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Jerry Goodisman
Syracuse University

Jean Paul Badiali
University Pierre et Marie Curie

Martin Luc Rosinberg
University Pierre et Marie Curie

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Contribution of the Metal to the Differential Capacity of an Ideally Polarizable Electrode

J.P. Badiali, University Pierre et Marie Curie
M.L. Rosinberg, University Pierre et Marie Curie
J. Goodisman, Syracuse University

Abstract

We consider the response of the metal in the ideally polarizable electrode to charging of the electrode, using a model for the metal surface in contact with the solvent of the electrolyte phase previously presented by us in this journal. We show that the effect of the solvent on the electrons of the metal cannot be considered to be simply that of a repulsive barrier. When the electrode charge varies, $q^M(\text{dip})$, the metal contribution to the double layer, is modified, implying a contribution which varies along the electrocapillary curve. By considering an electrostatic interaction between metal and solvent, we find an acceptable value for the contribution of the metal to the double-layer capacity. Furthermore, the introduction of appropriate parameters for the metals shows that one should expect $C_{\text{Ga}} > C_{\text{Hg}}$ at the potential of zero charge, in accord with experimental observations. The influence of the choice of parameters, particularly those which express the interpenetration of metal and solvent in our model, is discussed as well as other possible models. The different contributions of electrons of different metals probably need to be considered in evaluating models for the inner-layer contribution to the capacity.

Introduction

It is understood that any measurable parameter of a polarizable interface is a combination of properties of the metal, properties of the electrolyte phase, and their interaction, and that these three contributions cannot be separated experimentally. Thus, the idea of a correlation, between the potential of zero charge (pzc) of an ideally polarizable electrode and the electronic work function of the metal, has been accepted since the first work of A.N. Frumkin [1]. However, the work function, being a property of the interface between metal and vacuum, cannot alone characterize the contribution of the metal. The electric dipole layer on the metal surface, due to the non-coincidence of its electronic and ionic charges, is modified by the electrolyte phase. The contribution of this dipole layer to the electrode potential, which we denote by $g^M(\text{dip})$, may be considered to be the sum of X_M , the surface potential of the metal, and δX_m , representing the perturbation of the charge [End of page 73] distribution due to the solution. Bockris et al. [2,3], considering $\sim m$ at the pzc for various metals, have concluded it is negative and of magnitude 0.2-0.5 V. Of course the distributions of charges and molecular dipoles in the solution contribute to the determination of the pzc. Their contribution, which we will designate by $g^S(\text{dip})$, has been calculated for mercury using different models, and seems to be between -0.008 and -0.07V, depending on temperature [4-7]. Thus, the effect of δX_m seems much more important than $g^S(\text{dip})$ at the pzc. However, most electrochemists believe $g^S(\text{dip})$ to vary much more strongly with q_M than δX_m [8], so that only $g^S(\text{dip})$ makes an important contribution to the differential capacity of the electrode.

In a recent article [9], which we shall designate as Part I, we suggested an a priori calculation of δX_m at the pzc. Two models for the metal-solvent interaction were introduced, both giving δX_m of an acceptable size. The effect of changes in the properties of the metal and of the solvent was considered. In the present work, we use those models to calculate the effect of a change in the electrode charge on δX_m and hence the contribution of the metal to the capacity of the electrode. Calculations of the contribution of the electrolyte phase to the capacity and other

properties of the interface use a simplified model of the metal; here we do exactly the reverse. Thus, we do not pretend to calculate the capacity of any real interface. Rather, we hope that our calculations for *different* metals in contact with the *same* electrolyte may indicate whether the variation in properties of the metal itself is an important part of the variation of capacities between different interfaces. We are not concerned with the effect on properties of the interface of dissimilar adsorption of solvent on different metals. Such effects, suggested in the literature, may well be important, but they are properties of the solvent which depend indirectly on properties of the metal. To assess their importance properly, however, one must be sure that the direct contribution of the metal, if important, is taken into account when comparing a model for changed absorption with experiment.

For the contribution of the solvent, various models have been proposed [4,5,7,10]. (Additionally, several authors have attempted to relate the properties of the internal layer to electrostriction in the layer of water in contact with the metal [11]. In the present work, we will neglect such effects on the electronic profile.) Although our calculated capacities cannot be compared directly with experiment, *differences* in capacities for interfaces differing in metal phase may be comparable to differences in experimental capacities, if the electrolyte phase indeed behaves in the same way for these interfaces.

We denote the charge density on the metal side of the interface, i.e. the charge density of constituents of the metal, by q_M and the charge density of the electrolyte phase by q_s . In an ideally polarisable electrode, the two phases have no charged constituents in common [12]. Because there are no electric fields in the bulk of either phase, there must be overall electroneutrality: $q_M + q_s = 0$. Using the notation of Lange and Miscenko [13], we have for the total potential difference across the electrode ($V_{\text{metal}} - V_{\text{solution}}$)

$$V = g_s^M(\text{ion}) + g^S(\text{dip}) + g^M(\text{dip}) \quad (1)$$

[End of page 74] where $g_s^M(\text{ion})$ is the contribution of free charges, vanishing for $q_M = -q_s = 0$. The differential capacities are defined, in terms of eqn. (1), as follows:

$$\begin{aligned} \frac{1}{C(\text{ion})} &= \frac{\partial g_s^M(\text{ion})}{\partial q_M}; & \frac{1}{C^S(\text{dip})} &= \frac{\partial g^S(\text{dip})}{\partial q_M}; & \frac{1}{C^M(\text{dip})} &= \frac{\partial g^M(\text{dip})}{\partial q_M} \\ \frac{1}{C} &= \frac{\partial V}{\partial q_M} = \frac{1}{C(\text{ion})} + \frac{1}{C^S(\text{dip})} + \frac{1}{C^M(\text{dip})} \end{aligned} \quad (2)$$

