

Critical issues in applying electrokinetics to papermaking

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ABSTRACT: *The merit of microelectrophoresis is discussed in the light of a recent publication that presents highly controversial data which directly impact the credibility of this technique. The validity of the microelectrophoretic measurement, using fiber fines, has been fully confirmed by detailed theoretical work and is supported by various kinds of experimental evidence. The theory of microelectrophoresis is well understood, and the mobility measurement provides the best estimate of correct fiber potential. In contrast, the streaming potential measurement has many theoretical and physical difficulties, and the measured potentials represent only relative numbers. The "cationic demand plateau" allegedly shown by microelectrophoresis cannot be explained, and there is no reliable experimental proof to support its existence.*

KEYWORDS: *Cationic compounds, electrophoresis, fines, paper making, synthetic polymers, wet ends, zeta potential.*

During the past few decades, microelectrophoresis has been the most widely used technique for studying and controlling wet-end chemistry in the paper mill (1). It is fair to say that the information developed has formed a solid foundation for better understanding complex polyelectrolyte interactions and the chemistry of the wet end. This success can be attributed to the fact that electrophoretic mobility most accurately predicts the actual electrokinetic potentials of fiber fur-

nishes and that the measurements can be performed rapidly, before redistribution of adsorbed polymers and the associated shifts in surface potentials can occur. However, a recent publication in *Tappi Journal* (2), which compares streaming potential and microelectrophoretic measurements, presents highly controversial data that is bound to cause confusion in applying electrokinetic techniques to optimize wet-end chemistry. To keep our knowledge on solid ground, these issues must

be addressed in light of the industry's need for reliable wet-end process control.

Requirements of an electrokinetic technique

An electrokinetic technique should enable accurate assessment of charge-performance relationships of complex polyelectrolyte systems in the framework of existing mill conditions. It is always to the papermaker's benefit to investigate and rehearse the technical strategy before a machine trial is attempted. The parameters to assess include furnish cationic demand, effective charge of polymers to be used under ambient mill conditions, necessary polymer dosages for a balanced system, the best points of chemical additions, and a complete documentation of furnish charge as the stock moves toward the machine headbox.

In many cases, by necessity or by design, the furnish potentials may cross the isoelectric point more than once, with associated changes in the physical structure of furnish (drainage, retention) that are ultimately reflected in the performance of chemical additives. In certain grades, such as photographic, where high alpha-cellulose pulps of low cationic demand are used, the furnishes become strongly positively charged even with moderate levels of cationic wet-strength resins (3). To produce a high-wet-strength grade, more resin must be retained, which is well

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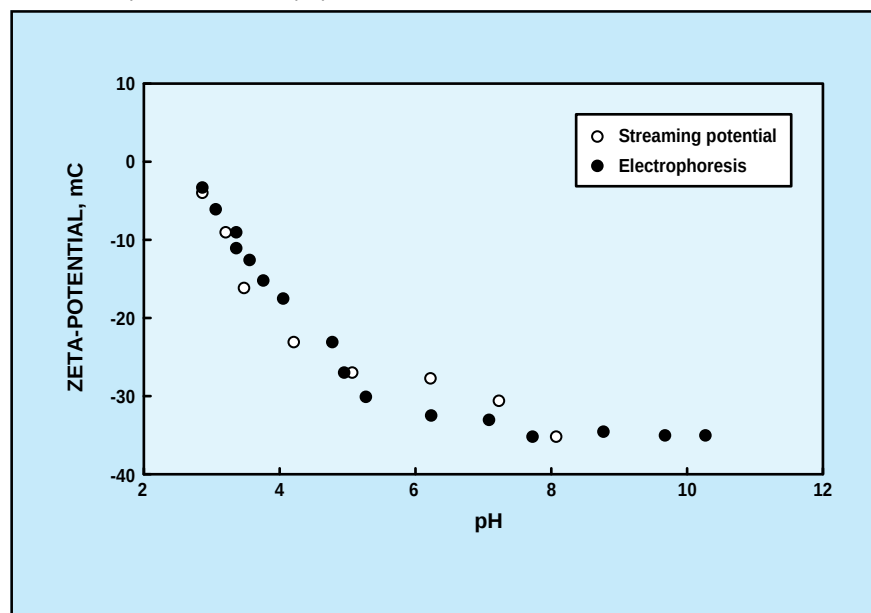
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beyond the amounts the furnish can adsorb without electrostatic interference from positive surface potentials. To alleviate the excess cationic charge and balance the system toward isoelectric or even slightly negative values, appropriate levels of anionic polymers, such as polyacrylamide dry-strength resins or carboxymethylcellulose, are added (4, 5). As the anionic polymers are introduced and the system swings back toward the isoelectric condition, strong coacervation of the cationic and anionic species sets in. This mechanism brings about major improvements in retention, drainage, and tray water cleanup. To properly monitor the wet-end chemistry, changes in the electrokinetic charge must be recorded with certainty and at more than one point of stock flow. This can be most conveniently done using microelectrophoresis. A measurement of the final charge near the machine headbox or wire provides much less insight into the subtleties of the wet-end process. It is the "charge history" that counts (5).

