Ion-Pair Correlation Function in Electric Double Layer Theory

Part 2.—Relevance to the Discreteness-of-Charge Effect

By Samuel Levine* and Gérard Féat†

Department of Mathematics, University of Manchester, Manchester M13 9PL

The expression derived in Part 1 for the ion-pair correlation function in the electric double layer is applied to two ions adsorbed on a plane (the i.h.p.) in the Stern inner region. For ions i and j, charges e_i and e_j at separation ρ on the i.h.p., the correlation function is

$$g^{(ij)}(\rho) = g^{(ij)}(\rho, \xi = 0) \exp\left[-\frac{1}{kT}\int_0^1 d\xi\,\{e_j\phi^{(i)}(\rho, \xi) + e_i\phi^{(j)}(\rho, \xi)\}\right],$$

where $\phi^{(i)}(\rho, \xi)$ is the potential due to ion i at distance ρ on the i.h.p. in the absence of ion j and $\phi^{(j)}(\rho, \xi)$ is defined similarly. Both ions are being charged to the same degree ξ. The potential $\phi^{(i)}(\rho, \xi)$ may be written as

$$\phi^{(i)}(\rho, \xi) = \xi e_i\phi_0(\rho) + \phi_a^{(i)}(\rho) + \phi_d^{(i)}(\rho, \xi),$$

where $\phi_0(\rho)$ is the potential due to a unit point charge, $\phi_a^{(i)}(\rho)$ arises from the removal of the mean surface charge density from the exclusion disc on the i.h.p. around i and $\phi_d^{(i)}(\rho, \xi)$ is due to the fluctuation in surface charge density on the i.h.p. beyond the exclusion disc. $\phi^{(j)}(\rho, \xi)$ can be expressed similarly. In the case of two oppositely charged ion species on the i.h.p., the contribution $\phi_a^{(i)}(0, 1)$ to the discreteness-of-charge potential at ion i is determined by adapting to two-dimensions the ion-pairing theory of Bjerrum and Fuoss, as extended by Poirier and DeLap. The results are applied to a study of ionized monolayers.

---

1. INTRODUCTION

In the preceding paper [1] (henceforth referred to as I) the pair correlation function $g^{(ij)}(12)$ was examined for two ions i and j situated at r_1 and r_2 in the diffuse layer. The eqn I(3.10) for $g^{(ij)}$ can be applied equally to two ions situated on the adsorption plane (the inner Helmholtz plane or i.h.p.) in the Stern region of the double layer, when $g^{(ij)}$ depends only on the separation $r_{12} = |r_1 - r_2|$ between the two ions. This is achieved by first regarding the Stern region as a part V_a of the volume V of the aqueous phase and, therefore, treating ion densities in the inner region as volume densities. In the theory presented in I, no assumptions have been made about the inhomogeneities in the dielectric constant at the interface and, in this respect, the approach in I has an advantage over that of Outhwaite.[2] In particular, the basic interaction potential $e_i e_j v(12)$ between two ions i and j has been left unspecified. In eqn I(3.10), it is only necessary to label the indices 1 and 2 with a dash to indicate that ions i and j are situated on the i.h.p. at positions r_1 and r_2 respectively.

In this paper we examine the relevance to the so-called discreteness-of-charge effect [3-5] of the two-dimensional pair correlation function for two ions adsorbed on the i.h.p. In previous papers on this effect, any use of the correlation function was based on the Kirkwood charging of one ion.[5] Most of the work was concerned with a single adsorbed ion species and, in this case, the lack of symmetry in the pair

correlation function affects the calculation of the discreteness-of-charge effect only slightly. The theory of the discreteness-of-charge effect for a mixture of cations and anions adsorbed on the i.h.p. hitherto has been largely qualitative.[6, 7] We shall demonstrate that for such a system, symmetry in the pair correlation function plays a significant role in this theory. A method based on the adaptation to two dimensions of the ion-pairing theory of Bjerrum,[8] Fuoss,[9, 10] Poirier and DeLap [11] is developed for determining the discreteness-of-charge potential of adsorbed ions in the mixture. A preliminary account of this approach has already been given with reference to the theory of electrode reactions.[12] Use of this ion-pairing method will be illustrated on adsorbed counter-ions in an ionized monolayer at the air/water interface.

The ion-pairing theory of Poirier and DeLap [11] as employed here, suffers from certain defects which are discussed below. However, it provides an approximate but feasible method of determining the discreteness-of-charge effect for a mixture of two ion species of opposite charge situated on the i.h.p. A more rigorous and comprehensive theory of ion-pairing in homogeneous symmetrical electrolytes has been developed by Stillinger et al.[13, 14] They are able to express the ion-atmosphere charge density in terms of a dielectric function depending on wave-length, which they determine approximately. They suggest that their general procedure should be adaptable to the description of the electric double layer, but this remains to be investigated.

2. SYMMETRY PROPERTIES OF THE PAIR CORRELATION FUNCTIONS

We consider an ion i, charge ξe_i, situated on the i.h.p. in the inner Stern region. Suppose that, in the formula I(3.8) for the self-atmosphere potential $\phi_1^{(i)}(r_2, \xi)$, the position r_1 of ion i is on the i.h.p. at the origin of coordinates and that r_2 is a point on the i.h.p. at distance ρ from the origin. $\phi_1^{(i)}(r_2, \xi)$ is the change in potential at distance ρ on the i.h.p. due to placing ion i, charge ξe_i, at the origin and it will be denoted by $\phi^{(i)}(\rho, \xi)$. It was explained in some detail in previous papers [5, 15-18] that this potential may be expressed as the sum of three terms which are written here as

$$\phi^{(i)}(\rho, \xi) = \xi e_i \phi_0(\rho) + \phi_a^{(i)}(\rho) + \phi_d^{(i)}(\rho, \xi). \tag{2.1}$$