We will suppose that $g^S(\text{dip})$ and $g^M(\text{dip})$ can be decoupled. The model we use is defined in section (I), with necessary formulae. Then we present results for gallium and mercury, the two metals for which experimental values are best established. We will examine in detail the capacity at the pzc in order to determine which parameters in the model have the greatest influence on the capacity. Then the effect of the charge on $^{\delta}X_m$ and the capacity will be calculated (section II). The discussion in section (III) considers other models which may be used for the metal.

(I) Model Used

Given the distributions of the various electrical elements (ions, molecules, and electrons) for a particular charge density q_M , one can use the Poisson equation to calculate V , the potential difference across the interface. From the dependence of V on q_M , one can calculate the capacity by differentiation.

If, as we suppose, there is no specific adsorption, the metal should be in contact with a monolayer of water, whose thickness is about 0.3 nm, as is generally considered in the classical models of the interface [14]. One generally takes the relative dielectric permittivity of this layer, ϵ_1 , to be about 6 [4,5,10]. Use of such a value often appears necessary to limit the potential drop in the interface [7]. Interpreting ϵ_1 as the permittivity of fixed dipoles [4], one may suppose that its value is independent of q_M . The polarisation of the monolayer associated with orientation of permanent dipoles appears in $g^S(\text{dip})$ and is not calculated here.

For highly concentrated solutions, the charge q^S is localized with respect to the direction perpendicular to the interface. The Gouy-Chapman theory of the diffuse part of the double layer shows, indeed, that the width of this charge distribution approaches zero as the concentration becomes very large. In our model, we assume the water monolayer is bounded by an ideal charged plane, beyond which one has unperturbed solvent with a dielectric

permittivity ($\epsilon_2 = 78$). In fact, our calculations [9] show that the choice of ϵ_2 does not have a great effect on the electron profile. The other side of the water monolayer is at a distance d_1 from the ionic profile of the metal, which is taken as a step (Fig. 1). The value of d_1 reflects the degree of interpenetration of the metal ions and the solvent molecules; its value is between 0 and R_c , the crystallographic radius of the ions. If $d_1 < R_c$, ions and solvent molecules coexist in some region of space. The region between 0 and d_1 is characterized by a permittivity of unity, as in the metal.

Only the profile of the electron density is to be determined. In an "exact" [**End of page 75**]

Fig. 1. Models used to discuss interaction of solvent molecules with metal electrons.

calculation, the electron density profile would be calculated for each configuration of the heavy particles (ions and molecules). We have used an approximate procedure which involves calculation of the profile for a mean configuration of these particles. In Part I we presented the model for the interface between metal and vacuum, and suggested two forms of the metal-solvent interaction. The particles of the solvent, as well as the ions of the metal, are represented by jelliums, and the electron-ion and electron-molecule interactions, which should depend on the configuration of ions and molecules, are replaced by interaction of the metal electrons with an external field, representing the mean effect of ions and molecules.

The jellium model for the interaction of electrons with ions of the metal is widely used [14]. As in Part I, we consider two types of interaction of electrons with the solvent: first, an electrostatic one, in which the water layer behaves as a uniform film of permittivity ϵ_1 , and, second, a short-range repulsion, expressed by a Harrison point-ion model. The interaction of electrons with ions of the solution is represented by the coulombic interaction with an ideal charged plane.

The form of the electron profile $n(z)$ is fixed a priori, with values of the parameters determined by minimisation of the surface energy. Thus,

$$\begin{aligned} n_-(z) &= \bar{n}_- (1 - A e^{\alpha z}), & z < z_0 \\ n_-(z) &= \bar{n}_- B e^{-\beta z}, & z \geq z_0 \end{aligned} \quad (3)$$

with $\bar{n}_-$ the mean electronic density in the homogeneous liquid phase. The continuity of n_- and its slope at z_0 require

$$A = \frac{\beta}{\alpha + \beta} e^{-\alpha z_0} \quad B = \frac{\alpha}{\alpha + \beta} e^{\beta z_0} \quad (4)$$

The global electroneutrality condition, $q_M + q_S = 0$, becomes [**End of page 76**]

$$q_M = -q_S = \int_{-\infty}^{\infty} [Z n_+(z) - n_-(z)] dz \quad (5)$$

with Z the charge of the ions and the ion density profile a step:

$$\begin{aligned} n_+(z) &= \bar{n}_+ / Z, & z > 0 \\ n_+(z) &= 0, & z \leq 0 \end{aligned} \quad (6)$$

Using eqns. (3)-(5) we find

$$z_0 = \frac{1}{\alpha} - \frac{1}{\beta} + \frac{q_S}{\bar{n}_-} \quad (7)$$

Thus, one has to determine α and β variationally for each value of q_s . The surface energy is, as in Part I,

$$U_s = U_{\text{kin}} + U_{\text{exc}} + U_{\text{inh}} + U_{\text{es}} + U_{\text{ps}} + U_{\text{B}} + U_{\text{ion}} \quad (8)$$

