Electrokinetic Properties of Polyformaldehyde Fibers

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Synopsis

Electrokinetic properties, namely, zeta potential (ζ), surface charge density (σ), and surface conductivity (K_s) of polyformaldehyde fibers [poly(oxymethylene) fibers] have been studied in the presence of direct dyes, with or without surfactants and an electrolyte. The anionic dyes increased the negative zeta potential of fibers. The increase in ζ was found to be a function of concentration and basicity of the dye in the streaming solution. Thus, the tetrabasic dye gave higher value of negative ζ than the equivalent concentration of the dibasic dye. The cationic surfactant brought about a decrease in negative ζ, giving a point of inflection, while the anionic surfactant increased it. The nonionic surfactant brought about a certain reduction in negative ζ, but failed to give a point of inflection. In the presence of a direct dye, the cationic surfactant brought about considerable reduction in negative ζ to give a point of inflection. The presence of an electrolyte in the streaming dye solution progressively lowered the negative ζ. In general, σ increased with the increase in the concentration of either a dye or an electrolyte in the presence of a given concentration of the dye in the streaming solution. Results on K_s indicated that the surface conductivity of the fibers is a function of concentration of dye, surfactant, and electrolyte. It was, however, observed to be independent of the nature of the surfactant. Although both the dibasic and tetrabasic direct dyes brought about an increase in K_s, the extent of increase was dependent upon the basicity of the molecules.

INTRODUCTION

Although poly(oxymethylene) was considered to be a promising raw material for the production of fibers, attempts in that direction could not give expected results for a long time. Investigations in the laboratories of E.I. du Pont de Nemours & Company carried out over a period of 18 years led to the discovery of thermally stable high molecular weight fiber-forming polyformaldehyde polymers.[1] Subsequently, a series of five papers from the same laboratories described various physical and chemical characteristics of the poly(oxymethylene) polymers.[2-6] These studies revealed that the chemical composition of the base polymer (unacetylated polyformaldehyde) was shown to be $(CH_2O)_n$ by analysis of the thermal degradation products. The endgroups of the base polymer were found to be hydroxyl and methoxy groups as revealed by infrared. The study of end group analysis by osmometry and the high degree of crystallinity of poly(oxymethylene) resins indicated that the polymer structure was linear rather than branched.[1]

In the early 1960's, Egorov and his colleagues[7-9] announced their results on the synthesis of poly(oxymethylene) fibers which they called polyformaldehyde fibers. The exact chemical structure of these fibers, however, was not disclosed. The chain breaking or degradation of poly(oxymethylene) and grafted po-

ly(oxymethylene) was studied by a number of workers.[10–13] Kimura, Yamauchi, and Sakurada[14] studied the grafting of poly(oxymethylene) filaments with styrene by using the irradiation technique. They found that the presence of methanol or dimethylformamide accelerated grafting. Lokhande et al.[15] reported the effect of electrolytes on the zeta potential of polyformaldehyde fibers. Yudin and his colleagues[16,17] carried out the modification of polyformaldehyde fibers with 5–10% triethylene glycol and obtained a twofold increase in dyeability with disperse dyes.

Recently, some work has been reported on the dyeability and mechanism of dyeing of polyformaldehyde fibers with disperse dyes and the effect of stretching on the internal structure of these fibers.[18,19] It has also been reported[20] that dyeing of polyformaldehyde fibers with reactive dyes could be carried out with some pretreatment of the substrate or by a suitable modification of the dyeing process. According to Akira and co-workers,[21] the dyeability of the poly(oxymethylene) fibers could be improved by catalytic sulfonation with gaseous sulfur trioxide diluted with nitrogen and air. Although studies on various aspects of polyformaldehyde fibers have been reported in the literature, information on electrokinetic studies of polyformaldehyde fibers is limited. The aim of the present paper is to report changes in zeta potential, surface charge density, and surface conductivity of these fibers in the presence of direct dyes, surfactants, and an electrolyte, and their mixtures in the streaming solution.

EXPERIMENTAL

Materials

Polyformaldehyde Fibers. This fiber was kindly supplied by the Kiev Technological Institute of Light Industries, Kiev (U.S.S.R.). It was prepared from the copolymer of formaldehyde and m-dioxane and was spun in the form of filaments on a laboratory spinning unit at the Institute. Important characteristics of the polyformaldehyde fibers were as follows: (a) Characteristic viscosity in dimethylformamide (DMF) determined at 150°C = 0.5 poise; (b) ratio of the comonomers:formaldehyde and dioxolan = 98:2; (c) draw ratio = 8; (d) molecular weight (number-average) = 50,000.

Chemicals, Dyes, and Surfactants. All reagents used in the present investigation were of "chemically pure" grade. The direct dyes, viz., Congo Red (C.I. Direct Red 28) and Chlorazol Sky Blue FF (C.I. Direct Blue 1), were purified before use. Commercial surfactants—anionic (Indopon T PDR), cationic (Taffulon), and nonionic (Noigen CS)—were used in this study.