$\phi_0(\rho)$ is the potential change at distance ρ due to a unit point charge at the origin $\rho = 0$, under the condition that no alteration in the mean charge distribution σ occurs on the i.h.p., when the unit charge is placed at the origin. $\phi_a^{(i)}(\rho)$, the so-called disc potential, is the change in potential at distance ρ, due to the removal of the charge of density σ from the exclusion area on the i.h.p. surrounding the ion i at the origin. Both $\phi_0(\rho)$ and $\phi_a^{(i)}(\rho)$ are independent of the charging parameter ξ. The third term $\phi_d^{(i)}(\rho, \xi)$ which proves to be the most difficult to determine, is the potential change at ρ due to the re-distribution of surface charge beyond the exclusion area when ion i is placed at the origin. These three potentials are so defined that all other accompanying changes in the charge distributions, both in the non-aqueous phase and in the diffuse layer, are automatically taken into account. The potential due to ion j, charge ξe_j, which corresponds to eqn (2.1) is

$$\phi^{(j)}(\rho, \xi) = \xi e_j \phi_0(\rho) + \phi_a^{(j)}(\rho) + \phi_d^{(j)}(\rho, \xi). \tag{2.2}$$

The reader is referred to the earlier papers [5, 15-18] for a full discussion of the physical basis of the relation (2.1) or (2.2).

Suppose now that ion i, charge e_i, and ion j, charge e_j, are situated on the i.h.p., at separation ρ. We shall consider the approximate forms for the pair correlation function which are based on eqn (3.14) or (3.15). These are obtained by retaining only the first term on the right-hand sides of the equivalent formulae I(4.8) and I(4.13)

respectively. Thus fluctuation potentials of the type $\phi_{12}^{(ij)}$, as introduced in paper I section 4, are ignored. Alternatively, as explained in I section 3, self-atmospheres of ions i and j are assumed additive and certain small terms relating to ion size are omitted. If we make use of eqn (2.1) and (2.2), the formula I(3.14) for the pair correlation function becomes

$$-kT \ln \left[g^{(ij)}(\rho)/g^{(ij)}(\rho, \xi = 0) \right] = \int_0^1 \left[e_j \phi^{(i)}(\rho, \xi) + e_i \phi^{(j)}(\rho, \xi) \right] d\xi$$

$$= e_i e_j \phi_0(\rho) + \left[e_j \phi_a^{(i)}(\rho) + e_i \phi_a^{(j)}(\rho) \right] + \int_0^1 \left[e_j \phi_d^{(i)}(\rho, \xi) + e_i \phi_d^{(j)}(\rho, \xi) \right] d\xi \quad (2.3)$$

recalling that omission of ξ denotes $\xi = 1$. On the other hand, use of eqn I(3.15) yields

$$-kT \ln \left[g^{(ij)}(\rho)/g^{(ij)}(\rho, \xi = 0) \right] = \tfrac{1}{2} \left[e_j \phi^{(i)}(\rho) + e_i \phi^{(j)}(\rho) \right]$$

$$= e_i e_j \phi_0(\rho) + \tfrac{1}{2} \left[e_j \phi_a^{(i)}(\rho) + e_i \phi_a^{(j)}(\rho) \right] + \tfrac{1}{2} \left[e_j \phi_d^{(i)}(\rho) + e_i \phi_d^{(j)}(\rho) \right]. \quad (2.4)$$

Now the leading terms in $\phi_d^{(i)}(\rho, \xi)$ and $\phi_d^{(j)}(\rho, \xi)$ are proportional to ξ and therefore the second integral in eqn (2.3) can be approximated by the last term in (2.4). However, the contributions to the right-hand sides of eqn (2.3) and (2.4) from the disc potential appear to differ by a factor of $\tfrac{1}{2}$. The origin of this disparity lies in the way in which ion-size has been taken into account. The detailed analysis in I section 3 shows that in the process of charging simultaneously ions i and j to obtain eqn (2.3), both ions of the pair are assigned a size, while all other ions are treated as point charges. Eqn (2.4) is obtained from eqn I(3.15), which becomes identical with eqn I(4.13). When the higher order fluctuation potential $\phi_{12}^{(ij)}$ is ignored, eqn I(4.13) in turn is derived from eqn I(4.11), which is based on charging either ion i only or ion j only and taking a suitable mean. At the end of I section 3, we described briefly the process of charging a single ion, leading to eqn I(3.18). Here only the " central " ion, which is being charged, is given a size, while all other ions are treated as point charges. The disc potential terms on the right-hand sides of eqn (2.3) and (2.4) refer, therefore, to different radii of the exclusion discs, those in eqn (2.4) being the larger. It does not seem possible to decide which of eqn (2.3) and (2.4) is the better approximation, without examining the higher order fluctuation potential $\phi_{12}^{(ij)}$. We should note that the potentials $\phi_d(\rho)$ will also differ in eqn (2.3) and (2.4), those in (2.3) being the larger.

The disc potential functions $\phi_a^{(i)}(\rho)$ and $\phi_a^{(j)}(\rho)$ depend on the mean charge density on the i.h.p. and on the ion sizes. If ions i and j carry charge of the same valency but opposite in sign and have equal exclusion areas, then $e_j \phi_a^{(i)}(\rho) = -e_i \phi_a^{(j)}(\rho)$, so that the disc potential terms cancel out in both eqn (2.3) and (2.4). In contrast, if eqn I(3.18) were applied to such oppositely charged ions i and j situated on the i.h.p., then

$$-kT \ln \left[g^{(ij)}(\rho)/g^{(ij)}(\rho, \xi_1 = 1, \xi_2 = 0) \right] = e_i e_j \phi_0(\rho) + e_j \phi_a^{(i)}(\rho) + e_j \phi_d^{(i)}(\rho) \quad (2.5)$$

which has a spurious non-vanishing disc potential term. This illustrates that eqn I(3.18) lacks symmetry in the pair correlation function. It should be stressed that the leading term on the right-hand side of eqn (2.5), $e_i e_j \phi_0(\rho)$, has the required symmetry.

