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ZETA POTENTIAL AS AN ANALYTICAL TOOL FOR GRAFT COPOLYMERS AND FOR POLYMER SURFACES

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ABSTRACT

Polymers with electrically charged groups exhibit a zeta potential when in contact with electrolyte solutions in water. This can be measured with solid polymers as fibers, foils, or granulates. The method of streaming potential/streaming current allows the determination of the carboxyl content of cellulose grafted with poly(acrylic acid). Since zeta-potential measurements concern the surface of the sample, the method yields information on the type of grafting; i.e., whether it takes place mainly on the surface or throughout the bulk. By measuring the pH dependence of the zeta potential it is possible to obtain the p*K* value of the charged groups. The significance of zeta potential as an analytical tool is emphasized.

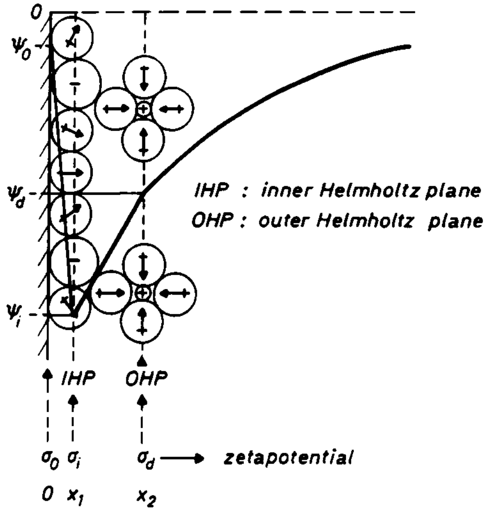


FIG. 1. The electrical double layer.

1. INTRODUCTION

Electrically charged particles in water form an electrical double layer. They are surrounded by a charge cloud which is sheared off during relative motion. In this way, electrokinetic phenomena are generated. They yield the charge of the particle in a given surrounding as a zeta potential (ZP). Figure 1 shows this well-known structural principle. Out of the various known electrokinetic measuring methods, we have mainly used streaming potential/streaming current. Figure 2 shows a typical measuring cell which contains the sample in solid form. When an aqueous medium, mostly an electrolyte solution, is pumped through, an electrical voltage can be measured at the electrodes, which allows the calculation of the zeta potential ζ. Recent developments have made it possible to determine the zeta potential of the surface of flat structures in a so-called flat cell (Fig. 3).

In this paper the zeta potential will be used only as an analytical tool; numerous other applications have been amply discussed in the literature [1]. The surface charges of the solid phase are produced mainly in two ways: either as bound dissociable groups or as charge carriers which are adsorbed from the environment. In the first case the dissociation can be

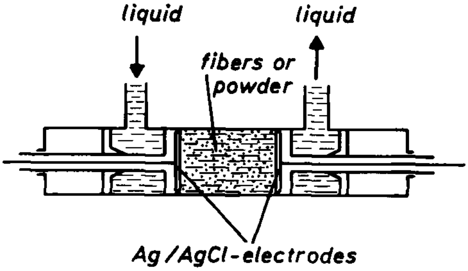


FIG. 2. Measuring cell for streaming potential.

characterized by measuring the zeta potential as a function of pH [1]; in the second, adsorption isotherms can be obtained from the zeta potential [2] and adsorption energies can be calculated [1]. In this connection we point out a rather new development, the so-called electroviscous fluids. They undergo a significant enhancement of viscosity in an electric field, which is explained by a distortion and overlapping of the charge clouds. Such electroviscous fluids find many practical applications.

2. GRAFT COPOLYMERS

Graft copolymers are molecular compound materials in which a backbone polymer carries other laterally bonded polymers. Of the different types of graft copolymers [3], the most important are listed in Fig. 4:

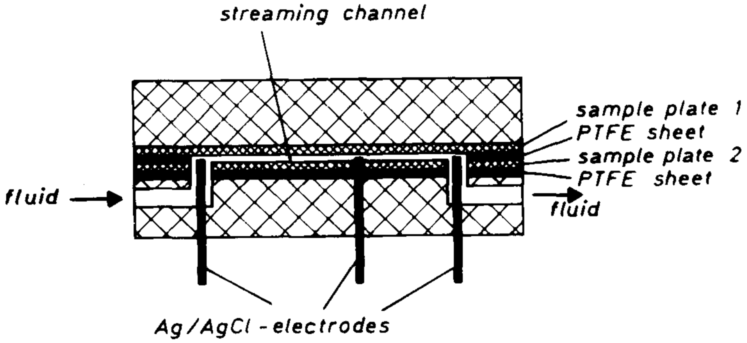
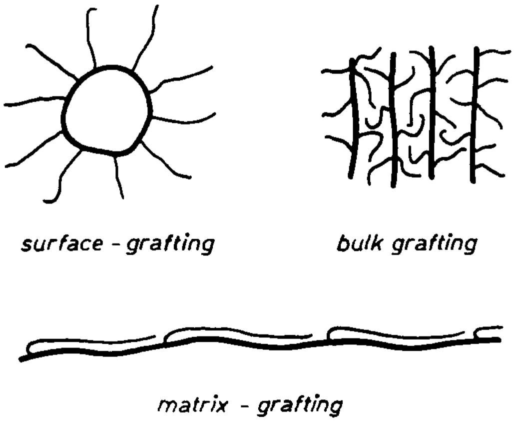


FIG. 3. The flat measuring cell.


surface - grafting

bulk grafting

matrix - grafting

FIG. 4. Grafting methods: surface grafting, bulk grafting, matrix grafting.