Purification of Direct Dyes

The direct dyes were purified according to the method recommended by Robinson and Mills.[22] Commercial dyes were dissolved in hot water to obtain fairly concentrated solutions and the hot solution was filtered. To the filtrate was added sodium acetate in order to precipitate the direct dye from hot, aqueous solution. The precipitate was filtered, redissolved in hot water, and reprecipitated by adding a fresh lot of sodium acetate. This procedure was repeated two to three times. The only electrolyte (impurity) in the dye was sodium acetate.
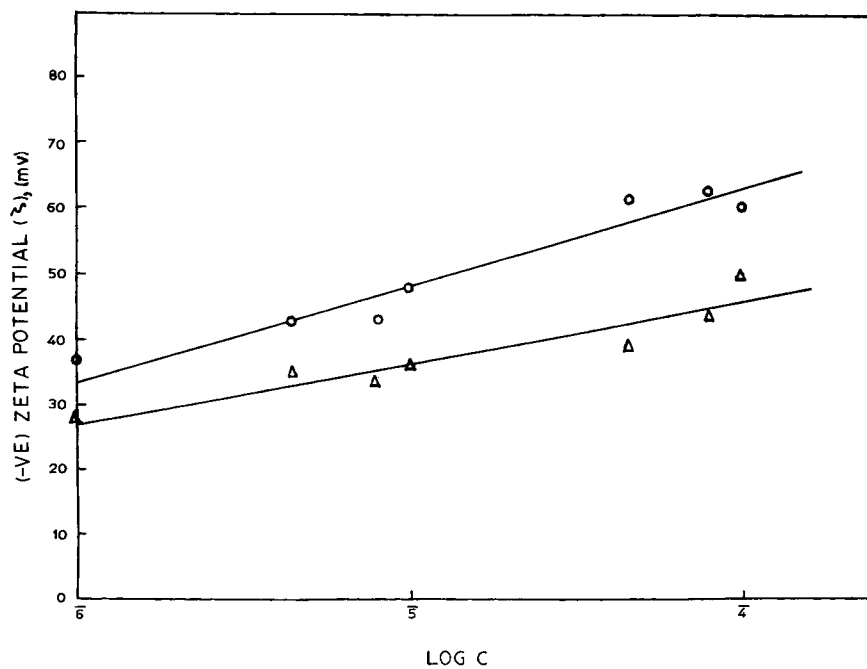
Fig. 1. Zeta potential of polyformaldehyde fibers vs. log of direct dye concentration: (△) Congo Red; (○) Chlorazol Sky Blue FF.
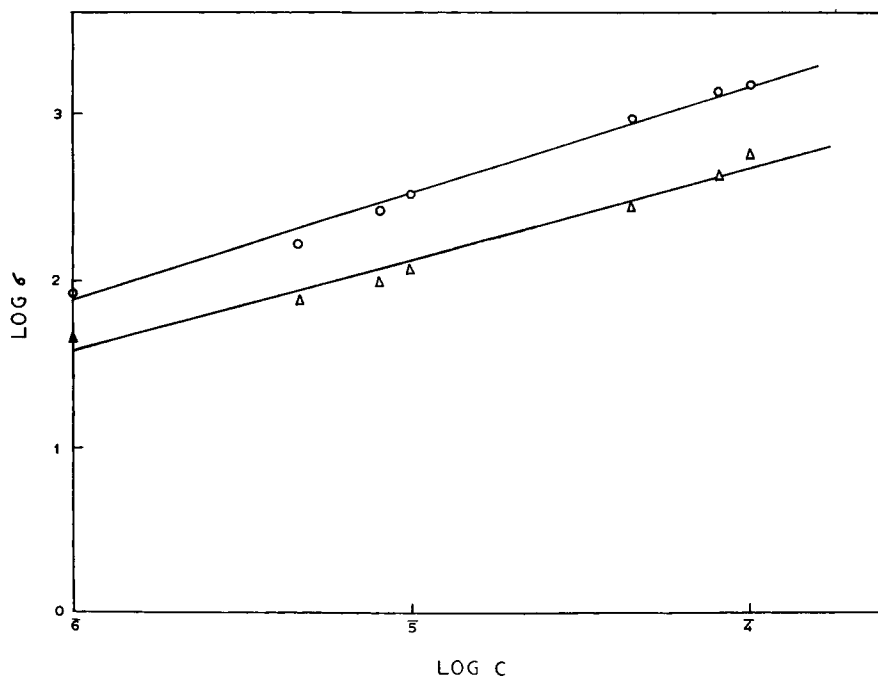

Fig. 2. Log of surface charge density of polyformaldehyde fibers vs. log of direct dye concentration: (△) Congo Red; (○) Chlorazol Sky Blue FF.
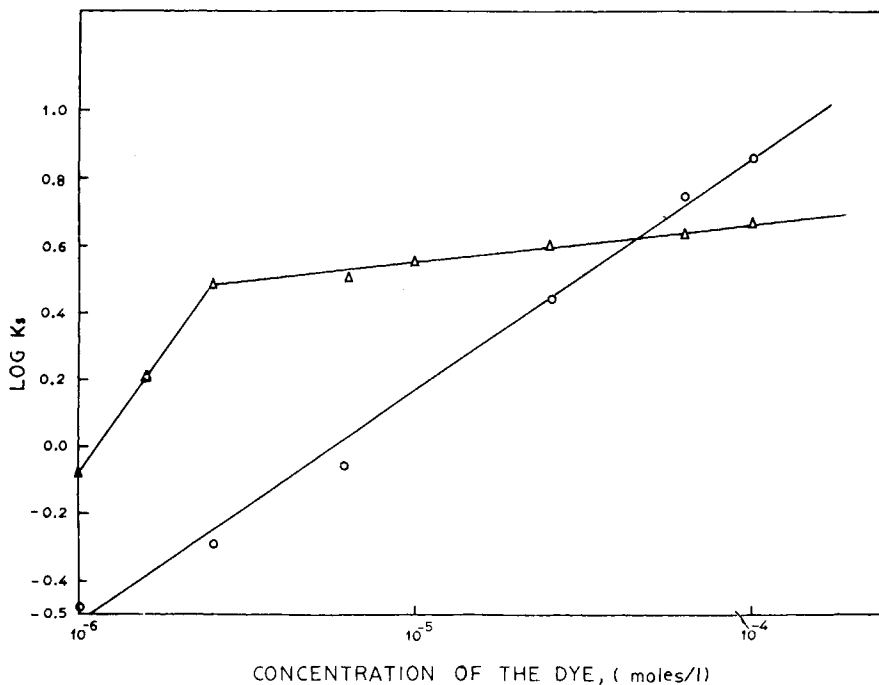
Fig. 3. Log of surface conductivity of polyformaldehyde fibers vs. concentration of direct dye: ($\triangle$) Congo Red; (O) Chlorazol Sky Blue FF.
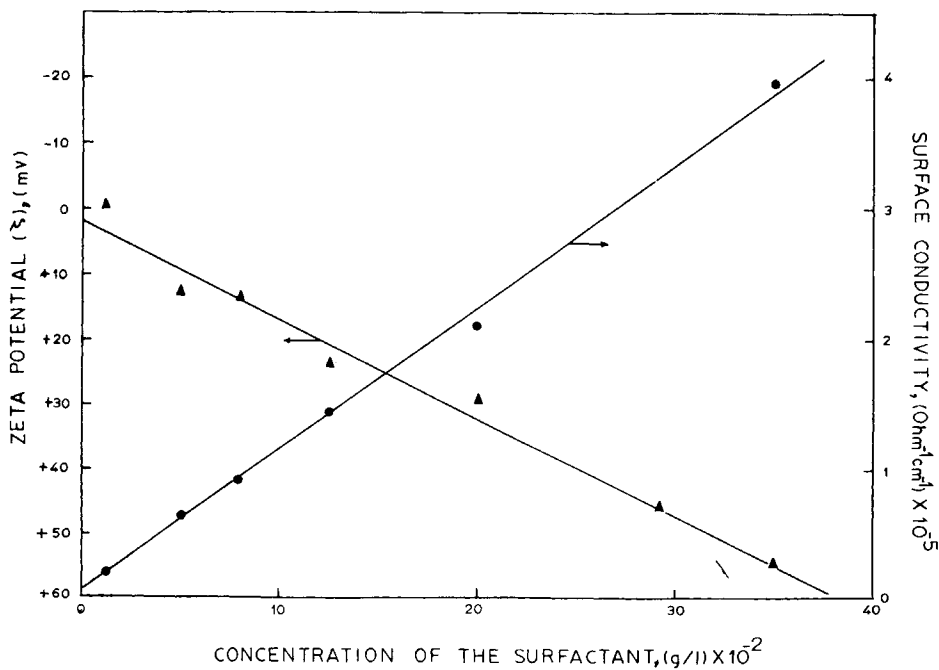

