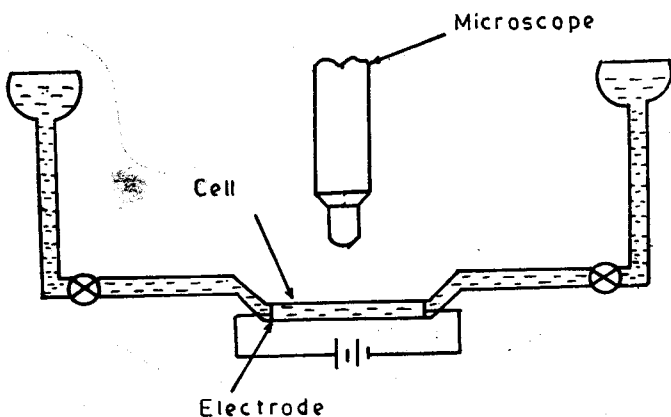
Rotating Prism Method :

The microscopic method is prone to time dependent errors such as convection current caused by heating of the sample, bubbles formed as gases come out of solution causing changes in the location of stationary layer, settling of particles, particle flocculation etc. Each of the above error can be reduced if the measurements are made quickly. This has been made possible by making measurements using a rotating prism inside the microscope [7]. The system consists of an appropriately shaped laser beam, which is used to illuminate the particles in the chamber. The image of particles is observed with the microscope (see Fig 4 (b)). The rate of rotation of prism is adjusted until the average particle motion caused by the applied electric field is cancelled by the prism rotation. If the rotation rate is too fast, the particles will appear to drift one way; if too slow, they will drift in the opposite direction. When the rotation is just right, the 'particle cloud' will appear stationary. Taking into account the rotating speed of the prism, the viscocity of the liquid and the applied electric field, the zeta potential of the particles is calculated.
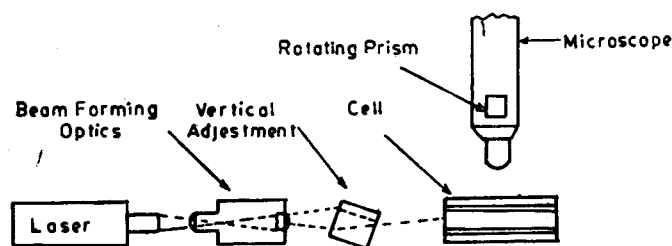

Fig.4 (b) Rotating Prism Method.

Since the method allows the measurement on a number of particles simultaneously, data are obtained quickly with less errors due to time dependent factors. The method is particularly suitable for high concentration systems, where conventional microelectrophoresis is impossible to use because individual particles can not be followed. Micro-electrophoresis has been successfully applied in a number of diverse areas such as kaolinite suspension, xylene emulsions, colloidal particles present in water supplies, cellulose and carbon black, becteria at different levels of pH, and normal and sick human red blood cells etc. [3, 8].

Moving Boundary Electrophoresis :

The method is found suitable for measuring the migration rate of particles in cases when the particles are too small to be seen by an ultra microscope or the particle concentration is too large so that individual particles ean not be traced. The schematic diagram of the apparatus is as shown in Fig. 4. (c). External electric field is applied to working electrodes placed in the side tubes to avoid disturbance by reaction products generated at the electrodes [2], while electrodes A and B are used only for measurement purpose. The boundary surfaces are established by filling the upper portion of the middle U-tube and side arms with colloid free supernatent liquid, and the lower portion of the middle U-tube with colloidal suspension. Under the influence of electric field, the particles move up in one arm and down in the other. From the shifting of boundaries, electrophoretic mobility may be found and the zeta potential can be calculated.
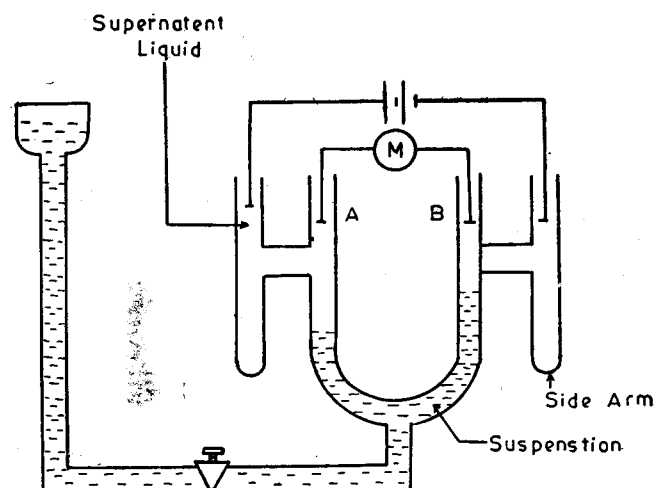

Fig.4 (c) Moving Boundary Electrophoresis.

