LETTERS TO THE EDITOR

Zeta Potential and Discrete vs. Uniform Surface Charges

Dear Sir:

There has been a wide spread use of surface charges, σ, since Abramson and Müller (1933) first calculated them from the zeta potential, $\bar{V}$, obtained from electrokinetic measurements. It has been convenient to express these results in terms of an average separation, b, between ionic charges, e, on the surface. The recent use of charges absorbed on cell membranes as significant factors in ion permeability behavior (Gilbert and Ehrenstein, 1969) has raised again the pragmatic question: Are the charge separations given by the assumption of uniformity useful approximations in cases for which the charges are assumed to be discrete?

CALCULATIONS

It is assumed that the net free charges are at the interface between aqueous and lipid phases with dielectric constants ϵ_a, ϵ_m and Debye reciprocal lengths κ_a, κ_m with $\kappa^2 = 8\pi ne^2/\epsilon kT$. Further sinh Ve/kT is approximated by Ve/kT to give the Poisson-Boltzman equations

$$d^2V/dx^2 = \kappa^2 V \tag{1}$$

for the plane problem and

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dV}{dr}\right) = \kappa^2 V \tag{2}$$

in the spherical case.

For uniform distribution with $\epsilon_m\kappa_m \ll \epsilon_a\kappa_a$ and in the aqueous phase

$$V = \bar{V}\exp\left(-\kappa x\right) \tag{3}$$

gives $\bar{V} = 4\pi\sigma/\epsilon\kappa$ at the interface. Elementary charges with the spacing b_0 in a hexagonal array given an average charge density $\sigma = 2e/\sqrt{3}\,b_0^2$ and the zeta potential

$$\bar{V} = \frac{e\kappa}{\epsilon}\cdot\frac{8\pi}{\sqrt{3}}\cdot\frac{1}{\kappa^2 b_0^2}. \tag{4}$$

The coefficient of $e\kappa/\epsilon$ is shown as a function of κb_0 in Fig. 1, (0).

The potential about a point charge, e, at the origin is $V = (A/r)\exp\left(-\kappa r\right)$ and if a is the distance of closest approach

$$V = \frac{e}{\epsilon}\cdot\frac{\exp(\kappa a)}{1 + \kappa_a}\cdot\frac{\exp(-\kappa r)}{r}. \tag{5}$$

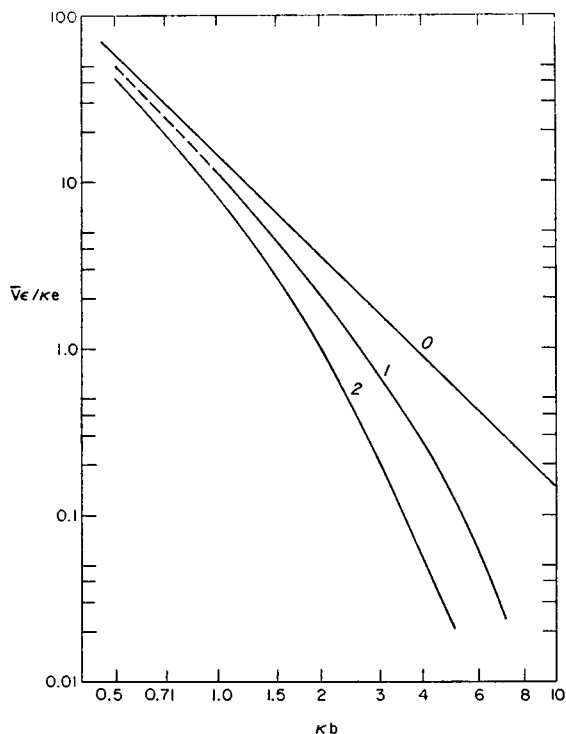With simple dielectrics and κ_a, $\kappa_m \to 0$, the potential about a point charge at the interface