Fig. 4. Zeta potential and surface conductivity of polyformaldehyde fibers vs. concentration of cationic surfactant (Taffulon): ($\blacktriangle$) zeta potential; ($\bullet$) surface conductivity.
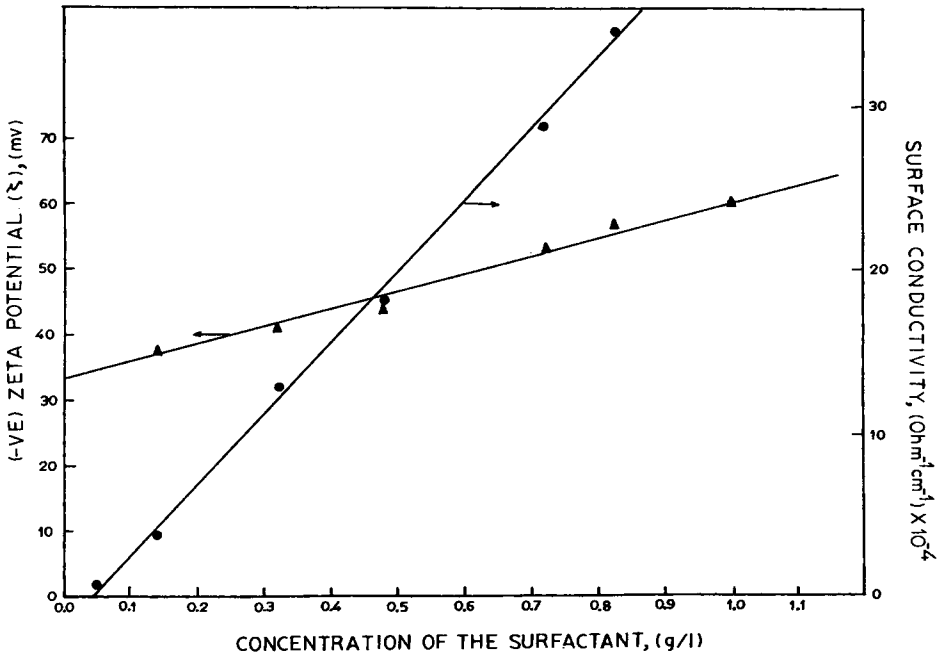
Fig. 5. Zeta potential and surface conductivity of polyformaldehyde fibers vs. concentration of anionic surfactant (Indopon T PDR): (▲) zeta potential; (●) surface conductivity.
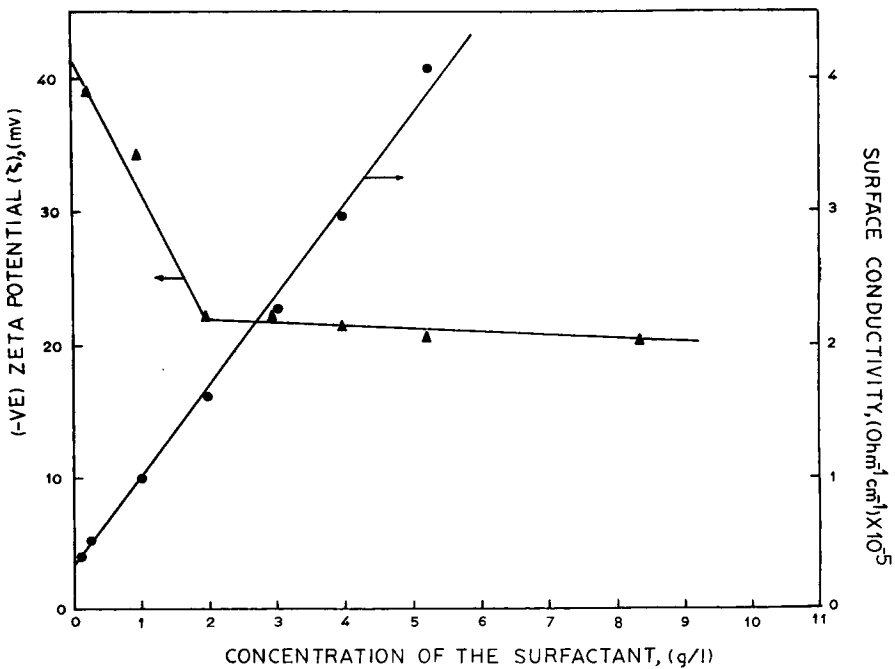

