DONNAN-E.M.F. AND SUSPENSION EFFECT

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ABSTRACT

The Donnan-e.m.f. may be defined as the e.m.f. of the cell obtained by connecting two identical electrodes by means of saturated KCl bridges to a suspension and its equilibrium liquid. The suspension effect is the difference in e.m.f. obtained in the conventional determination of the pH in a suspension and in its equilibrium solution. It is shown that the Donnan-e.m.f. and the suspension effect are identical. The Donnan-e.m.f. can be calculated from the chemical potentials and the transference numbers in the two liquid junctions. It is pointed out that the measured potential can not be separated into a "true" Donnan- or membrane-potential and two liquid junction potentials without arbitrariness. Explicit equations for the Donnan-e.m.f. are given for a number of typical cases. It appears that the classical equation for the Donnan-potential is in error if the mobilities of the gegenions are modified by the presence of the particles, which presumably is the case, unless the particle charge is extremely small.

1. INTRODUCTION

Recently (1–8) there has been a great deal of discussion of the suspension effect, that is, the difference in pH between a suspension and its equilibrium liquid, and of the relation between the suspension effect and the Donnan-potential. Although some of the contributions to this discussion have helped to clarify the situation, a completely satisfactory understanding has not been reached.

It is proposed to show in this paper that the suspension effect and the Donnan-potential are identical, and that attempts to separate the measured potential difference in the sum of a membrane-potential and a liquid junction (diffusion) potential are based on arbitrary assumptions. Moreover, it will be shown how the suspension effect can be calculated approximately from the composition of the system.

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2. THE RELATION BETWEEN THE SUSPENSION EFFECT AND THE DONNAN-POTENTIAL

The pH of a suspension is calculated from the e.m.f. of the following cell.

hydrogen electrode (or glass electrode) | suspension | saturated KCl | Hg_2Cl_2 | Hg

(Cell A)

We shall call this e.m.f. E_1, considering the calomel electrode as the positive pole. When the suspension is replaced by its equilibrium liquid, a different e.m.f. is found (E_2). The suspension effect may be defined as the difference between these two e.m.f.'s.

$$E_{\text{susp}} = E_1 - E_2 . \qquad [1]$$

As a rule it has the same sign as the electric charge of the particles.

The Donnan-potential is measured with the aid of cell B, where the suspension and its equilibrium liquid are separated by a membrane, which is impermeable to the suspended particles but not to any other component of the system.

A		B	C		D
		hydr. el.	hydr. el.		
Hg, Hg_2Cl_2	KCl (sat.)	equilibrium solution	suspension	KCl (sat.)	Hg_2Cl_2, Hg
		membrane			

(Cell B)

Hydrogen electrodes B and C are inserted in the equilibrium solution and in the suspension of the Donnan cell. The potentials of the four electrodes will be indicated as ψ_A, ψ_B, ψ_C, and ψ_D.

It has long been recognized (9–11) that the two hydrogen electrodes are at the same potential, because the circuit

hydrogen electrode B | equilibrium liquid | suspension | hydrogen electrode C

is in equilibrium and thus cannot perform work. Therefore

$$\psi_B = \psi_C . \qquad [2]$$

The suspension effect is defined as

$$E_1 - E_2 = (\psi_D - \psi_C) - (\psi_A - \psi_B) = \psi_D - \psi_A , \qquad [3]$$

which is just the e.m.f. of the Donnan cell.

In this paper we shall therefore mainly consider the e.m.f. of cell B.

$$E_{\text{cell B}} = \psi_D - \psi_A = \text{Donnan-e.m.f.} = \text{suspension effect.}$$

In the past a clear distinction has not always been made between the potential difference between the suspension and the equilibrium liquid, "which thermodynamically is not completely determined," (12, 13) and the e.m.f. of cell B, which is a well-defined quantity. Many authors take the point of view that the potential difference between the suspension and the equilibrium liquid is the "true Donnan-potential" and that the e.m.f. of cell B is an approximate value for it—approximate because of the presence of two liquid junctions. However, we avoid ambiguity in considering the potential of the complete cell rather than the potential difference between phases of unequal composition.