FIGURE 1 Computed potentials in units of $\bar{V}\epsilon/\kappa e$ as functions of hexagonal ion distribution with separation, b, and Debye length, $1/\kappa$. Line 0 is for the reference assumption of a uniform distribution of the charge. Curve 1 gives the potential at the center point between three charges. Curve 2 shows the extrinsic potential at point of closest approach to a single ion.

is the same in both dielectrics

$$V = \frac{2}{\epsilon_a + \epsilon_m} \cdot \frac{e}{r}.$$

However if $\kappa_m \to 0$ and V_a is cut down by κ_a, part of the distributed net counter ion charge, $-e$, will be required to satisfy boundary conditions at the interface. It will be assumed that, as for the plane case with $\epsilon_m\kappa_m \ll \epsilon_a\kappa_a$, the field is largely confined to the aqueous phase and equation 5 becomes

$$V = \frac{2e}{\epsilon} \cdot \frac{\exp(\kappa a)}{1 + \kappa a} \cdot \frac{\exp(-\kappa r)}{r}. \tag{6}$$

The potentials are calculated for hexagonal arrays of charges with the approximation $\exp \kappa a/(1 + \kappa a) = 1$ and for N charges at the distances $r = n\kappa b$

$$V = \frac{2e\kappa}{\epsilon} \sum N \frac{\exp(-n\kappa b)}{n\kappa b}. \tag{7}$$

The series were terminated at the terms less than one percent of the initial terms and the residuals evaluated by assuming uniform charge distribution farther out.

It seems entirely reasonable to assume that the site of entry of a permeating ion into the membrane is near the site of an adsorbed ion. The current popularity of this assumption is only a recommendation and it must be weighted by an estimate of the intuitive power of those who make it. The other extreme is to assume that the portals of entry are at the point of the zeta potential minimum—equidistant from three adjacent adsorbed charges. This leads to the coefficient of $e\kappa/\epsilon$ vs. κb_1 Fig. 1 (1) where the ion separation is b_1. The values for $\kappa b = 0.5$, 0.707 were only interpolated but it is apparent that $V \rightarrow \bar{V}$ as $\kappa b_1 \rightarrow 0$.

Considering now a single fixed ion at the origin as the point of entry for a permeating counter ion and the potential for $r = a$ as an approximation to the external ion cloud component of the measured membrane potential

$$\bar{V}(a) = 2e/\epsilon a(1 + \kappa a) + V_e \tag{8}$$

where V_e is the contribution of all other fixed ions in the plane. The first term is interesting because it is independent of the external fixed ion concentration and is not to be measured except with an electrode inside the membrane. It is a constant biasing potential at each side of the membrane and on our model is part of the potential difference between outside electrolytes and the membrane interior and may be called an intrinsic potential. Debye and Hückel (1923) give several values of a from 2.7 to 5 A and $1/\kappa = 3.1/\sqrt{\gamma}$ A where γ is mol/liter. Ignoring the complications at a concentration as high as 0.5 M we take $a = 4$ A and $1/\kappa = 4.4$ A. This intrinsic potential is then about 90 mv for $\kappa \rightarrow 0$ and is still 45 mv for $\kappa a \simeq 1$ as in seawater.

The extrinsic component of the zeta potential, V_e, may however be available experimentally as a difference from the base line where the separation, b_2, between ions adsorbed at the interface is large. V_e is calculated from eqn. 7 with the approximation exp $\kappa a/(1 + \kappa a) \simeq 1$. Again the coefficient of $e\kappa/\epsilon$ vs. κb_2 is shown on Fig. 1 (2). As was hoped for, $V_e \rightarrow \bar{V}$ when $\kappa b_2 \rightarrow 0$.

