ELECTROKINETICS

XVII. Surface Charge and Ion Antagonism*

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Abramson (1) made the suggestion that it would be interesting to recalculate the data of Bull and Gortner (2) on ion antagonism in such a manner as to determine the electrical charge per unit area which gives rise to the electrokinetic potential at the surface. The relation between the potential and charge for a plane surface is

$$\zeta = \frac{4\pi \sigma \lambda}{D}$$

(1)

where $\zeta$ is the potential, $\sigma$ is the charge per cm$^2$, $\lambda$ is the thickness of the double layer, and $D$ is the dielectric constant. In a sense, the charge is a more fundamental quantity than the potential. The presentation of these calculations together with others along similar lines is the purpose of this paper.

We wish to enter briefly into a discussion of the applicability of the conventional equation for the streaming potential to cellulose membranes such as were used by Bull and Gortner. Bull and Moyer (3) have discussed in some detail the relation between streaming potential and capillary size. In general, higher valence types reduce the critical radius. If the radii in these experiments are in the critical range, the mono- and divalent single salts should yield divergent values of $\sigma$ and the shapes of the concentration curves would be expected to differ. As will be shown, this is not the case. The shapes of the curves are completely analogous to those obtained

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with flat surfaces (1). We have determined the maximum pore radius in membranes such as those employed by Bull and Gortner by measuring the minimal air pressure required to force air through the cellulose membrane, using the formula (4),

$$P = \frac{2\gamma}{r}$$  \hspace{1cm} (2)

where $P$ is the pressure in dynes per cm., $r$ the radius, and $\gamma$ is the interfacial tension. We found a maximal pore radius of 6.5–6.8 $\mu$ in different membranes. In addition, the mean capillary radius was found to be 0.96 $\mu$ by the method of Bull and Moyer (3). This lies above the calculated critical radius (3).

A large number of the pores are above the critical range. A number, however, are no doubt below it. It is, therefore, difficult to say exactly what the true electrokinetic potential is in such cases. On one hand we have the results of Bull (5) who found a ratio of 0.28 between the electrokinetic potential of cellulose membranes in a $2 \times 10^{-4}$ M NaCl solution (as determined by the streaming potential method) and that determined by the electrophoresis of the same cellulose fibers in the same salt solution, which would indicate that the pore size in the membrane is considerably smaller than the critical size if no other factors enter in. On the other hand, Briggs (6) working with cellulose membranes of the same type as those employed by Bull and Gortner found the electrokinetic potential to be completely independent, over wide limits, of the tightness of the packing of the cellulose in the membranes. If the pore radii were in the critical range it would seem certain that correspondingly wide variations in the electrokinetic potential would have been observed. Since the membranes of Bull and Gortner were of the same type as Briggs', this indicates that their membranes were also above the critical range. For a more complete discussion of capillary size see (3). In any case, since all the measurements of Bull and Gortner were rigorously conducted under the same conditions the results have, at least, a relative significance and the data presented in this paper are to be considered in that light. For our present purpose this is sufficient.

\footnote{Chapters VI–VIII.}
Calculations

The following equation (1) was used for the calculation of the surface charge:

$$\sigma = \sqrt{\frac{NDkT}{2000\pi}} \sqrt{\sum c_i \left( e^{-\frac{z_i k T}{e}} - 1 \right) + \sum c_j \left( e^{\frac{z_j k T}{e}} - 1 \right)}.$$  \hspace{1cm} (3)

where $N$ is Avogadro’s number, $D$ is the dielectric constant, $k$ Boltzmann’s constant, $T$ the absolute temperature (298° K.), $c_i$ and $c_j$ the concentrations of the cations and anions in mols per liter, $z_i$ and $z_j$ the valences of the cations and anions, and $\sigma$ has the same sign as $\tau$. This is a perfectly general equation for all types of electrolytes but is valid only for plane surfaces. Potres above the critical range can undoubtedly be considered as plane surfaces. If one is dealing with a uni-univalent electrolyte the above equation reduces to

$$\sigma = 2 \sqrt{\frac{NDkT}{2000\pi}} \sqrt{c \sinh \frac{\frac{e \tau}{k T}}{2 k T}}.$$  \hspace{1cm} (4)

The results of these calculations are shown in Figs. 1–5. In all cases the charge shown ($\sigma$) is that obtained by subtracting the initial charge in distilled water ($\sigma_w$), which is due largely to carbonic acid, from the calculated charge ($\sigma_r$). The concentration of HCO$_3^-$ was taken as $2 \times 10^{-6}$ molar (1).4

Fig. 1 shows the rapid increase of the charge on the negative surface with the addition of potassium salts of various anions. Since the cation is the same, the different behavior should be due to the anions. The trivalent PO$_4^{3-}$ shows the largest effect, the divalent CO$_3^{2-}$ and SO$_4^{2-}$ next, and the monovalent Cl$^-$ least effect. The curves have the appearance of adsorption isotherms. Saturation has not been achieved. In this connection Moyer (8) was able to show that the charge on cholesterol particles in suspension followed Langmuir's adsorption isotherm when the charge was graphed against the OH$^-$ concentration. The data used in our calculations are from the paper by Bull and Gortner (9), who calculated the surface charge

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at that time by an entirely different technique and whose results are in essential agreement with those reported here.