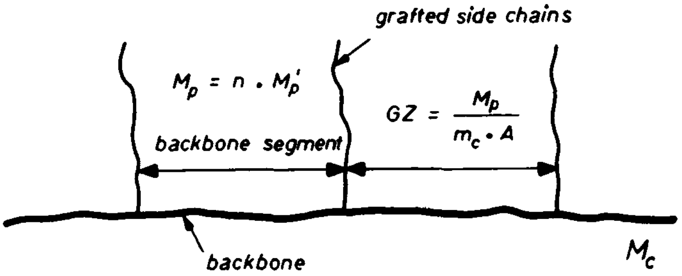
surface grafts, bulk grafts, and matrix grafts. Figure 5 schematically shows the structure of a graft copolymer together with the relevant characteristic parameters. For a description of these compound materials, we have introduced the characterization system shown in Fig. 6. For our discussion we need only the grafting yield A, which gives the brutto composition in % grafted polymer. As an interesting example of a special product, we mention our proposal for a superflocculant (Fig. 7). The charged grafted branches will form bonds, while the solid core secures fast sedimentation.

3. ZETA POTENTIAL MEASUREMENTS WITH GRAFTED FIBERS

We have grafted charged polymers onto cellulose as the backbone. The charged groups will produce a significant zeta potential. Figure 8 shows a regenerated cellulose fiber grafted with polyacrylic acid dispersed in water. The zeta potential is plotted against the grafting yield A. We find a linear correlation:

$$\zeta = a + bA$$

Further experiments showed that the zeta potential also correlates with other parameters derived from ζ. A typical example is the water retention



$M_t = M_p \bullet M_c$ $\qquad$ $n = \frac{M_c}{m_c \bullet GZ}$

M_t : Total molecular weight,
M_p : Total molecular weight of grafted material,
M_p' : Molecular weight of one grafted chain

M_c : Total molecular weight of backbone,
n : Number of grafted chains per backbone molecule

FIG. 5. A graft copolymer, shown schematically.

Grafting conversion	$U = \frac{G-C+H}{M}$	*Efficiency of polymerization*
Grafting ratio	$V = \frac{G-C}{G-C+H} = \frac{W}{U}$	*Ratio grafting to homopolymerization*
Grafting efficiency	$W = \frac{G-C}{M}$	*Efficiency of grafting*
Graft content	$A' = \frac{G-C}{G} = 1 - \frac{C}{G} = \frac{A}{1+A}$	*Fraction of backbone grafted*
Grafting yield	$A = \frac{G-C}{C} = \frac{G}{C} - 1 = \frac{A'}{1-A'} = \frac{U.M}{C}$	*Brutto - composition*
Chain ratio	$R_p = \frac{(G-C).m_c}{m_p . C}$	*Ratio length of side chains to length of backbone segment*
Glucose number	$GZ = \frac{M_p}{m_c . A}$	*Length of backbone segment*

Abbreviations :

G : *weight of graft product*
C : *weight of cellulose*
H : *weight of homopolymer*
M : *weight of monomer*

m_c : *molecular weight of the basic unit of backbone*
m_p : *molecular weight of the basic unit of the synthetic polymer*
M_p : *molecular weight of grafted synthetic polymer*

FIG. 6. Characterization of graft copolymers.

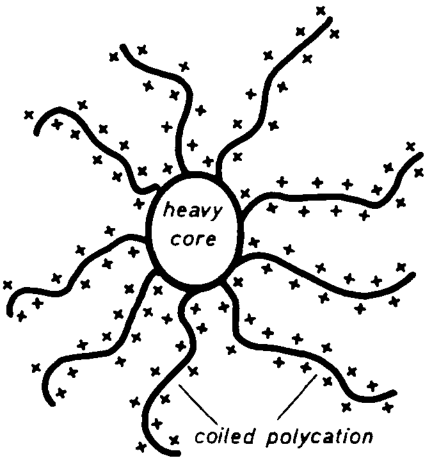


FIG. 7. A superflocculant.

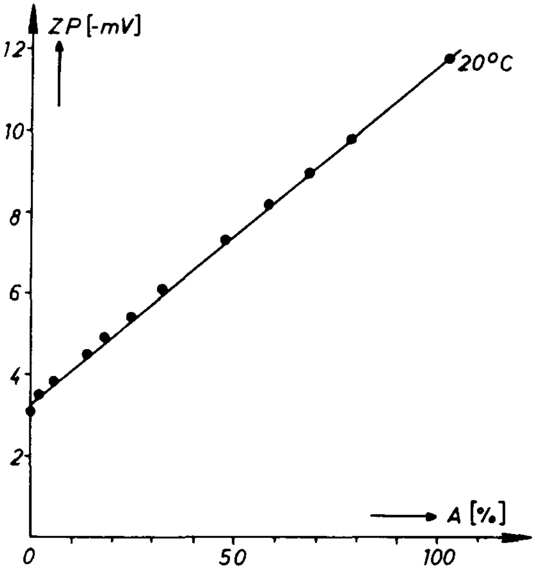


FIG. 8. Zeta potential as a function of grafting yield *A* for cellulose/PAS fibers.

