

A Critical Review on Zeta Potential Concept in Paper Sizing

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SUMMARY

With the help of electrical double layer theory proposed originally by Helmholtz and later modified by Smoluchowski, Stern etc., Zeta Potential concept is explained and its applicability to the elucidation of sizing mechanism evaluated. Critical appraisal of the literature review indicates, that sizing efficiency and retention is correlated quantitatively with Zeta Potential measured in terms of electrophoretic mobility of size precipitate, within the usual sizing pH range.

The role of Alum in furnishing hexahydrated tripositive ionic complex of Aluminium is highlighted and its binding capacity of cellulose and anionic sizing precipitate through its co-ordinate valencies pointed out.

INTRODUCTION

Internal sizing of paper with alum—rosin size is one of the most important and yet one of the most complex process of paper making. For a better understanding of this sizing, it is important to have an exact mechanism whereby alum “sets” the rosin size on the fibre can precisely be defined. The chemistry of alum—rosin size reaction, the complex products therein formed, and its subsequent adherence to the fibre surface deserves further study so as to put certain modification to the existing theories. Precipitation is a charge transfer phenomenon and adherence of precipitate on the surface is a surface phenomenon involving adsorption/absorption. The application of the above said phenomenon, fully to the water-fibre—rosin size—alum system without some reservations has been restricted because of the polyphase nature of the system and also by the wide variation of acidity which effect many radical changes in the system. Based on the critical evaluation of the different theories, it seems that the sizing of paper can satisfactorily be explained through “Electro Kinetic Theory”. Since the Electro Kinetic Theory deals with the surface phenomena, it should be remembered that not only the surface chemistry of the

fibre, but also the surface of suspension containing viz. rosin, aluminium rosinate and aluminium hydroxide are also important. An attempt has been made in this review to highlight the role of Electro Kinetic Potential (Zeta Potential) as a means of evaluating the water-fibre-rosin size-alum system and to delineate the individual roles of the variables so as to project a coherent theory.

ELECTRO KINETIC (ZETA) POTENTIAL- A CONCEPT

A colloidal particle in a polar liquid can get the electrical charge by a number of mechanisms, one of them is through “ionization”. The other mechanism being the adsorption of a cation or an anion from the bulk liquid, having a specific affinity to the particle. The Dipole-Dipole adsorption is yet another mechanism which results in the specific orientation of particular charge towards the outside of the particle, giving the particle specific residual and surface charge. The particle once in possession of a particular charge, the like charges are repelled away and the opposite charges are attracted towards it. So at any time, with reference to a particular charge on the particle, there will be on the average more ions of opposite than like sign in the vicinity of the charged particle. The excess opposite charge accumulates as a differential ionic layer called “Guoy—Chapmann” layer.

The distribution of this diffuse ionic layer of “Gegenions” (the Guoy-Chapmann Layer) in the liquid surrounding the ion species, strictly follows

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Poisson - Boltzmann's² equation. The movement of diffuse layer in the liquid creates a potential difference between the charged mobile layer and the surrounding bulk liquid. The Zeta Potential is then defined as the integral of the work done to transport an unit charge from an infinite source to a chosen arbitrary plane of shear³. For simplicity it has been assumed that the infinite source is the interior of the liquid and the arbitrary plane of shear is a point near the solid substance.

Representing a pad of fibrous mass as equivalent to a mass of fine capillaries, Quinkie⁴ observed electric osmotic phenomenon. He further observed that if the liquid is allowed to flow through the pad by the application of a pressure gradient, a flow of electrical charges occur.

The generated streaming current and its relationship, with the streaming potential and the resistance of the pad is given by Von Helmholtz⁵, which is modified and generalized afterwards by Smoluchowski, as follows⁶.

$$\frac{L}{P} = \frac{V}{PR} = \frac{F}{E} = \frac{DP}{4\pi\eta L} \zeta \quad (1)$$

In this equation, the electrical conductance is taken as that of the liquid in the pores and the pore factor ζ can be expressed as

$$\zeta = \frac{L}{CR} \quad (2)$$

where C is the bulk conductivity of the bulk liquid. Thus substituting the values of ζ in equation (1) gives

$$V = \frac{DP}{4\pi\eta C} \quad (3)$$

indicating the stream potential to be independent of the dimensions and conditions of the packing pad. The origin of surface electrical conductance, in addition to electrolytic conduction, depend on the electro osmotic transfer of current. So the value ζ in equation (3) is always too high. By replacing the electrolyte with the one of high concentration Briggs⁷ found the value of (ζ) and Briggs value of ζ has taken as the source of most of the Zeta-Potential data reported for fibres.