The terms U_{kin} , U_{exc} , and U_{inh} derive respectively from the kinetic, exchange, exchange-correlation and inhomogeneity energies of the electron gas; their expression in terms of α and β were given in Part I. When there is a surface charge, the values of α, β and z_0 change, but not the formal expressions. The electrostatic part of the surface energy is now written

$$\begin{aligned} U_{\text{es}} = 2\pi\bar{n}_-^2 & \left[\frac{-2\alpha}{\beta^3(\alpha+\beta)} e^{\beta z_0} - \frac{\alpha^2 e^{2\beta z_0}}{2\beta^3(\alpha+\beta)^2} \left(e^{-2\beta d_1} \left(1 - \frac{1}{\epsilon_1} \right) + e^{-2\beta d_2} \left(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_2} \right) \right) \right. \\ & + \frac{1}{6\alpha^3} + \frac{5}{6\beta^3} + \frac{1}{2\alpha\beta(\alpha+\beta)} - \frac{1}{3} \left(\frac{q_s}{\bar{n}_-} \right)^3 + \left(\frac{q_s}{\bar{n}_-} \right)^2 \left(d_1 + \frac{d_2 - d_1}{\epsilon_1} \right) \\ & \left. + 2 \left(\frac{q_s}{\bar{n}_-} \right) \frac{\alpha e^{\beta z_0}}{\beta^2(\alpha+\beta)} \left(e^{-\beta d_1} \left(1 - \frac{1}{\epsilon_1} \right) + \frac{e^{-\beta d_2}}{\epsilon_1} \right) \right] \quad (9a) \end{aligned}$$

for $z_0 < 0$ and, for $z_0 > 0$,

$$\begin{aligned} U_{\text{es}} = 2\pi\bar{n}_-^2 & \left[\frac{-2\beta e^{-\alpha z_0}}{\alpha^3(\alpha+\beta)} - \frac{\alpha^2 e^{2\beta z_0}}{2\beta^3(\alpha+\beta)^2} \left(e^{-2\beta d_1} \left(1 - \frac{1}{\epsilon_1} \right) + e^{-2\beta d_2} \left(\frac{1}{\epsilon_1} - \frac{1}{\epsilon_2} \right) \right) \right. \\ & + \frac{5}{6\alpha^3} + \frac{1}{6\beta^3} - \frac{q_s}{\bar{n}_-} \left(\frac{1}{\alpha^2} + \frac{1}{\beta^2} \right) + \frac{1}{2\alpha\beta(\alpha+\beta)} - \frac{2}{3} \left(\frac{q_s}{\bar{n}_-} \right)^3 \\ & \left. + \left(\frac{q_s}{\bar{n}_-} \right)^2 \left(d_1 + \frac{d_2 - d_1}{\epsilon_1} \right) + \frac{2q_s}{\bar{n}_-} \frac{\alpha e^{\beta z_0}}{\beta^2(\alpha+\beta)} \left(e^{-\beta d_1} \left(1 - \frac{1}{\epsilon_1} \right) + \frac{e^{-\beta d_2}}{\epsilon_1} \right) \right] \quad (9b) \end{aligned}$$

We characterize the ion-electron interaction by the pseudo-potential introduced by Heine and Animalu [15]

$$W(r) = A_0/Z \quad \text{for } r < R_M$$

[End of page 77]

$$W(r) = -1/r \quad \text{for } r \geq R_M$$

The values of A_0 and R_M are the same as in Part I. (In Table 1 of Part I read $-A_0Z$ instead of $-A_0$.) The pseudo-potential contribution U_{ps} is now

$$\begin{aligned} U_{\text{ps}} = 2\pi\bar{n}_-^2 & \left[\frac{2\alpha e^{\beta z_0}}{\beta^3(\alpha+\beta)} - \frac{\beta e^{-\alpha z_0 - \alpha R_M}}{\alpha^3(\alpha+\beta)} \left(1 + A_0 R_M + \frac{A_0}{\alpha} \right) - \frac{A_0 R_M^4}{8} - \frac{R_M^3}{6} \right. \\ & - \frac{\alpha e^{\beta z_0 - \beta R_M}}{\beta^3(\alpha+\beta)} \left(1 + A_0 R_M + \frac{A_0}{\beta} \right) + \frac{1}{3\alpha^3} - \frac{1}{3\beta^3} - \frac{1}{6} \left(\frac{q_s}{\bar{n}_-} \right)^3 - \frac{1}{2} \frac{q_s}{\bar{n}_-} \left(\frac{1}{\alpha^2} + \frac{1}{\beta^2} \right) \\ & + \frac{q_s}{\bar{n}_-} \left(\frac{A_0 R_M^3}{3} + \frac{R_M^2}{2} - \frac{A_0 \beta}{\alpha^2(\alpha+\beta)} + \frac{A_0 \alpha}{\beta^3(\alpha+\beta)} \right) \\ & - \left(\frac{A_0 R_M^2}{4} + \frac{R_M}{2} \right) \left(\frac{1}{\alpha^2} + \frac{1}{\beta^2} + \left(\frac{q_s}{\bar{n}_-} \right)^2 \right) + \left(\frac{A_0}{8} \right) \left(\frac{3}{\alpha^4} + \frac{3}{\beta^4} + \frac{2}{\alpha^2 \beta^2} \right) \\ & \left. + \frac{A_0 q_s}{\bar{n}_-} \left(\frac{1}{24} \left(\frac{q_s}{\bar{n}_-} \right)^3 + \frac{q_s}{4\bar{n}_-} \left(\frac{1}{\alpha^2} + \frac{1}{\beta^2} \right) + \frac{2}{3} \left(\frac{1}{\alpha} - \frac{1}{\beta} \right)^3 + \frac{1}{\alpha\beta} \left(\frac{1}{\alpha} - \frac{1}{\beta} \right) \right) \right] \quad (10a) \end{aligned}$$