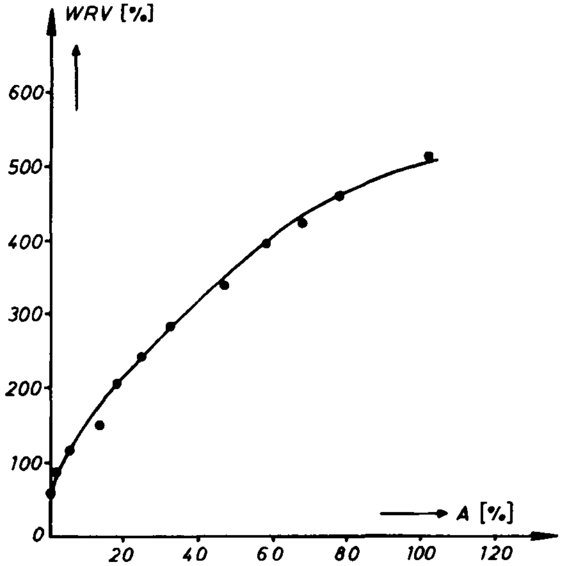


FIG. 9. Water retention (WRV) as a function of grafting yield A for cellulose/PAS fibers.

(WRV), practically a measure of the degree of swelling. As Fig. 9 shows, there is a clear correlation. The WRV increases with A, as expected. Of course there must also be a correlation between ZP and WRV (Fig. 10). For high grafting yield, saturation comes into play, the linearity is lost, and the WRV value increases less steeply.

The zeta potential measures only the surface charges. Therefore, differentiation between surface-grafted or bulk-grafted copolymers should be possible. Table 1 shows that this is actually so. A fiber grafted in a microwave stove is apparently a pure surface graft. Its negative zeta potential (−7 mV, A = 46%) is significantly higher than that of a sample grafted on a water bath (−3.6 mV, A = 44%) despite nearly the same grafting yield. In the latter case we obviously deal with bulk grafting. Staining with Victoria Blue corroborated this result (Fig. 11). On the left-hand side the fiber is stained over the whole cross section (ζ = −3.6). On the right-hand side, only the rim is dyed (ζ = −7.0 mV), which indicates surface grafting. In further experiments we have grafted other monomers. Two examples with methacrylic acid and acrylamide are shown in Fig. 12.

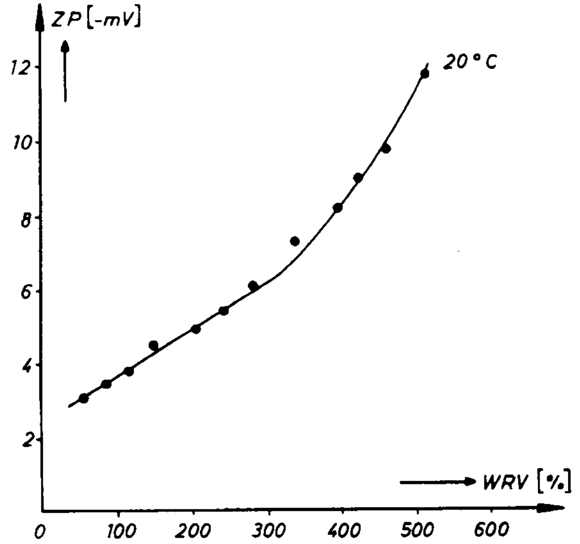


FIG. 10. Zeta potential as a function of water retention (WRV) for cellulose/PAS fibers.

Enhanced electrolyte concentration in the dispersion medium water will bring about a screening of the charges and thus a reduction of the ZP. This is demonstrated in Fig. 13, which shows the zeta potential for different NaCl contents, and in Fig. 14 the zeta potential as a function of both grafting yield *A* and NaCl content is shown. With increasing NaCl content the zeta potential is increasingly lowered with a higher grafting yield *A*. In accordance with the DLVO theory, this is caused by a compression of the double layer (bulk stress). Increasing the NaCl

TABLE 1. Zeta Potential and Method of Grafting

Method	*A*	ζ, mV	Type of grafting
Microwave stove	46	−7.0	Surface
Water bath	44	−3.8	Bulk