But Briggs failed to take account of the following complications. In the equation³ the dimensions of the pad is eliminated. Bikerman⁸ pointed out that the pads get swollen in the electrolyte and that the paths for the ionic transfer and fluid flow are unlikely to be identical as given in equation (2) So an appreciable amount of electricity can flow

through as well as around the fibres. A second but less serious complication arises from the ultra low frequency dispersion of electrical resistance. Extending the method of Neale and Peters^{9,10}, Goring and Mason¹¹ and then Chang and Robertson^{12,13} shown that

$$\frac{I\eta L}{PD} = \frac{A\delta}{8\pi} (1-\beta m) \quad (4)$$

where β is the effective volume of the swollen fibre, m , the density of the pad.

From the relation between the $\frac{I\eta L}{PD}$ and m ,

the Zeta Potential δ is calculated at the $n=0$ intercept point. The specific volume β and the specific surface σ are calculated from the slope and intercept of the rectilinear form of the Kozency-Carman^{14,15,16} permeability equation.

$$(Km^2)^{\frac{1}{3}} = \frac{1}{5.55\sigma^{\frac{1}{3}}} (1-\beta m) \quad (5)$$

Where $K = Q\eta L / PA$ the permeability coefficient,

and $Q = \text{Volume rate of streaming flow}$
Cm³/sec,

$A = \text{Area of cross section of pad}$
Cm²

THE THEORY OF ELECTRICAL DOUBLE LAYER

The change on the colloidal particle is due to polar characteristics of the liquid in which it is placed. The electrical double layer deals with the distribution of counter ions and co ions in the locality of the charged surface. The following given model has been adopted for further discussion (Fig. 1)¹⁷.

The concept of electrical double layer was first proposed by Von Helmholtz⁵. The double layer is assumed to be an electrical condenser in which the parallel plates are separated by a molecular distance. Approximating the surface of the particle as a plane, the adsorbed ion layer may be represented by a continuous distribution of charge over this surface. Because of the electrostatic attraction, the counter ions are drawn towards the particle and distributed uniformly. With the combined efforts of the electrical forces and the thermal agitation prevailing in the system, a diffuse ionic layer of "Gegenions" are formed (Guoy-Chapmann layer).