The situation with respect to the Donnan potential is closely similar to that in the determination of the pH. Likewise, the current definition of the pH is based not upon an alleged knowledge of the "activity of the hydrogen ions" but upon the total e.m.f. of the measuring cell, with inclusion of the liquid junction involved (14).

3. Expression for the e.m.f. of cell B.

Because the two calomel electrodes of cell B have the same composition and are in contact with identical solutions, the reactions at the electrodes do not influence the e.m.f. of the cell, which can therefore be described as the sum of three liquid junction potentials. If we number the four liquid sections of the cell I, II, III, and IV and the liquid junctions 1, 2, and 3 as follows:

I		II		III		IV
KCl (sat.)		equilibrium liquid		suspension		KCl (sat.)
	1		2		3	

the e.m.f., E, of the cell is given by (see, for example, reference 14, p. 220):

$$-EF = \int_{\mathrm{I}}^{\mathrm{IV}} \sum_i \frac{t_i}{z_i}\, d\mu_i\,, \tag{4}$$

where F is the Faraday, 96500 Coulombs, t_i the Hittorf transference number, z_i the valency with sign included, and μ_i the chemical potential of the ion i.

This equation, although correct, does not lend itself easily to calculations because it includes single-ion activities. To remedy this defect we add therefore to the right-hand side of Eq. [4]:

$$-\int_{\mathrm{I}}^{\mathrm{IV}} \sum_i t_i \frac{d\mu_R}{z_R} + \frac{\mu_R^{\mathrm{IV}}}{z_R} - \frac{\mu_R^{\mathrm{I}}}{z_R} = 0,$$

where R is a reference ion of valency z_R. (This method has been described in references 15 and 16.) As solutions I and IV are identical, this leads to:

$$-EF = \int_{\text{I}}^{\text{IV}} \sum_i t_i \left(\frac{d\mu_i}{z_i} - \frac{d\mu_R}{z_R}\right). \qquad [5]$$

All the chemical potentials are now combined in such a way as to refer to neutral substances. If for instance $i = \text{Cl}^-$ and $R = \text{K}^+$, $\frac{\mu_i}{z_i} - \frac{\mu_R}{z_R}$ just means $-\mu_{\text{KCl}}$.

The integral of Eq. [5] gives only contributions to the cell potential at places where the chemical potentials change, i.e., at the liquid junctions 1 and 3. *At the membrane 2, the chemical potentials of all the salts that can pass through the membrane do not change, because equilibrium is assumed to exist,* and for i = suspended particles, t_i is zero, because the particles cannot pass through the membrane.

Consequently we arrive at the equation:

$$E = \frac{1}{F}\left[\int_{\text{IV}}^{\text{III}} \sum_i t_i \left(\frac{d\mu_i}{z_i} - \frac{d\mu_R}{z_R}\right) - \int_{\text{I}}^{\text{II}} \sum_i t_i \left(\frac{d\mu_i}{z_i} - \frac{d\mu_R}{z_R}\right)\right]. \qquad [6]$$

The Donnan-e.m.f. and the suspension effect can be completely derived from the conditions at the two liquid junctions with saturated KCl, whereas the situation at the membrane does not enter into the final equation. This does not prove, however, whether there is or is not a potential difference between the suspension and its equilibrium liquid. Information on this potential difference simply can not be derived from the measurements with cell B nor, as far as we know, from any other measurement.

In order to treat the e.m.f. of the Donnan cell as the sum of two liquid junction potentials and a membrane potential, one adds the following expression to Eq. [4]:

$$-\int_{\text{II}}^{\text{III}} \sum_i t_i \frac{d\mu_R}{z_R} + \frac{\overset{\text{III}}{\mu_R}}{z_R} - \frac{\overset{\text{II}}{\mu_R}}{z_R} = 0,$$

and obtains:

$$E = \frac{1}{F}\Bigg[\underbrace{\int_{\text{IV}}^{\text{III}} \sum_i t_i \frac{d\mu_i}{z_i}}_{\text{A}} + \underbrace{\frac{\overset{\text{II}}{\mu_R} - \overset{\text{III}}{\mu_R}}{z_R}}_{\text{B}} - \underbrace{\int_{\text{I}}^{\text{II}} \sum_i t_i \frac{d\mu_i}{z_i}}_{\text{C}}\Bigg]. \qquad [7]$$