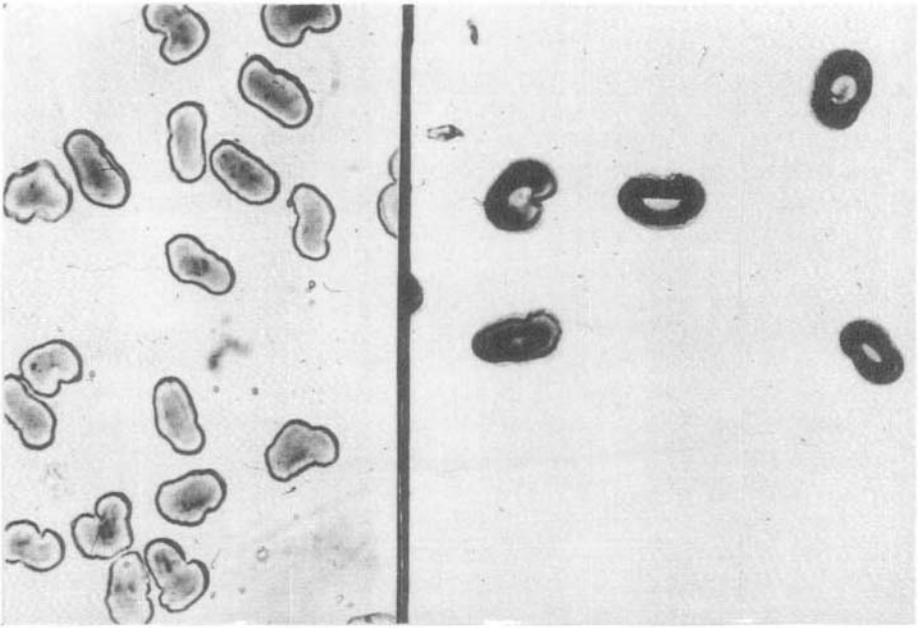


FIG. 11. Victoria Blue staining of fibers obtained by different grafting methods. Left: Stained over total cross section, $\zeta = -3.6$ mV. Right: Only rim stained, $\zeta = -7$ mV.

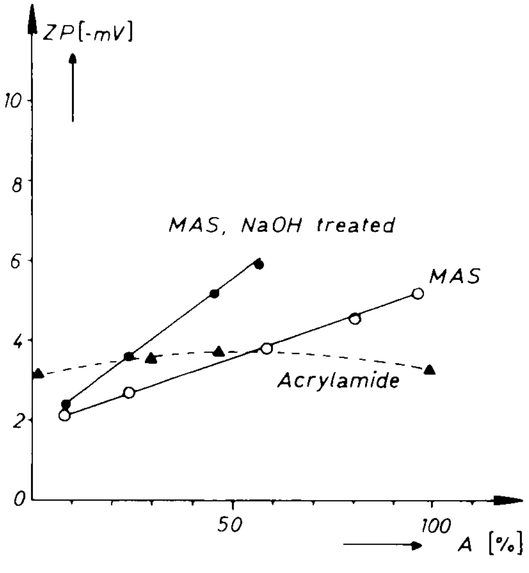


FIG. 12. Zeta potential as a function of grafting yield A for different monomers (MAS: methacrylic acid, acrylamide).

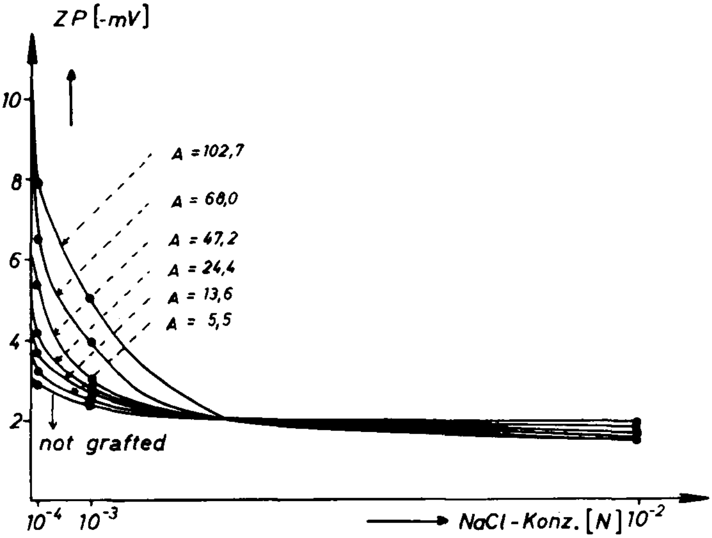


FIG. 13. Zeta potential as a function of NaCl content for different A values.

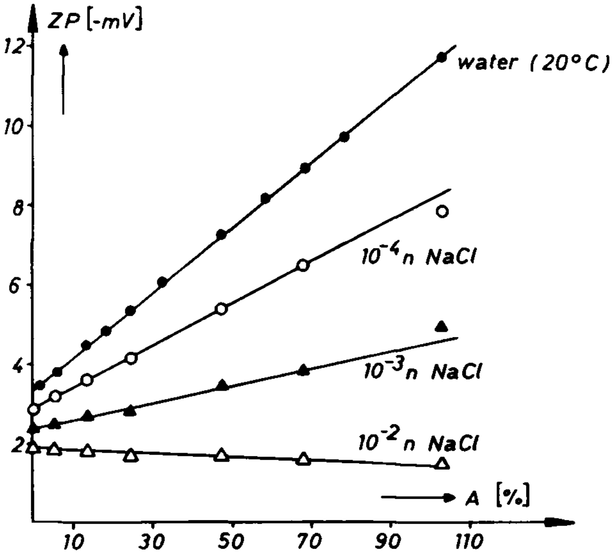


FIG. 14. Zeta potential as a function of grafting yield A for different NaCl contents.