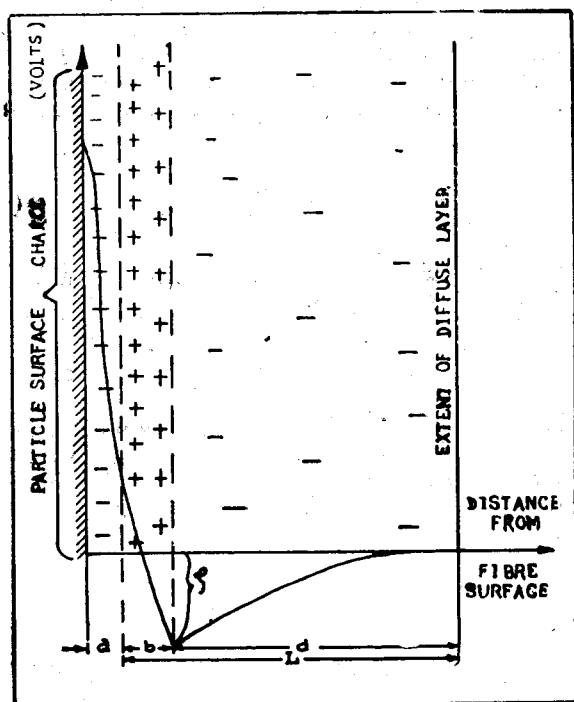


FIG. 1¹⁷

In contrary to the belief of Helmholtz, Guoy¹ showed that due to the presence of excess counter ions near the charged colloidal particle, the electrostatic attraction of the counter ions, further away from the particle are screened, and hence instead of a sharp potential gradient at the interface, the potential drops rapidly at first and then slows down with the increasing distance, coming to a Zero charge at distance infinite away from the particle surface. As to be expected, the attraction of the central colloid is the greatest, of course, close to itself. Due to this fact, the neutralizing counter ions are concentrated much more at these regions and becomes negligible as the distance further away. In addition to this the furtherance of the diffuse layer from the central colloid depends upon the charge of the bulk liquid and also on the concentration of the simple salts which gives the charge to this electrical system. An interesting aspect of this phenomenon is that the increase in the valency of the counter ions significantly affect the diffusion layer, because both the screening effect and the electric attractions are magnified. This is an important point in dealing with the sizing of the paper as a whole electro kinetic system, because the effect of polyvalent ion has as will be discussed later, a profound effect on the sizing efficiency.

STERN'S MODIFIED DOUBLE LAYER

Stern¹⁸ pointed out that Guoy-Chapmann, double layer theory, contains certain omissions and the assumptions made are not consistent to the charge evaluated for the system. He pointed out that all the counter ions and solvent molecules are not mobile. The narrow layer of counter ions always fixed to the surface at a closer distance. He has applied a correction for the finite size of the ions in the first layer adjacent to the charged surface. Due to the electrostatic and Van der Waals' forces, a specific ion adsorption is possible. This results in a compact layer of counter ions attached to the surface. According to him the double layer is in two parts: One, the layer which has approximately a single ion thickness, and remains fixed to the solid surface. The potential drop in this layer is therefore very sharp. The second part of the layer extends some distance into the liquid phase in diffused state. The free movement of the ions in this regions are affected by the thermal agitation but the distribution of positive and negative ion is not uniform, because of the preferential attraction of ions of opposite sign. The result is a gradual fall of potential into the bulk liquid where the charge distribution is uniform. The fixed layer to the surface is called Stern's rigid layer and the diffuse layer is called Guoy-Chapmann (Fig 2)¹⁷.

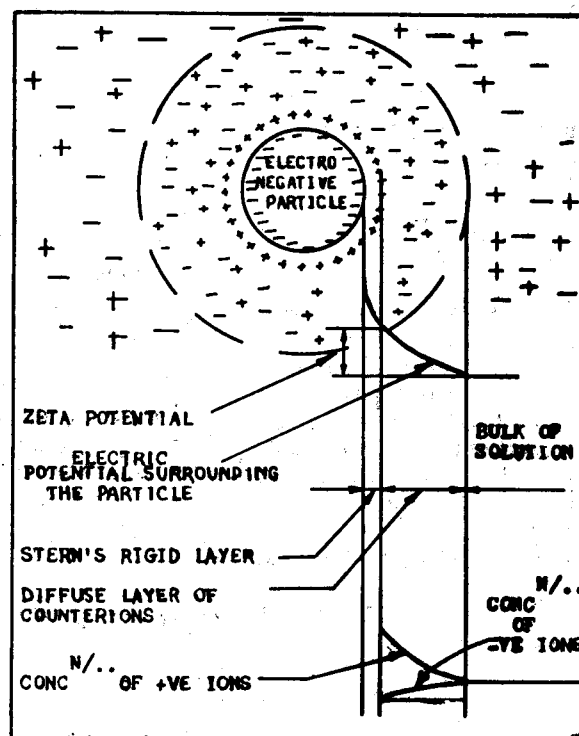


FIG. 2¹⁴ CONCEPT OF THE ZETA POTENTIAL

The region which separates the fixed stern layer and the Guoy-Chapmann diffuse layer is the plane of the shear. The work done to bring an unit charge from the interior of the liquid (where the charge distribution is uniform) to the surface of the Stern fixed layer, to make the unit charge immobile with respect to the mobile Guoy-Chapmann layer, is the Zeta Potential.

