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THE TIME-DEPENDENT CHANGE IN ZETA POTENTIAL OF PARTICLES WITH CATIONIC POLYMER

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ABSTRACT

According to Smoluchowski's and Komagata's theory, the electroosmotic and electrophoretic velocities vary with the depth of cell such that the distribution of velocities must be represented by a symmetrical parabola. However, in practical measurements of the electrophoretic velocities of sedimentary particles such as pulp fines and fillers, the distribution curve of velocities was found to be asymmetrical about the cell center. Thus use of the conventional method often gives rise to a serious error. The reasons for this are discussed and an improved method is proposed.

The time-dependent changes in zeta potentials (ZP) of clay and monodispersed polystyrene latex with added polyethyleneimine (PEI) or cationic polyacrylamide were investigated by the improved method. For instance, the ZP of clay, which was -42 mV originally, became +9 mV just after addition of PEI at a level of 0.1 % on clay, decreased rapidly at an initial stage, became -13 mV after 1 hr and finally reached -17mV. The rate of change in ZP varied widely with the degree of agitation, the addition level of polymer, the molecular weight and so on. The highest difference between initial and final ZP we have obtained hitherto is over 50mV. These phenomena must be closely related to the conformational change of polymers sorbed on solid surface and will offer important and fundamental information on how to use polymer additives in papermaking.

INTRODUCTION

A few years ago, The Retention and Drainage Subcommitee of the Tappi Papermaking Additives Committee sent out questionaires to determine exactly what types of wet-end chemistry measurements were being carried out at that time by papermakers and suppliers. Papermakers reported 51 different measurements, while suppliers reported 73, and a total of 93 different quantities were listed (1). The data indicate that pH is by far the most popular quantity, followed by headbox consistency, tray consistency, freeness and zeta potential (ZP) in that order. To the question asked in the survey, what additional wet-end chemistry measurements are needed, the total number of votes for cationic demand, charge, ZP etc. was 2.5 times the number cast for the second-place finisher, process stream solid/ash/fines concentration (1).

Electrokenetic measurements will become increasingly important as the fines content of the paper stock increases, a current trend occasioned by the increased use of hardwoods, system closure, paper recycling, and alkaline papermaking. It is generally known that the cationic demand, charge and ZP are closely related to each other. Huge numbers of reports have been published. The concept of the ZP once occupied a pre-eminent place in colloid chemical theory which plays an important part in the wet-end chemistry of papermaking but was, for a long time, under a cloud. One of the causes seems to be the low reproducibility of the data. Thus, our attention was first directed towards finding the detrimental factors and then developing an improved electrophoresis method, which could be widely used for fine particles.

The proposed method was used to investigate the time-dependent changes in ZP of solid particles such as clay and monodispersed polystyrene latex with cationic polymers under stirring. The results are discussed in connection with the conformational changes of polymers adsorbed onto a solid surface. Flocculation and retention are also discussed in connection with the bridging effect of polymers.

EXPERIMENTAL - MATERIALS AND METHODS

Materials

LBKP with a CSF of 350ml was used and the content of pulp fines which passed through the 200 mesh wire of Britt Dynamic Drainage Jar (DDJ) was 20%. Papermaking clay (Hydra Gross; average diameter listed in the catalogue as 0.25 μm), kaolin and polyethyleneimines (PEI) with various molecular weights were commercial products. Monodispersed polystyrene latex (PSL:IMMUTEX ~G2401, 0.429 ± 0.0008μm in diameter) and linear PEI (molecular weight 1,700) were kindly given by Nippon Synthetic Rubber Co. and Dr. Endo at Tokyo Institute of Technology respectively.

Zeta Potential Measurements

Zeta potential was determined by microelectrophoresis. The rectangular cell made of quartz had the following dimensions ; width x depth (inside dimension) = 23.0 x 0.95 mm: length x width x depth (outside dimension) = 75 x 25 x 3mm. The electrodes were composed of Pt-Hg-Hg $(NO_3)_2$-agar. A microscope (Type CHA ; Olympus Co.) with x10 object lens and x15 eyepiece was used. Lateral orientation of the cell was achieved by first laying the cell onto the horizontal microscope stage (horizontal orientation) and then rotating the whole microscope assembly through 90°, so that it "lay on its back", i.e. optical path - horizontal, microscope stage - vertical. It should be emphasized that a DC, constant current, source (model 6912, Metronix Co., Japan), was employed, in preference to the more usual constant potential source. One needs to use the value of the current for calculation of ZP or mobility, but the current often varies significantly during the measurement when the constant potential source is used.

Particles were well dispersed by the use of an ultrasonic generator (Bransonic 52) and, if necessary, desired amounts of NaCl and cationic polymers were added with stirring.

The velocities of 10 particles were measured microscopically at one level in the cell by changing the polarity after measurement of 5 particles. Then the above measurements were repeated at another level in the same cell, and the velocity distribution curve was drawn by the use of the least squares method. The electrophoretic velocities were obtained from Equation 3 derived by Mori and Okamoto. The ZP's were calculated from the above values using Smoluchowski's Equation. A personal computer was conveniently used for the calculation.

Flocculation and Retention Measurements

A well dispersed aqueous suspension (985 ml) of clay (300 mg) or PSL (60 mg as solid) was stirred at desired rpm using the propeller of the DDJ and 5ml of 1 N NaCl and 10 ml of aq. PEI with desired concentrations were added. The extent of flocculation was determined turbidimetrically.

Polymer retentions were estimated by the titration of centrifugal supernatants of filtrates by ultrafiltration with N/500 PVSK, known as the colloid titration (2).

The retention of fines in the dual polymer system was measured by the use of a DDJ according to Tappi T 261 pm. The typical stock consisted of 80% pulp, CSF 350ml, and 20% clay.

RESULTS AND DISCUSSION

Electroosmotic Flow in an Electrophoresis Cell

Eleltrophoretic Velocity Measurement

The electroosmotic flow of the liquid past the flat electrophoresis cell whose width is great compared with its thickness was first analyzed by Smoluchowski (3). Komagata (4) studied the more general case of a cell whose width is not great compared to its thickness. For these theories, it is prerequisite that the distribution of the electroosmotic velocity is a parabola symmetrical about the cell center. Therefore, the distribution of the observed electrophoretic velocities of particles must also be a symmetrical parabola. Hence, the electrophoretic velocity obtained at an upper stationary level is identical to that at a lower stationary level. When the cell is mounted horizontally, for instance, many investigators usually measure the velocity at an upper stationary level because the observation of particles at a lower stationary level is somewhat obscured by the unfocused particles deposited on the bottom of the cell.

In recent years, however, Mori et al (5) found that the distribution curves of migration velocities of various mineral particles were not symmetrical. We have also obtained similar results with respect to sedimentary particles such as pulp fines and fillers.

Mori and Okamoto (6) have derived a theoretical equation which can be applied to an asymmetrical distribution. The equation is as follows :-

$$U_{obs}(0,y) = AU_o\left(\frac{y}{d}\right)^2 + \Delta U_o\left(\frac{y}{b}\right) + U_o(1-A) + U_p \qquad (1)$$

$U_{obs}(0,y)$=observed velocity of particles at a depth (y):

(cell center;y=0, top surface;y=d, bottom surface;y=-d)

Up=electrophoretic velocity of particle

$U_o=(W_1 + W_0)/2$:(W_1;velocity of liquid at top surface,
(W_0;velocity of liquid at bottom surface)

$\Delta U_o=(W_1 - W_0)/2$

$A=1/(2/3 - 0.420166/K)$

K=ratio of cell width to thickness

If AUo is denoted by a, ΔUo by b, Uo(1 - A) + Up by c, y/b by Y and Uobs (0,y) by Z, Equation 1 becomes :-

$$Z = aY^2 + bY + c \qquad (2)$$

The observed velocities (Zi) are measured at several levels (Yi), and the coefficients a, b and c are calculated by the least squares method. The more precise electrophoretic velocity (Up) of particles at the true stationary level is uniquely determined from Equation 3 which is derived from the relation between Equation 1 and Equation 2.

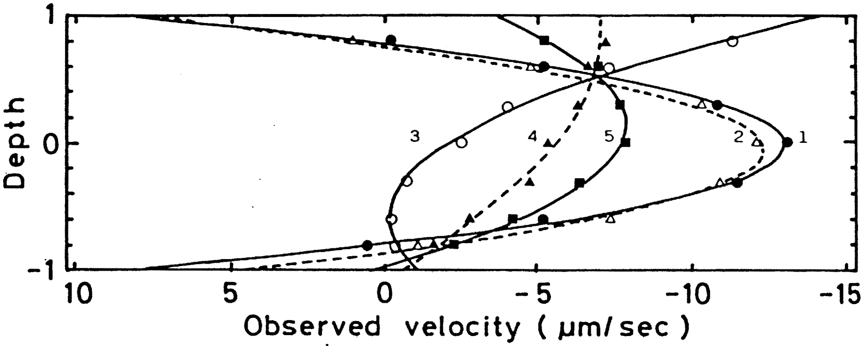

Fig 1—Velocity distribution curve of kaolin particles at a horizontal arrangement of a conventional cell or cell pretreated with PEI. (20 ± 1°C, pH 7.4, 0.27 mS/cm,0.25 mA)

No.1 and No.2; conventional cell, about 5% (No.1) or 50% (No.2) of the bottom surface area was covered with kaolin particles after measurements while the top surface area was little covered.

No.3; cell pretreated with PEI

No.4; cell washed with about 100 ml water after measurements of No.3

No.5; cell washed with about 100 ml water after measurements of No.4

Settling out of particles in No.3, 4 and 5 was similar to No.2

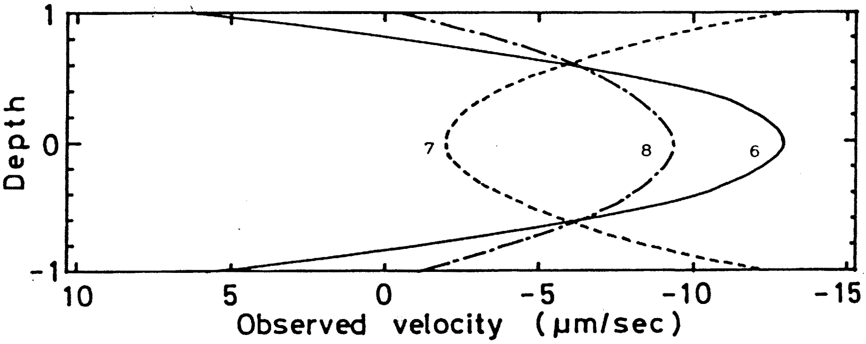

Fig 2—Velocity distribution curve of fine pulps at a horizontal arrangement of a conventional cell or cell pretreated with PEI. (20 ± 1°C, pH 7.5, 0.27 mS/cm,0.25mA)

No.6; conventional cell

No.7; cell pretreated with PEI

No.8; cell washed with about 500 ml water after measurements of No.7.