content reduces the influence of grafting yield on the zeta potential. The NaCl content also changes the pH value because it influences the dissociation. Figure 15 shows the pH value as a function of both grafting yield and NaCl content. On the basis of this and many other measurements, we have come to the conclusion that we should not measure single values of the zeta potential but rather a zeta potential curve, namely the function ζ(pH). It provides much more information than single measurements and should therefore be used for the characterization of a sample.

The temperature has little influence on ZP, as shown in Fig. 16. Apparently this is due to an inner compensation. The Brownian motion will increase with increasing temperature, thus making the double layer smaller, but this effect is small. Viscosity and conductance will approxi-

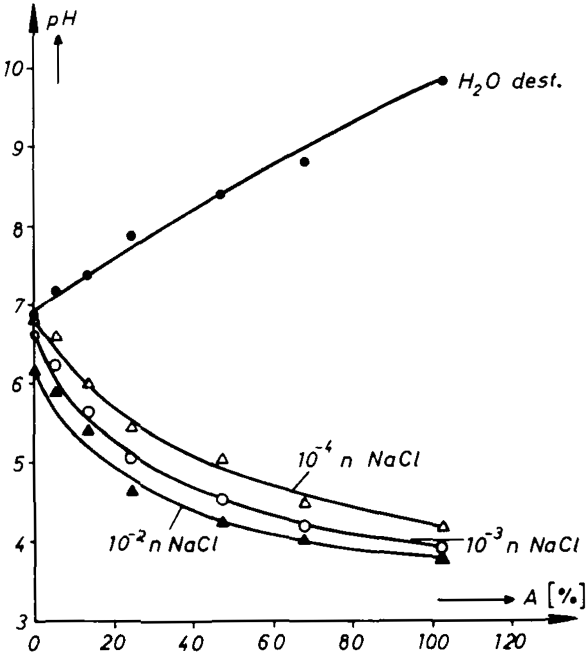


FIG. 15. pH value as a function of grafting yield A for different NaCl contents.

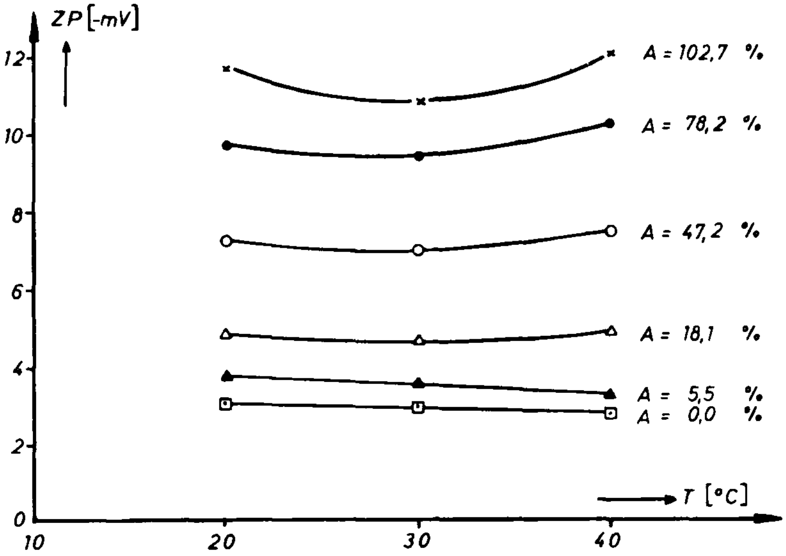


FIG. 16. Zeta potential as a function of temperature for cellulose/PAS fibers.

mately compensate each other. The dielectric constant ϵ will decrease, so that the product $\zeta \cdot \epsilon$ remains constant.

The dispersibility of grafted fibers will depend on the amount of hydrophilic acidic groups and thus on the zeta potential. Therefore it must increase with the grafting yield. Figure 17 shows the water dispersions of such grafted cellulose fibers with $A = 0$, 32, and 102%. Note that the dispersibility clearly increases with increasing grafting yield. As expected, it will decrease again after the addition of a neutral salt due to a decrease of the zeta potential.