The figure 2 shows the cross section of fibre having a negative charge placed in the water. The negative surface, by electrostatic force, attracts the positive ions (eg H^+), which may be originated from the bulk liquid or from the surface of the fibre itself. This charged system consists of the fibre (with a specific charge) and the neutralizing counter ion layers forming the double layer. The so called Stern's fixed layer is due to attachment of the counter ions to the fibre surface and larger the charge on the fibre more compact will be the Stern layer. This layer partly neutralizes the charge and electrostatic attraction of the colloid pushes the remaining counter ions further away from the fibre, but still being kept within the vicinity of the fibre, forming a diffuse layer. Since the diffuse layer is loosely bound to the colloid, it possesses some kind of mobility.

THE MEANING AND LIMITATIONS IN THE APPLICATION OF ELECTRO KINETIC THEORY TO THE PAPER SIZING

Considering the water-fibre-rosin size-alum system, it has been the objective of this paper, to discuss the individual role of these variable in terms of electro kinetic theory, measured in terms of either (i) electro osmosis (ii) electrophoresis (iii) streaming potential (iv) streaming current (v) sedimentation potential. In addition to this two things are to be studied. One is the formation of rosin complexes with alum and their subsequent adherence to fibre surface. Secondly the effect of polyvalent ions (both anions and cations) on the system and to the system environment before and after this addition.

BEHAVIOUR OF ALUM IN WATER

The dissociation products of alum in water is still a controversial subject. The dissociation of alum according to Price^{19, 20, 21, 22} and Cobb²³ etal results in the formation of aluminium ions of trivalency, which according to them, is the active agent that is taking part in the precipitation of rosin size. The polyvalent ions in the alum-water system is aluminium ($3+$) and sulphate ($2-$), Sieber²⁴ Lorenz and Ostwald^{25, 26, 27} believed that it is the aluminium hydroxide that is the active agent. But Ekwai²⁸, Guide²⁹, Strazdines³⁰ and

more recently Davison³¹ are of the opinion, that neither the aluminium ion as proposed by Price and others¹⁹⁻²³ nor the aluminium hydroxide as thought by Lorenz and others^{25, 26, 27} is the active agent but a more complex hexahydrated aluminium ion that is the active species in sizing the cellulosic fibres. The successive "hydroxylation" of this hexahydrated aluminium ion results to the system a number of complex aluminium compounds. Davison³¹ further proposed that, it is the hexahydrated trivalent aluminium ion, that is the starting point of the reaction with abietic acid (rosin) and the reaction is a successive one. One important point to be noted is that, an alum containing system contains a small amount of active acidity (its hydrogen ions) apart from a large reservoir of potential acidity due to the various species of aluminium ions. Matijevic^{32, 33} confirmed this facts pointed out by Ekwai²⁸, Guide²⁹, Davison³¹ and others³⁰ by showing that the hydrolysis product of $Al(NO_3)_3$ contains a complexed aluminium compound of the formula $Al_6(OH)^{3+}_{20}$.

ELECTRO KINETIC PROPERTIES OF ALUM-ROSLN SIZE PRECIPITATE AND THE SIZED FIBRE

The reaction products of alum-rosln size is yet another controversy. It is important to know the composition of size precipitate, because it has a pronounced effect on the sizing environment and the electro kinetic values of the system. By the bulk analysis of the precipitate. Ekwai²⁸ proposed that aluminium mono resinate, is the major contributor, but the size precipitate, in addition to this, contain di and tri resinates along with free acid. Stockigt and Klingner³⁴ holding that the dissociation of alum in water produces the alum and precipitate formed by the interaction of alum and a rosin hydrosol is a complex, which has been absorbed to the fibre Lorenz and Ostwald^{2, 26} attacked the problem by making observations on the direction of fibres in a size chemical suspension under the influence of an applied electrical field (electrophoresis) The migration of the fibres towards the anode on the application of electrical potential is reversed when alum is added to the system, thereby pronouncing that the addition of alum to the fibre suspension changes its charge from negative to a positive side. The addition of the positively charged alum to a system composed of negatively charged cellulose fibre and rosin size causes the lowering of the interfacial potential between the two negatively charged materials, to such a degree that the precipitation of the rosin on the fibre by the floccing action of the alum takes place.

