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Otto Halpern

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# On Electrophoretic Mobilities and the Isoelectric Point of Protein-Coated Particles

OTTO HALPERN, *Physics Department, New York University, University Heights*

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It is a fact known by experiment that quartz or glass particles of microscopic size suspended in a liquid and coated with a superficial layer of protein exhibit in almost every instance the same mobility in response to the application of an electric field. This indicates that their electrophoretic potential is independent of the size and shape of

the particles. Furthermore, the isoelectric point of these particles coincides with the isoelectric point of the proteinic ions in the solution. Some very general thermodynamic arguments are given in this paper indicating that we should expect a similar behavior as a consequence of simple model properties.

THE difference between the electric potential as it enters into the formulae of thermodynamics, and the electrophoretic potential as determined by kinetic experiments (experiments of flow in general) is now clearly recognized.<sup>1</sup> While the first refers to the electrical work done in the transference of a charged particle from one phase to another, and therefore can be due to excess charges in one phase as well as to double layers rigidly connected with one phase, an electrokinetic potential, in the second place, can only be observed provided one of the phases, which are in motion relatively to each other show an excess charge. Keeping this in mind, it is not difficult to understand that in extreme cases the two potentials might change in an opposite sense, with the variation of the ionic concentration, as has been found experimentally by Freundlich,<sup>2</sup> and interpreted later by Stern.<sup>3</sup>

From the preceding remarks it should not be expected that it would be possible to draw any inferences relative to electrokinetic potentials from thermodynamics. This is generally true, although in the case at present under consideration it seems as if the combination of a simple assumption touching the model properties of the protein with general thermodynamic arguments permits of an understanding of experimentally discovered uniformities of behavior.

<sup>1</sup> For a treatment of the theory and experiments pertaining to electrokinetic phenomena, see H. A. Abramson, *Electrokinetic Phenomena*, Chem. Cat. Co., New York. (In Press.)

<sup>2</sup> H. Freundlich, *Kapillarchemie*, Leipzig, Vol. I, 1932.

<sup>3</sup> O. Stern, *Zeits. f. Elektrochemie* 30, 508 (1924).

The theory of electrokinetic phenomena as developed by Helmholtz, Smoluchowski, and others shows that the electrokinetic potential  $\zeta$  of a particle is connected with its mobility  $u$  under the influence of an electric field by the relation

$$\zeta = (C\eta/D)u \quad (1)$$

( $\eta$  = coefficient of friction,  $D$  = dielectric constant). The numerical factor  $C$  is equal to  $4\pi$  for particles the radius of which is large as compared to the thickness of the ionic atmosphere surrounding the particles.

Proteins dissolved in a solution of known  $pH$  act as amphoteric electrolytes; they are able to ionize by parting with either  $H^+$  or  $OH^-$  ions. The dissociation equilibria are given by the relations

$$(C_+C_{OH^-})/C = K_+, \quad (2)$$

$$(C_-C_{H^+})/C = K_-, \quad (3)$$

where the notation is self-explanatory.

Combining the relations (2) and (3) with the expression for the solubility product of water

$$C_{H^+}C_{OH^-} = K \quad (4)$$

we obtain as a condition for  $C_+ = C_-$  the relation

$$C_{H^+} = [(K_-/K_+)K]^{\frac{1}{2}}. \quad (5)$$

The  $pH$  for which  $C_+ = C_-$  is called the isoelectric point. At this isoelectric point the protein particles do not show any mobility in the electric field. This can be understood by a slight reinterpretation of the thermodynamic formulae.  $C_+ = C_-$  does not mean that half of the

ions are positively, and the other half negatively charged, so that both types will move, only in opposite directions, but that every protein-particle is alternately positively and negatively charged, with the charge 0 in the time average. If the successive changes in the sign of the charge succeed each other fairly rapidly, the small motion in both directions becomes unobservable, the particles seeming to have the mobility 0.

If small particles of quartz or glass of microscopic dimensions but otherwise of arbitrary shape and size be immersed in the liquid it has been found by Abramson<sup>4</sup> that these particles coat themselves with a surface layer of protein, and subsequently show identical mobility in an electric field. Furthermore, the isoelectric point of the microscopic particles, i.e., the  $pH$  at which they show the mobility 0, coincides with the isoelectric point of molecularly dissolved protein. It is this general behavior which we are here trying to explain.