Another complicating factor that interferes with establishing accurate charge-performance relationships is the transient nature of the electrokinetic potential (4). On a paper machine, the contact times between chemical additives and paper furnish usually are very short. After initial adsorption, triggered by electrostatic forces, the cationic polymers tend to quickly redistribute to less accessible fiber domains and continue to interact with anionic polymers that had earlier been adsorbed on fiber surfaces (6). As a result, the furnish potential rapidly changes toward greater electronegativity. Therefore, any electrokinetic technique that requires extra handling or prolonged contact times is bound to produce results which will represent some deviation from the correct on-machine value.

In brief, a suitable technique must be fast and accurate and flexible

1. Comparison of zeta potential measurements of cellulose fibers by streaming potential and microelectrophoretic method (13)



enough to enable documentation of electrokinetic potentials at ambient mill conditions at all points of chemical introduction.

In the continuous quest for better process control tools, the most important criterion for choosing an electrokinetic technique is the accuracy of the measurement. Also important is whether the technique is adaptable for continuous on-line measurements (7). Since the practical application of electrokinetics for process control still is a developing field, the simultaneous pursuit of both goals is a commendable attitude. However, in the attempt to meet the second goal, no sacrifices can be made on the first. Papermaking is too complex and cost intensive to take a gamble on a new, inadequately proven process or analytical procedure.

Problem areas

On reviewing a recent publication (2) which compares microelectrophoretic measurement with streaming potential measurement, one comes face-to-face with a number of controversial issues which directly

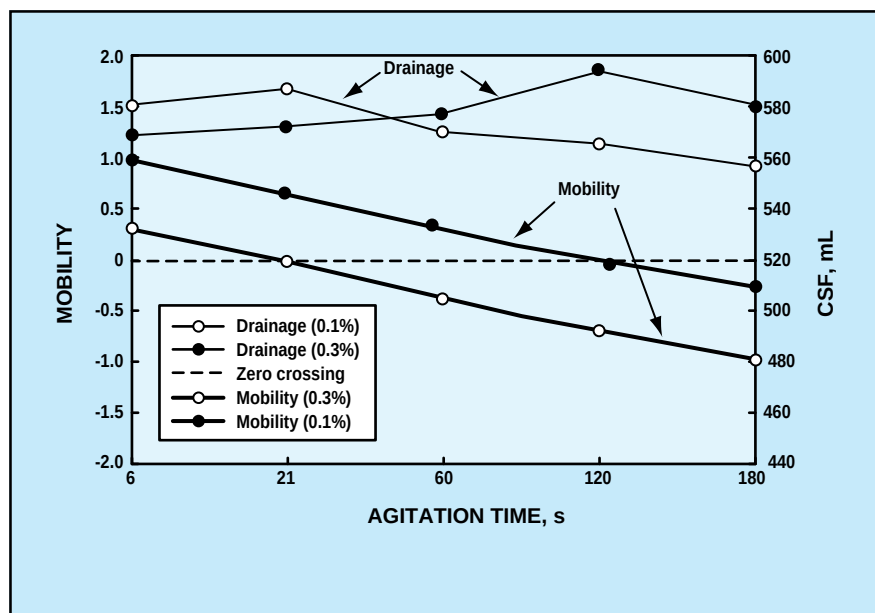
impinge on the credibility of the microelectrophoretic charge measurement. If not adequately dealt with, the ideas presented in the publication are bound to cause confusion and result in a setback in proper implementation of the well-established principles in research and for process control in the mill.

Most disturbing is the advocacy of the existence of a "cationic demand plateau" (2, 8) on the negative side of the zeta potential scale, and the explanations of the mechanisms of cationic polymer adsorption on furnish components are confusing. Also puzzling is the fact that on one hand the effort is made to prove the existence of a "cationic demand plateau" as a physical entity, but on the other hand it is suggested that the streaming potential measurement, which shows no plateau, is a better technique than microelectrophoresis.