The three terms of this expression can, however, be evaluated only when single-ion activities are known, and therefore an additional assumption has to be made. Some of the assumptions used in the past are:

1. The two liquid junction potentials A and C cancel.

2. The ion R (usually the gegenion is chosen) has identical activity coefficients in solution and suspension.

3. The ion R has identical activities on both sides of the membrane.

4. The membrane potential (part B) can be calculated from a model as the difference of the average potential of solution and suspension.

5. The membrane potential can be calculated from the osmotic pressure. None of these methods is at variance with thermodynamics. Provided we choose only *one* of these assumptions, we cannot run into conflict with experimental evidence, but we cannot learn anything from it either.

We may learn something from the examination of the complete cell potential by determining, experimentally or by calculation, relations among the transference numbers and the chemical potentials which will enable us to integrate Eq. [6]. Since the chemical potentials have the same values at the limits of integration of the two integrals, a finite value of the e.m.f. can be obtained only when the transference numbers are different in the suspension and in the equilibrium solution. This difference is due to the presence of the charged particles and the excess of ions in the double layers surrounding them.

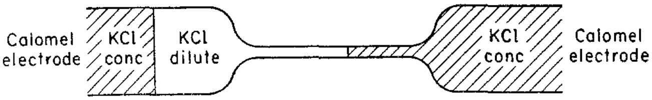

FIG. 1. Capillary effect, cell C.

In contradistinction to the usual theories, in which the Donnan potential is considered as an equilibrium quantity, related to ion activities in solution and suspension, we see here that the Donnan-e.m.f. is dependent upon mobilities also and that it can only be measured on a system that is *not* in equilibrium. The unequal distribution of ions between suspension and solution and the osmotic pressure, however, are independent of the presence of salt bridges and are characteristic of the Donnan equilibrium in the strict sense of the word.

In order to illustrate this point of view, we shall now give a few examples in which the integrals of Eq. [6] can be evaluated by assuming suitable relationships between transference numbers and chemical potentials. Since the major contributions to the integrals are made by the more dilute parts of the liquid junctions, the assumption of ideal behavior of the solutions as far as activity is concerned would be a good starting point. The cases to be treated will be of increasing order of complexity.

4. CAPILLARY EFFECT IN KCl

Loosjes (17) discovered that something analogous to the suspension effect can be measured in cell C, in which the suspension of cell B is replaced by a capillary. The capillary wall carries an electrical double layer and shows a certain amount of surface conductance. As this surface conductance presumably is carried by the gegenions (in this example cations), the transference number of the cations in the capillary will be increased above the value for the bulk of the solution.

The e.m.f. of cell C can be derived from Eq. [6], taking K$^+$ ions as the reference ions R.

$$\begin{aligned} E_{\text{capillary effect}} &= \frac{1}{F}\left[\int_{\text{KCl conc.}}^{\text{KCl dil.}} (-t_{\text{Cl}}\, d\mu_{\text{KCl}})_{\text{cap.}} + \int_{\text{KCl conc.}}^{\text{KCl dil.}} (t_{\text{Cl}}\, d\mu_{\text{KCl}})_{\text{wide tube}}\right] \\ &= \frac{1}{F}\int_{\text{KCl dil.}}^{\text{KCl conc.}} \left[t_{\text{Cl(cap.)}} - t_{\text{Cl(wide tube)}}\right] d\mu_{\text{KCl}}\,. \end{aligned} \qquad [8]$$

If $t_{\text{Cl}} = t$ in the wide tube and we assume that the surface conductance in the capillary is completely carried by an excess of K$^+$ ions, we find:

$$t_{\text{Cl(cap.)}} = \frac{t\pi r^2 \lambda c}{\pi r^2 \lambda c + 2\pi r \sigma} = \frac{t}{1 + \dfrac{2\sigma}{\lambda c r}}, \qquad [9]$$

where λ is the equivalent conductance of KCl, c the concentration of the solution, r the radius of the capillary, and σ the specific surface conductance along the glass wall.