Measurements were carried out in concentration as low as possible and the amount of settling particles was extremely small

$$Up = c + a(1/3 + 0.420166/K) \qquad (3)$$

Although calculations by the least squares method for a quadratic equation are rather complicated, a personal computer is now readily available for rapid calculation. Alternatively if a computer is not available, the calculations are simplified when the measurements of Uobs are carried out at symmetrical levels about the cell center. Then, the coefficients a, b and c are evaluated by fitting the next equations to experimental measurements:-

$$a=\frac{N\Sigma Yi^2Zi - \Sigma Yi^2\Sigma Zi}{N\Sigma Yi^4 - (\Sigma Yi^2)^2},\quad b=\frac{\Sigma YiZi}{\Sigma Yi^2},\quad c=\frac{\Sigma Zi - a\Sigma Yi^2}{N} \qquad (4)$$

where N is the number of measuring levels. If the measurements are always carried out at the same levels, $N, \Sigma Yi^2$ and ΣYi^4 became constant and, therefore, ΣZi, $\Sigma YiZi$ and ΣYi^2Zi only need to be calculated each time.

Experimental Results

Now, let us present some experimental results and try to consider why the distribution of electrophoretic velocities results in asymmetry.

Fig.1 shows the distributions of migration velocities of kaolin particles in a conventional cell or the cell pretreated with PEI. All curves are asymmetrical. The cell is composed of quartz the surface charge of which is moderately negative in a conventional state. If kaolin particles of lower surface charge than that of the quartz settle out upon the bottom, then the bottom surface charge must be reduced, and the velocity of electroosmotic flow near the bottom surface will decrease also. This reasoning is supported experimentally (No.1 and No.2 in Fig.1).

If the cell is pretreated with cationic polymer such as PEI it is expected that the surface charge of the cell becomes positive due to the adsorption of it and the electroosmotic flow is changed to the opposite direction. The results in No.3 (Fig.1) and No.7 (Fig.2) are in accord with this expectation.

When a part of the PEI was desorbed in turn from the cell by washing with water, distribution curves of Uobs returned gradually to ordinary states (Nos. 4, 5 and 8).

It is noteworthy that there is only one stationary level in the cases of Nos. 3 and 4, because Up is located in a midway position between Uobs of the upper and lower sides of the cell. This is believed to be due to the charge of the bottom wall becoming negative through the settling out of negatively charged kaolin particles while the charge of the top wall is positive.

Fig. 3 shows the effects of PEI on the distribution curves of Uobs of kaolin particles and the electrophoretic velocities (Up) at the true and so-called (Komagata's) stationary levels. Various curves indicate that the electroosmotic flows are greatly affected by the settling out of particles and/or the adsorption of PEI. In the case of No.12, there is only one stationary level. This is thought to be due to the charge of the bottom wall becoming positive through the settling out of positively charged kaolin particles while that of the top wall is still negative.

For most purposes, it is practical to place the cell in a horizontal position, but the settling out of particles is unavoidable and the electroosmotic flow results in an asymmetrical parabola in almost all cases. Since the system is closed and therefore the net flow of liquid through the cell must be zero, Up determined by Mori-Okamoto's equation is in theoretical agreement with the mean value of velocities at both upper and lower stationary levels obtained from Komagata's equation.

Influence of Particle Concentration

As the amount of particles sedimented during the measurement changes with the concentration of the sample, the bottom surface charge also changes in a similar way. Thus the particle concentration must play an important role in ZP measurement.

Figs. 4 and 5 show the ZP's of clay and pulp fines respectively measured at concentrations of 5 to 1,050 ppm using a horizontal arrangement of a flat cell.

In the case of clay (Fig.4), the ZP's obtained from the lower and upper stationary levels change with concentration, as expected. The former values (A) were always higher than the later ones (B) and the A/B ratio occasionally went up to over 4.

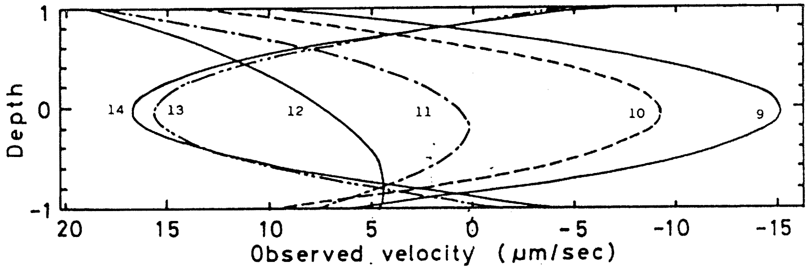

Fig 3—Effect of PEI on distributions of migration velocities and Up of kaolin particles at a horizontal arrangement of a flat cell.
(20±1°C, pH 7.6-7.8, 0.26-0.28 mS/cm, 0.25 mA)

No.		9	10	11	12	13	14
PEI (ppm)		0.1	0.5	1.0	2.0	5.0	12.0
unadsorbed PEI (ppm)		0	0	0	0.2	3.1	10.0
Up determined by eq.3 (µm/sec)		-7.2	-2.0	5.0	8.8	9.0	9.1
Up at a so-called stationary level (µm/sec)	upper	-6.1	-0.5	8.0	13.0	7.9	8.4
	lower	-8.3	-3.3	2.0	4.6	9.9	9.6
	average	-7.2	-1.9	5.0	8.8	8.9	9.0

Kaolin (1.0 g) was added into 1000 ml tap water containing desired amount of PEI with stirring, allowed to stand for about an hour and the supernatants were used for measurements. Concentrations of PEI were determined by colloid titration method (2)

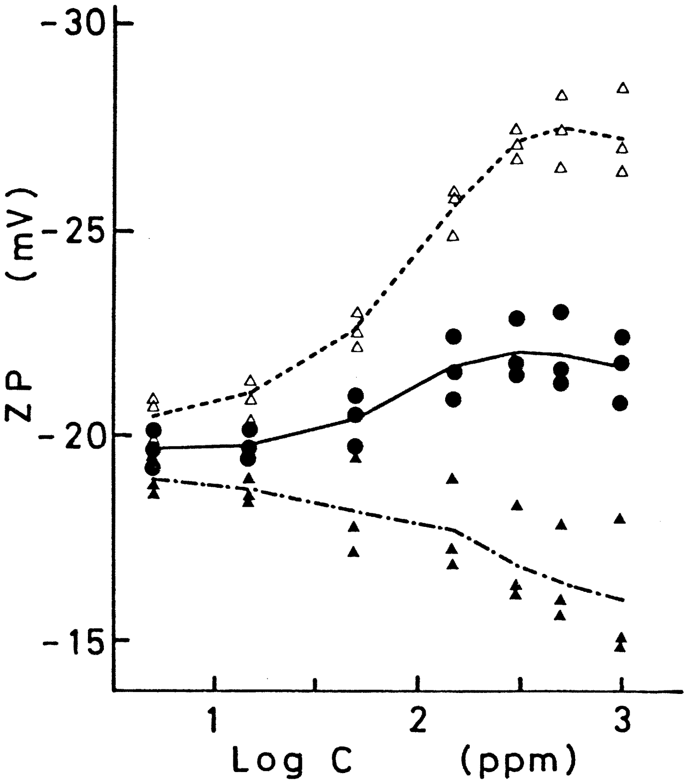

Fig 4—The zeta potential of clay particles measured in the concentration (C) of 5 to 1000 ppm at a horizontal arrangement of a flat cell.
(20-22°C, pH 7.8, 0.32 mS/cm, 0.35 mA)

--△--; Observed ZP at lower stationary level
_.▲._; Observed ZP at upper stationary level

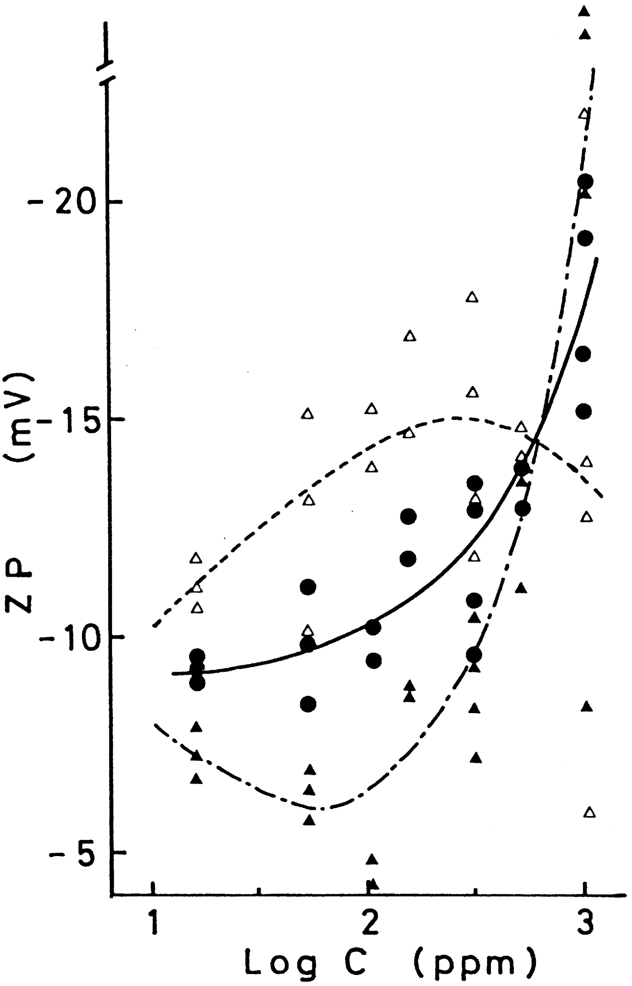

Fig 5—The zeta potential of pulp fines measured in the concentration (C) of 15 to 1050 ppm at a horizontal arrangement of a flat cell
(23-25°C, pH 7.5, 0.32 mS/cm, 0.35 mA)