for $z_0 < 0$ and

$$\begin{aligned}
U_{ps} = 2\pi\bar{n}^2 \left[\frac{2\beta e^{\alpha z_0}}{\alpha^3(\alpha + \beta)} - \frac{\beta e^{-\alpha z_0 - \alpha R_M}}{\alpha^3(\alpha + \beta)} \left(1 + A_0 R_M + \frac{A_0}{\alpha} \right) - \frac{A_0 R_M^4}{8} - \frac{R_M^3}{6} \right. \\
- \frac{\alpha e^{\beta z_0 - \beta R_M}}{\beta^3(\alpha + \beta)} \left(1 + A_0 R_M + \frac{A_0}{\beta} \right) + \frac{1}{3\beta^3} - \frac{1}{3\alpha^3} + \frac{1}{6} \left(\frac{q_s}{\bar{n}_-} \right) + \frac{1}{2} \frac{q_s}{\bar{n}_-} \left(\frac{1}{\alpha^2} + \frac{1}{\beta^2} \right) \\
+ \frac{q_s}{\bar{n}_-} \left(\frac{A_0 R_M^3}{3} + \frac{R_M^2}{2} - \frac{A_0 \beta}{\alpha^3(\alpha + \beta)} + \frac{A_0 \alpha}{\beta^3(\alpha + \beta)} \right) \\
- \left(\frac{A_0 R_M^2}{4} + \frac{R_M}{2} \right) \left(\frac{1}{\alpha^2} + \frac{1}{\beta^2} + \left(\frac{q_s}{\bar{n}_-} \right)^2 \right) + \frac{A_0}{8} \left(\frac{3}{\alpha^4} + \frac{3}{\beta^4} + \frac{2}{\alpha^2 \beta^2} \right) \\
\left. + \frac{A_0 q_s}{\bar{n}_-} \left(\frac{1}{24} \left(\frac{q_s}{\bar{n}_-} \right)^3 + \frac{q_s}{4\bar{n}_-} \left(\frac{1}{\alpha^2} + \frac{1}{\beta^2} \right) + \frac{2}{3} \left(\frac{1}{\alpha} - \frac{1}{\beta} \right)^3 + \frac{1}{\alpha\beta} \left(\frac{1}{\alpha} - \frac{1}{\beta} \right) \right) \right] \quad (10b)
\end{aligned}$$

for $z_0 > 0$.

The energy associated with the non-coulombic part of the electron-molecule interaction is designated by U_B . It is written

$$U_B = N \int w(\vec{r}_i - \vec{r}) n(z) P(\vec{r}_i) d\vec{r}_i dz \quad (11)$$

Where $P(\vec{r}_i) d\vec{r}_i$ gives the probability that one of the N molecules in the layer is [End of page 78] within the volume $d\vec{r}_i$ at $\vec{r}_i$. The electron-molecule pseudo-potential $w(\vec{r}_i - \vec{r})$ is approximated by the Harrison model

$$w(\vec{r}_i - \vec{r}) = \bar{\beta} \delta(\vec{r}_i - \vec{r}) \quad (12)$$

If all these molecules can be assumed to have their centres at $\frac{1}{2}(d_1 + d_2)$, we may write for $P(\vec{r}_i)$, $S^{-1} \delta(z_1 - \frac{1}{2}d_1 - \frac{1}{2}d_2)$, S being the total surface of the layer. Then

$$U_B = \lambda n \left(\frac{1}{2}d_1 + \frac{1}{2}d_2 \right) \quad (13)$$

where λ is $N\bar{\beta}/S$. The term U_{ion} in eqn. (8) describes the inter-ionic correlations, and does not enter the determination of α and β , which are found from

$$(\partial U_s / \partial \alpha)_\beta = 0 \quad (\partial U_s / \partial \beta)_\alpha = 0 \quad (14)$$

By integrating the Poisson equation, we find the potential difference across the interface in terms of $n(z)$. The result is ($V = V_{metal} - V_{solution}$)

$$\begin{aligned}
V = 4\pi q_M \left(\frac{q_M}{2\bar{n}_-} + d_1 + \frac{d_2 - d_1}{\epsilon_1} \right) \\
+ 4\pi\bar{n}_- \left[\frac{1}{2} \left(\frac{1}{\alpha^2} + \frac{1}{\beta^2} \right) + \frac{\alpha e^{\beta z_0}}{\beta^2(\alpha + \beta)} \left(\frac{e^{-\beta d_2}}{\epsilon_2} + \frac{e^{-\beta d_1} - e^{-\beta d_2}}{\epsilon_1} - e^{-\beta d_1} \right) \right] \quad (15)
\end{aligned}$$

which can be written

$$V = g_s^M(\text{ion}) + g_s^M(\text{dip}) \quad (16)$$

where

$$g_s^M(\text{dip}) = 4\pi q_M \left(\frac{q_M}{2\bar{n}_-} + d_1 + \frac{d_2 - d_1}{\epsilon_1} \right) \quad (17)$$