The ultra filtrate of the suspension is frequently used as the supernatent liquid. However, if the conductivities of the suspension and ultra filtrate are different, the discontinuous change in potential gradient at the place of boundaries leads to error. In that case, a suitable supernatent liquid must be found by checking the composition of the suspension. Density of the particles must be close to that of the suspending liquid to avoid the error due to gravitational forces. The method has given accurate results for electrolyte solutions, however due to the problem of selecting correct supernatent liquid, the applicability of the method to colloidal systems is restricted. It has been used for the study of the effect of several electrolytes on platinum, gold, silver, bismuth, lead, iron and selenium sols, the effect of electrolytes on latex emulsions and arsenic trisulfide, and ferric oxide sols [3].

Electrophoretic Transfer :

Another method used for measuring electrophoretic mobility was developed by Sennett etal [3]. The apparatus (see Fig. 4 (d)) consists of a container filled with suspension under study, in which is immersed a bracket that supports two electrodes placed opposite each other. The electrode on the left, is completely accessible to the solution, while the electrode on the right is placed at the closed end of a cell that has a restricted tubular opening directly between the two electrodes. The electrode in the cell must be reversible; Ag-AgCl and zinc have both been used successfully. To measure mobility with this device, the cell and container are filled with the speciman suspension. When an electric field is impressed between the two electrodes, particles having an electric charge will migrate either into or out of the cell (depending upon the sign of the cell electrode). After a short time, there will be a change in composition of the cell contents because of the migration of the particles. The change may be determined by analysis, and from this concentration change the mobility and zeta potential of the particles can be calculated.
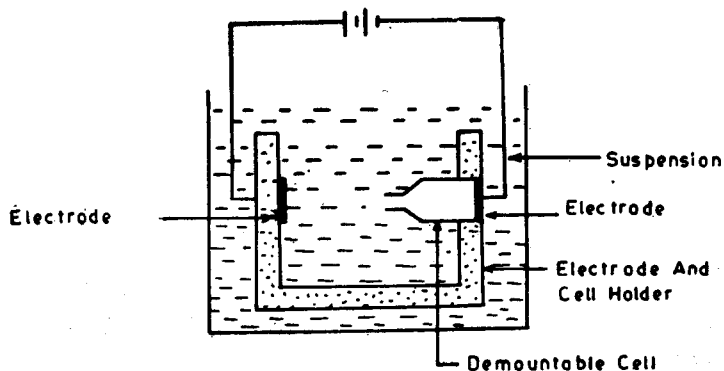

Fig.4 (d) Electrophoretic transfer.

The method has been used for studying Kaoline-water systems. It is particularly suitable for systems containing particles large enough to preclude the use of microelectrophoresis or moving boundary method.

MIGRATION POTENTIAL :

When small particles suspended in a liquid are forced to move either due to gravitation force or centrifugal force, a difference in potential is observed in the direction of movement. This potential difference is known as migration potential and is found to be related to zeta potential of the system. The phenomenon is opposite to that of the electrophoresis.

Sedimentation Potential :

The potential difference produced by particles falling through a suspending medium under the force of gravitation is known as sedimentation potential. Assuming particles of uniform size, zeta potential may be given by the following equation [3].

$$\zeta = \frac{3\,\eta\,\lambda\,E_D}{Dr^3\,(\rho-\rho')ng} \qquad \ldots\ldots\ldots (18)$$

where r represents the particle radius, $(\rho-\rho')$ represents the difference in specific gravity. n represents the concentration and g represents the accleration of gravity. Fig. 5 shows schematic diagram of an apparatus that can be used for measuring sedimentation potential.
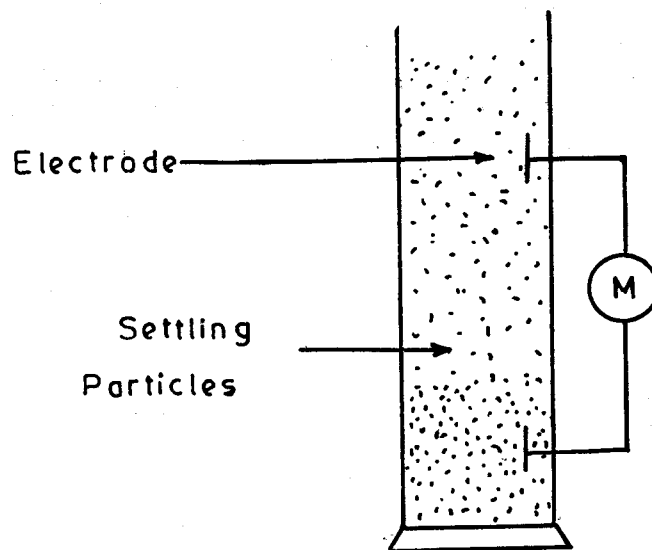

Fig. 5. Apparatus for measuring sedimentation potential.

The method was first applied to water and water solutions of Aluminium chloride, Barium chloride and Sodium chloride by Quist et al [9] and has been used for the measurement of zeta potential of glass, fused silica, silicon. fused alumina in KCl and $BaCl_2$ solutions, and quartz in KCl solutions [3,4,10].