--△-- ; Observed ZP at lower stationary level
_.▲._ ; Observed ZP at upper stationary level

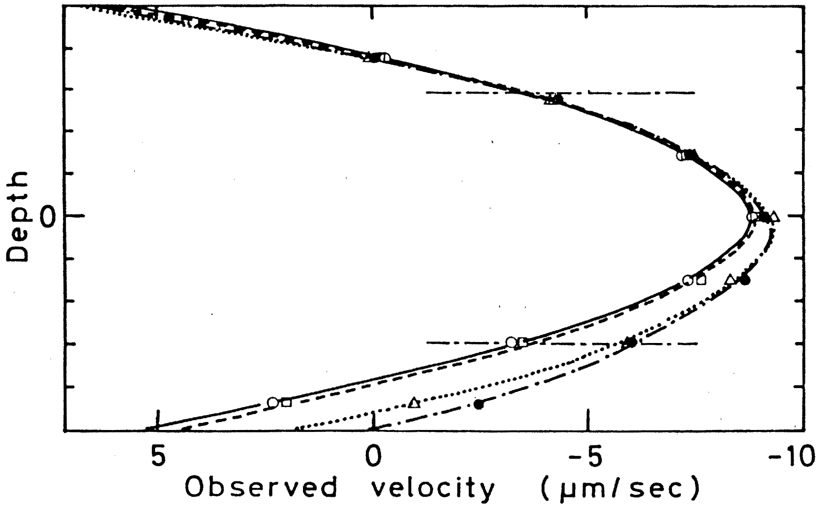

Fig 6—Velocity distribution curve of clay particles in various concentrations at a horizontal arrangement of a flat cell. (20-22°C, pH 7.8, 0.32 mS/cm, 0.20 mA)
Concentration of clay (ppm); ○ :5, □ :15, △ :150, ● :500

The mean values of ZP's at the two stationary levels also changed with the particle concentration and passed through a maximum at about 300 ppm. These phenomena are attributable to the settling of particles which occurs gradually during the measurement. Usually it takes 5 to 10 minutes to make the measurements at seven levels, which were carried out from top to bottom side. Just after the measurements, few particles were observed on the top surface. About 15% of the bottom was covered when the concentration was 50ppm and all areas of the bottom were covered at 500ppm.

Fig.6 shows the velocity distribution curves for clay concentrations of 5, 15, 150, and 500ppm. The velocities measured at initial stages are almost the same regardless of particle concentration, but those measured at last stages varied considerably with concentration.

The cell used was made of quartz whose ZP is assumed to be about -40 mV. When the clay with a lower ZP (absolute value) than quartz settles on the bottom, the charge of the bottom is reduced and then the electroosmotic flow toward the cathode which is the opposite direction to the electrophoresis is also reduced. Consequently, the electrophoretic velocities are apparently accelerated and this results in high values. However, when the concentration is high enough to cover the bottom quickly, the electrical changes occurring during measurements become small and the maximum seems to appear.

On the other hand, the maximum did not exist in the case of pulp fines which passed through 200 mesh wire although great differences in ZP's between the upper and lower stationary levels were detected (Fig. 5). It is thought that the fairly long fine pulps settle unevenly on the bottom, changing the electroosmotic laminar flow into turbulent and/or vortical flow when the concentration is too high, such as 1,050ppm. In fact the 200 mesh passed fraction contained fibers about 300μm long which could be occasionally flocculated and the height of sedimented fibers was 250μm in places which corresponded to 1/4 of the cell depth.

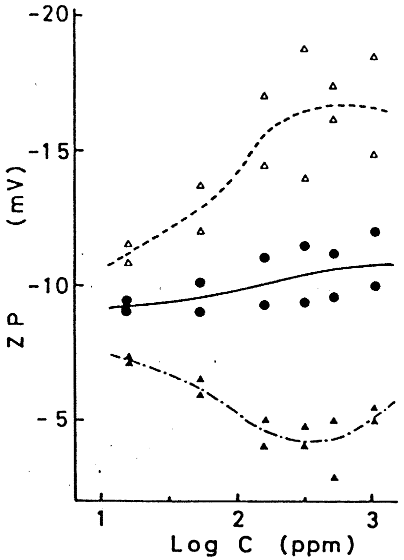

Fig 7—The zeta potential of pulp fines measured at a concentration (C) of 15 to 1050 ppm in a horizontal arrangement of a flat cell with 3.92 mm height. (20-23°C, pH 7.5, 0.32 mS/cm, 0.35 mA)

···△··· ; Observed ZP at lower stationary level

—·▲—· ; Observed ZP at upper stationary level

When the measurements were carried out in a deeper cell (4mm), the results were similar to those for clay obtained by use of the regular cell (1mm) as seen by comparison of Fig. 4 and Fig. 7.

At any rate, it is noteworthy that experimental results on ZP are considerably influenced by the particle concentration whenever the cell is mounted horizontally. If it is unavoidable to use the cell in a horizontal arrangement, the particle concentration must be as low as possible. However, it may often take a long time to make the measurements because of the few visible particles.

Lateral Arrangement of the Cell

If particles are of such size and density that they settle rapidly and disappear from a visual field, then it is difficult to make accurate measurements. This led Hartman et al (7) to propose that the electrophoresis cell be mounted laterally. In this case, both settling and convective trends are perpendicular to the direction of the electrophoresis in the cell. By measuring migration times between vertical lines in the microscope field, one can determine directly the electrophoretic velocity of the particle and ignore the component in the perpendicular direction due to settling or convection. Although this arrangement is ideal in principle, it is pointed out that in practice it has more convective disturbance than the horizontal arrangement, and, whenever possible, the horizontal is the preferred arrangement (8).

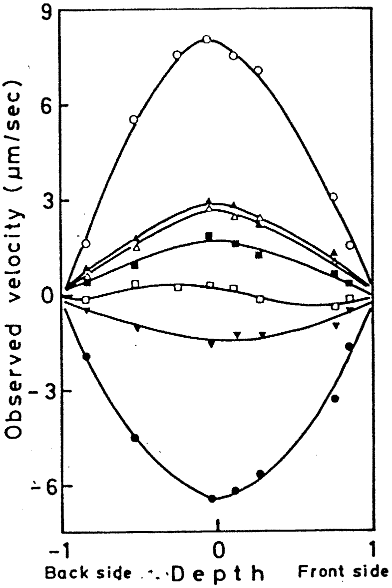

Fig 8—The falling or rising velocity of clay particles at a lateral arrangement of a flat cell under the microscope illumination shaded by water in the glass cell with a base 5x2 cm and a height of 5 cm. Degree of shade under a full scale(10.0) illumination(%);

○ :none, ■ :50, □ :55, ▼ :65, ● :100

▲ ; At 6.8 scale illumination without shade,

△ ; Shaded with light blue heat filter at a full scale illumination.

In last two cases, the visible particles were reduced to one-half or less than that.

But it has been stated that the horizontal arrangement is not preferable for sedimentary particles such as fillers and pulp fines. We tried, therefore, to find out a method for preventing the vertical movements of particles by balancing the settling and the convection.

After several attempts, it was found useful to cover an appropriate area of the illumination lens with an adiabatic body such as a water tank according to the degree of convective and settling disturbances.

Fig.8 shows the falling or rising velocities of clay particles in a laterally arranged cell under microscope illumination shaded to various levles by water in the glass cell without an electric field. In this case, aqueous $CuSO_4$ although this has generally been recommended for reducing heat, was not suitable because many particles go out of view. When 55% of the illumination area was covered, observed velocities of clay particles were almost zero. Under the same condition, the ZP's of clay measured in various concentrations are shown in Fig.9.

The ZP's are almost constant in a wide range of particle concentration. The ZP's at the two stationary levels were close to each other contrary to the results (Fig.4) in the horizontal arrangement of a cell.

The results concerning pulp fines are similar to the above as shown in Fig.10. In this case, however, it is preferable for the particle concentration to be lower than 100ppm since the reproducibility of the data is somewhat poor at concentrations over 100ppm because of the turbulent flow caused by sedimentation of long and/or flocculated pulp fines.

When the measurements are carried out at just one stationary level, the uncertainty in focus, besides the difference of electrical character between both walls of the cell, often leads to pretty large errors. The errors in focussing are almost cancelled by measuring velocities at both upper and lower levels and averaging since the distance between both stationary levels can be maintianed exactly by setting mechanically the dial of the microscope. The errors in the two electrophoretic velocities then compensate each other.