and $g_s^M(\text{dip})$, the remainder of eqn. (15), carries the dependence on α and β . The quantities $g_s^M(\text{ion})$ and $g_s^M(\text{dip})$ have meanings consistent with the normal usage of electrochemists. Thus, $g_s^M(\text{ion})$ vanishes when the charge q_s vanishes, so that $V = g_s^M(\text{dip})$ at the pzc. On the other hand, $g_s^M(\text{dip})$ disappears when α and β become infinite, i.e. when the profiles of positive and negative charge density become steps, so that the dipole of the metal surface disappears. (Note, however, that the values α and β depend on q_s , since q_s affects U_s .) In the absence of solvent, $g_s^M(\text{dip})$ is only the surface potential of the metal.

Associated with $g_s^M(\text{ion})$ and $g_s^M(\text{dip})$ are the capacities $C(\text{ion})$ and $C(\text{dip})$ (cf. eqn. 2). According to eqn. (16)

$$\frac{1}{C} = \frac{\partial V}{\partial q_M} = \frac{1}{C(\text{ion})} + \frac{1}{C(\text{dip})} \quad (18)$$

The layer of water molecules, whose thickness is represented by $d_2 - d_1$, is assumed incompressible, and if d_1 is itself constant,

$$\frac{1}{C(\text{ion})} = \frac{4\pi(d_2 - d_1)}{\epsilon_1} + 4\pi d_1 + 4\pi \frac{q_M}{\bar{n}_-} \quad (19)$$

[End of page 79] The first term in eqn. (19) is the inherent capacity of a water monolayer, with fixed permanent dipoles. It is present in most models of the double layer, e.g. refs. 2, 3 and 13. The second term is due to a zone of permittivity unity located between the last ions of the metal and the layer of solvent. This term tends to decrease $C(\text{ion})$. The term in q_M is related to the distance $(q_M/\bar{n}_-)$ a step profile for the electrons must be displaced in the present model to maintain overall electroneutrality for a surface charge q_M

The dipolar contribution, $C(\text{dip})$, depends on the charge via z_0 , α and β . A more realistic representation of the solvent would, of course, include a contribution to $C(\text{dip})$ of the permanent dipole moments of water molecules, whose orientability by an electric field would perhaps depend on the strength of their interaction with the metal. Although the permanent dipole moments probably make the major contribution to the interfacial capacity, they can be omitted when one is interested in comparing the electronic contributions of different metals.

Among the parameters of the model are geometric parameters (d_1 and d_2), electrical properties (ϵ_1 and ϵ_2) and those defining the interactions (A_0 , R_M , λ). For all these, except λ , we use the values given in Part I. Section II presents the results for the mercury and gallium electrodes.

(II) Results

In Part I we considered separately the two ways of representing the metal-solvent interaction (dielectric film and barrier). Either is capable of giving δX_m a value of about -0.5 V at the pzc. We now show what these models give for the capacities. We have considered the barrier model by itself, the dielectric film model by itself and the two simultaneously. Thus, the value $\lambda = 0.3$ for the barrier gave an acceptable value for δX_m in Part I. According to eqn. (13), λ is related to the density of adsorbed molecules, N/S , and to the strength of the pseudo-potential β . Taking $N/S \sim 10^{15} \text{ cm}^{-2}$ (0.027 au) [14] and $\beta \sim 15$ au, of the size found for metals, we have $\lambda \sim 0.4$.

Tables 1 and 2 summarize, for Hg and Ga respectively, some results for $d_1 = R_c$. In each case, we have given results for $\alpha = \beta$ and for independent variation of α and β . In certain cases there are important differences in the results, although they are qualitatively the same. Here, $C(\text{ion})$ is calculated from eqn. (19), the capacitance C from the change in V with q_M ; from C and $C(\text{ion})$ we obtain $C(\text{dip})$. The last, like $C^S(\text{dip})$ [3], is a negative contribution, making $C > C(\text{ion})$. The introduction of d_1 and the existence of $g^M(\text{dip})$ affect C in opposite directions.

The tables show that, with $\epsilon_1 = \epsilon_2 = 1$, we obtain values of C which are very small compared to experimental values ($C_{\text{exp}} \sim 25 \mu\text{F cm}^{-2}$ for Hg and $\sim 120/\mu\text{F cm}^{-2}$ for Ga [16,17]. Using the present model, the capacity of the system C_T is given by

$$C_T^{-1} = C^{-1} + C^S(\text{dip})^{-1} \quad (20)$$

where $C^S(\text{dip})$ results from orientation of solvent dipoles. To obtain $C_T \sim C_{\text{exp}}$, one must have values for $C^S(\text{dip})$ which are much smaller than those generally accepted **[End of page 80]**

TABLE 1

Properties of the Hg electrode at the pzc; $d_1 = R_c = 2.12$ au. For the bare surface $\chi_M = 5.37$ V for $\alpha \neq \beta$ and 5.74 V for $\alpha = \beta$