Let us denote by  $\mu^i$ ,  $\mu_+^i$ ,  $\mu_-^i$ , respectively, the specific thermodynamic potential of the neutral, the positively, and the negatively ionized protein molecule in the surface of the particle denoted by  $i$ . We are considering for the following purposes the surface layer of adsorbed proteins as a phase in the thermodynamic sense, which assumption is very nearly correct, since the surface layer contains a large number of molecules. Removal or addition of a protein particle would influence the thermodynamic properties but very slightly. We shall furthermore assume that the *individual* specific thermodynamic potentials of the neutral, positively, and negatively charged protein particles apart from the concentration terms are all changed by the same amount through the process of adsorption. This assumption seems justified in view of the fact that the protein particles are giant molecules containing thousands of atoms, so that the change in free energy produced by adsorption will probably affect very little, if at all, the ionogenic properties of the protein. Our second assumption would be untenable if we were dealing, for example, with comparatively small molecules or ions, with which the adsorption would strongly influence the ionization properties.

<sup>4</sup>H. A. Abramson, J. Phys. Chem. **35**, 289 (1931); J. Gen. Physiol. **15**, 575 (1932).

In the case of thermodynamic equilibrium the following relation, as one out of the series of many similar, must hold

$$\mu_+^i + e\Delta_i = \mu_+ = \mu_+^k + e\Delta_k. \quad (6)$$

In Eq. (6),  $\Delta$  stands for the electrical potential difference in the thermodynamic sense. Eq. (6) simply states that there must be equilibrium between any ion on the surface of any particle and the same ion in solution, and therefore between any two identical ions on the surfaces of two particles selected arbitrarily. According to our assumption as to the influence of adsorption we are justified in equalizing  $\mu_+^i$  and  $\mu_+^k$ , so that Eq. (6) reduces to

$$\Delta_i = \Delta_k. \quad (7)$$

This relation was to be expected from the general behavior of "large electrodes" in electrochemistry.

Nevertheless, since  $\Delta$  might still contain, as mentioned above, potential differences due to double layers rigidly connected to the particle, Eq. (7) *does not express* the equality of the electrophoretic potentials (i.e., the equality of the mobilities). To derive this second result we write the equilibrium condition Eq. (6) in the form

$$\mu_{+0}^i + RT \log C_+^i + e\Delta_i = \mu_{+0} + RT \log C_+, \quad (8)$$

$$\mu_{-0}^i + RT \log C_-^i - e\Delta_i = \mu_{-0} + RT \log C_-, \quad (9)$$

where we have assumed, as is certainly correct, that we are dealing with an ideal mixture. We subtract Eq. (9) from Eq. (8), and apply the resulting equation

$$\begin{aligned} \mu_{+0}^i - \mu_{-0}^i + RT \log (C_+^i/C_-^i) + 2e\Delta_i \\ = \mu_{+0} - \mu_{-0} + RT \log (C_+/C_-) \end{aligned} \quad (10)$$

to the isoelectric point

$$C_+ = C_-, \quad C_+^i = C_-^i.$$

At this isoelectric point there is no more excess charge present on the particle (mobility 0), so that any difference in potential would be due to double layers. Rewriting Eq. (10) we obtain

$$2e\Delta_i = \mu_{+0} - \mu_{+0}^i - (\mu_{-0} - \mu_{-0}^i), \quad (11)$$

in which the right-hand side is 0 (or at all

events very small), according to our second assumption. This shows for our model the absence of potential differences due to dipole layers, and therefore leads, with the help of (7), to the desired result: the potential difference due to excess charge and (therefore the mobility) is the same for all particles, independently of size and shape.

It becomes quite obvious in our presentation

that the identity of the isoelectric point for free and adsorbed particles is by no means necessary, and in the case of proteins is due to the fact that adsorption apparently does not influence the ionogenic properties. In more general cases in which the dissociation is changed by adsorption the identity of the isoelectric point is not to be expected, and then our conclusions would become invalid.