We have investigated the zeta potential of several synthetic fibers. Table 2 gives a few examples. The finish had been removed by extraction. In the streaming potential method, the porosity of the fiber bundle (plug) in the cell will influence the electrokinetic effects. In order to obtain absolute figures, extrapolation to zero density of the fiber bundle (infinitely diluted plug) should be performed (method of Goring-Mason). Figure 18 shows such a plot for polyamide fibers reacted with 1-fluoro-2,4-dinitrobenzene. The zeta potential is obtained from the ordinate at $c = 0$. In Fig. 19 the zeta potential of dinitrophenylated poly-

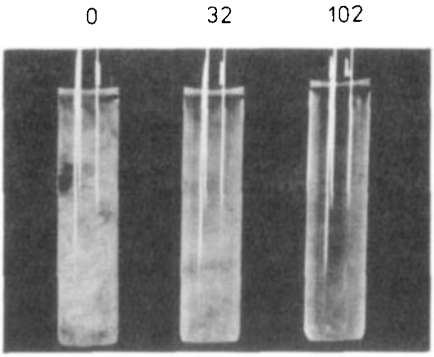


FIG. 17. Dispersibility of cellulose/PAS fibers as a function of zeta potential and grafting yield values shown.

amide fibers is shown [4]. Here, too, we find a clear effect: the negative ZP is lowered with an increasing amount of dinitrophenyl groups (DNP), so the DNP content can be calculated from the measured ZP.

Finally, in Fig. 20 we show the ZP of the natural fibers wool and silk, and in Fig. 21 of a bleached spruce sulfite pulp. Here the ZP depends strongly on the purification method.

TABLE 2. Zeta Potential of Various Fibers

	Zeta potential, mV	
Sample	Not extracted	7 h methanol extracted
Cellulose acetate, no finish	−14.5	—
Cellulose acetate, with finish	−21.0	−11.8
Polyamide (Perlon), unstretched	−22.2	−17.8
Polyamide (Perlon), stretched	−22.1	−12.4
Polyester (Trevira), no finish	−42.3	−24.6
Polypropylene (Daiwabo PP), no finish	−14.6	−22.4
Polyacrylonitrile (Dralon), no finish	−25.6	−35.1
Polyurethane (Dorlastan), no finish	−7.8	−3.0
Glass fiber, no finish	−64.4	−84.7

4. EVALUATION OF ZETA POTENTIAL CURVES

Since the zeta potential as a function of the pH value reflects the degree of dissociation, it can be used to obtain the dissociation constant and the pK value. The isoelectric point (IEP) can be directly read off this curve at $\zeta = 0$. Such investigations are particularly interesting for plane surfaces and can be performed in a flat cell. For complete dissociation we obtain a plateau of the zeta potential (Fig. 22). The theory of Börner [5] allows the calculation of the pK value from this plateau; Eq. (1) shows the formula.

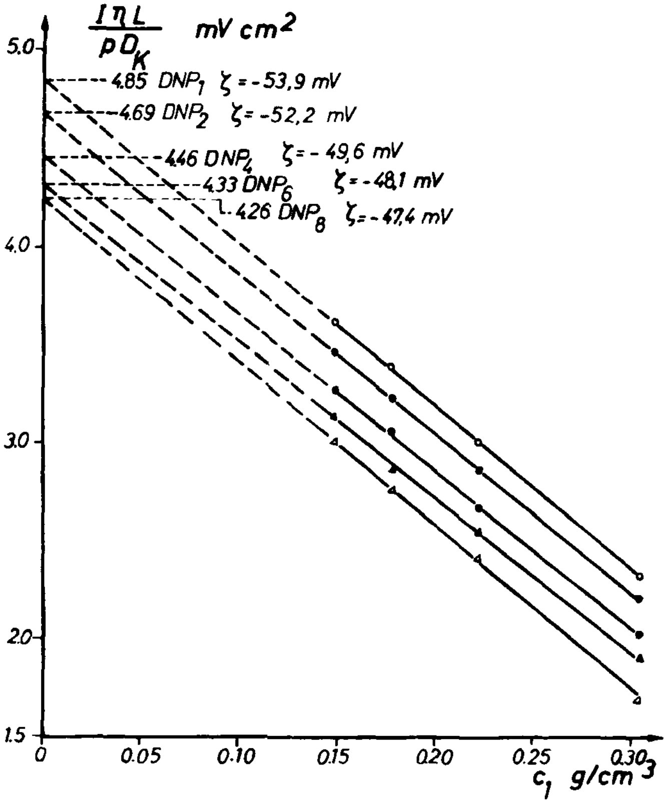


FIG. 18. Zeta potential of dinitrophenylated polyamide fibers (Goring-Mason plot).

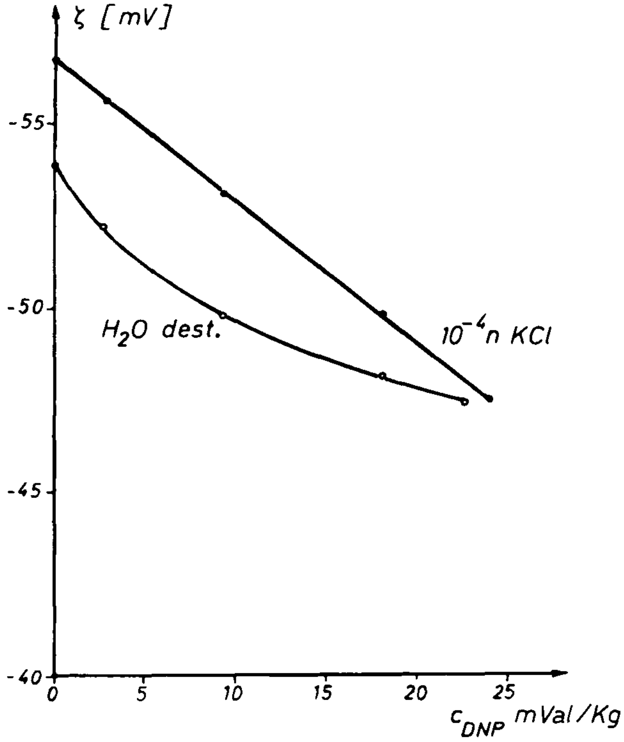


FIG. 19. Zeta potential of dinitrophenylated polyamide fibers as a function of DNP content.