With only one ion species i on the i.h.p., $j = i$ and eqn (2.3) simplifies to

$$-kT \ln \left[g^{(ii)}(\rho)/g^{(ii)}(\rho, \xi = 0) \right] = e_i^2 \phi_0(\rho) + 2 e_i \phi_a^{(i)}(\rho) + 2 e_i \int_0^1 \phi_d^{(i)}(\rho, \xi) \, d\xi, \quad (2.6)$$

whereas (2.4) reduces to

$$-kT \ln \left[g^{(ii)}(\rho)/g^{(ii)}(\rho, \xi = 0) \right] = e_i \phi^{(i)}(\rho) = e_i^2 \phi_0(\rho) + e_i \phi_a^{(i)}(\rho) + e_i \phi_d^{(i)}(\rho). \qquad (2.7)$$

Here again the radius of the exclusion disc in eqn (2.7) must exceed that in eqn (2.6). In the previous work, where the adsorption of only one ion species on the i.h.p. was considered, the pair correlation function was based on eqn I(3.18). For species i this leads to eqn (2.7) provided $g^{(ii)}(\rho, \xi = 0)$, the pair correlation function when both ions of the pair at separation ρ are uncharged, is replaced by $g^{(ii)}(\rho, \xi_1 = 1, \xi_2 = 0)$, the correlation function when only one of the pair of i ions is uncharged. We have shown in I section 4 that the difference can be expressed in terms of the higher order fluctuation potential $\phi_{12}^{(ii)}$. Thus, to the approximation where $\phi_{12}^{(ii)}$ is neglected, either eqn (2.6) or (2.7) can be used.

The potentials $\phi_0(\rho)$ and $\phi_a^{(i)}(\rho)$ in (2.7) have been expressed in integral form and numerical values obtained at a metal/electrolyte interface.[16-18] An approximate method of determining the potential $\phi_d^{(i)}(\rho)$ in eqn (2.7), is as follows. The change in the surface density of ions at distance ρ, due to the presence of ion i at $\rho = 0$, is

$$\Delta \sigma^{(i)}(\rho) = e_i \nu^{(i)} [g^{(ii)}(\rho) - 1], \qquad (2.8)$$

where $\nu^{(i)}$ is the mean surface density of i ions on the i.h.p. Substituting for $g^{(ii)}(\rho)$ from eqn (2.7), assuming $g^{(ii)}(\rho, \xi = 0) = 1$ and retaining only linear terms in the fluctuation potential $\phi^{(i)}(\rho)$, we obtain

$$\Delta \sigma^{(i)}(\rho) \approx -\frac{e_i^2 \nu^{(i)}}{kT} \phi^{(i)}(\rho). \qquad (2.9)$$

The potential $\phi_d^{(i)}(\rho)$ can be written as

$$\phi_d^{(i)}(\rho) = 2\pi \int_{a_i}^{\infty} \rho' \Delta \sigma^{(i)}(\rho') M(\rho, \rho') \, d\rho'$$

$$\approx -\frac{2\pi e_i^2 \nu^{(i)}}{kT} \int_{a_i}^{\infty} \rho' \phi^{(i)}(\rho') M(\rho, \rho') \, d\rho' \qquad (2.10)$$

where a_i is the radius of the exclusion disc surrounding ion i and $M(\rho, \rho')$ is defined as the change in potential at a point on the i.h.p., distant ρ from the origin, due to a charged ring on the i.h.p. with centre at the origin, of radius ρ' and having unit total charge. On substituting the second equation in eqn (2.7), (2.10) becomes a linear integral equation [19] in $\phi_d^{(i)}(\rho)$, bearing in mind that $\phi_0(\rho)$ and $\phi_a^{(i)}$ can be calculated. Approximate solutions of this integral equation have been obtained at the mercury/ aqueous electrolyte interface.[16] This method of finding $\phi_d^{(i)}(\rho)$ cannot be extended directly to the determination of $\phi_d^{(i)}(\rho, \xi)$ in eqn (2.6), when both i ions of the pair at separation ρ are being charged simultaneously. When eqn (2.4) is used with different ion species i and j, two coupled linear integral equations in $\phi_d^{(i)}(\rho)$ and $\phi_d^{(j)}(\rho)$ are obtained. In the following section we shall develop an approximate, but simpler, ion-pairing method of estimating $\phi_d^{(i)}(\rho)$, in the case of two oppositely charged ion species on the i.h.p.

3. ION-PAIRING THEORY IN TWO DIMENSIONS

We shall employ here the "unlike-partners" only definition of an ion-pair as described by Poirier and DeLap.[11] Two species of oppositely charged univalent ions i and j, having mean number densities $\nu^{(i)}$ and $\nu^{(j)}$ (where in general $\nu^{(i)} \neq \nu^{(j)}$) and carrying charges e_i and e_j (where $e_i = -e_j$), respectively, are assumed to be situated on the i.h.p. Let $G^{(ij)}(\rho) d\rho$ be the probability of finding an ion j at distance

ρ from an ion i, in a circular ring of thickness $d\rho$, under the following special restriction. The condition is imposed that when the ion-pair i and j are on the i.h.p. at separation ρ then *neither* ion has another unlike partner at any distance less than ρ. For simplicity the distance of nearest approach between ions i and j will be equated to a_i, the radius of the exclusion area of ion i. Then

$$p^{(ij)}(\rho) = \int_{a_i}^{\rho} G^{(ij)}(\rho')\, d\rho', \tag{3.1}$$

is the probability of finding ion j at any distance ρ' from the ion i in the range (a_i, ρ) such that at each distance ρ' neither i nor j ion has a second unlike partner at a distance less than ρ'. The quantity

$$P^{(i)}(\rho) = 1 - \int_{a_i}^{\rho} G^{(ij)}(\rho')\, d\rho', \tag{3.2}$$

is the probability that ion j is *not* found in the range (a_i, ρ) subject to no other unlike partner in the specified vicinity as described above. $P^{(j)}(\rho)$ is defined similarly. The function $G^{(ij)}(\rho)$ is given by

$$G^{(ij)}(\rho) = 2\pi\rho v^{(j)} g^{(ij)}(\rho) P^{(i)}(\rho) P^{(j)}(\rho), \tag{3.3}$$

where $g^{(ij)}(\rho)$ is the pair correlation function between ions i and j which was discussed in the preceding section. The factors $P^{(i)}(\rho)$ and $P^{(j)}(\rho)$ are required to ensure that ions i and j do not have another unlike ion partner within a radius ρ on the i.h.p. The corresponding probability of finding an ion i at distance ρ from ion j is

$$G^{(ji)}(\rho) = 2\pi\rho v^{(i)} g^{(ji)}(\rho) P^{(i)}(\rho) P^{(j)}(\rho). \tag{3.4}$$