Fig. 6. Zeta potential and surface conductivity of polyformaldehyde fibers vs. concentration of nonionic surfactant (Noigen CS): (▲) zeta potential; (●) surface conductivity.
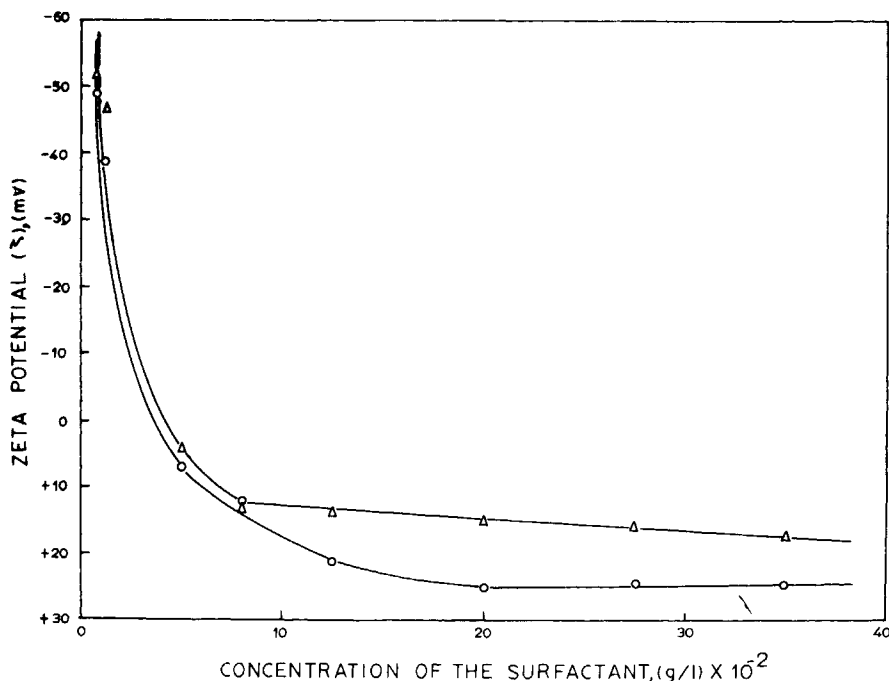
Fig. 7. Zeta potential of polyformaldehyde fibers vs. concentration of cationic surfactant (Taffulon) in the presence of direct dye (1×10^{-5} mole/l.): (△) Congo Red; (○) Chlorazol Sky Blue FF.

The dye was then extracted for 16 hr with absolute alcohol in a Soxhlet extraction unit to remove sodium acetate from the dye. The dye was then crystallized twice from 50% ethanol–water mixture. All the dyes were preserved in a desiccator over P_2O_5 at about 30°C.

Streaming Potential Method

Streaming potential of the polyformaldehyde fibrous plug was measured by the method described by Kale, Lokhande, Rao, and Rao.[23]

Knowing the streaming potential and the resistance of the plug, the zeta potential was calculated by using the Helmholtz-Smoluchowskii equation:

$$\zeta = 6.75 \times 10^7 \times \frac{4\pi\eta\chi E_s}{DP}$$

where ζ = zeta potential (mV); η = viscosity of solution (poises); χ = specific conductivity of the solution in the plug of fibers (ohm^{-1} cm^{-1}); D = dielectric constant of solution; P = pressure in the cell (cm Hg); and E_s = streaming potential (mV).

Surface charge density was calculated from the equation

$$\sigma = \left(\frac{2NKTD}{\pi}\right)^{1/2} \sinh \frac{e\zeta}{2KT}$$

where σ = surface charge density (e.s.u./cm^2); N = number of cations or anions per ml in bulk of solution; K = Boltzmann constant (1.37×10^{-16} ergs/degree);
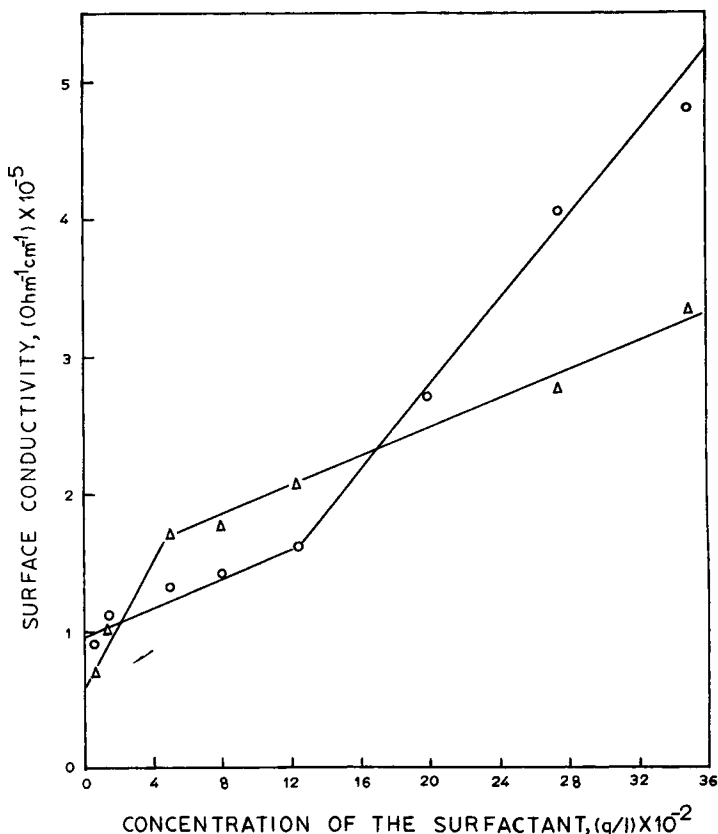
Fig. 8. Surface conductivity of polyformaldehyde fibers vs. concentration of cationic surfactant (Taffulon) in the presence of direct dye (1×10^{-5} mole/l.): ($\triangle$) Congo Red; ($\bigcirc$) Chlorazol Sky Blue FF.