$$\mathrm{p}K = \mathrm{pH} + 0.434\left\{\frac{F\zeta}{RT} + \ln\left[\frac{\sinh\left(-\frac{F\zeta_{\mathrm{Pl}}}{2RT}\right)}{\sinh\left(-\frac{F\zeta}{2RT}\right)} - 1\right]\right\} \tag{1}$$

If we apply these considerations to acidic groups occurring in foils of cellulose and other polymers, it is possible to characterize the surface charge and to estimate by means of the pK value its acidic strength. We have investigated various foils. Figure 23 shows a filter material with pK = 5, corresponding to a weak acid. Figure 24 shows polypropylene with pK = 4.9. After treatment of this foil by corona discharge, the pK is reduced to 4.5 (Fig. 25). Obviously, additional COOH groups have

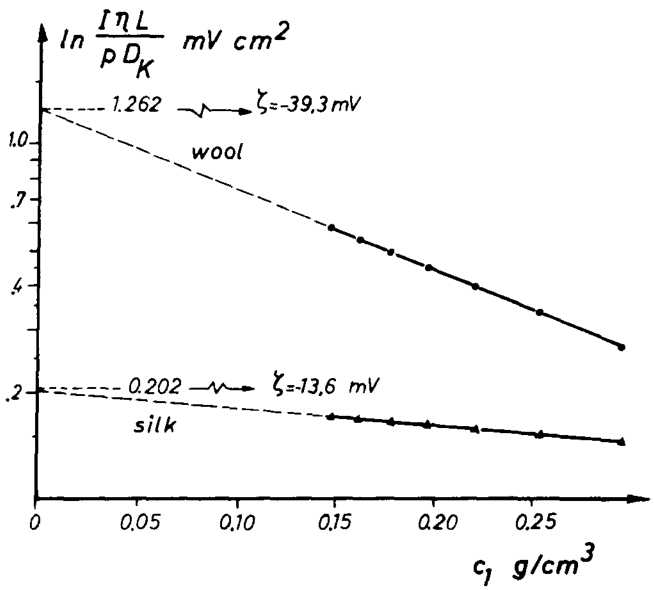


FIG. 20. Zeta potential of wool and silk (Goring-Mason plot).

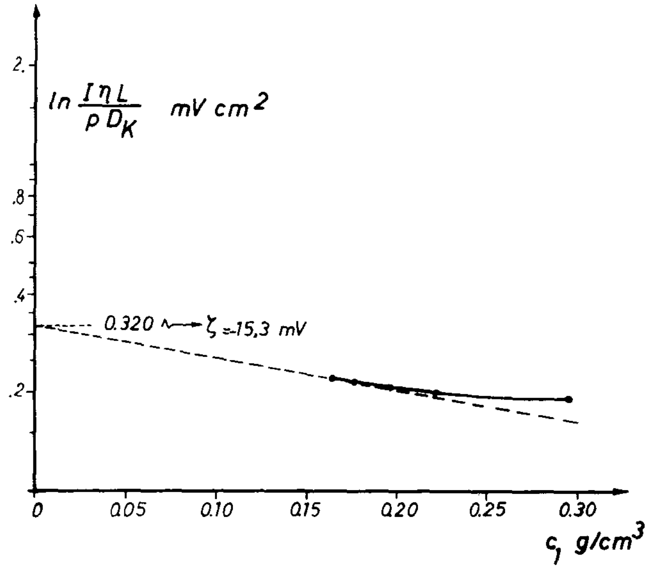


FIG. 21. Zeta potential of pulp (bleached spruce sulfite) (Goring-Mason plot).

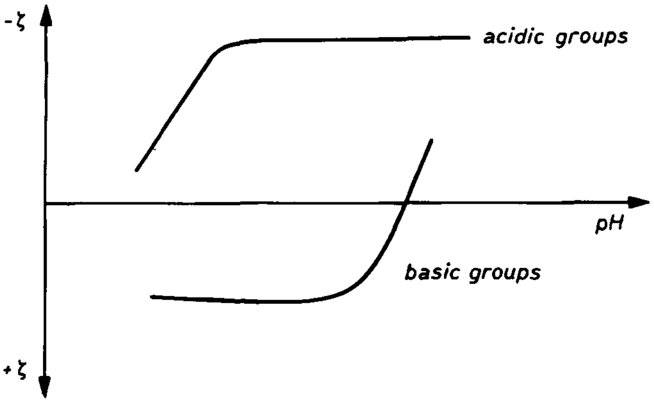


FIG. 22. ζ–(pH) curves for acidic and alkaline groups, shown schematically.