![Graph showing electric charge density of a cellulose surface in various potassium salt solutions.]

**Fig. 1.** The electric charge density of a cellulose surface in various potassium salt solutions.

Fig. 2 shows the calculations for ThCl₄, the data being taken from the paper by Bull and Gortner (9). Again the result is in essential agreement with that obtained by these two workers. This case is
interesting because an actual reversal of the sign of the charge is encountered. The curve has the shape predicted by Müller (10).

Fig. 3 shows the variation of the charge with temperature, using $1 \times 10^{-4}$ N NaCl as the electrolyte. The data for the calculations are taken from the paper by Bull and Gortner (11) together with some additional unpublished data of the above authors. Since in these data no measurements for the calculation of $\sigma_w$ are available, all data are calculated as $\sigma_T$. The difference between $\sigma$ and $\sigma_T$ is, however, constant and very small for such high values of $\sigma_T$. Fig.
4 shows the graph of \( \ln \sigma \) against \( 1/T \). The slope of such a curve is equal to \(-\Delta H/R\) (by the van't Hoff equation), provided \( \sigma \) is a measure of the equilibrium constant of adsorption, where \( \Delta H \) is the heat of the adsorption reaction and \( R \) is the gas constant. When plotted by the method of least squares, two straight lines are obtained giving heats of adsorption of \(-2870\) calories and \(-846\) calories. The break comes at 39\(^\circ\). In this connection, it is interesting that the specific heat of water shows a rather sharp minimum at 37.5\(^\circ\). Inasmuch as the adsorption of ions probably involves the desorption of water, the break in the heat of adsorption of the charge is probably due to the change in the heat of desorption of water at this point. It is interesting that \( \kappa \) (the reciprocal of the thickness of the double layer) was found to remain constant or to increase with increasing temperature. This is a somewhat unexpected result since one might expect that the increased kinetic energy of the ions at higher temperatures would result in a greater thickness. The explanation is no doubt to be found in the smaller dielectric constant at higher temperatures, thus resulting in an increased force of attraction between the ions and the charged wall.

The variation of the charge with the addition of chlorides of various
The concentration is given in terms of anion equivalency but other methods of plotting give the same result. The data are taken from the paper by Bull and Gortner (2). The MgCl₂ curve was repeated because of a disagreement between the unpublished results of Briggs and those of the above authors. The new data for MgCl₂ have been used here. These data agree closely with the CaCl₂ data. As can be seen, the charges produced by the single salts rise much higher than...
those for the salt mixtures. Here is a completely different picture from that shown by a plot of the electrokinetic potentials against concentration (2). Unquestionably, ion antagonism is exhibited and the effect increases in the higher concentrations where our calculations are most accurate. This, to our knowledge, is the first time ion antagonism has been directly traced to electrical effects. Evidence is not lacking to confirm the conclusion. There is, for example, a marked ion antagonism between LiCl and MgCl₂, BaCl₂, AlCl₃, and CeCl₃ in the flocculation of As₂S₃ sols (12). It is known that the surface charge is very important in the stability of these sols. Ion antagonism has also been observed in the coagulation of proteins (12). It is interesting to speculate on the reason why the charge with the salt mixtures is lower than that with single salts. It seems probable that in the case of salt mixtures the cations are adsorbed to a certain extent independently of one another, thus resulting in a higher cation adsorption while the chloride adsorption is much the same in the two cases; this, of course, results in a smaller net negative charge. This seems to be borne out by the fact that the charge decreases as the cation mixture is changed, in the order: uni-univalent > divalent—univalent > di-divalent. It is difficult to interpret this ion antagonism in terms of ion antagonism in biological systems as the concentrations in biological systems are so uncertain. It is not impossible, however, that the two are of the same nature.

**SUMMARY**

1. The question of the critical pore diameter for streaming potential is discussed.
2. The surface charge is calculated for cellulose in contact with solutions of K₃PO₄, K₃CO₃, K₃SO₄, KCl, and ThCl₄.
3. The surface charge of cellulose in contact with a solution of 2 × 10⁻⁴ N NaCl is calculated as a function of temperature and is found to show a sharp break at 39°. This is interpreted in terms of the change of the specific heat of water.
4. A marked ion antagonism is found in NaCl:KCl, KCl:MgCl₂,

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*Since each ion follows its own adsorption isotherm, halving the concentration of each produces a proportionately greater total adsorption.*
NaCl: MgCl₂, NaCl: CaCl₂, KCl: CaCl₂, CaCl₂: MgCl₂ mixtures when the surface charge is calculated as a function of concentration.

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