We now apply the condition that the pair correlation function for ions i and j on the i.h.p. is symmetrical with respect to i and j, i.e.,

$$g^{(ij)}(\rho) = g^{(ji)}(\rho). \tag{3.5}$$

From eqn (3.3), (3.4) and (3.5)

$$v^{(i)} G^{(ij)}(\rho) = v^{(j)} G^{(ji)}(\rho). \tag{3.6}$$

Using eqn (3.6), $P^{(j)}(\rho)$ may be expressed in terms of $P^{(i)}(\rho)$. Thus

$$P^{(j)}(\rho) = 1 - \int_{a_i}^{\rho} G^{(ji)}(\rho')\, d\rho' = 1 - \frac{v^{(i)}}{v^{(j)}} \int_{a_i}^{\rho} G^{(ij)}(\rho')\, d\rho'$$

$$= 1 - \frac{v^{(i)}}{v^{(j)}}[1 - P^{(i)}(\rho)]. \tag{3.7}$$

On substituting eqn (3.3) into (3.2), differentiating the resulting form for eqn (3.2) with respect to ρ and making use of eqn (3.7), we obtain

$$\frac{dP^{(i)}(\rho)}{d\rho} = -2\pi\rho v^{(j)} g^{(ij)}(\rho) P^{(i)}(\rho) \left[1 - \frac{v^{(i)}}{v^{(j)}} + \frac{v^{(i)}}{v^{(j)}} P^{(i)}(\rho) \right]. \tag{3.8}$$

Integration yields

$$P^{(i)}(\rho) = \frac{[v^{(j)} - v^{(i)}]\, e^{-B}}{v^{(j)} - v^{(i)}\, e^{-B}}, \tag{3.9}$$

where, if

$$\Delta v = v^{(j)} - v^{(i)}, \tag{3.10}$$

$$B = 2\pi\Delta v \int_{a_i}^{\rho} \rho' g^{(ij)}(\rho')\, d\rho'. \tag{3.11}$$

From eqn (3.7)

$$P^{(i)}(\rho)P^{(j)}(\rho) = \frac{\Delta v}{v^{(j)}}P^{(i)}(\rho)\left[1+\frac{v^{(i)}}{\Delta v}P^{(i)}(\rho)\right],\qquad(3.12)$$

and therefore, making use of eqn (3.9), the expression (3.3) for $G^{(ij)}(\rho)$ can be expressed in terms of the pair correlation function, namely

$$G^{(ij)}(\rho) = 2\pi\rho v^{(j)}g^{(ij)}(\rho)(\Delta v)^2\frac{e^{-B}}{[v^{(j)}-v^{(i)}e^{-B}]^2}.\qquad(3.13)$$

If ions i and j are assigned equal exclusion areas on the i.h.p. then their disc potential functions are equal and eqn (2.3) simplifies to

$$-kT\ln\left[g^{(ij)}(\rho)/g^{(ij)}(\rho,\xi=0)\right] = e_i e_j\phi_0(\rho)+e_i\int_0^1\Delta\phi_d(\rho,\xi)\,d\xi,\qquad(3.14)$$

where $\Delta\phi_d = \phi_d^{(j)}-\phi_d^{(i)}$. In the Bjerrum–Fuoss theory of strong electrolytes,[8, 9] a minimum is sought in the function which corresponds to our $G^{(ij)}(\rho)$ at $\rho = \rho_c$, say. For $\rho < \rho_c$ it is assumed that the ion pair correlation function is given by its form at infinite dilution of electrolyte (characterised by the unscreened basic Coulomb interaction energy of an ion pair). In the present problem, the analogous approximation is to retain the dominant term $e_i e_j\phi_0(\rho)$ only on the right-hand side of eqn (3.14), neglecting the integral of the potential $\Delta\phi_d$. Thus we replace eqn (3.14) by

$$g^{(ij)}(\rho) = g^{(ij)}(\rho,\xi=0)\exp\left[-\frac{e_i e_j\phi_0(\rho)}{kT}\right].\qquad(3.15)$$

On equating to zero the derivative of eqn (3.13) with respect to ρ and making use of eqn (3.11) and (3.15) we obtain the relation

$$0 = 1+\frac{\rho e_i}{kT}\frac{d\phi_0(\rho)}{d\rho}-2\pi\rho^2\Delta v g^{(ij)}(\rho)\frac{[1+v^{(i)}e^{-B}/v^{(j)}]}{[1-v^{(i)}e^{-B}/v^{(j)}]}.\qquad(3.16)$$

Assuming a solution exists, $G^{(ij)}(\rho)$ is a minimum at the root $\rho = \rho_c$ of this equation.