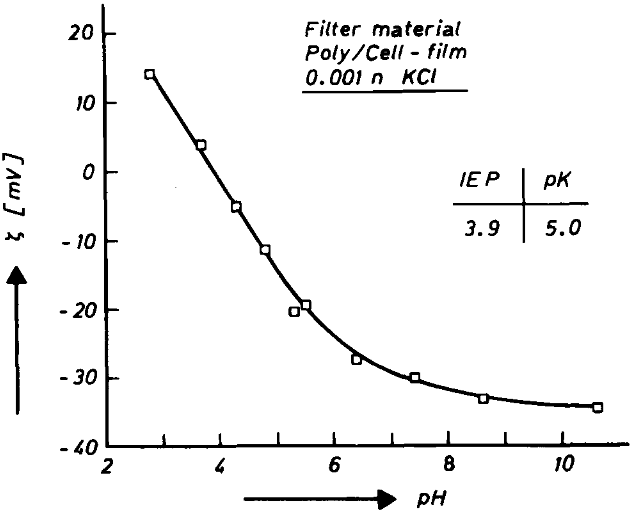


FIG. 23. ζ–(pH) curve of filter material.

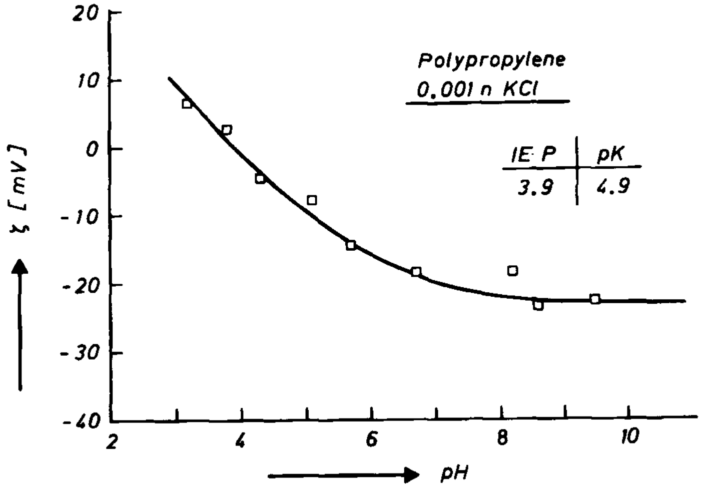


FIG. 24. ζ—(pH) curve of polypropylene.

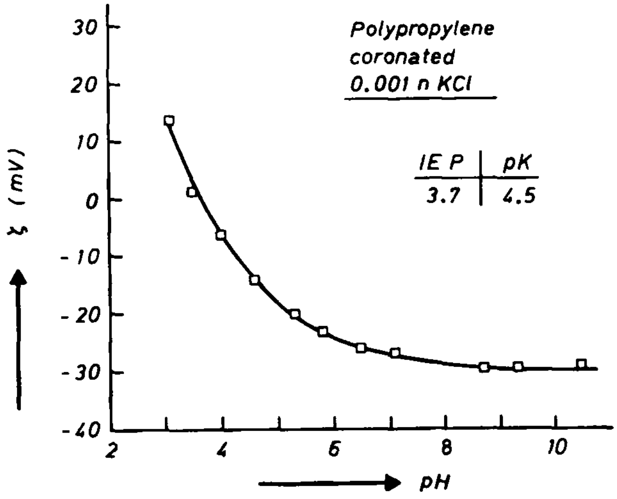


FIG. 25. ζ—(pH) curve of coronated polypropylene.

been formed, and they enhance the acidic strength. The IEP has also changed; it shows a slight rise. The results of several such evaluations are compiled in Table 3.

5. CONCLUSION

In conclusion, we may state that the zeta potential is well suited for analytical investigations with various materials, in our case fibers and foils. However, we must not forget that the zeta potential we measured is an average (mean zeta potential). The individual zeta potentials can only be obtained with pure substances. Finally, we may add that the flat cell is also suited for polyelectrolyte titrations, which directly give us the number of charges.

For biopolymers, the electric conditions of the surface, and thus the zeta potential, will be particularly important. However, here probably both the average charge and the charge pattern of the surface will be of interest. A determination of this charge pattern would be highly desirable, but so far no suitable method of measurement exists. In biochemistry, mainly gel electrophoresis is used. Recently, carrier-free electrophoresis has become possible by means of Doppler laser light scattering. It allows for the absolute determination of the zeta potential. Therefore, in this field, too, zeta potential measurements represent a valuable analytical tool.

TABLE 3. pK Values and IEP of Various Polymeric Materials

	IEP	p*K*
Polymer/cellulose 50/50	3.9	5.0
PS	4.9	5.2
PP-K coronated	3.7	4.5
PP-K 35 μm	3.9	4.9
PP-K 100 μm	–	4.9
PVA	3.7	4.5

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