(a) $\alpha \neq \beta$			
	$\lambda = 0.3, \epsilon_1 = 1$ $\epsilon_2 = 1$	$\lambda = 0, \epsilon_1 = 6$ $\epsilon_2 = 78$	$\lambda = 0.3, \epsilon_1 = 6$ $\epsilon_2 = 78$
α	0.795	0.861	0.800
β	1.117	0.926	1.099
$-\delta\chi_m$	0.21	0.23	0.37
$C(\text{ion})$	2.14	5.46	5.46
$-C^M(\text{dip})$	9.30	10.35	12.22
C	2.78	11.56	9.87
(b) $\alpha = \beta$			
	$\lambda = 0.3, \epsilon_1 = 1$ $\epsilon_2 = 1$	$\lambda = 0, \epsilon_1 = 6$ $\epsilon_2 = 78$	$\lambda = 0.3, \epsilon_1 = 6$ $\epsilon_2 = 78$
α	0.938	0.892	0.931
$-\delta\chi_m$	0.42	0.20	0.63
$C(\text{ion})$	2.14	5.46	5.46
$-C^M(\text{dip})$	7.40	8.64	10.02
C	3.03	14.81	11.98

TABLE 2

Properties of the Ga electrode at the pzc; $d_1 = R_c = 1.17$ au. For the bare surface $\chi_M = 10.51$ V for $\alpha \neq \beta$ and 10.50 V for $\alpha = \beta$

(a) $\alpha \neq \beta$			
	$\lambda = 0.3, \epsilon_1 = 1$ $\epsilon_2 = 1$	$\lambda = 0, \epsilon_1 = 1$ $\epsilon_2 = 78$	$\lambda = 0.3, \epsilon_1 = 6$ $\epsilon_2 = 78$
α	0.772	0.962	0.814
β	1.078	0.707	0.929
$-\delta\chi_M$	0.83	0.67	1.47
$C(\text{ion})$	2.45	7.91	7.91
$-C^M(\text{dip})$	8.33	12.92	15.77
C	3.46	20.40	15.87
(b) $\alpha = \beta$			
	$\lambda = 0.3, \epsilon_1 = 1$ $\epsilon_2 = 1$	$\lambda = 0, \epsilon_1 = 1$ $\epsilon_2 = 78$	$\lambda = 0.3, \epsilon_1 = 6$ $\epsilon_2 = 78$
α	0.909	0.818	0.865
$-\delta\chi_M$	0.94	0.70	1.64
$C(\text{ion})$	2.44	7.91	7.91
$-C^M(\text{dip})$	6.31	10.95	12.15
C	4.07	28.42	22.63

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[4,5,7,10]. Thus, the barrier without dielectric appears unrealistic. When one considers the dielectric film without the barrier ($\lambda = 0, \epsilon_1 = 6, \epsilon_2 = 78$), one obtains values of C_T which are much closer to the experimental ones. Note that C for mercury is about half C for gallium. If we suppose that we have the *same* layer of solvent molecules at the two metals, we can use eqn. (20) to compare our results with experiment. In Table 3 we give values of C_T calculated with different choices for $C^S(\text{dip})$. In all cases we find C_{Ga} to be $> C_{Hg}$. It is seen that C_T can agree with experiment with a value for $C^S(\text{dip})$ that is consistent with contemporary estimates of the latter quantity. At the same time, $\delta\chi_m$ has a reasonable size.

When the film and barrier are used simultaneously, the capacities are not greatly modified. On the other hand (see Tables 1 and 2), $\delta\chi_m$ approximately doubles in size compared to the model with film but without barrier.

The effects of changing d_1 appear in Tables 4 and 5, where we present results for $d_1 = R_c, R_c/2$, and $R_c/4$ with $\lambda = 0, 0.3$ and 0.6 . No $\alpha \neq \beta$ solutions could be found for $d_1 = 0, \lambda = 0.3$ or 0.6 with mercury, and for similar

cases with gallium. These cases are physically unreasonable since the electrostatic forces would be very large: with $d_1 = R_c/4$ one already has most of the electronic charge on the electrolyte side of the surface; our assumed form of the profile is inadequate to represent the piling up of charge which should occur near the barrier, and other forms should perhaps be tried. The potential drop V is shown as a function of d_1 in Fig. 2. For $\lambda = 0$, V varies by < 0.5 V; however, the variations in V are much more important for $\lambda = 0.3$ or 0.6 . The profiles in this case are highly deformed for a given d_1 and $|\delta_{x_m}|$ grows as d_1 diminishes (Fig. 2). At the same time, it becomes more difficult to perturb the profile by placing a charge in the solution and $C(\text{dip})$ grows. One can say that the profile is frozen in place by the barrier. An extreme case is that of mercury (Table 4b) with $\lambda = 0.6$ and $d_1 = 0$: a charge of $1 \mu\text{C cm}^{-2}$ changes $g_s^M(\text{dip})$ by 3 mV.

