

Enhancement of Adsorption of Organics at High-Area C Electrodes by Variation of Potential and Surface Charge

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Use of high specific-area C materials, e.g. granular activated charcoals, has been employed extensively for clean-up of organic and other impurities in waste-waters and in preparative organic chemistry in final work-up stages. For a number of applications, use of C powders or granules is inconvenient (except in fluidized-bed systems) and in most of such processes the aspect of control of electrode potential has been ignored, except in preparative electro-organic chemistry at bulk C and in the use of C electrodes for electrolytic Cl₂ (old technology) or F₂ production.

In the present work, we report the use of a high specific-area, woven C-cloth electrode material ("Spectracarb 2225"), having a real area of ca. 2500 m² g⁻¹. The C-cloth can be spirally wound into compact cylindrical electrodes, provided with a suitable gold wire current collector, that have excellent mechanical integrity compared with packed C particles or granules.

Using such electrodes, we have been able to demonstrate major effects of variation of electrode potential (controlled in a 3-electrode cell) on adsorption of organics such as aniline, pyridine, bipyridyls, 1,4-pyrazine, xanthate, and various other heterocycles at electrodes of the above kinds.

The electrodes are characterized by their interfacial capacitance, determined by cyclic voltammetry, which enables also the extents of electrosorption of the organics to be evaluated as a function of surface charge density, q . Electrosorption was studied both under galvanostatic (positive and negative) current control and potentiostatic control enabling comparisons between these conditions to be evaluated. Comparisons were also made with behavior observed under open-circuit conditions. The electrical behavior of such high-area electrodes has to be considered in terms of their porous structure, as in the treatments of de Levie [1] and of Conway [2] in terms of double-layer Supercapacitors.

Extents of adsorption of the organic adsorbates were quantitatively monitored, *in situ*, by means of UV-Vis spectrophotometry [3,4] employing a quartz cuvette sealed to the bottom of a V-shaped electrochemical cell that could be placed inside the spectrometer chamber, darkened by a black curtain. The spectroscopic technique was employed in a computer-controlled Cary spectrophotometer enabling *kinetics* as well as extents of adsorption to be recorded as a function of time. The observed kinetics were usually found to be dependent on the structure of the adsorbed organic and, in the case of isomers, specifically on their configuration. Adsorption extents and rates were also very dependent on whether (for the case of the N-bases) they were protonated (acid pH) or not. These observations indicated the importance of electrostatic interaction with the C surface and the role of hydrophobic adsorption, also proved by comparative experiments in non-aqueous solvents, and in aqueous/non-aqueous solvent mixtures.

The electrode-potential (and conjugate surface charge-density) dependence of electrosorption of small organics has been the subject of much earlier work at the Hg/aq. solution interface, as in the seminal works of Frumkin [5], Butler [6] and of Parsons [7], who also provided theoretical bases for the effects of electrode potential on organic molecule adsorption (such as *n*-amylalcohol) originating from electrostatic polarization energies of solute and solvent in the electrode/solution interphase.

We show, probably for the first time, that the same principles apply at the high-area C electrodes leading to the observed major effects of electrode polarization at C on the adsorption of the organics, as may be expected.

Applications to environmental chemistry will be discussed, where the controllable effects of varied potential and surface charge-density are particularly useful.

References

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