We must discuss these many controversial issues in a systematic manner for the sake of clarity:

1. To support the existence of a "cationic demand plateau" the work of Onabe (9) is cited as an important reference (2). Onabe used the Chang and Robertson method

2. Correlation of mobility with drainage in a dynamic system (bleached sulfite, pH 6.0, 0.1–0.3% cationic promoter)



(10), which in principle is similar to the streaming potential measurement since both use a fiber pad. What Onabe shows is a well-known plateau on the positive side of the zeta potential scale. This merely confirms the principle that electrostatic repulsion obstructs further adsorption of a cationic polymer once the fibers have become strongly positively charged (4). But this plateau has no functional relationship to the “cationic demand plateau” on the negative side.

2. In proposing mechanisms for cationic polymer adsorption, the author seems to rely on the ideas proposed by Soremark and Linstrom (11). These workers conjectured that cellulose fines are more anionic and more mobile than the large fibers. Therefore, the fines may adsorb cationic polymers at a faster rate and become positively charged while the large fibers remain electronegative.

This theory cannot be supported for several reasons. Common sense dictates that fines, which largely consist of fibrillar material that has been peeled off the

primary wall of fibers, have the same composition as the potential-determining surface of fibers. Hence, the negative potentials of the fines and fibers must be the same. Theoretical work by Jaycock and Pearson (12, 13) has fully confirmed this hypothesis.

- In rationalizing the adsorption mechanisms, certain key parameters deserve consideration. The adsorption of cationic polymers primarily occurs via the route of coulombic force interactions. The radii of gyration of a typical polyamine-type cationic polymer (DADM) of 0.4×10^6 MW and a cationic polyacrylamide of 14×10^6 MW are 1.1×10^{-4} mm and 3×10^{-4} mm, respectively (14, 15). Obviously, the cationic polymers are of much smaller dimensions and are much more mobile than fiber fines. Electrostatic forces act over much longer ranges than physical forces; therefore, the electrostatic attraction between the cationic polymer and anionic cellulosic components will be the main driving force for adsorption (16). This automatically provides that a cationic polymer will adsorb on cellu-

lose fibers and fines similarly and that at any time during the adsorption process the fines and fibers will have identical surface potentials. The fact that fines adsorb more polymer on a weight basis as a result of their large surface area may be mistaken as an indication that fines are more cationic than fibers.

3. Detailed studies have shown that changes in surface potential have a profound effect on the hydrodynamic surface area of fibers (σ) and, consequently, the drainage and retention responses (5, 17). If a “cationic demand plateau” were real, there should be commensurate trends in drainage and retention when a plateau is reached, but such evidence has not been found.

The arguments concerning the existence of a “cationic demand plateau” have a long history (18), and many efforts have been made to settle this controversy (5) by cooperation among different laboratories using similar fiber furnishes and various types of instrumentation.

4. Reference 2 does not cite any pertinent publications (4, 19) which cover the dynamic aspects of charge decay (or “changing pattern of charge”) at greater depth. The discovery of this important phenomenon is to be credited to the versatility of the microelectrophoretic technique, without which the rapid changes in surface potentials would not be documented (19). In this context, it is regrettable that no microelectrophoretic data on the “changing pattern of charge” are shown to make the comparison of the two techniques meaningful.

In summary, the referenced publication (2) arbitrarily favors the streaming potential measurement as a more viable technique without supporting that conclusion with valid experimental data. It fails to discuss

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these issues in the light of published information, thereby unjustifiably downgrading the credibility of the microelectrophoretic technique.

Theoretical aspects

The main thrust here is to resolve the controversies that impact the mobility measurement in the context of comparing the efficiency of microelectrophoresis with that of the streaming potential measurement.

Jaycock and Pearson (12, 13) have done the most theoretical work in comparing the zeta potentials derived from mobility measurements on fiber fines with zeta potentials obtained by streaming potential techniques. These authors conclude that:

1. The streaming potential technique is time consuming and has theoretical difficulties in interpreting the charge; different methods of calculation produce different answers.
2. Only extrapolation to 0% pad consistency, using the Chang and Robertson method (10), produces consistent results which, within the experimental error, agree with the zeta potentials derived from mobility measurements, as shown by **Fig. 1**.
3. Since the microelectrophoretic measurements can be performed much faster than streaming potential measurements, these authors switched to microelectrophoresis in the rest of their work.

Schempp (20) made a thorough investigation of variables that affect the streaming potential measurement, with the following conclusions:

1. The zeta potential values of the same furnish are grossly different if different methods are used for calculation.
2. Various physical factors, such as sample size, changes in pad con-

sistency, uniformity of packing, fines content (recycled broke), and changes in refining have major effects on the magnitude of the measured potential.