In Fig. 3 we have shown calculated results for the variation of $g_s^M(\text{dip})$ with charge. (If the corresponding quantities for the solvent were known, we could construct an electrocapillary curve). The quantity

$$\Delta g = g_s^M(\text{dip}) - [g_s^M(\text{dip})]_{q_M=0} \quad (21)$$

directly gives the effect of the electrode charge on the electron density profile. We

TABLE 3

Values of C_T at the pzc for different choices of $C^*(\text{dip})$; α independent of β and $\epsilon_1 = 6$, $\epsilon_2 = 78$, $d_1 = R_c$; C in $\mu\text{F cm}^{-2}$

$-C^*(\text{dip})$	25	30	35	40	50
$C_{T,\text{Hg}} \lambda = 0$	21.50	18.81	17.26	16.26	15.04
$C_{T,\text{Hg}} \lambda = 0.3$	16.31	14.71	13.75	13.10	12.30
$C_{T,\text{Ga}} \lambda = 0$	110.87	63.75	48.90	41.60	34.40
$C_{T,\text{Ga}} \lambda = 0.3$	43.46	33.69	29.04	26.31	23.25

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TABLE 4

Capacities in $\mu\text{F cm}^{-2}$ for Hg; $\epsilon_1 = 6$, $\epsilon_2 = 78$, $R_c = 2.12$ au

(a) $\alpha \neq \beta$					
d_1	R_c	$R_c/2$	$R_c/4$	0	
C	11.56	18.43	25.80	40.37	$\lambda = 0$
$-C^M(\text{dip})$	10.35	15.23	20.23	31.49	
C	9.87	16.13	26.59		$\lambda = 0.3$
$-C^M(\text{dip})$	12.22	17.27	19.77		
C	9.55	17.64	64.63		$\lambda = 0.6$
$-C^M(\text{dip})$	12.74	15.82	13.72		
$C(\text{ion})$	5.46	8.36	11.31	17.69	
(b) $\alpha = \beta$					
d_1	R_c	$R_c/2$	$R_c/4$	0	
C	14.81	25.69	39.22	80.00	$\lambda = 0$
$-C^M(\text{dip})$	8.64	12.36	15.94	22.72	
C	11.98	17.54	22.22	31.75	$\lambda = 0.3$
$-C^M(\text{dip})$	10.02	15.90	23.14	39.96	
C	10.46	13.80	16.00	18.70	$\lambda = 0.6$
$-C^M(\text{dip})$	11.40	21.07	38.88	328.60	

TABLE 5

Capacities in $\mu\text{F cm}^{-2}$ for Ga; $\epsilon_1 = 6$, ϵ_2 , $R_c = 1.17$ au

(a) $\alpha \neq \beta$					
d_1	R_c	$R_c/2$	$R_c/4$	0	
C	20.40	29.74	37.80	49.30	$\lambda = 0$
$-C^M(\text{dip})$	12.92	17.48	21.01	27.57	
C	15.87	20.53	28.00	36.07 ^a	$\lambda = 0.3$
$-C^M(\text{dip})$	15.77	23.38	26.07	27.50 ^a	
C	15.80	29.11			$\lambda = 0.6$
$-C^M(\text{dip})$	15.94	49.30			
$C(\text{ion})$	7.91	10.43	13.51	17.69	
(b) $\alpha = \beta$					
d_1	R_c	$R_c/2$	$R_c/4$	0	
C	28.42	40.29	74.85	115.17	$\lambda = 0$
$-C^M(\text{dip})$	10.95	15.00	16.49	20.90	
C	22.63	32.77	45.62	76.50	$\lambda = 0.3$
$-C^M(\text{dip})$	19.15	16.40	19.20	23.02	
C	18.61	24.12	30.28	41.87	$\lambda = 0.6$
$-C^M(\text{dip})$	13.75	19.98	24.40	30.64	

^a For $d_1 = R_c/8$; no solution was found for $d_1 = 0$.

Fig. 2. Variation of electrode potential with choice of d_1 for various λ : (a) with α fixed equal to β ; (b) with $\alpha \neq \beta$ allowed.

Fig. 3. Effect of electrode charge on the surface dipole potential of the metal; $\alpha \neq \beta$, $\lambda = 0.3$, $\epsilon_1 = 6$, $\epsilon_2 = 78$.

Fig. 4. Effect of electrode charge on capacity; $\alpha \neq \beta$, $\lambda = 0.3$.

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have shown Δg as a function of q_M for $\lambda = 0.3$, $\epsilon_1 = 6$, $\epsilon_2 = 78$. The dependence of Δg on the charge is evident. We remark that, in the literature, this dependence is often ignored [8].

The variations of C with electrode charge q_M , shown in Fig. 4, also arise from $g_s^M(\text{dip})$. It must be remembered that the present model neglects electrostrictive phenomena that might alter d_1 and d_2 , and in this way lead to a modification of the electronic profile by the permanent dipoles of the solvent molecules in the electrolyte phase, whose organization depends on the charge. Furthermore, we have kept ϵ_1 constant. These conditions are quite restrictive, and certainly cannot be justified far from the pzc. Introduction of a detailed model for the solvent dipoles would clearly represent an important step forward, and we hope to attempt this in the future. A combination of such

a model and a model like ours for the electrons would have to explain the independence of differential capacities on the nature of the metal [18] for very negative metal charges ($\sim 15 \mu\text{C cm}^{-2}$).

(III) Discussion

The model we have constructed for the metal seems fairly realistic for the metal since, as we showed in I, it leads to acceptable values for the work functions for a series of metals. Two quantities specific for each metal enter this model: the electronic density and the ion-electron pseudo-potential. Two models for the coupling between metal and solvent were introduced in I, each emphasising one kind of interaction: electrostatic for the film, quantum mechanical core repulsion for the barrier. While either model can give δX_m of an acceptable size, they respond quite differently to a layer of charge in the solution. The barrier by itself leads to dipole orientation capacities which are too small, and the model cannot be retained.

