EXPERIMENTAL AND THEORETICAL ANALYSIS OF THE SURFACE CHEMICAL EFFECTS IN THE ADSORPTION OF AROMATICS CONTAINING ELECTRON-WITHDRAWING AND ELECTRON-DONATING FUNCTIONAL GROUPS

Ljubisa R. Radovic and Joshua I. Ume
Fuel Science Program
Department of Materials Science and Engineering
The Pennsylvania State University, University Park, PA 16802

INTRODUCTION

Adsorption of organic water pollutants onto activated carbon surfaces has been studied extensively and a very voluminous literature is available on this increasingly important environmental problem [1]. From a practical point of view, the adsorption capacity of an activated carbon depends on (a) the nature of the adsorbent (e.g., functional groups present, surface area and pore size distribution), (b) the nature of the adsorbate (e.g., functional groups present, polarity, molecular weight, solubility and pK_a or pK_b for weak electrolytes), and (c) solution conditions (e.g., pH, temperature and adsorbate concentration). From a fundamental standpoint, the central issue is how to account simultaneously for the well documented importance of (a) pH of the aqueous solution, and (b) surface chemistry of the adsorbent. In other words, the relative importance of electrostatic and dispersive adsorbate/adsorbent interactions is of interest.

We have been interested in these fundamental issues for some time now. We concluded that, while electrostatic interactions are important, they are often not as dominant as they are in the adsorption of inorganics [3]: π-π dispersion interactions are often more important for the adsorption of aromatic solutes. On the other hand, electrostatic repulsion appears to be much more important for the adsorption of aliphatic anions.

The remaining key questions seem to be related to the special features of phenol adsorption [4] and the complex behavior of natural organic matter [5]. In the present study, we focus on the former issue. We contrast the behavior of three chemically different carbons in adsorbing two vastly different aromatic solutes: benzoic acid is a strong acid (pK_a=4.2; H_2O solubility = 0.29/100) possessing the electron-withdrawing COOH (or COO^-) group, while phenol is a weaker acid (pK_a=10.0; H_2O solubility = 6.7/100) that possesses the electron-donating OH (or O^-) group. The chemical differences among carbons are produced by incorporating O- or N-containing functional groups, or by removing O functional groups and stabilizing free carbon surface sites against room-temperature oxidation [6].

EXPERIMENTS AND THEORY

Batch equilibrium adsorption tests, as a function of pH, adsorbate concentration and carbon surface chemistry, were performed as described elsewhere [2].

The key equations describing competitive Freundlich-type adsorption on amphoteric carbon surfaces, in terms of fractional surface coverage θ of molecules (M) and ions (M^+ or M^-) of a partially dissociated organic solute on a heterogeneous surface, are the following [7]:

$$\theta = \theta_M + \theta_{M\pm} = \frac{C_\alpha}{C_1}(\frac{C_1}{C_1 + K})^n$$

$$C_\alpha = [M] + \frac{\alpha[M^\pm]}{K_q} \quad \text{and} \quad C_1 = [M] + \frac{[M^\pm]}{K_q}$$

where K_q and K are the electrostatic and dispersion adsorption potentials, n is a surface heterogeneity parameter and α represents the fraction of the surface accessible to the coionic adsorbate species.

RESULTS AND DISCUSSION

Figures 1-4 are illustrations of the interplay of electrostatic and dispersion forces in the adsorption of benzoic acid and phenol on chemically modified carbon surfaces. The results of these parametric sensitivity studies will be discussed in more detail at the Conference. For example, conversion of an 'acidic' carbon to a 'basic' carbon (Figures 1 and 3) increases the point of zero charge from 3 to 10, and this is beneficial for the adsorption of benzoate anions at high pH. The relative changes in the dispersion potentials between benzoic acid and phenol will be of special interest.