In a previous paper[12] an electron-transfer electrode reaction at a mercury–aqueous electrolyte interface was considered for a model in which the surface densities on the i.h.p. of reacting and non-reacting ion species i and j, respectively, were such that $v^{(i)} \ll v^{(j)}$. Also the pair correlation function between i and j was based on eqn I(3.18) so that $e_i\phi_0(\rho)$ in eqn (3.15)-(3.16) was replaced by the sum $e_i\phi_0(\rho)+\phi_a^{(i)}(\rho)$, but it has been explained above that this inclusion of the disc potential gives the poorer approximation. The influence of ion pairing between species i and j on the kinetics of the electron transfer was investigated. The quantity required, $\phi_d^{(i)}(0)$, is the mean potential at the centre of ion i due to the fluctuation in surface charge density on the i.h.p. beyond the exclusion radius a_i of the reacting i ion. This can be obtained from the first equation in (2.8) by putting $\rho = 0$. Since $M(0,\rho') = \phi_0(\rho')$[5] eqn (2.8) yields

$$\phi_d^{(i)}(0) = 2\pi\int_{a_i}^\infty\rho'\Delta\sigma^{(i)}(\rho')\phi_0(\rho')\,d\rho'.\qquad(3.17)$$

An approximate expression for eqn (3.17) was obtained as follows.[12] A solution to eqn (3.16) was found at $\rho = \rho_c$, say, and it was assumed that

$$g^{(ij)}(\rho) = 1,\ \rho > \rho_c.\qquad(3.18)$$

This means that the density of the non-reacting j ions on the i.h.p. in the vicinity of a reacting i located at the origin $\rho = 0$ is assigned its mean value beyond the distance

$\rho = \rho_c$. The mean surface charge density σ on the i.h.p. was then imagined to be removed from the disc of radius ρ_c, centre at origin. A "fraction of a j ion", $\rho^{(ij)}(\rho_c)$, where $p^{(ij)}(\rho)$ is defined by eqn (3.1), was then brought into the area between $p = a_i$ and $\rho = \rho_c$ to form an ion-pair with ion i situated at $\rho = 0$. This process yields for eqn (3.17) the relation

$$\phi_d^{(i)}(0) = -2\pi\sigma \int_{a_i}^{\rho_c} \rho' \phi_0(\rho')\,\mathrm{d}\rho' + \phi_p^{(i)}(0), \qquad (3.19)$$

where

$$\phi_p^{(i)}(0) = e_j \int_{a_i}^{\rho_c} G^{(ij)}(\rho')\phi_0(\rho')\,\mathrm{d}\rho'. \qquad (3.20)$$

The first term in eqn (3.19) may be added to the disc potential at the origin $\phi_a^{(i)}(0)$ to give a disc potential corresponding to a radius ρ_c, which we denote by

$$\phi_{\rho_c}^{(i)}(0) = -2\pi\sigma \int_0^{\rho_c} \rho' \phi_0(\rho')\,\mathrm{d}\rho'. \qquad (3.21)$$

The approximations in the above method of determining eqn (3.17) lie in the assumption eqn (3.18) and in the use of the function $G^{(ij)}(\rho)$ in eqn (3.20). From the definition of $G^{(ij)}(\rho)$, only one ion of species j is permitted in the area $\rho = a_i$ to $\rho = \rho_c$. Also no account is taken of the possible presence of a second i ion in this area. The errors in $\phi_p^{(i)}(0)$ due to these two restrictions partly compensate each other.

In the adaptation of the theory described above to an ionised monolayer at an air/water interface, which is described in the next section of this paper, no solution is found to eqn (3.16), which must, therefore, be replaced by some other criterion which gives a cut-off distance ρ_c. In the three relations eqn (3.18), (3.20) and (3.21), which are still used, the distance ρ_c is fixed by assuming that the magnitude of the quantity $e_i^2\phi_0(\rho_c)$ is equal to or less than kT. Also in the formulae (3.11) and (3.13) we shall substitute (3.15) for $g^{(ij)}(\rho)$ and assume $g^{(ij)}(\rho, \xi = 0) = 1$. The use in eqn (3.20) of the resulting approximate expression for $G^{(ij)}(\rho)$ yields the potential $\phi_p^{(i)}(0)$. An approximation to $g^{(ij)}(\rho)$ which is better than eqn (3.15) would be based on eqn (2.3) or on the simpler version eqn (3.14). This involves determining the potential functions $\phi_d^{(i)}(\rho, \xi)$ and $\phi_d^{(j)}(\rho, \xi)$ in terms of integrals similar to eqn (3.20) with $\phi_0(\rho)$ replaced by $M(\rho, \rho')$ [which was introduced in eqn (2.8)], but it seems premature to attempt this formidable task, bearing in mind that the use of $G^{(ij)}(\rho)$ in eqn (3.20) is an approximation.

4. APPLICATION TO IONIZED MONOLAYER

The model of the electric double layer at a completely ionized monolayer adopted here has been described in a previous paper [7] and is illustrated in fig. 1. We consider a film of sodium octadecyl sulphate spread at the air or oil/aqueous electrolyte interface. The charge centres of the head-group ions SO_4^- are situated on the primary plane, which corresponds to the i.h.p. in the inner region at the mercury/aqueous electrolyte system. In principle, it is sufficient to specify the density of SO_4^- on the primary plane and the method of statistical mechanics should provide the distribution of adsorbed Na^+ ions. It is convenient to regard these adsorbed ions as divided into two groups. In one group the Na^+ is bound to a SO_4^- and its centre is situated on the boundary between the monolayer or inner region and the diffuse layer, commonly known as the outer Helmholtz plane or o.h.p. The other group consists of mobile Na^+ ions which are able to penetrate into the monolayer region between the head-group ions. By treating each group as part of a surface phase, one assigns a chemical