Considering KCl as an ideal solute we have:

$$\mu_{\text{KCl}} = \mu_0 + 2RT \ln c \qquad [10]$$

and considering the surface conductance constant,[1] the e.m.f. of the capillary effect becomes:

$$\begin{aligned} E_{\text{cap. eff.}} &= \frac{2RT}{F} t \int_{c_{\text{dil.}}}^{c_{\text{conc.}}} \left(\frac{1}{1 + \dfrac{2\sigma}{\lambda r c}} - 1\right)\frac{dc}{c} = -\frac{2RT}{F} t \int_{c_{\text{dil.}}}^{c_{\text{conc.}}} \left(\frac{1}{c} - \frac{1}{c + \dfrac{2\sigma}{\lambda r}}\right) dc; \\ &= -\frac{2RT}{F} t \ln \frac{c_{\text{conc.}}\left(c_{\text{dil.}} + \dfrac{2\sigma}{\lambda r}\right)}{c_{\text{dil.}}\left(c_{\text{conc.}} + \dfrac{2\sigma}{\lambda r}\right)}\,. \end{aligned} \qquad [11]$$

When the surface conductance is small even in the dilute solution and negligible in the concentrated one, Eq. [11] can be approximated by

$$E_{\text{cap. eff.}} = -\frac{2RTt}{F}\frac{2\sigma}{r\lambda c_{\text{dil.}}}\,. \qquad [12]$$

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[1] Although this is rather a crude approximation, it is permissible because what little reliable data we have on surface conductance indicate that there is only a slight variation of surface conductance with concentration.

The right-hand terminal of cell C is negative; the e.m.f., inversely proportional to the radius of the capillary and the conductance of the dilute solution, and virtually independent of the concentration of the concentrated one—all in agreement with Loosjes' results. From the e.m.f.'s as measured, a specific surface conductance of the order of 2×10^{-7} mho is derived—not an improbable value for the soft glass used (Corning 015). Unfortunately Looseјes did not measure the surface conductance, so that a direct check is not possible.

For comparison with later examples we point out that the capillary effect does not depend on the surface charge but on the surface conductance, that is, on the number of ions in the surface multiplied by their mobility.

5. Suspension Effect and Donnan-e.m.f.

Considering now a suspension of negatively charged particles, and taking again K^+ as the reference ion, the equation [6] for the Donnan-e.m.f. can be written as follows:

$$E_{\text{Donnan}} = \frac{1}{F}\int_{\text{susp.}}^{\text{KCl sat.}} \left[t_{\text{Cl}}\, d\mu_{\text{KCl}} - \sum_{i \neq \text{K,Cl}} t_i \left(\frac{d\mu_i}{z_i} - d\mu_{\text{K}}\right)\right] - \frac{1}{F}\int_{\text{solut.}}^{\text{KCl sat.}} \left[t_{\text{Cl}}\, d\mu_{\text{KCl}} - \sum_{\substack{i \neq \text{K,Cl} \\ \text{part.}}} t_i \left(\frac{d\mu_i}{z_i} - d\mu_{\text{K}}\right)\right]. \qquad [13]$$

In order to proceed, an assumption has to be made about the liquid junction between the suspension and the saturated potassium chloride. We will suppose that the concentrations of particles and all other ions of the suspension are constant and that the only variation in the liquid junctions is a gradient of the KCl concentration. This assumption makes calculations very easy, and results are only slightly different from the ones obtained with a Henderson-type boundary.