T = absolute temperature (°K); D = dielectric constant of solution; e = electronic charge; and ζ = zeta potential (mV).

Specific conductivity of streaming solution (K_a) and of the plug (K_c) was also determined. Surface conductivity of the fibers (K_s) was obtained by taking the difference between K_c and K_a.

RESULTS AND DISCUSSION

Effect of change in concentration of direct dyes on the electrokinetic properties of polyformaldehyde fibers has been given in Figures 1–3. In general, there seems to be an increasing trend in absolute values of all the three electrokinetic properties, viz., zeta potential (ζ), surface charge density (σ), and surface conductivity (K_s), as a result of progressive increase in the dye concentration in the streaming solution.

From Figure 1, it can be seen that a linear relationship exists between ζ and log C in the case of both dyes studied. The increase in the negative value of zeta potential of polyformaldehyde fiber in the presence of a direct dye may be attributed to the presence of dye anions on the surface of the fiber in an adsorbed state, possibly through the nonspecific forces between the dye and the hydro-
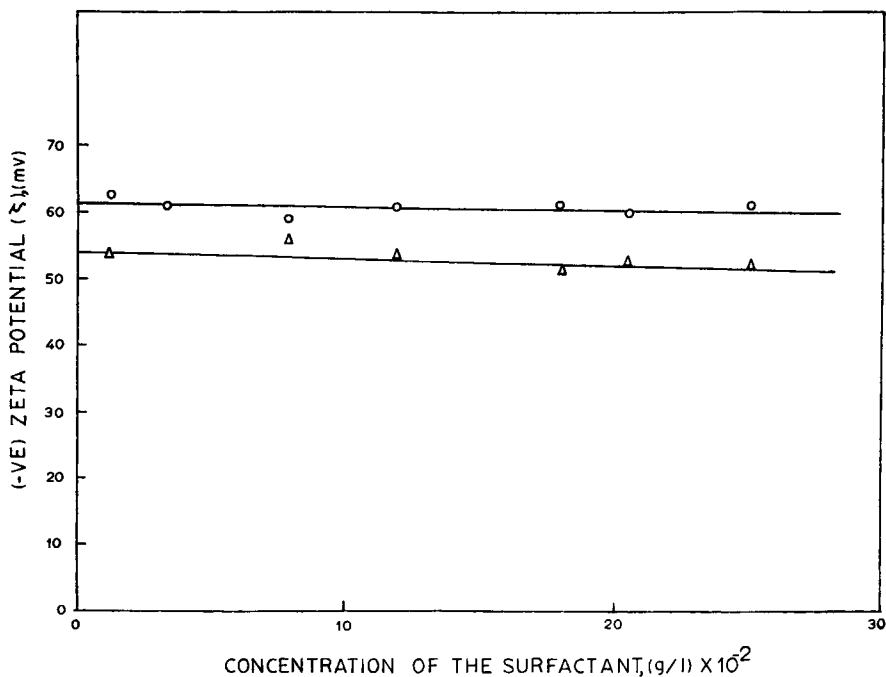
Fig. 9. Zeta potential of polyformaldehyde fibers vs. concentration of anionic surfactant (Indopon T PDR) in the presence of direct dye (1×10^{-5} mole/l.): ($\triangle$) Congo Red; ($\bigcirc$) Chlorazol Sky Blue FF.

phobic surface of the fiber. The negative values of the zeta potential are higher in the case of Chlorazol Sky Blue FF (C.I. Direct Blue 1) than in the case of Congo Red (C.I. Direct Red 28) for equivalent concentration of dye in the streaming solution. This may be due to the higher basicity of the dye anion of Chlorazol Sky Blue FF (C.I. Direct Blue 1) (tetrabasic) as compared to that of Congo Red (C.I. Direct Red 28) (dibasic).

From Figure 2, it can be seen that a linear relationship exists between the log–log plot of the surface charge density (σ) and the concentration (C) of direct dyes in the streaming solution. As in the case of zeta potential, surface charge density also increased with an increase in the dye concentration. This may be attributed to the dye anions present on the surface of the fiber. In this context, it is significant that at a given concentration of the dye in the streaming solution, the surface charge density values for the tetrabasic Chlorazol Sky Blue FF are higher compared to those for the dibasic Congo Red.

Figure 3 gives results on surface conductivity of fibers in the presence of direct dyes in the streaming solution. The surface conductivity (K_s) increases with increase in the concentration of dye in the streaming solution. A linear relationship exists between log K_s versus C. The trend, however, seems to be different for different dyes studied, and while in the case of Chlorazol Sky Blue FF there is a progressive increase in the surface conductivity, such a trend could not be observed in case of Congo Red. After an initial fast increase, there was a break in the conductivity curve, after which the rate of increase slowed down to a considerable extent. Such a break in the curve may be due to the saturation of
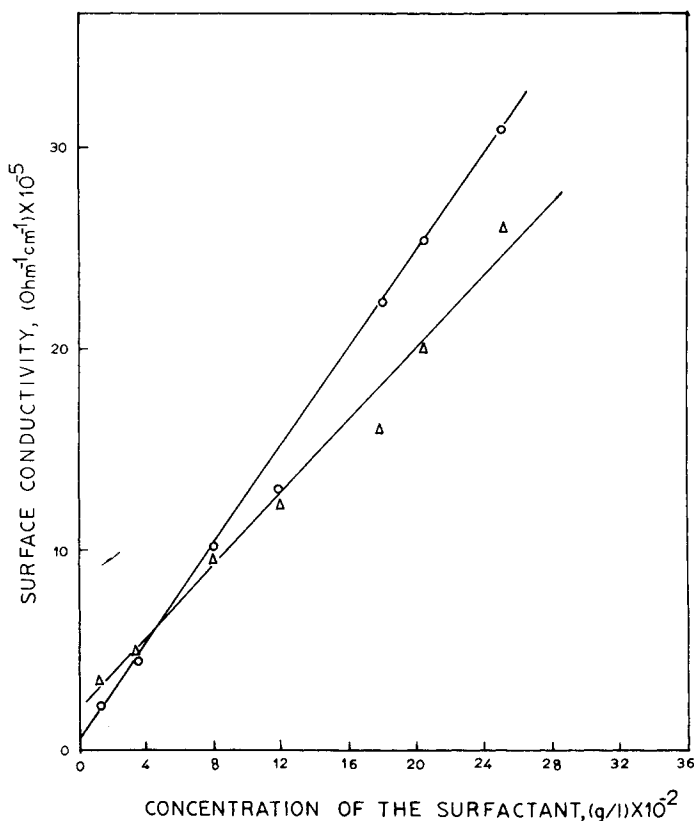
Fig. 10. Surface conductivity of polyformaldehyde fibers vs. concentration of anionic surfactant (Indopon T PDR) in the presence of direct dye (1 × 10⁻⁵ mol/l.): (△) Congo Red; (○) Chlorazol Sky Blue FF.