They pointed out that sizing efficiency is highest at the iso electric zone, where the sum of the Zeta Potential as distinguished from the Nernst Potential is zero. It may be explained that an excess addition of alum disturbs the electrical double layer by contracting the Stern fixed layer surrounding the negatively charge fibre. With an excess of positive ions in the system because of the presence of H^+ resulting out from the dissociation of alum, the double layer totally collapse, by the attainment of positive charged by fibre, resulting in the mutual repellency of rosin size and fibre which is otherwise would be minimum at the nearest iso electric point. Reversion of this phenomenon takes place with insufficient alum addition. Kanamaru and Tsuchina³⁴ confirmed this fact.

Collins, Davis, Rowland and Hotz^{6,37} carried out further study in this field, pertaining the effect of iso electric point, attributed that the most important questions concerning the alumina is the exact location of iso electric point and the effect of adsorbed ions and the pH on the magnitude and sign of the electrophoretic charge, by making a comparative study between $AlCl_3$ and $Al_2(SO_4)_3$ for precipitation of rosin. The instantaneous values of electrophoretic velocity of floccs of $AlCl_3$ were much nearer to equilibrium values than that of alum. They established the fact that the zones of precipitation and peprization at various pH, centres more around the alumina rosin complex than of aluminium resinate, thereby giving the necessary stress to the school of thoughts of Ekwai²³. With the precipitation of prosize of sodium rosinate with alum and aluminium chloride they have pointed out that the change of the electrostatic charge from $\pm$ ve to $-ve$ value changes around 5.5 to 6.0 pH at which the maximum sizing is obtained.

By studying the relationship between the physico chemical properties of the size precipitate and sizing in a sodium aluminate—sodium abietate-perchloric acid system, Guide⁸ showed that the electro kinetic potentials of the size precipitate particles and cellulose fibres are the most important forces governing the deposition of precipitate on the fibre. Considering the system as two solid surfaces possessing definite amount of Zeta Potential, the two variables are to be considered as a part of a single system in which the fibre surface is the charged colloidal particle. The electro kinetic potential between this surface and the rosin size are opposite in nature and are attracted to each other. If on the other hand the sign of potential is same, and the absolute value of the potentials are high enough to overcome thermal and mechanical agitation, the precipitate is repelled away from the fibre surface and little deposition occurs.

Though his findings were in confirmation with the proposed theory of Ostwald and Lorens,^{25,26} he has contradicted with them in one respect. The negative charge on the cellulose fibres is very high. The addition of excess alum in presence of rosin size rather modifies the negative charge of size complex than that of cellulose fibres. Thode et al,^{39,41} are in agreement with this point proposed by Guide⁸, but they pointed out that the alum charge used by other workers may be much low as compared with the amount used by Ostwald and Lorenz^{25,26}. The change on the fibre definitely reverse back at a higher alum concentration. They carried out experiments both in the presence and absence of rosin (Fig.)⁴⁰. But one thing is much clear. The addition of excess of alum in presence of size chemical rathera modifies the charge on the size complex than that of cellulose fibres.