a. Ideal Behavior

The simplest possible assumption about the relation between transference numbers and chemical potentials is that of ideal behavior of all components with respect both to activity and mobility. In that case the following relations can be used to transform Eq. [13]:

$$t_{\text{Cl}} + \sum_{i \neq \text{K,Cl}} t_i = 1 - t_{\text{K}}$$

$$d\mu_{\text{KCl}} = RT\frac{dc_{\text{K}}}{c_{\text{K}}} + RT\frac{dc_{\text{Cl}}}{c_{\text{Cl}}} \qquad [14]$$

$$d\mu_i(i \neq \text{K, Cl}) = 0; \qquad d\mu_{\text{K}} = RT\frac{dc_{\text{K}}}{c_{\text{K}}}$$

$$dc_{\text{K}} = dc_{\text{Cl}}.$$

With the aid of the relations [14], Eq. [13] is transformed into

$$E_{\text{Donnan}} = \frac{RT}{F}\int_{\text{susp.}}^{\text{KCl sat.}}\left[\left(\frac{t_{\text{Cl}}}{c_{\text{Cl}}} - \frac{t_{\text{K}}}{c_{\text{K}}}\right)dc_{\text{K}} + \frac{dc_{\text{K}}}{c_{\text{K}}}\right] - \frac{RT}{F}\int_{\text{solut.}}^{\text{KCl sat.}}\left[\left(\frac{t_{\text{Cl}}}{c_{\text{Cl}}} - \frac{t_{\text{K}}}{c_{\text{K}}}\right)dc_{\text{K}} + \frac{dc_{\text{K}}}{c_{\text{K}}}\right].$$

The first terms of the two integrals give a very small contribution, which is proportional to the difference in mobility of the Cl^- and the K^+ ions and which will be neglected.

Then we obtain the simple result:

$$E_{\text{Donnan}} = \frac{RT}{F}\ln\frac{c_{\text{K, equil. sol.}}}{c_{\text{K, suspension}}}. \qquad [15]$$

When the only ions in the system are K^+ and Cl^- and when the concentration of particles is small, the distribution of ions is given by the relation:

$$c_{\text{K, suspension}} = c_0 + \frac{c_P}{2},$$

where c_P is the equivalent concentration of suspended particles, and c_0 is the concentration of KCl in the equilibrium solution, both expressed in equivalents per unit volume.

With this relation Eq. [15] simplifies to:

$$E_{\text{Donnan}} = -\frac{RT}{2F}\frac{c_p}{c_0}. \qquad [16]$$

So, although our approach has been different, we obtain in this ideal case the classical equations for the Donnan potential.

The assumption of ideal behavior in a suspension or in a polyelectrolyte is, however, often quite unrealistic. Not only will the distribution of ions deviate from the ideal one, forcing us to introduce activity coefficients, but the mobility of the ions in the neighborhood of the suspended particles will also be modified by electric and hydrodynamic interaction.

We shall now show that even for the limiting case of small particle concentrations, especially the modified mobilities affect the Donnan-e.m.f. seriously.

b. Nonideal Distribution: Nonideal Mobilities

A very important reason for departure from ideal behavior is the high concentration of ions around the suspended particles. When the charge density on the particles is very low, half of this charge is compensated by an excess of gegenions, and the other half by a deficiency of ions of the same sign of charge as the particles. When the particle charge is high, the gegenions compensate more than ½, say a fraction x of the particle charge, and the deficiency of ions of the same sign compensates less than ½, say a fraction y, even when the concentration of particles is very low. This asymmetry is the more pronounced the smaller the concentration of electrolyte (18; cf. 19, p. 191 ff.)

Considering a suspension of negatively charged particles in KCl, in equilibrium with a KCl solution of concentration c_0, the concentrations of K^+ and Cl^- ions will be:

$$\begin{aligned} c_K &= c_0 + xc_P \\ c_{Cl} &= c_0 - yc_P; \\ x + y &= 1. \end{aligned} \qquad [17]$$

This amounts to taking the activity coefficient of KCl for small values of c_P equal to:

$$f_\pm = 1 - \frac{x - y}{2} \frac{c_P}{c_0} \qquad [18]$$

if we assume the activity coefficient in the solution to be equal to one.

The mobilities of the ions will be affected as well. We expect some of the Cl^- ions close to the particles to have an increased mobility, and the K^+ gegenions will certainly have a lower mobility than normal.