potential to an adsorbed ion and this is equated to the chemical potential of the ion in the bulk electrolyte to give an adsorption isotherm. The chemical potential of the adsorbed ion will have various electrical and entropic contributions, which depend on the particular geometrical and dielectric model assumed for the monolayer region. The derivation of these isotherms will be the subject matter of later papers. Here we wish to illustrate the use of ion-pairing theory to evaluate the discreteness-of-charge potentials. We, therefore, specify the surface density of adsorbed Na^+ ions in each group and, for simplicity, imagine the centres of the mobile ions to be situated in the same plane as the SO_4^- ions, i.e., on the primary plane. No other ion species from the aqueous substrate is permitted to cross the o.h.p. into the monolayer region.
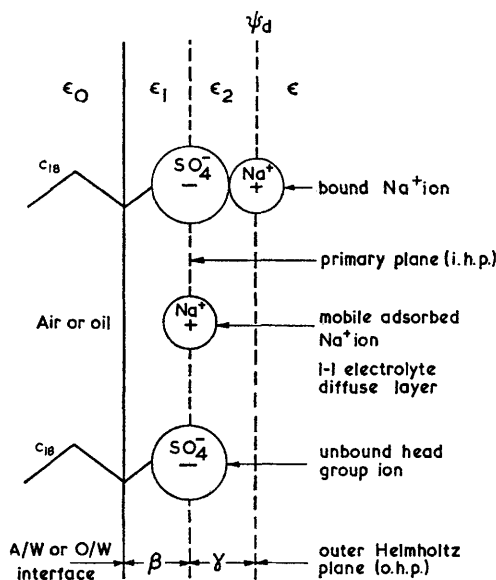

FIG. 1.—Model of electric double layer for completely ionized monolayer.

The " inner zone " and " outer zone " of the monolayer region (fig. 1) have thicknesses β and γ respectively. The monolayer region is inhomogeneous with a dielectric constant increasing with distance from the non-aqueous phase, but we have chosen a simple step-function variation. The mean dielectric constants of the (isotropic) non-aqueous medium, inner and outer zones and aqueous medium are ε_0, ε_1, ε_2 and ε respectively. Any local dipole effects attributed to the ion-pairs SO_4^--bound Na^+ are ignored. Let $v^{(i)}$ be the surface density of mobile Na^+ ions and $v^{(J)}$ that of the unpaired SO_4^- ions (those unbound to Na^+ ions). Introducing the reciprocals $A^{(i)} = 1/v^{(i)}$ and $A^{(J)} = 1/v^{(J)}$, i.e., the areas per mobile Na^+ ion and unpaired SO_4^- ion respectively, the surface charge density on the primary plane is

$$\sigma = -e_0\left(\frac{1}{A^{(J)}} - \frac{1}{A^{(i)}}\right), \qquad (4.1)$$

where e_0 is the proton charge and $A^{(J)} < A^{(i)}$. For a 1–1 electrolyte in the aqueous phase, application of the Gouy–Chapman theory to the diffuse layer yields for the potential at the o.h.p.

$$\psi_d = \frac{2kT}{e_0} \sinh^{-1}\left(\frac{2\pi e_0 \sigma}{\varepsilon kT \kappa}\right), \qquad (4.2)$$

where κ is the Debye–Hückel parameter. If c is the electrolyte concentration in mol dm^{-3} and N Avogadro's number, $\kappa = (8\pi e_0^2 Nc/\varepsilon \, kT)^{\frac{1}{2}}$.

We require the basic potential $\phi_0(\rho)$ which depends on β and γ, the dielectric constants of the different regions, the potential ψ_d and the electrolyte concentration c. If linear terms only in the self-atmosphere of fluctuation potential are retained, then for the particular monolayer model chosen here [5]

$$\phi_0(\rho) = \frac{2}{(\varepsilon_1 + \varepsilon_2)} \int_0^\infty J_0(k\rho) H(k) \, dk, \tag{4.3}$$

where J_n denotes the Bessel function of the first kind of order n, and introducing

$$\alpha = \frac{1}{2}\left(1 + \frac{k^2}{\kappa^2}\right)^{\frac{1}{2}}, \qquad \xi = \tanh^2\left(\frac{e_0\psi_d}{4kT}\right), \qquad h = 1 + \frac{2\xi}{\alpha(1-\xi)[2\alpha+1-\xi(2\alpha-1)]},$$

$$f_{21} = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1}, \qquad f' = \frac{\varepsilon}{\varepsilon_2}\left(1 + \frac{\kappa^2}{k^2}\right)^{\frac{1}{2}}, \qquad f_2'' = \frac{(1-hf')}{(1+hf')}, \tag{4.4}$$

$$D = \varepsilon_0[1 - f_{21}\,e^{-2k\beta} - f_2''\,e^{-2k\gamma}(f_{21} - e^{-2k\beta})] +$$
$$\varepsilon_1[1 + f_{21}\,e^{-2k\beta} - f_2''\,e^{-2k\gamma}(f_{21} + e^{-2k\beta})],$$

$$H(k) = \frac{(1 + f_2''\,e^{-2k\gamma})}{D}[\varepsilon_0(1 - e^{-2k\beta}) + \varepsilon_1(1 + e^{-2k\beta})]. \tag{4.5}$$

The potential change at the centre of a disc of radius a_i on the primary plane, due to the removal of the surface charge density σ from the disc is given by

$$\phi_a^{(i)}(0) = -\frac{4\pi\sigma a_i}{(\varepsilon_1 + \varepsilon_2)} \int_0^\infty \frac{J_1(ka)}{k} H(k) \, dk, \tag{4.6}$$

where σ is related to ψ_d by eqn (4.2). It is seen that this disc potential depends on the radius a_i as well as on the different parameters listed above for $\phi_0(\rho)$.

Substituting the expression (4.3) for $\phi_0(\rho)$ into eqn (3.15) and choosing $g^{(ij)}(\rho, \xi = 0) = 1$ the function $G^{(ij)}(\rho)$ is determined numerically from eqn (3.11) and (3.13). The fraction of an ion-pair formed between Na$^+$ and SO$_4^-$ in the range $\rho = a_i$ to $\rho = \rho_c$, $p^{(ij)}(\rho_c)$, is given by eqn (3.1), where ρ_c is obtained from the condition $e_0\phi_0(\rho_c)/kT = \frac{1}{4}, \frac{1}{2}$ or 1. Typical computed values of ρ_c and $p^{(ij)}(\rho_c)$ are shown in table 1. The areas of unpaired SO$_4^-$ and Na$^+$ ions, $A^{(j)}$ and $A^{(i)}$ respectively, have been varied under the condition that the sum of the densities of these two ions on the primary plane remain fixed at