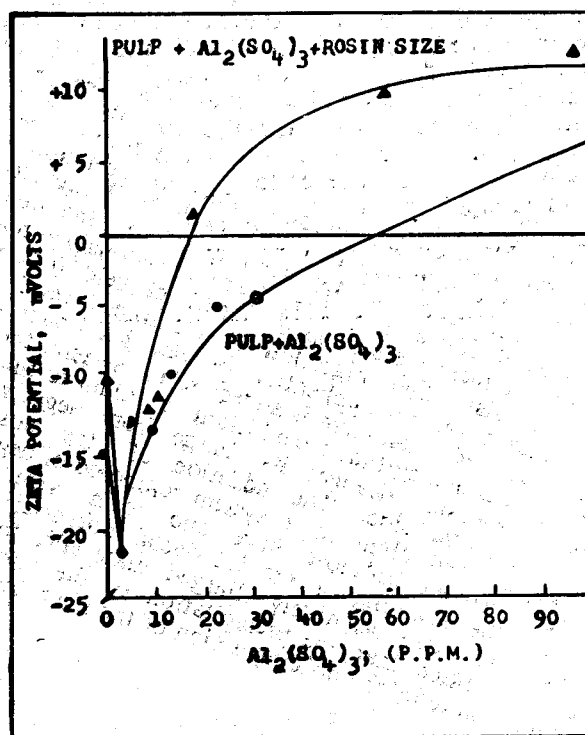


FIG. 3⁴⁶ EFFECT OF ALUM ON ZETA POTENTIAL OF PULP FIBRES

Referring the equation(4) and (5) the Zeta Potential is calculated by varying the concentrations of the electrolytes in the system. The specific charge on fibres can also be calculated from the above said equations (viz. from equation⁵). But the addition of polyvalent ions to the sizing environment and its consequences are still a doubtful vogue. Thode et al^{30,40} tried to explain this by the application of equations 4 and 5 and concluded that certain foreign

materials added to the sized pulp system changes the electro kinetic potential of the cellulosic fibre appreciably as well as the rosin size. The addition of citrates and ferrocyanides to the system definitely shows a variation in the electrophoretic mobility and therefore on the net potential charge, because of preferential adsorption of the foreign cation of the rosin-alum complex takes place and the electrophoretic potential reverts back from positive to negative value (fig. 4 & 5) thereby adversely affecting

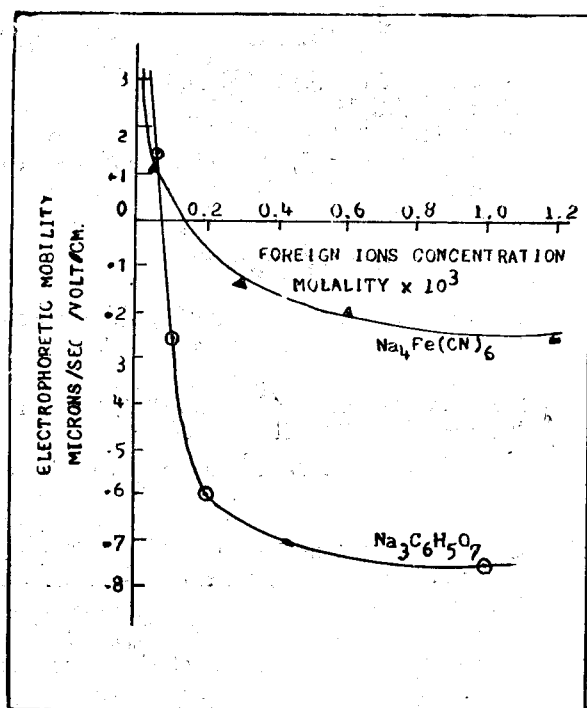


Fig. 4³⁹ EFFECT OF FOREIGN IONS ON THE ELECTROPHORETIC MOBILITY OF ROSIN-ALUMINIUMCHLORIDE COMPLEX

the sizing efficiency. Thode et al^{41,42} further studied the effect of metal ions especially that of Mg^{2+} on the sizing precipitate and the sizing environment. The electrophoretic mobility of the system decreases by the addition of polyvalent cations like Ca^{2+} , Mg^{2+} and this is more predominant if the system is subjected to agitation resulting in "Slack" size. Thode et al^{40,41} in addition to this, studied the effect of free rosin on the system and based on the estimated electrophoretic mobility, showed that the addition of free rosin produce & insignificant effect on mobility, thereby pointing out that the qualitative role of free rosin and the claims raised by other workers are still dubious