3. The streaming potential is not a viable technique.

A pure pulp, such as used by Jaycock and Pearson, does not contain any chemical additives. Such pulp is ideally suitable for comparing the microelectrophoretic and streaming potential techniques because the electrokinetic potentials are stable. If a cationic polymer is added to the fiber furnish, the potential will be subject to rapid change, and such a comparison would not be possible. Microelectrophoresis is the only technique that is capable of capturing fast changes in the fiber potentials.

Microelectrophoresis has been the preferred technique for studying electrokinetic phenomena in colloid and biological sciences, and it has also found application in analytical research, such as in studying adsorption phenomena or titrating the charge of polyelectrolytes (21). The theoretical principles of this technique are most rigorously understood, and the measured mobility best represents the actual electrokinetic potential. For particles which are the size of fibers or fiber fines, whatever their shape and orientation, the mobility (M) calculated from electrophoretic measurements can be converted to the zeta potential (Z), using the equation of Smoluchowski (13):

$$Z = M(4\pi\eta/\Theta)$$

where

η = viscosity of surrounding medium

Θ = dielectric constant.

As an approximation, the following expression can be used:

$$Z = M \times 12.8$$

As a further refinement, the mobility calculation can be greatly simpli-

fied by precalibrating the cell to obtain a cell factor (F). Then,

$$M = F/\text{particle velocity}$$

The mobility measurement can be performed rapidly, which is essential to determine undistorted charge-performance relationships.

The versatility of the microelectrophoretic technique can be best appreciated by correlating the mobility with changes in drainage of a system where the stock is subjected to continuous shear. A bleached sulfite pulp was treated with 0.1% or 0.3% of a polyamine-type cationic polymer with an estimated molecular weight of about 75,000. The stock was continuously agitated in a high-shear mixer, and samples were periodically withdrawn for drainage (Canadian Standard Freeness) and mobility measurements. As shown in **Fig. 2**, the fibers initially assumed positive potentials which rapidly changed toward greater electronegativity. Of particular interest is the fact that the drainage maxima at both polymer dosage levels coincided with zero charge. Under high shear, the polymer-fiber bridges are broken up, so the shifts in drainage responses are directly attributable to changes in the electrokinetic potentials. When potential decreases, the electrostatic repulsions diminish, and the hydrodynamic surface area (σ) is reduced (17, 22). This translates directly into increased drainage. The fact that the mobility measurements so faithfully correlate with physical changes of the whole furnish is compelling evidence that the charge, measured on fines, truly represents the charge of the entire fiber furnish.

Practical aspects

Every mill chemist or researcher in the laboratory may have a different procedural approach toward solving technical problems. Nevertheless, I'd like to suggest some proven approaches for better process control

and optimization of wet-end chemistry:

- As a rule of thumb, a thorough investigation of the chemical and furnish variables should precede any attempt at a machine run. Every step in stock treatment should involve thorough documentation of the electrokinetic responses so the behavior of the furnish and the underlying colloidal phenomena are better understood.
- The papermaking furnish during polymer addition is a live and rapidly changing body. Most useful are those analytical techniques that accurately document changes during the wet-end stage. By analogy, a good technique must score right on the bull's eye. Having a tight group off the target is of little value.
- The choice of chemical additives and the procedural details must evolve from thorough knowledge of pertinent technical literature and specific recommendations from knowledgeable suppliers.
- For preliminary testing of polymeric additives, or for effecting quick changes on-machine, a simple drainage tube may serve as one of the more useful tools. A quick drainage measurement immediately indicates if the polymer moves the system in the right direction, since changes in drainage and observation of the drainage filtrate always correlate with changes in first-pass retention (22). An immediate mobility reading on the filtrate produces an

accurate performance-charge relationship, which adds badly needed confidence that the system is under control.

- Once the process is well understood, it is appropriate to take some shortcuts and rely on monitoring the wet-end chemistry with a reliable on-line measurement, a place where some newer types of instrumentation (23, 24) might find their niche.

Conclusions

1. Good control of the wet-end process requires assessment of all important factors, such as polymer charge and functionality under ambient mill conditions, furnish cationic demand, and reliable documentation of electrokinetic charge at more than one point of stock flow.
2. Microelectrophoresis satisfies these requirements best. The theory of this technique is well understood, and the mobility best represents the real surface potential of a papermaking furnish.
3. The pad techniques, such as streaming potential, are subject to many difficulties, which may give rise to serious deviations from the correct values. The nature and extent of such deviations must be thoroughly assessed before relying on such methods for on-line process control.
4. The existence of a "cationic demand plateau" on the negative side of the zeta potential scale

lacks adequate experimental evidence. 

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