the available effective surface area of the fiber by the dye ions. Beyond this stage, even though the concentration of dye in the streaming solution is progressively increased, there may not be an equivalent increase in the surface conductivity of the fibers.

Such a situation did not arise in the case of Chlorazol Sky Blue FF, possibly because of its tetrabasic nature, and surface saturation might not have been easily possible as a result of greater repulsion between fiber and the dye anion bearing four negatively charged sites. This contention seems to be logical as the absolute values of the surface conductivity of the fibers for a given concentration of a dye in the streaming solution are lower in case of the tetrabasic Chlorazol Sky Blue FF than those in the case of dibasic Congo Red. This situation is reversed at higher concentrations of dyes in the streaming solution, possibly because the fiber surface is still receptive as far as Chlorazol Sky Blue FF is concerned, while it is completely saturated with the dye ions in the case of Congo Red.

Figures 4–6 give results on the effect of change in concentration of cationic, anionic, and nonionic surfactants in the streaming solution on zeta potential and surface conductivity of polyformaldehyde fibers. A linear relationship exists between each of the two properties and the concentration of surfactant in the streaming solution.
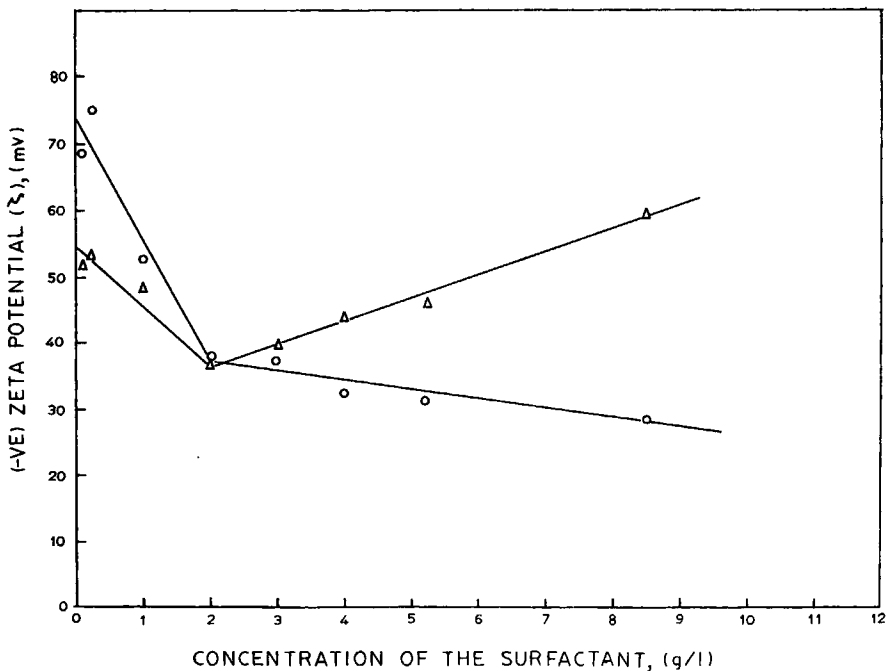
Fig. 11. Zeta potential of polyformaldehyde fibers vs. concentration of nonionic surfactant (Noigen CS) in the presence of direct dye (1×10^{-5} mole/l.): ($\triangle$) Congo Red; ($\bigcirc$) Chlorazol Sky Blue FF.

The zeta potential of the fibers progressively decreases with an increase in the concentration of cationic surfactant as a result of neutralization of the negative charge by the cations of the surfactant. Surface conductivity, on the other hand, continues to increase as a result of increased amount of cations adsorbed on the surface of the fibers. In order to maintain the electrical neutrality, anions of the surfactant molecules are also pulled in the close vicinity of the fiber surface, thereby bringing about compression in the electrical double layer and increasing the surface conductivity of the fibers (Fig. 4).

From Figure 5, it can be seen that the reverse is true with respect to changes in zeta potential with change in the concentration of anionic surfactants in the streaming solution. Thus, the negative zeta potential increases with increased amount of anions present in the immovable part of the electrical double layer at the fiber–liquid interface. Surface conductivity, however, increases in the same manner as in the case of cationic surfactant.