That this is by no means a small effect may be illustrated by the case of the AgI sol., where the mobility of the counterions is only 20% to 25% of the normal value (20; cf. 19, p. 239). Investigations on ion exchange (21; cf. 19, p. 176 ff.) in the double layer of AgI have shown that this cannot be ascribed to incomplete dissociation between particle and counterions. Another example of a large change in mobility is given by the negative transference-number of the counterions of some paraffin-chain salts (22).

These facts can be taken into account by placing the contribution of the K^+ and Cl^- ions to the conductance equal to

$$\begin{aligned} c_K\lambda_K &= \lambda_0(c_0 + uc_P) \\ c_{Cl}\lambda_{Cl} &= \lambda_0(c_0 - vc_P) \end{aligned} \qquad [19]$$

where λ_0 is the limiting equivalent conductance of Cl^- or K^+, and u and v are constants. This means that from now on we neglect the small difference in limiting equivalent conductance of K^+ and Cl^-.

The following values for the mobility coefficients in the case of small c_P can be calculated from Eq. [19]:

$$\lambda_K/\lambda_0 = 1 - (x - u)\frac{c_P}{c_0}$$

$$\lambda_{Cl}/\lambda_0 = 1 + (y - v)\frac{c_P}{c_0}.$$

There are no simple relations between u, v, and x, y although v should not be very different from y but u should be considerably smaller than x, so that

$$u + v < 1. \qquad [20]$$

Applying now Eq. [13] for the case considered here we find:

$$E_{\text{Donnan}} = \frac{1}{F}\int_{\text{susp.}}^{\text{KCl sat.}} \left(t_{\text{Cl}}\, d\mu_{\text{KCl}} + \frac{t_P}{z_P}\, d\mu_{PK_z}\right) - \frac{1}{F}\int_{\text{sol.}}^{\text{KCl sat.}} t_{\text{Cl}}\, d\mu_{\text{KCl}} \qquad [21]$$

where t_P is the transference number and z_P the valency of the particles and μ_{PK_z} the chemical potential of a particle with its z gegenions.

In order to eliminate μ_{PK_z} we apply the Gibbs-Duhem relation to a suspension and to the liquid with which it is in equilibrium. We find

for the solution $\qquad 55\, d\mu_{\text{H}_2\text{O}} + c d\mu_{\text{KCl}} = 0,$

for the suspension $\qquad 55\, d\mu_{\text{H}_2\text{O}} + (c - yc_P)\, d\mu_{\text{KCl}} + \frac{c_P}{z_P}\, d\mu_{PK_z} = 0,$

where 55 represents the number of moles of water in a liter.

From these relations we derive

$$\frac{1}{z_P}\, d\mu_{PK_z} = y d\mu_{\text{KCl}} \qquad [22]$$

and consequently the equation for the e.m.f. becomes

$$E_{\text{Donnan}} = \frac{1}{F}\int_{\mu_0}^{\text{KCl sat.}} (t_{\text{Cl, susp.}} - t_{\text{Cl, sol.}} + yt_P)\, d\mu_{\text{KCl}} \qquad [23]$$

where μ_0 is the chemical potential of KCl in the suspension or the solution.

The transference numbers and the chemical potentials to be substituted in Eq. [23] are:

$$\begin{aligned} t_{\text{Cl, susp.}} &= \frac{c - vc_P}{2c + (u - v + r)c_P} \\ t_{\text{Cl, sol.}} &= \tfrac{1}{2} \\ t_P &= \frac{rc_P}{2c + (u - v + r)c_P} \\ d\mu_{\text{KCl}} &= 2RT\,\frac{dc}{c} \end{aligned} \qquad [24]$$

where r is the ratio of the mobility of a particle to that of a free K^+ or Cl^- ion. Assuming that y, u, v, and r are independent of the KCl concentration (or taking suitable averages for them) we find:

$$E_{\text{Donnan}} = -\frac{RT}{F}\int_{c_0}^{c\,\text{sat.}} \frac{(u + v + (1 - 2y)r)c_P}{2c + (u - v + r)c_P}\,\frac{dc}{c}. \qquad [25]$$

