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The Role of Metal Structure in Determining Solvent Orientation at the Electrode/Solution Interface

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The role of molecular packing on the dielectric properties of a solvent monolayer at a polarizable interface is examined for a hexagonally close packed system and a less well packed square lattice. Dipole-dipole interactions within the monolayer are considered both perpendicular and parallel to the geometrical electrode/solution interface. In both systems, dipoles with their vectors parallel to the interface predominate near the point of zero charge on the metal. As the charge on the metal increases, a capacity peak is observed whose value is much larger for the hexagonal lattice than the square one. Comparison with experimental data for single crystal silver electrodes demonstrates that the the differences observed between capacity data on different low index faces cannot be due to differences in solvent molecule packing, but instead can be attributed to the presence of chemisorbed solvent molecules.

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The Role of Metal Structure in Determining Solvent Orientation at the Electrode/Solution Interface

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It is well known that double layer properties for aqueous solutions depend on both the nature of the metal and on its structure [1]. In the case of silver electrodes, Valette and Hamelin [2] demonstrated that the effect of the solvent on inner layer properties is best determined in the presence of NaF as electrolyte, the fluoride anion being only very weakly adsorbed. The value of the inner layer capacity has a maximum value at a charge density of 4.5 μC cm^{-2} for the low index planes of silver, the highest value being observed for the (110) face and the lowest for the most densely packed face, namely, the (111) orientation. The maximum value of the inner layer capacity is more than 100 μF cm^{-2} for all three low index faces and falls off to considerably lower values when the electrode charge density changes so that only one maximum is seen on the inner layer capacity - charge density curve within the polarizable range on a silver electrode [2]. Valette [3] fitted data for the inner layer capacity against charge density obtained for the (110) silver face in water to a simple model in which the predominant species at the interface are water clusters and showed that the essential features of the capacity curve could be attributed to cluster reorientation.

The purpose of the present study was to determine whether a three state model with orientable solvent dipoles [4] can describe the differences observed with change in the nature of the face of the crystal exposed. In this regard, the (100) and (111) faces of a face centered cubic crystal have quite different atomic arrangements, and therefore different coordination numbers of the metal atoms with nearest neighbours in the exposed crystal face. Thus, the (100) face has a square lattice of atoms with each atom having four nearest neighbours, whereas the (111) face has a hexagonally close packed arrangement, each atom having six nearest neighbours [1]. If the solvent molecules in the first monolayer at the interface follow the metal pattern, then one expects differences in the dipolar interactions in the monolayer and in its resulting dielectric properties [5, 6]. In developing a model to describe the properties of a dipolar monolayer it is important to consider lateral interactions between dipoles adsorbed with their vectors parallel to the interface [7, 8]. A method of incorporating these interactions within the context of the three state model based on the Kikuki method [9] was described recently [10] in which the basic unit consisted of a triangular cluster. In the present paper, this method is applied to clusters containing four molecules either in a square arrangement or a hexagonally close packed configuration (see Figure 1). It is readily apparent that the effects of lateral interactions are more important in the hexagonally close packed lattice.

Inner layer capacity against charge density curves were estimated for the two lattices using the methods described previously [10]. The partition function for a given value of the local field $\mathcal{E}$ was estimated on the basis of the 81 possible configurations for the four member cluster considering three possible orientations of each dipole, namely "up", "down" and "parallel" with respect to the geometrical electrode/solution interface. Thus, the partition function is given by

$$q = \sum_{i=1}^{81} e^{-U_i/kT} \qquad (1)$$

where $U_i = (U_{ex} + U_{zz} + U_{xy} + U_{im})_i$ (2)

The contributions to the internal energy of configuration, i, come from interaction of the dipoles with the external field (U_{ex}), interactions between nearest neighbours in the direction of the field (U_{zz}), interaction between nearest neighbours parallel to the interface (U_{xy}), and interaction with images in the electrode (U_{im}). For a given local field, $\mathcal{E}$, the average orientation in the monolayer is

$$<s> = \frac{-kT}{4p} \frac{\partial \ln q}{\partial \mathcal{E}} \qquad (3)$$

where p is the magnitude of the dipole moment and the parameter s has values of +1 when the dipole has its positive end pointing to the surface ("up"), -1 for the opposite orientation ("down"), and 0 when the dipole is parallel to the surface ("parallel"). The expression for the potential drop across the monolayer is given by

$$\Delta\phi = \frac{\sigma d_e}{\varepsilon_0} + \frac{N_T <s> p}{\varepsilon_0} \qquad (4)$$

and that for the reciprocal of the inner layer capacity by

$$\frac{1}{C_i} = \frac{d_e}{\varepsilon_0} + \frac{N_T p}{\varepsilon_0} \frac{\partial <s>}{\partial \sigma} \qquad (5)$$

where d_e is the effective thickness of the inner layer, N_T, the number density of solvent dipoles in the monolayer, and ε_0, the permittivity of free space. Estimation of $<s>$ requires knowledge of the effective coordination number beyond the cluster. In the absence of imaging ($U_{im} = 0$), this was assumed to be 11.03 - 6 = 5.03 for a hexagonal lattice and 9.03 - 4 = 5.03 for a square lattice [9]. When imaging is included these values change to 7.87 for the hexagonal lattice and 7.41 for the square lattice [9, 10].