Centrifugation Potential :

If a sol is centrifuged, the potential difference developed between two points in the sol at different

distances from the axis of rotation, is known as centrifugation potential. It is related to the zeta potential of suspension by the following expression [11] :

$$\zeta = \frac{12\pi\eta\lambda V_{CP}}{m'nDw^2(R^2_2 - R^2_1)} \qquad \ldots\ldots \quad (19)$$

In the above equation, V_{Cp} represents the centrifugation potential, W represents the angular speed of rotation, R_1 and R_2 represent the distances from the axis of the two points between which centrifugation potential is measured, while m'n represents the apparent mass of the dispersed substance. The method has been applied in the study of AgI and AS_2S_3 sols in KI and KNO_3 solutions [11].

ELECTROKINETIC SONIC AMPLITUDE

Electrokinetic sonic amplitude is the most recently developed attempt of measuring electrokinetic charge reliably, and involves the generation and detection of ultra sonic waves in a suspension of particles [12,13]. When a high frequency sinusoidal potential is applied to an electrode assembly in a suspension of charged particles, an ultrasonic wave is emitted due to the interaction of oscillating electric field and the charged layers surrounding the particles. The amplitude of the ultrasonic wave, termed as electrokinetic sonic amplitude (ESA), increases or decreases as the effective charge in the charge layers surrounding the particles changes. A comparison of ESA to zeta potential indicates that the two quantities are closely related.

The instrumentation consists of a sensor which houses three ultrasonic transducers and an electrode assembly. Charged particles or droplets in the sample act in conjuction with the electrode assembly to form an electrochemical ultrasonic transducer. Radio frequency electrical pulse is applied to the electrode assembly resulting in the emission of an ultrasonic pulse. The pulse propagates through the fluid and is detected by a conventional ultrasonic transducer. The transducer produces an electrical signal which is amplified and measured. The remaining two transducers measure the ultrasonic attenuation of the sample. The information is used to correct the amplitude of the ESA signals for any energy lost in propagating through the sample.

The method offers several advantages over the conventional methods of measuring electrophoretic mobility and streaming potential. Measurenents can be made faster, with less labour and in suspensions having concentrations ranging from a few hundred parts per million to 70% solids by weignt. Sensors are in direct contact with the suspension but do not obstruct or interfere with liquid flow for greatest measurement accuracy. Unbleached fibre and clay systems were used to evaluate the ESA measurements through variation in pH, particle concentration, lignin and calcium concentration [12].

CONCLUSIONS :

A number of methods applied for the measurement of zeta potential have been summarized and discussed. Each of the methods has advantages and disadvantages and has found applications accordingly. Todate microelectrophoresis and streaming potential methods are the most widely used methods.

ACKNOWLEDGEMENT

REFERENCES :

1. Torbjorn Helle, "Colloidal Mechanism Relevant to Paper Making", Lecture Notes for NORAD course on Pulp and Paper Technology, NTH, Trondheim, Norway.

2. R, Kruyt, Colloidal Science, Vol. I Edition—1952.

3. Paul Sennett and J P. Olivier. "Colloidal Dispersion Electrokinetic Effects and the Concept of zeta Potential." Industrial and Engineering Chemistry, Vol. 57 No. 8, August 1965.

4. Charu Bhusan Roy, "Determination of Zeta Potential of Quartz Particles in Dilute Solutions of KCl," Jour. Indian Chemical Society, Vol. 38, No. 11, 1961.

5. R.J. Hunter and A.F. Alexander, "Some Notes on the Measurement of Electrokinetic Potentials", Journal of Colloidal Science, 17, 781-788, 1962.

6. A.S. Buchanan and E. Heymann, "Determination of Electrokinetic Potentials in concentrated solutions by the Streaming Current Method," Journal of colloid science 4, 137, 1949.

7. Philip J. Goetz and J. G. Penniman, "A New Technique for Microelectro phoretic Measurements" American Laboratory, October 1976.

8. Norman Street, Effect of a Polyanion on the Rheology of a Kaolinite Suspension". Journal of Colloid Science 12, 1—9, 1957.

9. J.D. Quist and E.J Roger Washburn, "A Study in Electrokinetics," J. American Chemical Society, Vol. 62, Nov. 1940.

10. C.I. Dulin and G.A.H. Elton, "Determinations of Electrokinetic Charge and Potential by the Sedimentation Method Part—I Silica in Aqueous Solutions of Potassium Chloride" J. Chemical Society, 61, 148, 1952.

11. A.J. Rutzers and P. Nagels, "Centrifugation Potentials in Sols of Silver Iodide," Nature, March 28, 1953.

12. Allan M. Springer and Thomas E. Taggart, Quantitative Evaluation of Alternative Methods of Determining Total Charge," Tappi Journal, May 1986.

13. MATEC. "The Ultrasonic Alternative to zeta Potential Measurements, MATEC, INC, Warwick, R.I.. U.S A.