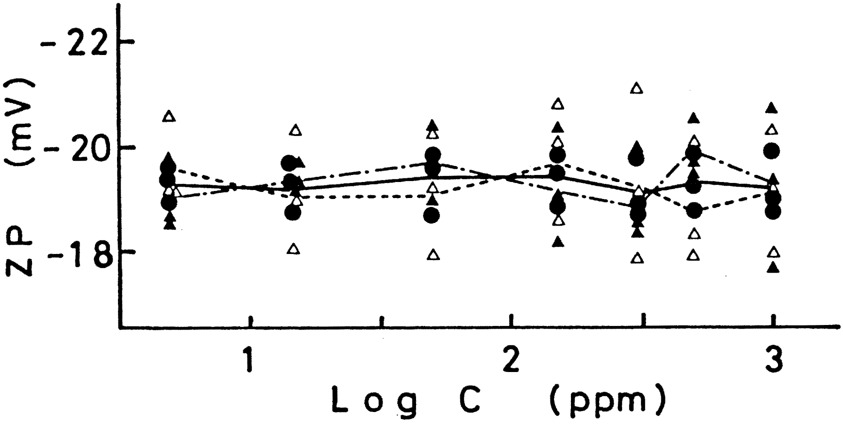

Fig 9—The zeta potention of clay particles measured in the concentration (C) of 5 to 1000 ppm at a lateral arrangement of a flat cell.
(20-22°C, pH 7.8, 0.32 mS/cm, 0.35 mA)

---△--- ; Observed ZP at backward stationary level
—▲— . ; Observed ZP at forward stationary level

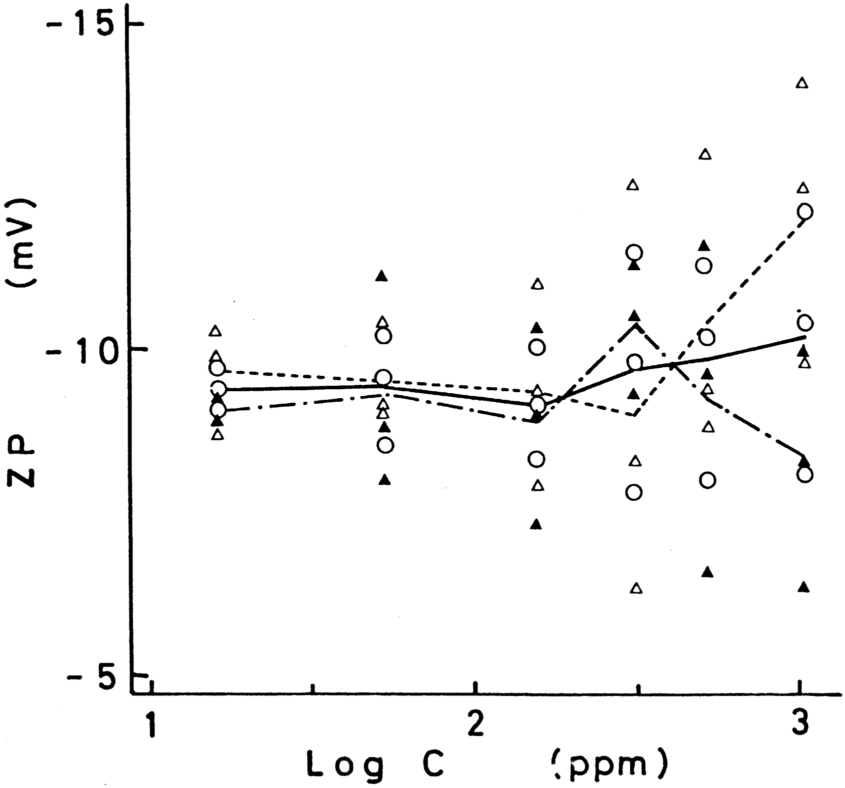

Fig 10—The zeta potential of pulp fines measured at a concentration (C) of 15 to 1050 ppm in a lateral arrangement of a flat cell.
(20-23°C, pH 7.5, 0.32 mS/cm, 0.35 mA)

---△--- ; Observed ZP at backward stationary level
—▲– . ; Observed ZP at forward stationary level

At present, a more sophisticated apparatus in which you can select either the lateral or the horizontal arrangement of a cell is available from Mitmura Riken Co., (Hongo. Tokyo 113).

The Change in ZP of Particles by Agitation

During recent years many workers have made an effort to elucidate the relationship between fines retention and ZP. In these studies, several workers have found that the ZP's or electrophoretic mobilities of fines treated with cationic polymer change to increasingly negative values with increased time and degree of agitation.

Rinke (9) stated that the redistribution of adsorbed cationic polymer within the flocs decreased the surface charge and that the rate of release of anionic interior particles is increased when the severity of the agitation is increased. Strazdins (10) studied the influence of agitation on the ZP of pulp fines with cationic polymer and concluded that the decreases in ZP occured through the creation of a negatively charged surface and the diffusion of polymer into the micropores. In the study on a microcrystalline cellulose-ionic polymer system, Gossens et al (11) also recognized the diffusion, but did not support the creation of the new surface. Arvela (12) and Stratton et al (13) also found that the ZP of white water with cationic polyacrylamide (C-PAM) became more negative with increasing time. On the other hand, Lindstrom et al (14) found the mobilities of pulp fines with C-PAM not changed by agitation. However, the mobility of the fines in the mixture of fines and fibers increased rapidly toward the positive side after the addition of C-PAM, decreased gradually, and reached an equilibrium value. They explained that the adsorption was faster to the fines than to the long fiber fraction, and a desorption from the fines and adsorption to the coarse fibers occurr with increasing time.

The data obtained so far concern cellulose materials such as pulp and microcrystalline cellulose. It is well known that cellulosic materials are porous and may be fragile under strong agitation. Thus the various explanations described above can be possible. However, several questions occur to us: Are the cationic polymers so movable on the negative charged surface? Why does the decrease of ZP also take place under gentle stirring? etc.

Therefore, we used the clay and monodispersed polystyrene latex as more simplified and stronger particles.

Fig.11 and Fig.12 show the changes in ZP of clay particles with various addition levels of high molecular weight PEI (80,000) and various degrees of agitation respectively. The clay was well dispersed in pure water using an ultrasonic generator before adding NaCl and PEI. When PEI was added under agitation of 750rpm at the level of 0.1% on clay (original ZP of -42 mV), the ZP increased rapidly to +9 mV after which it decreased and reached -17 mV. It is also shown that the rates of change in ZP increase with increasing degree of agitation at the same addition level of PEI and increase with decreasing addition level under the same degree of agitation (Fig.12).

It is interesting that the equilibrium values of ZP at a certain addition level are almost the same despite the large difference in stirring. This may indicate that the disruption of clay does not take place. This fact is also illustrated in the system of clay-methylene blue (MB) which is a cationic dye.

Fig.13 shows that no change in ZP takes place due to agitation when MB is added at high levels and the changes in ZP are much smaller and slower than those observed with PEI even at low addition levels. As the adsorption of MB onto clay is almost 100% at below 0.83% MB on clay as shown in Fig.14, a small portion of MB may penetrate into micropores or small gaps in the clay during stirring because of it's low molecular size. Further, the degree of agitation had little influence in contrast to the clay-PEI system.

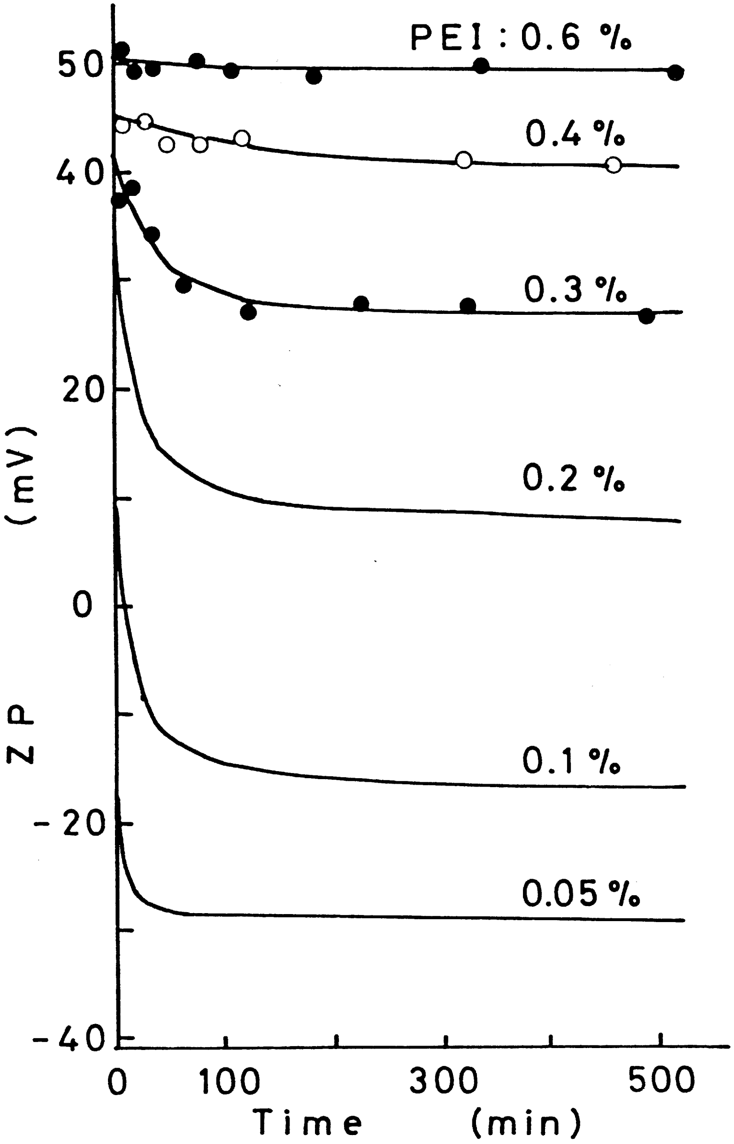

Fig 11—Change in zeta potential of PEI-treated clay at various addition levels with agitation of 750 rpm. (18-21°C, pH 6.0, 0.50 mS/cm, 0.60 mA, NaC1 0.0045 M) Clay; 300 ppm, Molecular weight (MW) of PEI; 80,000

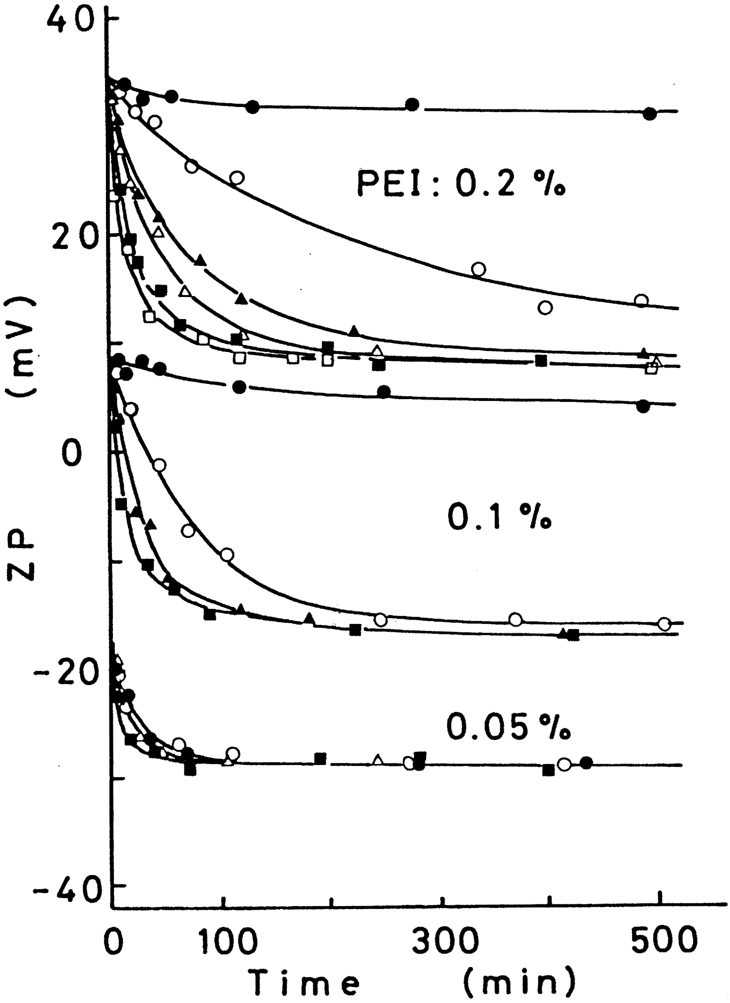

Fig 12—Change in zeta potential of PEI-treated clay at various addition levels under various turbulences. (Conditions are the same as those in Fig.11)