Capacity curves estimated for the two configurations are shown in Figure 2. The symmetrical nature of the results with respect to the point of zero charge (p.z.c.) is due to the fact that no difference in chemical interaction with the metal is assumed between the "up" and "down" orientations. Dipoles in the parallel orientation predominate at the p.z.c. in the hexagonal lattice (Figure 3). This result is clearly due to the fact that lateral interactions were considered. As the electrode charge density is made more positive, the fraction of "down" dipoles increases and that of "parallel" dipoles decreases. This leads to the capacity maximum near 9 μC cm^{-2}. The same changes are also accompanied by an increase in the fraction of "up" dipoles which are present in clusters favored by the net local field. However, their concentration is approximately an order of magnitude lower, and decreases at higher charge densities. When the present results are compared to those obtained without consideration of lateral interactions, the importance of these interactions is readily apparent.

Capacity curves for the square lattice are similar in shape but the capacity maxima are much less pronounced

(see Figure 2). At the p.z.c., the fractions of dipoles in the three orientations are equal (Figure 4). In fact, the fraction of dipoles favored by the external field and the fraction "parallel" remain equal up to rather high charge densities. These results again demonstrate the importance of considering lateral interactions in developing models for solvent structure at polarizable interfaces.

Comparison of the present results with experimental data [2, 3] leads to the conclusion that the presence of chemisorbed water molecules at the interface must be considered in developing a suitable model for the inner layer. Further results for the interfacial capacity in the presence of chemisorbed "down" dipoles will be presented. In addition, the effect of increasing the size of the elementary cluster is considered.

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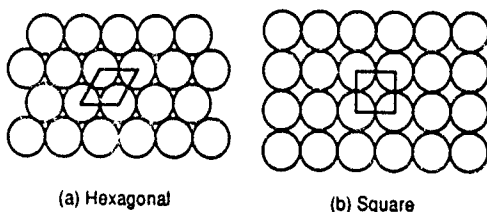10. W.R. Fawcett, J. Chem. Phys., 93 (1990) 6813.

Figure 1. The arrangement of dipolar spheres in (a) a hexagonal lattice and (b) a square lattice. The centers of four adjacent molecules are joined to indicate the units of one cluster used to develop the partition function for a monolayer of dipolar spheres.
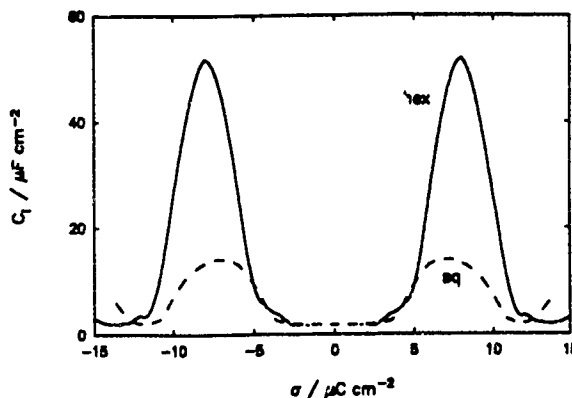

Figure 2. Inner layer capacity plotted against charge density for a dipolar monolayer in a hexagonal lattice (hex) or a square lattice (sq). The molecular dipole moment was assumed to be 1.8 Debyes and the diameter 0.32 nm. Other details are given in the text.
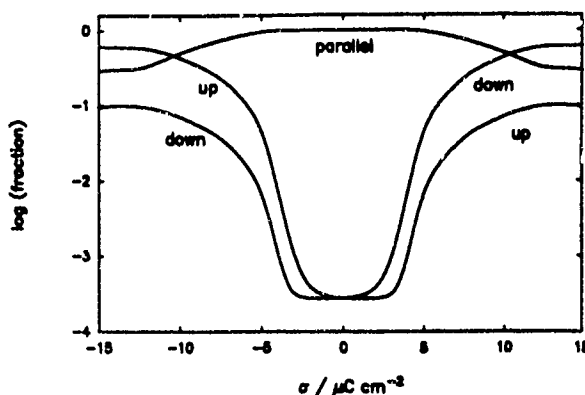

Figure 3. Fractions of molecular dipoles in a hexagonal lattice in the "up", "down", and "parallel" orientations plotted against electrode charge density.
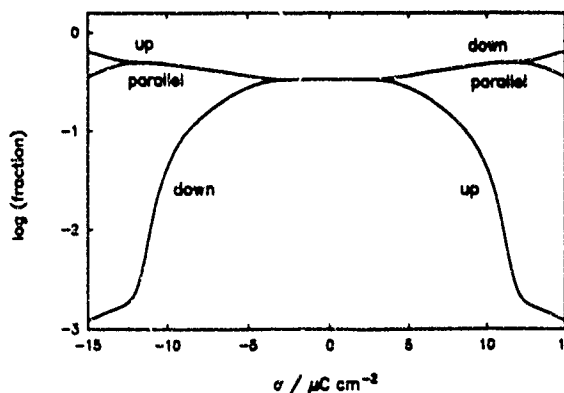

Figure 4. As in Figure 3, but for a square lattice.