With respect to the nonionic surfactant (Fig. 6), there is a break in the zeta potential–surfactant concentration plot giving initially a rapid decrease in the negative value of zeta potential followed by much slower decrease with further increase in the concentration of the nonionic surfactant in the streaming solution. The nonionic surfactant molecules sit on the surface of the fiber as a result of nonspecific interaction forces between the fiber and the surfactant molecules, thereby reducing the negatively charged surface area of the fiber. This gives rise to the very fast reduction in the negative zeta potential up to a stage when the fiber surface is saturated with the neutral molecules of the surfactant. This gives rise to a sharp break in the curve, beyond which stage the decrease in the negative value of zeta potential is reduced to a considerable extent as a result
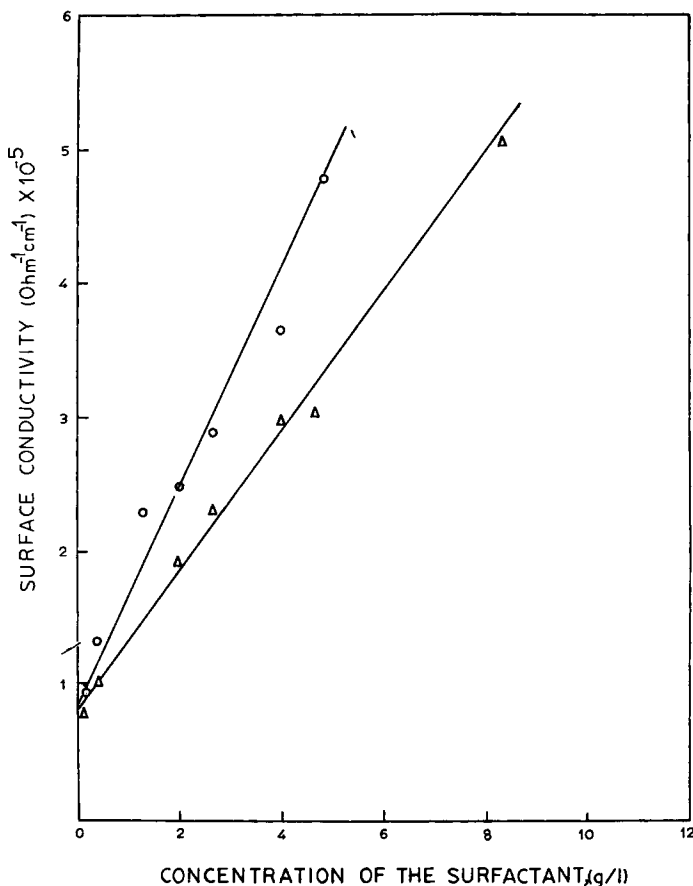
Fig. 12. Surface conductivity of polyformaldehyde fibers vs. concentration of nonionic surfactant (Noigen CS) in the presence of direct dye (1×10^{-5} mole/l.): ($\triangle$) Congo Red; ($\bigcirc$) Chlorazol Sky Blue FF.

of an equilibrium established between the surfactant molecules on the surface of the fibers and those which are in the movable part of the electrical double layer. Although such equilibrium is shifted toward further neutralization of the negative charge, such a shift is marginal with further increase in the concentration of the nonionic surfactant, since the forces of attraction between the fiber and the nonionic surfactant molecules are very labile; and perhaps only because of this, a point of inflection could not be obtained in this case unlike the cationic surfactant. Surface conductivity, however, increased linearly with the increase in concentration of the nonionic surfactant as a result of increased activity of the surface dye to the presence of nonionic surfactant molecules in its close vicinity.

Direct dye concentration in the streaming solution was kept constant at 1×10^{-5} mole/l., while the surfactant concentrations were varied from 0 to 0.4 g/l. In general, the results indicate the influence of the type of surfactant use in the direct dye solution on zeta potential and the surface conductivity of polyformaldehyde fibers. Thus, from Figures 7, 9, and 11 it can be seen that the zeta potential decreases rapidly, describing a hyperbolic curve, and giving a point of inflection in the case of cationic surfactant (Taffulon). The anionic surfactant
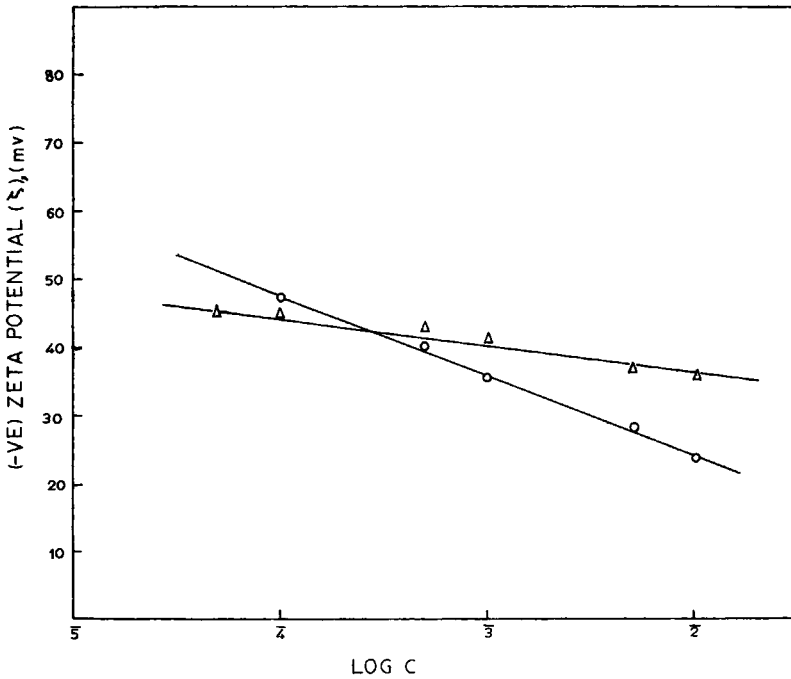
Fig. 13. Zeta potential of polyformaldehyde fibers vs. log of electrolyte concentration in the presence of direct dye (1 × 10⁻⁵ mole/l.): (△) Congo Red; (O) Chlorazol Sky Blue FF.
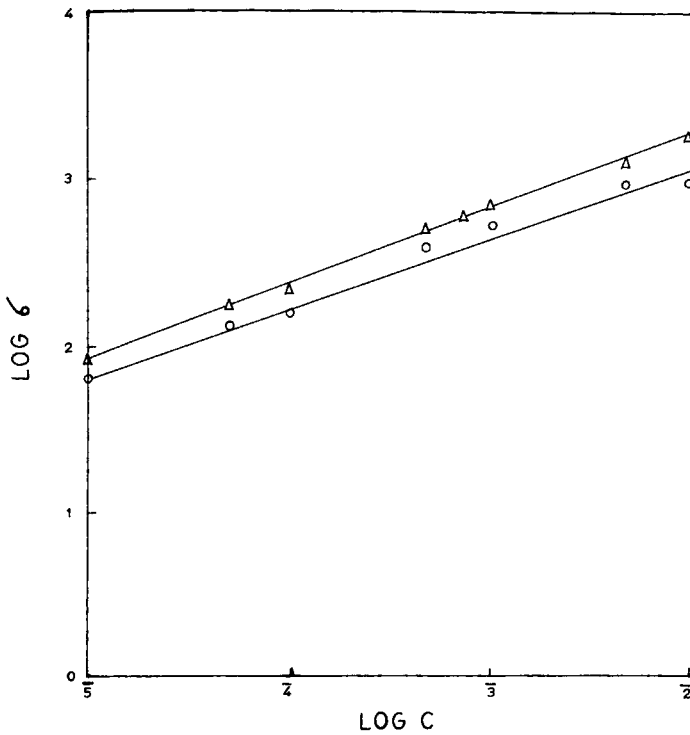