$$\frac{1}{A^{(j)}} + \frac{1}{A^{(i)}} = \frac{1}{550}A^{-2}. \tag{4.7}$$

Values are given of the charge density σ on the primary plane, of the potential at the o.h.p. and of the two disc potentials $\phi_a^{(i)}(0)$, where a_i is the exclusion radius of Na$^+$ and $\phi_{\rho_c}^{(i)}(0)$, where ρ_c is the cut-off distance in our ion-pairing model. These two potentials are expressed in energy units of kT (1 kT corresponds to 24.4 mV at $T = 10°$C, one of the temperatures in the experiments of Mingins et al.)[20] The potential $\phi_p^{(i)}(0)$ at the centre of Na$^+$, which is due to the formation of ion-pairs with the SO$_4^-$, is obtained by numerical integration of eqn (3.20). The main contribution to the discreteness-of-charge potential at the centre of an Na$^+$ ion, situated on the primary plane, is the sum $\phi_p^{(i)}(0) + \phi_{\rho_c}^{(i)}(0)$ consisting of two terms with opposite

signs. We find that the change in $\phi_p'^{(i)}(0)$ is very much less than that in $\phi_{\rho_c}^{(i)}(0)$, with variation in either σ or ρ_c. The above sum provides a negative potential energy term for the Na^+ ion, which decreases in magnitude with increase in $|\sigma|$. When the areas $A^{(i)}$ and $A^{(j)}$ approach each other, the surface charge density σ tends to zero and this produces the sharp drop in $\phi_{\rho_c}^{(i)}(0)$ shown in table 1. The ideal situation in the ion-pairing approximation would be one where $p^{(ij)}(\rho_c) \approx 1$, *i.e.*, each Na^+ ion is virtually paired-off with a SO_4^- ion. It is observed that the values of the ion-pairing fraction $p^{(ij)}(\rho_c)$ calculated in table 1 all exceed $\frac{1}{2}$. As expected, for given $\phi_0(\rho_c)$ this fraction decreases with increase in the concentration ratio of Na^+ to SO_4^-. As ρ increases, the function $G^{(ij)}(\rho)$ diminishes more rapidly than $\rho g^{(ij)}(\rho)$, with which it should

TABLE 1.—ION-PAIRING CHARACTERISTICS BETWEEN Na^+ AND SO_4^- ON THE PRIMARY PLANE IN MONOLAYER AT AIR/WATER INTERFACE

$T = 10°C$, $c = 0.0316 \text{ mol dm}^{-3}$ (1–1 electrolyte), $\varepsilon_0 = 1$, $\varepsilon_1 = 20$, $\varepsilon_2 = 40$, $\varepsilon = 84.15$, $\beta = 3$, $\gamma = 2$, $a_i = 5$ (all distances in Å and areas in (Å)^2). Areas per ion $A^{(j)}(SO_4^-)$, $A^{(i)}(NA^+)$; ρ_c accurate to nearest $\frac{1}{4}$Å, σ in $\mu C \text{ cm}^{-2}$, ψ_d in mV.

$A^{(j)}$	$A^{(i)}$	σ	ψ_d	$\dfrac{e_0^2 \phi_0(a_i)}{/kT}$	$\dfrac{e_0 \phi_a^{(i)}(0)}{/kT}$	d_m
600	6600	−2.42	−48.1	2.35	0.73	26.3
700	2567	−1.66	−35.4	2.46	0.50	28.4
800	1760	−1.09	−24.3	2.53	0.34	30.4
900	1414	−0.65	−14.8	2.57	0.20	32.2
1000	1212	−0.29	−6.7	2.59	0.09	34.0

$(e_0^2 \phi_0(\rho_c)/kT = 1)$

$A^{(j)}$	$A^{(i)}$	ρ_c	$p^{(ij)}(\rho_c)$	$\dfrac{e_0 \phi_p^{(i)}(0)}{/kT}$	$\dfrac{e_0 \phi_{\rho_c}^{(i)}(0)}{/kT}$	$\dfrac{\rho_c}{/d_m}$
600	6600	8.75	0.70	−1.24	1.08	0.33
700	2567	9.25	0.68	−1.24	0.79	0.33
800	1760	9.50	0.64	−1.20	0.54	0.31
900	1414	9.75	0.60	−1.14	0.33	0.30
1000	1212	9.75	0.55	−1.05	0.15	0.29

$(e_0^2 \phi_0(\rho_c)/kT = \frac{1}{2})$

600	6600	12.5	0.86	−1.34	1.34	0.48
700	2567	13.3	0.83	−1.34	1.00	0.47
800	1760	14.0	0.79	−1.31	0.70	0.46
900	1414	14.3	0.74	−1.24	0.43	0.44
1000	1212	14.5	0.68	−1.15	0.20	0.43

$(e_0^2 \phi_0(\rho_c)/kT = \frac{1}{4})$

600	6600	17.0	0.94	−1.37	1.55	0.65
700	2567	18.25	0.92	−1.37	1.17	0.64
800	1760	19.5	0.88	−1.34	0.83	0.64
900	1414	20.0	0.84	−1.28	0.51	0.62
1000	1212	20.5	0.78	−1.19	0.24	0.60

be compared. For example, from $\rho = 5$ to $\rho = 10$ Å, $G^{(ij)}(\rho)$ drops by a factor of ~ 11, compared with ~ 2.5 in $\rho g^{(ij)}(\rho)$. This follows from eqn (3.3) since $G^{(ij)}(\rho)$ differs from $\rho g^{(ij)}(\rho)$ by the factors $P^{(i)}(\rho)$ and $P^{(j)}(\rho)$, both of which are fractions diminishing with increase in ρ. The resulting rapid decrease in $G^{(ij)}(\rho)$ with increase in ρ leads to the property that the expression (3.20) for $\phi_p^{(i)}(0)$ increases with ρ_c only slightly for given areas $A^{(i)}$ and $A^{(j)}$.

