

## Effect of the Nature of the Metal on the Dielectric Properties of Water at the Electrode Solution Interface

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Structuring of the liquid usually occurs at the solid/solution interface as a consequence of specific interactions between the two phases [1, 2]. As a result, the orientation polarizability of polar molecules is influenced with modification in the apparent dielectric properties of the liquid phase. The orienting effect of the solid surface induces modifications in the liquid to a depth depending on the nature and strength of the interactions.

Metal surfaces can be divided into hydrophilic and hydrophobic [3] depending on whether or not they tend to bind water molecules strongly through their oxygen atom with increased dipole alignment perpendicular to the solid surface. Hydrophobic metals exert their orienting effect just on the first monomolecular layer of water. Beyond this layer, the diffuse region exhibits the apparent dielectric behaviour of the bulk liquid. Enhanced apparent permittivity is exhibited by the monomolecular layer of water at hydrophilic metals as compared to the hydrophobic ones. Consistently, the strong structuring of the compact layer is expected to drive similar enhancement also in the apparent permittivity of the diffuse layer.

Among the sp (non-catalytic) metals it has been shown [4, 5] that Au is the most hydrophobic and Ga the most hydrophilic one. The apparent failure of the Gouy–Chapman theory for the diffuse layer at Ga was first pointed out by Frumkin and Grigoryev [6]. No similar effect is exhibited by any of the other sp metals. Transition metals are on the contrary all strongly hydrophilic. Thus, failure of the Gouy–Chapman theory for these metals may also be predicted. It will be shown that the sole sufficiently reliable results are available [7] for Fe and they give evidence that this may in fact be the case. The difference between Ga and Fe lies in the reduced orientation polarizability of water in the compact layer at Fe as compared to the former metal.

A possible model will be discussed to explain the above results consistently with conclusions drawn earlier [4] on the basis of independent observations. The structuring of the liquid is expected to give rise to dielectric anisotropy at the interface in the compact layer [8] which can penetrate into the diffuse layer depending on the hydrophilicity of the solid surface. Attempts will be made to relate ionic adsorption on different metals to dielectric aniso-

tropy. The apparent permittivity is also expected to depend on the sign of the charge density on the metal since the surface becomes more hydrophilic the more positive is the charge. The type of solvent–adsorbate interaction is thus expected to depend on the charge sign. This will be discussed on the basis of the asymmetric behaviour observed [9] in the adsorption of neutral molecules on Hg about the potential of zero charge. This effect is expected to increase as the hydrophilicity of the metal increases but data on this aspect are still lacking.

### References

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### Molecular Models for the Structure of Solvent in an Interphase

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In the last two decades a considerable effort has been expended on the development of molecular models for the solvent in an interphase especially for the mercury–aqueous solution interphase. The great majority of this work originates in the model proposed by Watts-Tobin [1] in which the solvent dipoles are assumed to be able to take up two orientations. This model and developments of it have been remarkably successful in representing the experimentally observed properties of mercury electrodes in aqueous and many non-aqueous solutions. Nevertheless, this type of model was subjected to a rather fundamental criticism by Cooper and Harrison [2] who showed that non-physical results could be obtained using not-unreasonable values of the parameters of the model. This difficulty can be overcome

by careful choice of the details of the model, but the basic criticism has never been satisfactorily answered.

In the present work the origin of the difficulty pointed out by Cooper and Harrison is explored and it is demonstrated that the Watts-Tobin model rests on an invalid postulate. Once this postulate has been abandoned, it becomes possible to develop a more consistent model of solvent in the interphase.

The first steps of this development will be outlined.

#### References

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