Fig. 14. Log of surface charge density of polyformaldehyde fibers vs. log of electrolyte concentration in the presence of direct dye (1 × 10⁻⁵ mole/l.): (△) Congo Red; (O) Chlorazol Sky Blue FF.
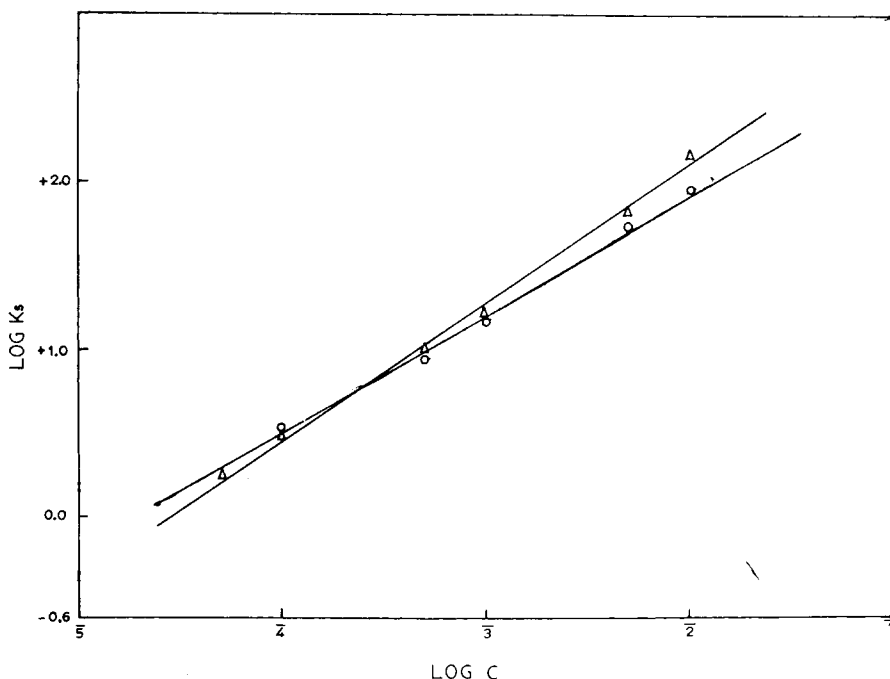
Fig. 15. Log of surface conductivity vs. log of electrolyte concentration in the presence of direct dye (1×10^{-5} mole/l.): ($\triangle$) Congo Red; ($\bigcirc$) Chlorazol Sky Blue FF.

(Indopon T PDR), on the contrary, seems to have a negligible influence on zeta potential (Fig. 9). Nonionic surfactant (Noigen CS) exhibits an entirely different behavior; and although no point of inflection was obtained either for Congo Red or Chlorazol Sky Blue FF, the zeta potential decreased rapidly in the initial stages for both the dyes studied up to a certain concentration of the nonionic surfactant. Beyond this concentration, the rate of decrease was considerably slowed down for Chlorazol Sky Blue FF, while it increased in the case of Congo Red. The difference in behavior of the two direct dyes may be attributed to their differences in basicity. Surface conductivity, however, increased linearly with the progressive increase in the concentration of the anionic, cationic and nonionic surfactants studied (Figs. 8, 10, and 12).

Figures 13–15 give the effect of electrolyte concentration on the electrokinetic properties of polyformaldehyde fibers in the presence of direct dyes. Figure 13 illustrates the results on zeta potential. The addition of electrolyte brings about partial neutralization of the negative charge on the surface of the polyformaldehyde fibers and hence the drop in the negative value of zeta potential.[15] If an anionic dye such as a direct dye molecule is present in such a system, an increased amount of dye may be adsorbed on the less negatively charged surface of the fiber. Consequently, the dye anions which are adsorbed on the surface of the fiber will have a tendency to some extent to cancel the neutralizing effect of the salt. The drop in the negative zeta potential of the system, therefore, depends upon the extent of the neutralizing effect of the electrolyte.

For a given concentration of a dye in the streaming solution, the drop in the negative zeta potential of the polyformaldehyde fibers will be higher at higher concentrations of electrolytes. Thus, in the case of Congo Red and Chlorazol

Sky Blue FF, there is a progressive decrease in the negative zeta potential with increase in the concentration of sodium chloride in the streaming solution. The tetrabasic Chlorazol Sky Blue FF, however, shows lower negative zeta potential of the polyformaldehyde fibers at higher concentrations of the electrolyte as compared to the zeta potential values in the case of dibasic Congo Red. This may be attributed to the decreased adsorption of the tetrabasic dye as compared to the dibasic dye. This observation is in agreement with the adsorption of direct dyes of different basicities on cellulosic fibers.[24]

From Figures 14 and 15, it can be seen that linear log–log correlations exist between the surface charge density and surface conductivity of the polyform-aldehyde fibers on one hand, and the concentration of electrolyte in the streaming solution on the other in the presence of direct dyes. The σ and K_s values increase with increase in the concentration of sodium chloride in the streaming solution, possibly owing to the increased adsorption of the dye anions on the surface of the fibers.

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