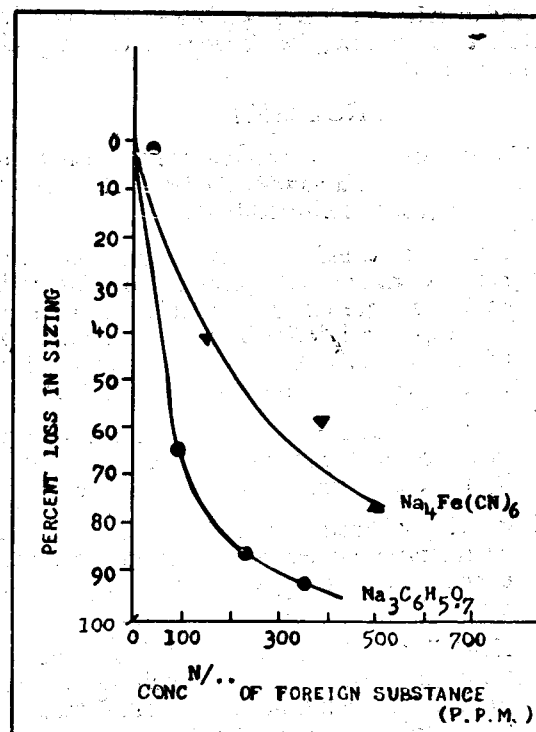


FIG. 5³⁹ EFFECT OF FOREIGN IONS ON THE SIZING EFFICIENCY

Strazdines⁴³ contradicted the views of Thode et al^{40,41} and shown that metal ions at an acidic pH rather results a better sizing. He pointed out that some sizing could be obtained with any metal ion that forms an insoluble hydrozide which show a strong interaction with the monomolecular rosin films. Sulphate and citrate ions, due to their coordination with alum, were found to exert strong contraction effects on rosin films, which results in a reduction of the electrophoretic charge of the underlying aluminium lattice, their presence in a little more quantity certainly improves the sizing. But he argued that the reason for the poor sizing in presence of large excess of these ions may be due to the Columbic attraction between the highly negative rosin size and trivalent aluminium species which forms an excessive agglomeration thereby collapsing the whole electrical double layer. The advantage of using alum as a precipitor of rosin size over the others are its ability to form readily positively charged polymeric complexes in a tolerable acidic system, and formation of a compact positive layer with rosin size containing the sulphate ion, that moderates or buffers the positive charge activity on the complexes formed in the system and thus providing conditions for uniform unimpaired

rosin deposition on cellulose fibres, making it less accessible to chelation with organic acids especially to lactic acid.

CONCLUSION

The following conclusions have been made, based on the critical appraisal of the Zeta Potential concept in sizing of cellulosic fibre.

- (i) Sizing mechanism involves three successive steps consisting of (a) formation of potentially low free surface energy precipitates, (b) adhesion of the precipitates on to the cellulose fibres (c) transformation of the wet size precipitate fibre surface to a stable low free surface.
- (ii) Electro Kinetic Potential (or Zeta Potential) of the rosin size precipitate is a major contributing factor in influencing sizing efficiency.
- (iii) Positively charged, aluminium ions act as an "electrostatic adhesive" between negatively charged cellulose and negatively charged rosin.
- (iv) Zeta Potential measured in terms of electrophoretic mobility of size precipitate, appears to bear a close relationship to sizing efficiency, atleast within the usual sizing pH range.
- (v) Alum furnishes hexahydrated tripositive ionic complex of aluminium which binds cellulose and anionic size precipitate together through its coordinate valencies. During sizing reactions hexahydrated tripositive ionic complex is formed which is capable of binding strongly the anionic groups (particular hydroxyl groups) through its co-ordinate valencies. Thus, aluminium can coordinately bind both cellulose and anionic sizing materials together.
- (vi) An increase in the electro kinetic potential of the size precipitate is accompanied by an increase in size precipitate retention.

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NOMENCLATURE

- A = Area of the cross section of the pad, cm^2 .
 C = Bulk conductivity (of the bulk liquid), mhos.
 D = Dielectric constant, c.g.s
 E = Potential difference across the pad, causing electro osmosis, volts.
 F = Volume rate of electro-osmotic flow (zero external hydraulic resistance) cm^3/sec .

- I = Streaming current (at zero external resistance), amps.
 K = Permeability coefficient.
 L = Thickness of pad, cm.
 M = Density of the pad, gm/cm^3 .
 P = Pressure differential across the pad causing stream kg/cm^2 .
 Q = Volume rate of streaming flow, cm^3/sec .
 R = Resistance of the pad, ohms.
 V = Streaming potential (at infinite electrical resistance), volts.

GREEKS

- η = Viscosity of the liquid, poises.
 δ = Zeta Potential.
 σ = Pore factor.
 β = Hydrodynamic effective specific volume of the swollen fibre, cm^3/gm .
 σ = Specific surface.

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