Stirring (rpm); ● 80, ○ 170, ▲ 300, △ 400, ■ 750, □ 2000

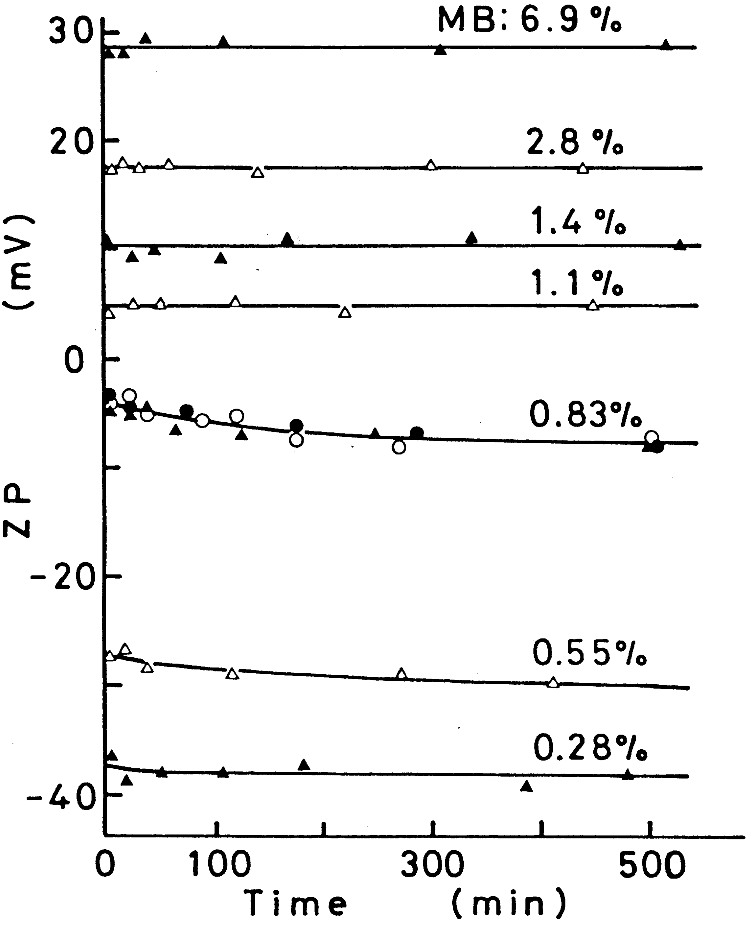

Fig 13—Change in zeta potential of MB-treated clay at various addition levels under various turbulences. (18-21°C, pH 5.7, 0.50 mS/cm, 0.60 mA, NaC1 0.0045 M) Clay; 300 ppm, Stirring (rpm); ○ 150, ▲ △ 750, ● 2000

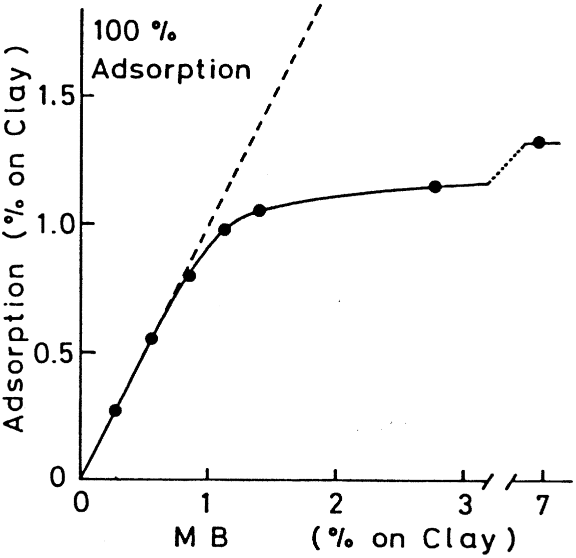

Fig 14—Adsorption of MB onto clay. (20°C, pH 5.7, NaC1 0.0045 M)

The above results suggest that the changes of ZP in clay-PEI system are not dependent on both the disruption of particles and penetration of PEI into pores.

The same trend was observed with regard to the uniform polystylene latex (PSL 0.429 μm in diameter). Results are shown in Fig.15. It was reconfirmed that the rates of change in ZP increased with decreasing addition level of PEI under the same degree of agitation. The PSL has a smooth surface without such big pores that polymers can penetrate. Observations by scanning electron microscope did not indicate the disruption of particles after agitation. These facts suggest that the time dependent change in ZP can occur even though the cationic polymers do not penetrate into pores of particles and/or that the new surfaces with negative charges do not appear.

Therefore an alternative explanation is required. We would like to propose a new hypothesis, that the change in ZP may be attributed to conformational changes of polymers on solid surfaces.

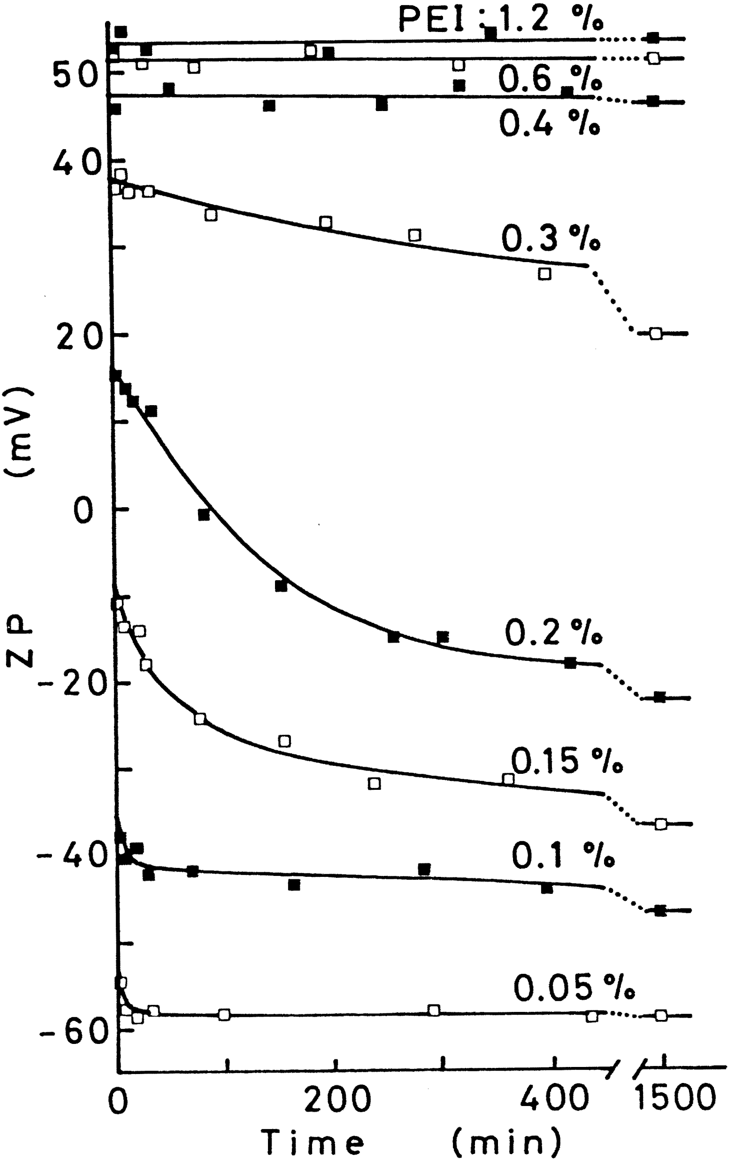

Fig 15—Change in zeta potention of PEI-treated PSL at various addition levels with agitation of 750 rpm. (18-21°C, pH 6.0, 0.50 mS/cm, 0.60 mA)
PSL; 60 ppm, MW of PEI; 80,000

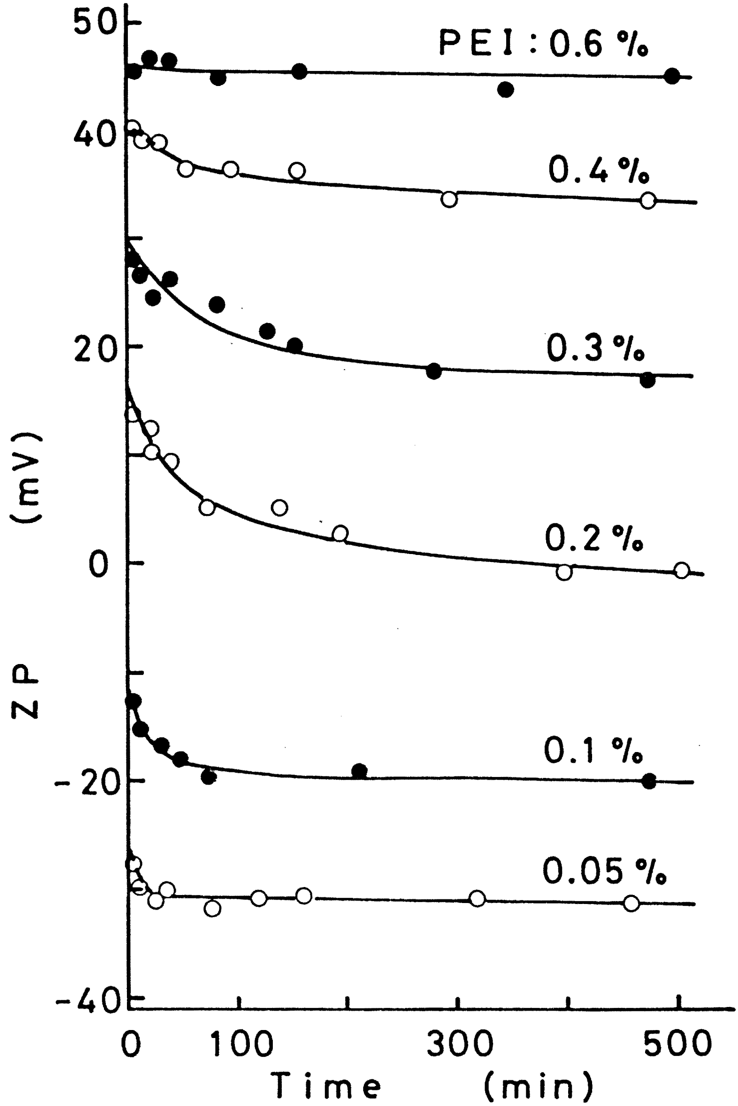

Fig 16—Change in zeta potential of PEI-treated clay at various addition levels with agitation of 750 rpm. (Conditions are the same as those in Fig.11 except MW of PEI) MW or PEI; 1,800