INTERPRETATIONS

It had been feared that the zeta potential as computed for a uniform distribution might be quite different from that at an adsorbed charge portal, and indeed the factor of as much as $30 \times$ at large κb in Fig. 1 seemed to confirm this intuition. This was not a result that could be used for an easy interpretation of experimental data and several alternative expressions of the calculations were even more obscure. The only operationally useful procedure that has been found is the following: Given a zeta potential, $\bar{V}$, measured at a known external κ; On the usual assumption of a uniformly distributed adsorbed charge density, the equivalent hexagonal ion separation, b_0, is found by equation 4; With κb_0 now determined, the alternative interpretations of $\bar{V}$ are available from their respective curves (1) for κb_1 and (2) for κb_2 of Fig. 1. These have been plotted in Fig. 2 in the forms b_1/b_0 and b_2/b_0 as functions of the known κb_0.

For a high average adsorbed charge density in a concentrated electrolyte, κb_0 is quite small and b_0, b_1 and b_2 approach equality. At 0.5 M, $1/\kappa = 4$ A and for $b_0 = 2$ A, $\kappa b_0 = 0.5$ and $b_1 = 1.85$ A, $b_2 = 1.7$ A. But these values clearly indicate that they are of no more than casual interest. For the same ionic strength and $b_0 = 12$ A (Gilbert and Ehrenstein, 1969) we have $b_1 = 8.8$ A, $b_2 = 7$ A which are again of ionic dimensions and not of any great precise value. If we have a value (Chandler et al. 1965) of $1/\kappa = 40$ A and $b_0 = 29$ A we
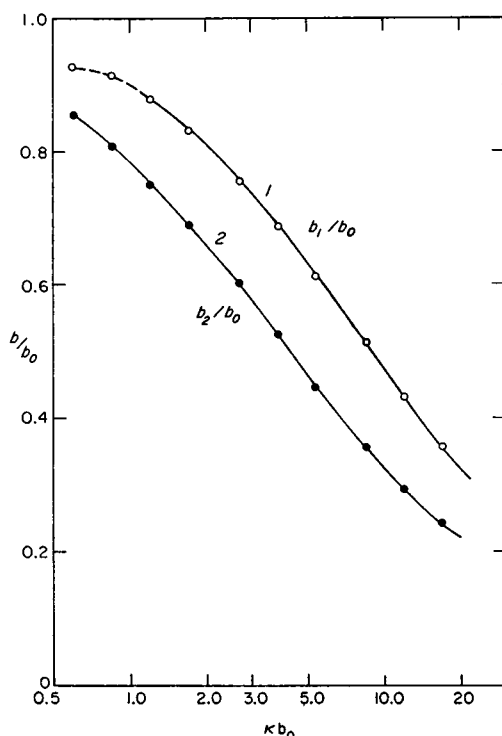
FIGURE 2 Hexagonal ion separations b_1 and b_2 of Fig. 1 relative to b_0, the uniformity reference, from curves *1*, *2*, and *0* respectively for various values of $\bar{V}_\epsilon/\kappa e$ shown as functions of κb_0.

find $b_1 = 27$ A, $b_2 = 24$ A. Here again the differences between b_1 and b_2 are probably not significant but the absolute values may have some meaning.

CONCLUSION

The general conclusion to be drawn is that the densities of adsorbed ions which are estimated from zeta potential measurements on the assumption of a uniform charge distribution are about as accurate as is useful at the present time. The various estimates of charge separations from 10 A to 1000 A have not yet been of crucial importance in problems of membrane structure or function. The potential measurements themselves and such an interpretation are not always entirely free from criticism.

A thousandfold range either of ionic strength or of estimated charge density is found to require no more than an order of magnitude correction for the estimate of the density. This correction is about the same whether the portals are between the adsorbed ions or the portal and the adsorption site are essentially parts of the same local structure. In the latter case, a more detailed analysis is needed and the significance of the intrinsic potential should be considered more carefully.

Certainly there can be no great objection to the primitive calculations of charge separation when they are considered primarily as convenient expressions of experimental data. Other

examples of such utility may be the Goldman (1943) permeabilities and Solomon (1968) pore diameters.

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