In considering the film model or the film + barrier model, we showed the important influence of d_1 on C (Tables 4 and 5). The parameter d_1 , specific to our model, expresses the degree of metal-solution interpenetration. No spatial separation between metal and solution is assumed; on the contrary, there is a region of space, defined by d_1 , in which metal ions, electrons and solvent molecules coexist. We have assumed that the value of d_1 should be related to the crystallographic ion radius of the metal.

In order to compare calculated capacities with experiment, we would need values for $C^S(\text{dip})$. Table 3 shows that, with $C^S(\text{dip}) = -25 \mu\text{F cm}^{-2}$ and $d_1 = R_c$, we obtain $C_T = 111 \mu\text{F cm}^{-2}$ for Ga and $21 \mu\text{F cm}^{-2}$ for Hg, in reasonable accord with experimental values. We note that only the orders of magnitude are significant since, for example, using independently variable parameters α and β leads to values for C somewhat different from imposing $\alpha = \beta$. In addition, the ionic concentration profile used is too simple, and we have neglected any coupling between $C^S(\text{dip})$ and $C^M(\text{dip})$.

As in all double-layer treatments, the problem of the proper dielectric function remains to be solved [11]. Note, however, that the same solvent film, with capacity $\epsilon_1/(d_2 - d_1)$, has been used for both metals, so that the difference in capacities we [End of page 85] find between Ga and Hg is due to the introduction of parameters specific to the metals ($A_0, R_M, R_c, \bar{n}_-$). In all cases, we find a larger capacity for Ga than for Hg. This may be considered as the main physical result of this work. The school of Frumkin [5,10,16,17] has ascribed the larger values of C_{Ga} to a specific (adsorptive) interaction between water and the metal, which is larger for Ga than for Hg. Our finding, that the smaller values of R_c for Ga already makes C_{Ga} larger because it allows the solvent molecules to interact more strongly with the charges of the metal, is not necessarily in contradiction with the model of Frumkin and co-workers. However, it appears that, before parameterising a model for specific adsorption to account for different observed capacities, one should remove from the observed values an important direct contribution of the metal electrons.

A simple model for the contribution of the metal to the double-layer capacity was recently presented [19]. Assuming the electron density may be described by the Thomas-Fermi model, the capacity is found to be

$$C_{\text{TF}} = 4\pi/\lambda_{\text{TF}} \quad (22)$$

where λ_{TF} is the Thomas-Fermi length. Table 6 gives λ_{TF} and C_{TF} for our metals: they are seen to be quite similar. Since spatial separation between metal and solution is assumed, the respective potential differences are additive and

$$C^{-1} = C_{\text{TF}}^{-1} + (C^{\text{sol}})^{-1}; \quad (C^{\text{sol}})^{-1} = [C(\text{ion})]^{-1} + (C^S)^{-1} \quad (23)$$

To obtain C close to C_{exp} with C_{TF} of Table 6, one would require the capacity of the solvent C^{sol} to be negative, which is unreasonable. Note that C^{sol} includes the contribution of free charges in the electrolyte. An improved theory by Newns [20] shows that, instead of λ_{TF} , values about twice as large should be used, as given in Table 6 (λ_N). With the resulting capacities C_N , negative values for C^{sol} are still needed.

Another simple model for surfaces [11] considers free electrons in contact with an infinitely high and thick repulsive wall. The capacity in this case is (see Appendix)

$$C_B = 4\pi/d, \quad d = 3\pi/8k_F$$

with k_F the Fermi momentum of the metal electrons. The values for C_B , given in Table 6, are between C_{TF} and C_N , again implying negative capacities for the solvent.

TABLE 6

Properties of models invoking spatial separation between metal and solution: $\lambda_{TF}, \lambda_N, 3\pi/4k_F$ in au; C_{TF}, C_N, C_B in $\mu F\text{ cm}^{-2}$

	λ_{TF}	C_{TF}	λ_N	C_N	$3\pi/4k_F$	C_B
Ga	0.945	17.68	1.837	9.18	1.338	12.49
Hg	1.042	16.05	2.128	7.85	1.630	10.25

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All the above models imply complete spatial separation between metal and solvent, and seem less realistic than those presented in this work.

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Appendix

For free electrons against an infinite wall located at $z = 0$, the electronic density profile is given by

$$n_-(z) = \bar{n}_- \left(1 + \frac{3 \cos x}{x^2} - \frac{3 \sin x}{x^3} \right), \quad x < 0 \quad (A1)$$

where $x = 2k_F z$. Taking the distribution of positive charges as a step

$$\begin{aligned} n_+(z) &= \bar{n}_+, \quad z < -b/2k_F \\ n_+(z) &= 0, \quad z \geq -b/2k_F \end{aligned} \quad (A2)$$

we use the electroneutrality condition

$$q_M = \int_{-\infty}^0 [n_+(z) - n_-(z)] dz \quad (A3)$$

to find the value of b . The result is

$$b = \frac{3\pi}{4} - \frac{2k_F q_M}{\bar{n}_-} \quad (A4)$$

Using the charge density $n_+ - n_-$, we solve the Poisson equation to obtain for the potential difference

$$V = \frac{k_F}{3\pi} \left(3 - \frac{b^2}{2} \right) \quad (A5)$$

Here V depends on q_n through b (eqn. A4). The capacity is obtained by differentiation

$$\frac{dV}{dq_n} = \frac{-k_F b}{3\pi} \frac{db}{dq_n} = \frac{2k_F^2 b}{3\pi \bar{n}_-}$$

at the pzc this becomes $k_F^2/2\bar{n}_-$.

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