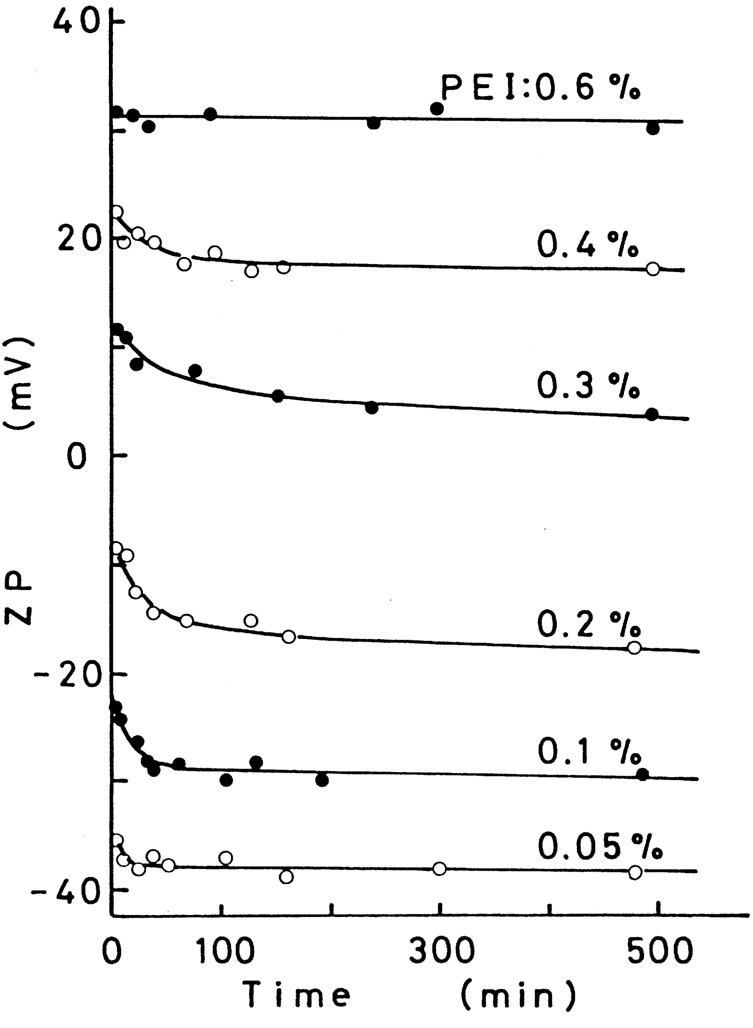

Fig 17—Change in zeta potential of linear PEI-treated clay at various addition levels with agitation of 750 rpm. (Conditions are the same as those in Fig 11 except characters of PEI) MW of linear PEI; 1,700

It is well known that polymers are dissolved in a shape of a coil and polyelectrolytes take more expanded conformation because of electrostatic repulsive force. It is reasonable to postulate that the polycations are at first adsorbed in a random coil onto the negatively charged surface and become flatter depending on the mutual interaction between surface and polymer.

Brooks (15) has shown the model for treating the effect of adsorbed polymer on ZP, which allows for the possibility of a shift in shear plane as well as a modified ion distribution in the diffuse layer. Some other workers (16) discussed the effect on the ZP of an adsorbed layer of polyelectrolyte, although many problems still remain to be elucidated.

Some other experimental evidence was obtained to support our hypothesis. Figs. 16 and 17 show the time-dependent changes in ZP of clay added at various levels of low molecular weight PEI(MW : 1,800) and linear chain PEI (MW : 1,700) respectively.

From data in Figs. 11, 16 and 17 the differences between initial and equilibrium ZP's were drawn to show the effects of molecular weight and molecular form on changes in ZP. As PEI's are of commercial origin except the linear PEI, they are highly branched. As shown in Fig. 18, the differences in ZP are bigger in high rather than low, molecular weight PEI and also in branched rather than linear PEI.

Fig. 19 shows the changes in ZP in Clay-poly (trimethylaminoethymethacrylate) (P.QDM) system. The coil of P.QDM is expected to be more expanded than that of PEI because it is a linear molecule and it contains the quarternary amino group. If the configuration of P.QDM adsorbed on an oppositely charged clay is extremely flat, the ZP seems not to be changed. However, for instance, the difference in ZP between the highest and equilibrium values reached over 50 mV at the polymer addition level of 0.2% based on clay. The molecular weight of P.QDM used is estimated to be considerably higher than that of high molecular weight PEI because of the higher viscosity. These results also support our hypothesis.

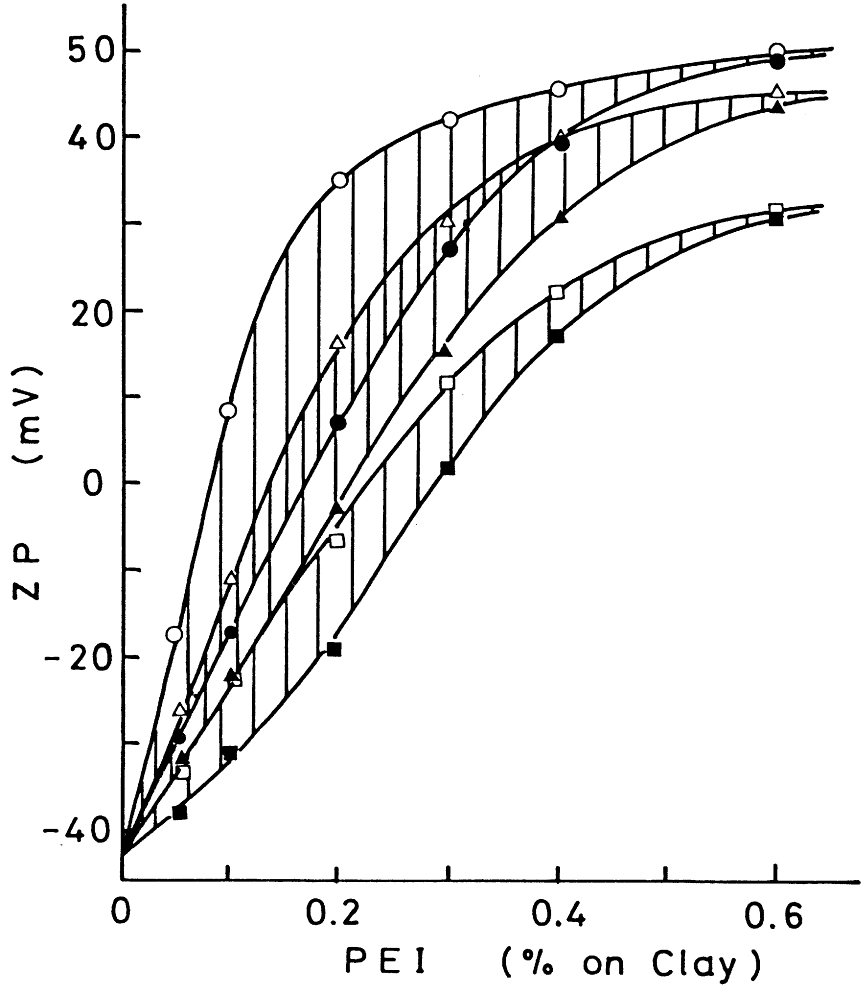

Fig 18—Difference in zeta potential of PEI-treated clay between initial and equilibrium stages at various addion levels. (Conditions are shown in Figs 11, 16 and 17)

○ ● ;MW of PEI 80,000, △ ▲ ;MW of PEI 1,800, □ ■ ;MW of linear PEI 1,700, ○ △ □ ;at initial stage, ● ▲ ■ ;at equilibrium stage