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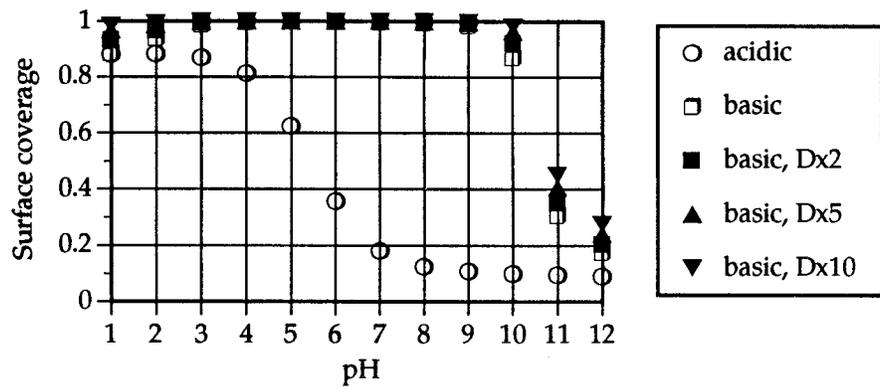
Figure 1. Combined effects of electrostatic and dispersive interactions on changes in phenol uptake upon thermal treatment of an 'acidic' carbon and its conversion to a 'basic' carbon. (The dispersion potential is enhanced by a factor of 2, 5 or 10.)
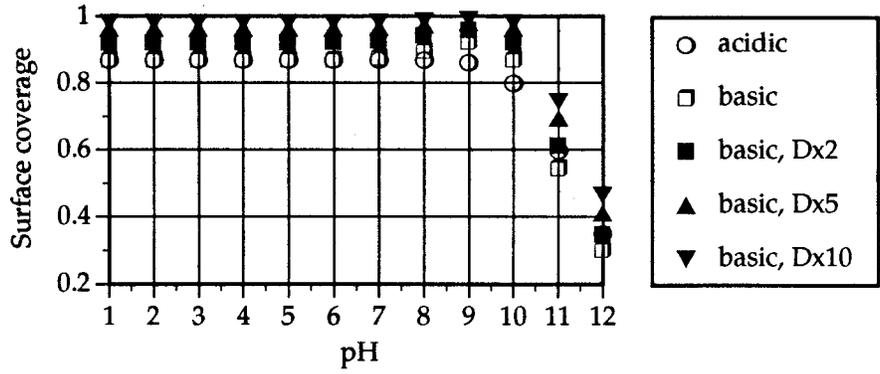
Figure 2. Combined effects of electrostatic and dispersive interactions on changes in phenol uptake upon surface oxidation of a 'neutral' carbon and its conversion to an 'acidic' carbon. (The dispersion potential is reduced by a factor of 2, 5 or 10.)
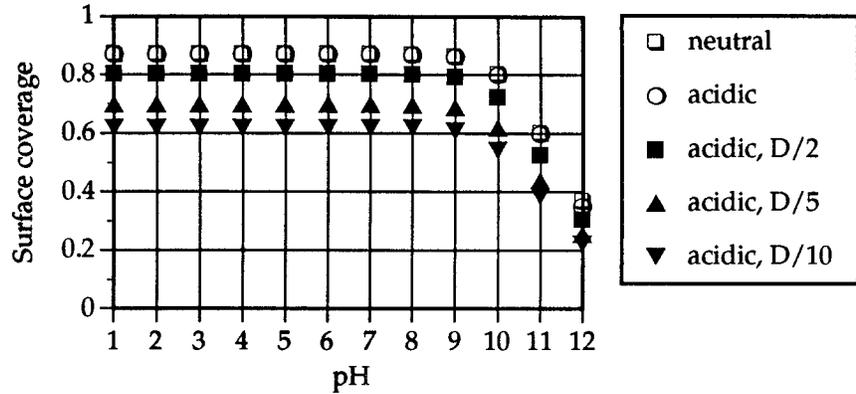
Figure 3. Combined effects of electrostatic and dispersive interactions on changes in benzoic acid uptake upon thermal treatment of an 'acidic' carbon and its conversion to a 'basic' carbon. (The dispersion potential is enhanced by a factor of 2, 5 or 10.)

Figure 4. Combined effects of electrostatic and dispersive interactions on changes in benzoic acid uptake upon surface oxidation of a 'neutral' carbon and its conversion to an 'acidic' carbon. (The dispersion potential is reduced by a factor of 2, 5 or 10.)