

# Investigating the thermodynamic causes behind the anomalously large shifts in $pK_a$ values of benzoic acid-modified graphite and glassy carbon surfaces

Abiman, P.<sup>1</sup>, Crossley, A.<sup>2</sup>, Wildgoose, G.G.<sup>1</sup>, Jones, J.H.<sup>3</sup> and Compton, R.G.<sup>1</sup>

<sup>1</sup> Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, United Kingdom

<sup>2</sup> Materials Department, University of Oxford, Parks Road, Oxford, OX1 3PH, United Kingdom

<sup>3</sup> Chemical Research Laboratory, University of Oxford, Mansfield Road, Oxford, United Kingdom

## Abstract

The difference between the values of 4-carboxyphenyl groups, covalently attached to either graphite (BAcarbon) or glassy carbon (BA-GC) surfaces, and benzoic acid in solution is explored using Potentiometric titration and cyclic voltammetry. In solution, benzoic acid has a  $pK_a$  of 4.20 at 25°C. However, the observed  $pK_a$  value on the graphitic surfaces shows significant deviations, with BAcarbon exhibiting a large shift to higher  $pK_a$  values ( $pK_a = 6.45$ ) in contrast to BA-GC, which is shifted to lower  $pK_a$  values ( $pK_a = 3.25$ ). Potentiometric titrations at temperatures between 25 and 50°C allowed us to determine the surface  $pK_a$  of these materials at each temperature studied and hence to determine the enthalpy, entropy, and Gibbs' energy changes associated with the ionization of the carboxylic acid groups. It was found that the endialpic contribution is negligible and that the changes in surface  $pK_a$  values are entropically controlled. This suggests that solvent ordering/disordering around the interface strongly influences the observed  $pK_a$  value, which then reflects the relative hydrophobicity/hydrophilicity of the different graphitic surfaces.

## Indexed keywords

**Engineering controlled terms:** Cyclic voltammetry; Enthalpy; Entropy; Gibbs free energy; Graphite; Titration

**Engineering uncontrolled terms:** Benzoic acid; Carboxyphenyl groups; Glassy carbon surfaces; Potentiometric titration

**Engineering main heading:** Thermodynamics