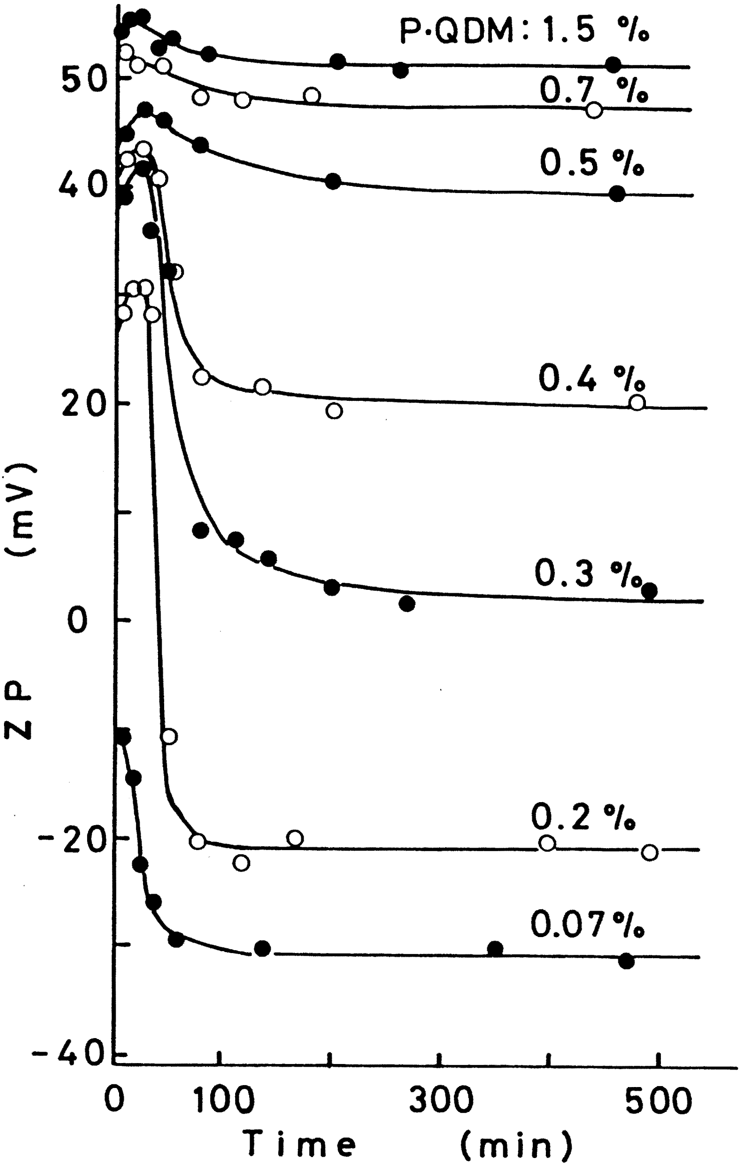

Fig 19—Change in zeta potential of P·QDM-treated clay at various addition levels with agitation of 750 rpm. (18-21°C, pH 5.8, 0.50 mS/cm, 0.60 mA, NaC1 0.0045 M) Clay; 300 ppm

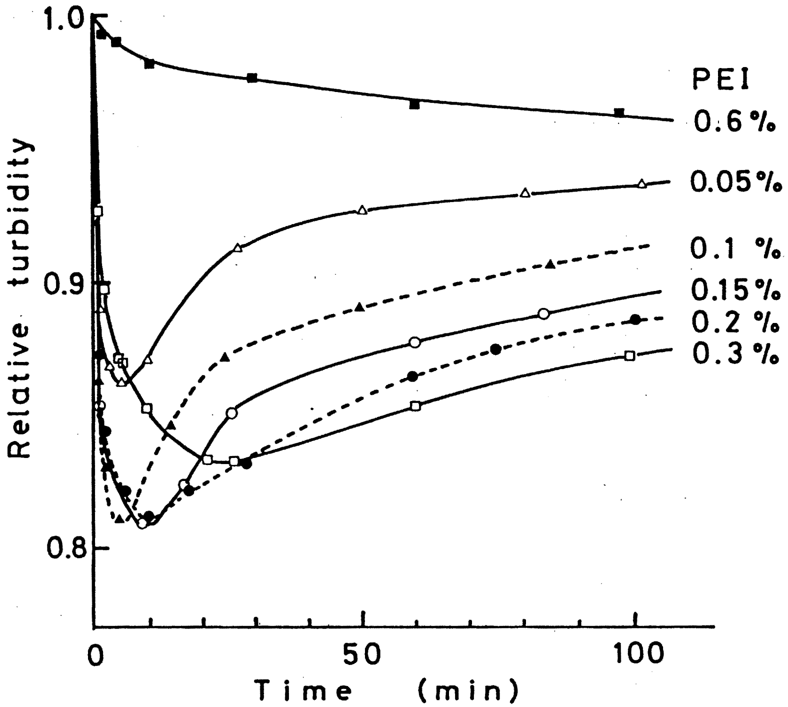

Fig 20—Effects of PEI dosage and agitation on flocculation of clay. (18-20°C, pH 6.0, NaC1 0.0045 M) Clay; 300 ppm, 750 rpm

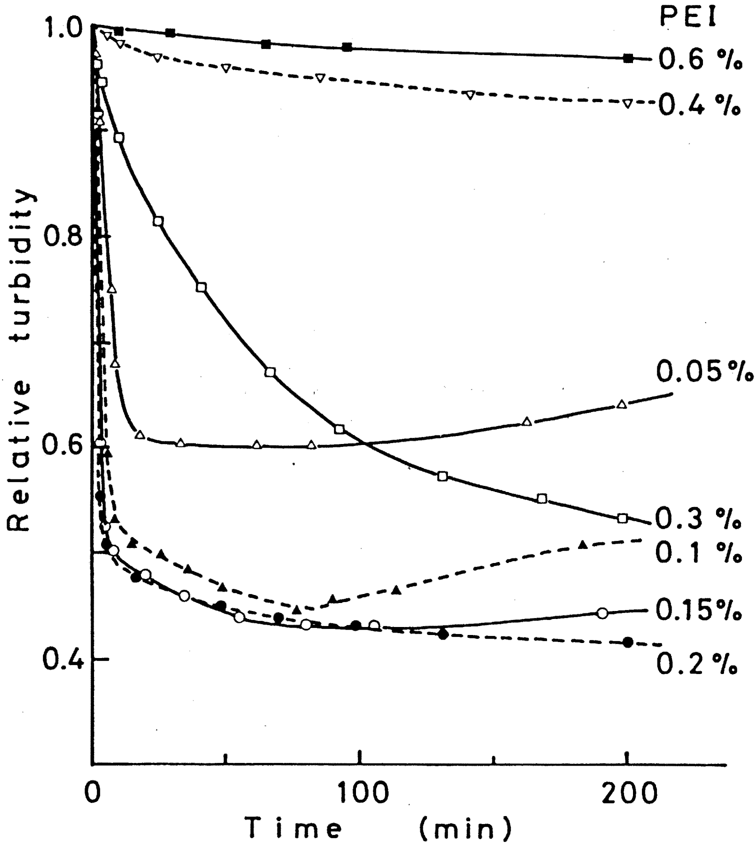

Fig 21—Effects of PEI dosage and agitation on flocculation of PSL. (18-20°C, pH 6.0, NaC1 0.0045 M) PSL; 60 ppm, 750 rpm

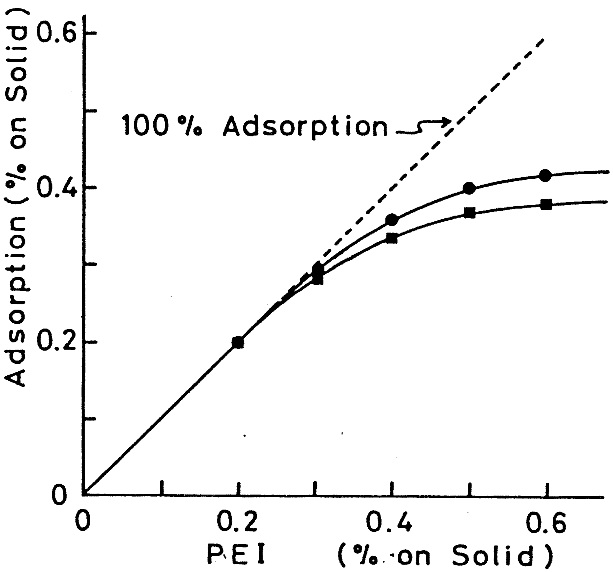

Fig 22—Adsorption of PEI onto clay and PSL. (20°C, pH 6.0, NaC1 0.0045 M) MW of PEI; 80,000, ● ;Clay, ■ ;PSL

Flocculation

The flocculation results evaluated from relative turbidities are shown in Figs. 20 and 21 with respect to clay-PEI and PSL-PEI respectively.

The flocculations of both clay and PSL occured very quickly when the addition levels of PEI were below 0.1% for clay and 0.2% for PSL and the equilibrium ZP's were negative as shown in Figs. 11 and 15. This suggests that enough room of negative particle surface still remains to be bridged by another particle with attached cationic polymer.

Fig. 22 shows the relation between PEI dosage and percentage adsorption concerning PSL and clay.

The diameter of PSL is 0.429 ± 0.0008μm and the specific gravity is 1.05. Thus the surface area is $13.3m^2/g$. It is estimated that the monomer unit of PEI occupies an area of about 20 A^2.

As shown in Fig.22, the adsorption is almost 100% at the polymer addition level of 0.3% on PSL. The surface area of PSL occupied by polymer is then 8.4m^2/g which corresponds to 63% of the total area of the particle if the polymer is adsorbed in a flat configuration. Although the occupied area at the first stage of adsorption must be smaller that 63% because of existence of loops and tails, it may be possible that the bridging is retarded by the electro-repulsive force between adsorbed polymers.

Experimental results show that the flocculation decreases dramatically at the addition level of PEI over 0.3% (Fig.21). At such a high level, the positive ZP is kept in equilibrium as shown in Fig. 15 and then the chance for bridging must be reduced. On the other hand, at a low addition level of PEI such as 0.05%, the flocculation takes place quickly, but not to the same extent. This indicates that the adsorption of PEI onto PSL and the bridging are fast because the negative surface available for bridging is vast, but the resistance of the floc to hydrodynamic shear is not high because of the low bridging density.

At the medium addition level of PEI between 0.1 - 0.2% both the chance for bridging and the density of bridging are considerably higher and then the flocculation occurs more easily (Fig.21).

Similar results are also obtained with respect to the clay-PEI system. Figs. 22 and 20 show the adsorption and flocculation behaviour. It was confirmed that the flocculation of clay occurred most readily in a similar manner as the above when the addition level of PEI was 0.1-0.2%, at which the bridging effect seems to be high since the behaviour of adsorption of the PEI and the change in ZP were similar to those of PSL.

It is also possible to account for the flocculation behaviour by the attraction between positive and negative regions of particles, namely the so-called patch model. However, the time dependent changes in ZP can not be explained by the patch model.

