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DOUBLE LAYER STRUCTURE AND ELECTRODE KINETICS.(U)
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The modular "systems" formalism for the description of the admittance of electrode kinetics was applied to membranes, especially to the cases in which membrane-soluble ions cross the membrane, or where ion transport is facilitated by cation carriers, or proton transport by weak acids. The expressions include the effects of the ionic displacement current, which was studied separately in greater detail. Two manuscripts surveyed double layer effects on membranes and at electrodes, while an extensive review discussed the mathematical modeling of ion transport through membranes. Some problems were

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The above research program encompassed theory, development of new instrumental methods as well as experimentation. Its accomplishments will be discussed in this order. Numbers in parentheses will refer to the attached list of publications.

The modular "systems" formalism for the description of the admittance of electrode kinetics was applied to membranes, especially to the cases in which membrane-soluble ions cross the membrane (7), or where ion transport is facilitated by cation carriers, or proton transport by weak acids (13). The expressions include the effects of the ionic displacement current, which was studied separately in greater detail (4). Two manuscripts surveyed double layer effects on membranes and at electrodes (1,14), while an extensive review discussed the mathematical modeling of ion transport through membranes (3). We also treated some problems which occur in the application of admittance measurements to a fixed or rotating disk electrode (8).

A new method to analyze electrocapillary data was developed, based on Fourier transformation (2). This efficient method has since been applied successfully in our work on sucrose adsorption, see below. The sampling problem of measurements on a dropping mercury electrode was addressed (12). It was found that the usual errors involved in sampling on the growing mercury surface can be reduced more than an order of magnitude, from over one percent to less than one per mille, by either using averaging over the sampling interval or, for "instantaneous" measurements, by taking into account the transfer function of the specific detector used.

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A novel method was devised and tested to obtain admittance data on time-varying objects such as a dropping mercury electrode (11). The technique is the digital analog of synchronous detection, with the additional advantages of high speed (even faster than Fourier transformation) and simultaneous detection at a number of different frequencies. It uses the Hadamard transform algorithm.

Extensive double layer studies were made at the water-membrane and water-mercury interfaces. The effect of the neutral compound phloretin, which can modify membrane permeability more than thousandfold by changing the existing dipole potential, could be interpreted quantitatively (5). The effect was used to determine the nature of the phloretin adsorption isotherm.

A boxcar integration method was developed which allows us to measure short-lived transients with our PDP-11 minicomputer. The method yields a time resolution of 0.1 μs and has been used effectively to establish that the anomalous behavior of dipicrylaminate is due to ion pairing (15).

Extensive ion probe measurements using perbromate, and a combination of dc, ac and pulse polarography, were made in order to measure possible specific adsorption of both fluoride anions and alkaline earth cations on mercury. The fluoride data tested whether the method is useful up to high ionic strengths, where the more classical methods fail; no internal inconsistencies were observed (9). In the case of the alkaline earth cations, the method appears to yield results which are too high, most likely as the result of a "dynamic discreteness-of-charge effect, whereby the probe ion is attracted to the vicinity of the oppositely charged, specifically adsorbed ion, and hence oversamples its presence (10).

During efforts to find additional probe ions we found that tetrathionate, a likely candidate, is specifically adsorbed onto mercury even at very low (10^{-4} to 10^{-5} M) concentrations, and is therefore not useful as a probe (6).

Using our fully computer-controlled maximum bubble pressure instrument, we have studied the adsorption of sucrose on Hg from aqueous NaCl solutions (16). Sucrose was selected because it is adsorbed over the entire range of experimentally accessible potentials, and NaCl because activities of the ternary system sucrose-NaCl-water are available. The data obtained show that the mutual effects of sucrose and chloride adsorption are very small, and can be neglected to a first approximation. These measurements also confirm, at least qualitatively, our earlier probe results on specific adsorption of alkali cations (17).

Cumulative list of publications

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17. R. de Levie and M. Krishnan, On subequivalent specific adsorption of ions, in preparation.

Respectfully submitted,

Robert de Levie

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