

Parsons R & Zobel F G R. The interphase between mercury and aqueous sodium dihydrogen phosphate. *J. Electroanal. Chem.* 9:333-48, 1965.
[Department of Physical Chemistry, University of Bristol, England]

In this paper we investigated the extent to which HPO_4^- ions were specifically adsorbed at a mercury/aqueous electrolyte interphase. Sensitive tests were developed for weak specific adsorption. In the region of negative charges on the mercury, the negative adsorption of the anion was used to estimate the effective thickness of the Helmholtz layer, which was shown to be about equal to the diameter of a water molecule and somewhat dependent on the interfacial charge. [The $SC^{1/2}$ indicates that this paper has been cited in over 170 publications.]

Roger Parsons
Department of Chemistry
University of Southampton
Southampton SO9 5NH
England

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In the early 1960s I was interested in the adsorption of organic ions and molecules at the mercury/aqueous solution interphase. Although many measurements had been published on this subject, they were done almost without exception in a base electrolyte such as sodium sulphate or potassium chloride where the anion was specifically adsorbed. This meant that the organic species was competing with anion adsorption at least when the mercury was positively charged. The analysis was therefore more complex and difficult to reconcile with simple models of the interphase. A few measurements had been done with NaF as a base electrolyte since F^- is scarcely adsorbed on Hg. However, NaF is difficult to purify and has other objectionable properties. We were therefore looking for another base electrolyte with a very weakly adsorbed anion. NaH_2PO_4 appeared promising since old measurements by M. Gouy¹ in 1903 showed that there was no adsorption at mercury when its charge was zero.

A large section of Frank Zobel's thesis in 1963 at the University of Bristol was devoted to a careful experimental study of this system together with the development of sensitive ways of detecting and measuring specific adsorption when it is weak. This is difficult because electrostatic adsorption is always present and may mask nonelectrostatic adsorption. One of these tests was the plot of the reciprocal of the measured differential capacity of the interphase against the reciprocal of the differential capacity,

calculated at the same mercury charge, from the Gouy-Chapman (diffuse layer) theory. This has become known as a Parsons-Zobel (P-Z) plot and is the reason this paper is frequently cited.

More recently, the P-Z plot has been used with experimental results on solid metals as a measure of surface roughness. For a uniform but rough surface, the slope of this plot becomes less than unity, and its reciprocal can be interpreted as the ratio of true to projected surface of the electrode. The condition of uniformity is important, as Georges Valette and Antoinette Hamelin first showed.² A polycrystalline surface is made up of elements having different interfacial capacity, and the explanation of a nonunit P-Z slope is more complex. The use of the P-Z plot alone can be misleading, and it always needs to be supplemented by other types of experimentation; nowadays, a great range is available.

The original experiments have been used again recently in a note I wrote with Lesser Blum and Douglas Henderson.³ In it the deviations from the P-Z line at high concentrations were compared favourably with a much more sophisticated model of the electrolyte (a mixture of hard spheres in the mean spherical approximation) and used to suggest that the electron distribution in the surface of the metal makes a substantial contribution to the observed capacity.

Although I think that the P-Z plot is a useful and graphic way of presenting the data, it is not an aspect of my work that, at the time, I would have expected to be widely cited. The calculation of Helmholtz layer thickness as a function of charge seems to me of greater interest. It was based on earlier work by A. Frumkin⁴ and J.E.B. Randles,⁵ and although approximate, it does give a real idea about the dimensions of this region. Perhaps the thermodynamic basis does not make it appeal to a wide public.

The original aim of the work was not achieved. The H_2PO_4^- adsorbed more strongly than F^- , so we did not find a good substitute for NaF as a base electrolyte. However, no one else subsequently succeeded in this aim. Perhaps it should be remarked that the relative adsorbability of ions differs to some extent with the nature of the metal.

The study of electrode interphases remains an important and active area, although the emphasis has shifted to more realistic models and to experiments with solid electrodes that can now be obtained with well-defined surfaces.

1. Gouy M. Sur la fonction électrocapillaire (Electrocapillarity). *Ann. Chim. Phys.* 29:145-241, 1903.
(Cited 65 times since 1955.)
2. Valette G & Hamelin A. Structure et propriétés de la couche double électrochimique à l'interphase argent/solutions aqueuses de fluorure de sodium (Structure and properties of double electrochemical films at sodium fluoride aqueous solution/silver interphases). *J. Electroanal. Chem. Interfac.* 45:301-19, 1973. (Cited 125 times.)
3. Blum L, Henderson D & Parsons R. The mean spherical approximation capacitance of the double layer for an electrolyte at high concentration. *J. Electroanal. Chem. Interfac.* 161:389-92, 1984.
4. Jofa S & Frumkin A. Electrocapillary curves of concentrated solutions of acids.
Acta Physicochim. URSS 10:473-80, 1939.
5. Randles J E B & Harrison J A. Informal meeting on electrochemistry. Newcastle. April 1959. (Unpublished report.)