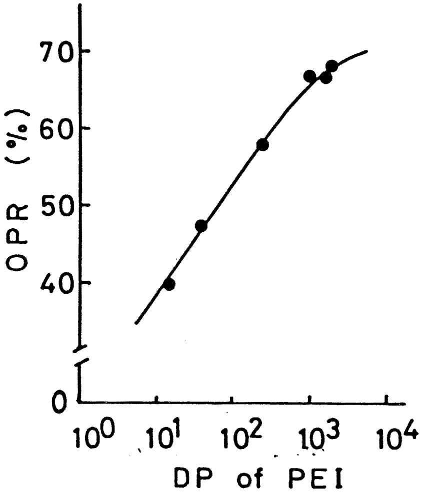

Fig 23—Effect of DP of PEI on OPR of fines in dual polymer system.
PEI; 0.05 % on solid (added first), A-PAM; 0.05 % on solid (after 0.5 min), Agitation; 1,000 rpm

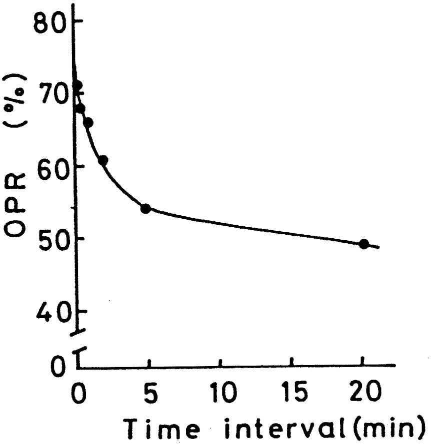

Fig 24—Effect of time interval between the additions of PEI and A-PAM on OPR of fines in dual polymer system.
PEI;0.05 % on solid(added first). A-PAM;0.05 % on solid(after certain min), Agitation; 1,000 rpm

Retention of Fines in Dual Polymer System

In the bridging model of flocculation, polymer molecules adsorb on the surface of the particle or fiber in a series of loops, trains and tails and these loops are able to interact with other particle surfaces when they extent out into the solution beyond the electric double layer. Unbehend (17) has suggested that the hydrodynamic forces at the particle surface cause a reconformation of the polymer chain by the flattening of the loops which reduces the retention, and introduces the concept of hard and soft flocculation. This concept is widely accepted, but little is known about an experimental technique for following the process of flattening of loops.

In addition, Britt et al (18) have shown that the most tenacious flocculation forms through the dual polymer system of sequential treatment of stock first with PEI followed by a long chain anionic polymer.

Then, it is easy to expect that the longer the loops and tails of PEI are, the higher the retention of fines in paper stock is, because the bridging by a long chain anionic polymer occurs more effectively.

Fig. 23 shows the effects of molecular weight (MW) of PEI in the dual polymer system on the one pass retention (OPR) of fines. In fact, the OPR increased with an increase of MW of PEI.

Fig. 24 shows the effects of time intervals between the additions of PEI (0.05%) and anionic polyacrylamide (0.05%) on the OPR. The stirring was continued at 1,000rpm during the experiment. The OPR was reduced rapidly to a certain level within 5 minutes and gradually after that. The pattern of decrease in OPR was very similar to that in ZP shown in Fig. 11.

These results support again our idea that the decrease in ZP during stirring depends on the conformational change of polymer on solid surfaces.

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Transcription of Discussion

SESSION 7 ADDITIVES

Chairman J.C. Roberts

The Time-dependent Change in Zeta Potential of Particles with Cationic Polymer

by H. Tanaka

Dr. T. Lindström STFI, Stockholm, Sweden

I would like to say first that I think yours was a very nice presentation. I think you have added a new dimension to our understanding of these phenomena by doing these experiments with latex particles.

However, in practical papermaking situations, this is not the most important effect and I would advocate my own hypotheses of 1975 of fibre fines transfer of polymer. We know from the transient surface potentials, first published by Strazdins, that the migration process into the cell wall is the critical factor in polymer adsorption kinetics.

Recently, we have performed some experiments which generate more data on this hypothesis. I would just like to explain the rationale for our hypothesis on this subject.

Mostly with papermaking systems, we are dealing with fibres and fines. We can only measure the electrophoretic mobility of the fines. We think this is the cause of this specific phenomena.

If you measure the electrophoretic mobility of the fines particle after different times of addition in the presence of coarse fibres, you will observe those transient phenomena. This is in contrast to experiments with the fines fraction only where you will not record these transient phenomena in our experience. We only see the transient phenomena in the presence of the coarse fibres.

Our explanation for this is that, initially, the polymer adsorbs onto both the fines and the coarse fibres simultaneously, but then after some time, we have a transport phenomena of polymer from the fines onto the coarse fibre fraction. We can substantiate this by determining the amount of polymer on the fines particles after various times of addition. We have also used microcrystalline cellulose as well as fines particles. More important is that these transport phenomena are not present if you replace the coarse fibres with, for instance, non porous material. So, the phenomena seems to be related to the porosity of the coarse fibre fraction. The explanation for this is that if you have the cellulose fibres, together with fines particles for example, and then add cationic polymer, we will get a very fast adsorption onto the fines particles, but the adsorption onto the fibre is quite slow. As time goes on, the polymer will actually rearrange and go into the porous system of the fibre cell wall which means we are opening up negative charges on the fibre surfaces leading to a transfer from the fines (which are cationic) onto the large porous fibres which are negatively charged. The difference between fines and coarse fibres is the diffusion distance. The cell wall is quite thick, in the order of several microns, whereas the fines particle has a thickness of about 0.1 micron and therefore the diffusion distance into the interior of the fines particle is very short which means that the adsorption is more rapid.

This explanation is important for practical systems although I have to congratulate you on a beautiful piece of work.

Dr. H. Tanaka May I ask Dr. Lindström how he measured the adsorption rate for fibre and fines? How did you separate them?

Lindström You take a Britt jar type of device and filter off the fines.

Tanaka Do you use nitrogen analysis?

Lindström No, these polymers are radioactively tagged.

Dr. B.A. Nazir Wiggins Teape R & D, Beaconsfield, Bucks

Regarding the measurement of electrophoretic mobility, you spent some time in explaining the way the cell should be set up, horizontal, lateral or vertical, whether it should be screened by water or some type of heat filter. These procedures are well known, (see, for example, A.L. Smith in "Dispersion of Powders in Liquids" edited by G.D. Parfitt, Elsevier, 1969). People measuring electrophoretic phenomena are already taking these precautions. The important question is how long does it take to make a measurement? Your Figures 11 and 12 indicate how rapidly particle mobility can change with time.

Tanaka In five minutes, we take 10 measurements at the upper stationary level and 10 at the lower stationary level.

Nazir By the time you move from the upper to the lower stationary level, things might have changed. In fact, from your figures, it would appear that even in five minutes, the mobility could have changed significantly.

Tanaka That happens if you mount the cell horizontally. If you mount the cell laterally, then that problem is eliminated. That was the point I was making at the beginning of my paper.

Even if the cell is mounted laterally and/or the measurements are carried out quickly, however, it is highly recommended that one at least measures the particle velocities at the two stationary levels (so-called Komagata's) and use the mean value for calculation of ZP or mobility, especially in the case of the use of an old cell or the successive use of a cell without washing each time. Among thousands of measurements, there was almost no case in which the values at two stationary levels were the same. It is theoretically proved that the mean value represents the true one, namely the value at the real stationary level where the liquid velocity is zero (6).

Also I would like to emphasize that a DC, constant current, source should be employed, in preference to the more usual constant potential source because one needs to use the value of the current for calculation of ZP, but the current often varies suddenly and significantly during the measurement when the constant potential source is applied.

E. Strazdins Consultant, Fairfield, U.S.A.

(Written Contribution) I think we are moving into dangerous ground in attempting to rationalize these mechanisms. For the sake of clarity I would like to respond by commenting on some aspects of Dr. Tanaka's work and then to Dr. Lindström's contribution on the polymer redistribution mechanism.

Dr. Tanaka's work encompasses many procedural and mechanistic aspects of the microelectrophoresis technique. He presents a wealth of information that is of value to those who might get deeply immersed in experimentation with microelectrophoresis or with instrument design. To those who may use this technique merely to diagnose chemical balance of their system, such a complex array of data may become a burden or even give an impression that the technique is unreliable. Since the first application of this technique (1) we have accumulated a wealth of technically useful data which has served well to optimize the application of all chemical additives (2). No major problems have been experienced with settling or dissymmetry of the stationary layers. If the operator uses common sense and develops some basic skills he should have no problem in getting uniform and correct data. It goes without saying that the cell must always be adequately equilibrated with the suspension used for measurement; measurements must be performed fast, before settling, thermal overturn or gassing at the electrodes becomes significant interferences.

In regard to the observed changes in zeta potential (or charged decay) the results obtained on the clay and PSL suspensions are logical and consistent. However, I would like to offer another mechanism to explain the changes in the zeta potentials towards greater electronegativity. The clay and PSL spheres are inpenetrable and any decrease in the initially high positive charge may come about through a time-dependent interaction of the cationic PEI with the underlying anionic polyelectrolytes, such as emulsifiers or colloid stabilisers that are adsorbed on the particle surfaces. Even in the case of cellulose fibres, one never sees a pure surface. It always contains some amount of re-deposited lignins, degraded hemicelluloses or other anionic polyelectrolytes. All these material can rearrange and interact with the adsorbed cationic polymers in a time-dependent manner. The particular rate of charge decay will obviously depend on a large number of factors.

The trends in turbidity and charge vs time could be rationalised by more heavily leaning on the significance of the transient and the final zeta potentials. Thus, for instance, the results of Figure 15 and Figure 21 clearly indicate the significance of the system being close to, or having passed through the zero charge domain at the 0.2% PEI doseage level as a stabilising factor. Conversely, the electric static repulsions are a strong destabilising factor, either when the system is excessively electronegative or when the suspension charge is swiftly reversed to strongly positive at the highest PEI levels, even at the expense precluding effective bridging.

Finally, I want to thank Dr. Lindström for the excellent documentation of the polymer transfer from fine particles to the more penetrable long fibre fraction (3). We have supported this kind of mechanism from the very beginning of the charge decay study, since it is inherent to the measurement procedure that the transient charge of the whole furnish is reflected to the charge of the fines, implying a redistribution of polymer between the stock components (4). I could not conceive a mechanism that assumes the fines being chemically different from the potentially determining fibre surfaces and that the fines would become cationic while the long fibres are still anionic. Polymer does not know the difference between surfaces. The adsorption of polymer on fines vs the long fibres occurs in proportion to their relative surface areas.

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