On integration this leads to

$$E_{\text{Donnan}} = -\frac{RT}{F}\,\frac{u + v + (1 - 2y)r}{u - v + r}\ln\frac{c_{\text{sat.}}}{c_0}\,\frac{c_0 + \dfrac{u - v + r}{2}\,c_P}{c_{\text{sat.}} + \dfrac{u - v + r}{2}\,c_P}, \qquad [26]$$

which usually can be simplified to

$$E_{\text{Donnan}} = -\frac{RT}{F}\,\frac{u + v + (1 - 2y)r}{u - v + r}\ln\left(1 + \frac{u - v + r}{2}\,\frac{c_P}{c_0}\right), \qquad [27]$$

and which, in the case of small concentrations of particles, can be further simplified to

$$E_{\text{Donnan}} = -\frac{RT}{2F}\,\frac{c_P}{c_0}\left[u + v + (1 - 2y)r\right]. \qquad [28]$$

We see that even in the case of small particle concentrations the Donnan-e.m.f. is not determined in a simple way by the charge of the particles but mainly by the contribution to the conductance of the ions in the double layer. The fact that the mobility of the counterions is much lower than normal (it may even be negative) and that $u + v$ is always smaller than one (see Eq. [20]), explains why the Donnan-e.m.f. is often found to be lower than the value calculated from the ideal equation. This lower value need therefore not necessarily reflect incomplete dissociation, nor can it give much information on the activity coefficients of the system.

When the charge density on the particles is high, v and y will be quite low and may be neglected. In that case the Donnan-e.m.f. and the contribution of the particles plus gegenions to the conductance (micellar conductance) are both determined by $u + r$, and Eq. [27] can be written

$$E_{\text{Donnan}} = \frac{RT}{F}\ln\frac{\text{conductance of suspension}}{\text{conductance of equil. solution}},$$

showing clearly the close analogy to the capillary effect (Eqs. [11] and [12]).

Not a single Donnan system has been investigated in sufficient detail to test the Eqs. [26]–[28] quantitatively. Information on the mobilities of all components of the system would be particularly desirable.

Incidentally Eq. [26] is rather similar to an equation obtained by Jenny c.s. (1) for the suspension effect. They applied it to compressed plugs of clay and other ion exchange materials. It should be remarked that in such cases, although the particles are fixed with respect to the apparatus, their Hittorf transference number is not zero, because electro-osmosis drives the solvent through the plug. An approach using "reduced" transference numbers (23, 24) instead of Hittorf ones appears more natural, although both methods are correct and finally lead to the same result.

6. SEPARATION OF THE CELL POTENTIAL INTO THREE CONTRIBUTIONS

If an attempt is made to separate the cell potential into three contributions by using Eq. [7], one encounters the following difficulty. The total cell potential contains mobilities according to Eqs. [26]–[28], but the true membrane-potential $\frac{1}{Fz_R}(\mu_R^{\text{II}} - \mu_R^{\text{III}})$ should depend only upon activities. Consequently the assumption that the two liquid junction potentials cancel would imply that the activity of the R ion is connected in a very special way with the mobilities of the ions of the system, even in the limit of a very small concentration of particles. On the other hand, any other plausible assumption on the single-ion activities would lead to a value for the liquid junction potentials which is significantly different from zero, even if the particle concentration is small. Since it is at any rate impossible to test assumptions of this nature experimentally, the discussion on the Donnan potential in the sense of a potential difference between suspension and solution loses much of its attraction, and it appears more satisfactory to concentrate on the Donnan-e.m.f., that is, on the e.m.f. of the total cell.

7. FINAL REMARKS

The Donnan potential has often been used to determine particle charges (25, 26). It is now evident that this is only justified when the charge density on the particles is small, so that all electrostatic and hydrodynamic interaction may be neglected. A small value of the Donnan-e.m.f. in itself, which can also be obtained by a small concentration of particles, or a high concentration of electrolyte, is not a sufficient condition.

Finally it should be remarked that Loosjes in his thesis (17) suggested an explanation for the capillary effect and for the suspension effect based upon the different contributions of the surface of the capillary or the particles and the bulk of the liquid to the conductivity of the system. Quantitatively his explanation comes therefore rather close to the one offered in this paper.

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