The present method of evaluating the discreteness-of-charge effect at an ionized monolayer supersedes the earlier attempt by Levine *et al.*[6] In the latter work the potential which corresponds here to the sum $\phi_p^{(i)}(0) + \phi_{p_c}^{(i)}(0)$, gave a negative potential energy term for the Na$^+$ ion which increased in magnitude with increase in $|\sigma|$ by $\sim 2.5\,kT$ over a range in $A^{(j)}$ of 100 to 1000 Å^2. Here we calculate the opposite trend of $\sim -1\,kT$ in a range 600 to 1000 Å^2 for $A^{(j)}$. However, in place of condition (4.7), an adsorption isotherm for the Na$^+$ ion was assumed and the ratio $A^{(i)}/A^{(j)}$ was found to vary from 1.1 to 3.2 as $A^{(j)}$ increased from 100 to 1000 Å^2. It is observed that here $|\phi_p^{(i)}(0)| > \phi_{p_c}^{(i)}(0)$ for such area ratios. Indeed $\phi_{p_c}^{(i)}(0) \to 0$ as $A^{(i)} \to A^{(j)}$, *i.e.*, the ion-pairing term $\phi_p^{(i)}(0)$ becomes dominant when the density of Na$^+$ ions on the i.h.p. approaches that of the SO$_4^-$ ion. The quantity $|\phi_p^{(i)}(0)|$ will reach a maximum when $p^{(ij)}(\rho_c) = 1$ and it appears that the energy associated with $\phi_p^{(i)}(0)$ will not exceed $-1.5\,kT$ for the relevant parameters chosen. Larger ion-pairing energies are obtained by choosing a smaller distance of nearest approach between Na$^+$ and SO$_4^-$ ions or smaller dielectric constants for the inner region. To obtain more information on the trend of the discreteness-of-charge potentials an adsorption isotherm for the Na$^+$ ion is required, but this is not attempted here.

The approximations in the calculations shown in table 1 need to be discussed. The function $G^{(ij)}(\rho)$ is so defined that only one SO$_4^-$ ion is allowed in the region $a_i < \rho < \rho_c$. To test whether this condition is reasonable, we have compared in the table ρ_c with the nearest neighbour distance d_m between SO$_4^-$ ions for the different areas $A^{(j)}$, assuming regular two-dimensional hexagonal close packing of these ions. For $e^2\phi_0(\rho_c)/kT = \frac{1}{4}$, the ratio ρ_c/d_m is becoming large enough to cast doubt upon the above restriction. Of course the condition (3.18) becomes a better approximation the larger the value of ρ_c, but this improvement is offset by the increase in the probability that a second SO$_4^-$ or Na$^+$ ion is situated in the region $a_i < \rho < \rho_c$. The usefulness of the ion-pairing method is reduced by the absence of a minimum in $G^{(ij)}(\rho)$, as is found in the Bjerrum–Fuoss theory for homogeneous electrolytes.[8-10] Nevertheless, it does provide values for $\phi_p^{(i)}(0)$ and hence $\phi_d^{(i)}(0)$ which are otherwise difficult to determine in the case of two oppositely charged ion species on the i.h.p.

The discreteness-of-charge potentials obtained here are required in order to find an adsorption isotherm for the adsorbed counter-ions. A knowledge of the adsorption isotherm permits the determination of the surface potential and surface pressure of an ionized monolayer as functions of surface density of SO$_4^-$ ions, the electrolyte concentrations and the temperature. The work on such calculations, which can be compared with experiment, will be reported in later papers.

[1] G. R. Féat and S. Levine, *J.C.S. Faraday II*, 1977, **73**, 1345.
[2] C. W. Outhwaite, *Mol. Phys.*, 1974, **27**, 561.
[3] C. A. Barlow and J. R. Macdonald, *Adv. Electrochem. Electrochem. Eng.*, 1967, **6**, 1.
[4] S. Levine, J. Mingins and G. M. Bell, *J. Electroanalyt. Chem.*, 1967, **13**, 280.
[5] S. Levine, K. Robinson, G. M. Bell and J. Mingins, *J. Electroanalyt. Chem.*, 1972, **38**, 253.
[6] S. Levine, J. Mingins and G. M. Bell, *J. Phys. Chem.*, 1963, **67**, 2095.
[7] G. R. Féat and S. Levine in *Advances in Chemistry Series*, 144, ed. E. D. Goddard (1975), p. 98.
[8] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, 1949), p. 409.
[9] R. M. Fuoss, *Trans. Faraday Soc.*, 1934, **30**, 967.
[10] H. Reiss, *J. Chem. Phys.*, 1956, **25**, 400.
[11] J. C. Poirier and J. H. DeLap, *J. Chem. Phys.*, 1961, **35**, 213.
[12] W. R. Fawcett and S. Levine, *J. Electroanalyt. Chem.*, 1975, **65**, 505.
[13] F. H. Stillinger and R. Lovett, *J. Chem. Phys.*, 1968, **48**, 3858, 3869.

[14] F. H. Stillinger and R. J. White, *J. Chem. Phys.*, 1971, **54**, 3395, 3405.

[15] S. Levine, J. Mingins and G. M. Bell, *Canad. J. Chem.*, 1965, **43**, 2834.

[16] S. Levine and K. Robinson, *J. Electroanalyt. Chem.*, 1973, **41**, 159.

[17] K. Robinson and S. Levine, *J. Electroanalyt. Chem.*, 1973, **47**, 395.

[18] S. Levine, K. Robinson and W. R. Fawcett, *J. Electroanalyt. Chem.*, 1974, **54**, 237.

[19] G. M. Bell and S. Levine, in *Statistical Mechanics, Foundations and Applications*, Proc. I.U.A.P. meeting, Copenhagen, ed. T. A. Bak (Benjamin, New York, 1966).

[20] J. Mingins and B. A. Pethica, *Trans. Faraday Soc.*, 1963, **59**, 1892; *J.C.S. Faraday I*, 1973, **69**, 500.

(PAPER 6/795)