INTERACTION OF GRAPHITIC CARBONS WITH SULPHUR CONTAINING COMPOUNDS

A.J. Groszek,
Microscal Ltd. 79, Southern Row, London W10 5AL. U.K.

Introduction

The author has found previously that graphitic basal planes adsorb preferentially n-paraffins dissolved in a low molecular weight solvents, as well as water soluble alcohols, acids, phenols and, more recently, transition metal compounds, both ionic and non-ionic, from solutions in water (2, 3). The latter adsorptions have been found to be especially strong at low surface coverage,up to 5% of the basal plane areas in graphitized carbons adsorbing irreversibly metal compounds such as $HgCl_2$ and $KPtCl_6$.

Previous work of the author also indicated that certain low molecular weight sulphur containing compounds such as sodium thiosulphate and sodium sulphide are preferentially adsorbed from dilute aqueous solutions suggesting that the graphitic basal planes may have a 'special relationship' with certain types of sulphur present in water soluble compounds (4). To verify this hypothesis a series of adsorption studies have been carried out with urea and thiourea having the same chemical structures, but with the sulphur atoms in thiourea replacing oxygen in urea. Similar work was also carried out with Na_2S, as opposed to NaOH. The results illustrate the striking affinity of the graphitic basal place surface for sulphur.

Experimental: Adsorbents and Adsorption/ Calorimetric Measurements

The active carbon used was a commercial material Chemviron BPL, having a BET N_2 surface area of $1000m^2/g$ and the polar surface of $53.6m^2/g$. Graphon was a graphitized carbon black with a BET N_2 surface of $85m^2/g$ and the polar surface of $0.14\ m^2/g$. The surface areas of the polar sites were determined microcalorimetrically (5). Urea and thiourea had purities exceeding 99% water was of HPLC grade supplied by Aldrich Chemicals. Adsorption was measured using a flow method in which the solutes remaining in solution after percolation through a small bed of adsorbent in the cell of a Microscal Flow Microcalorimeter (FMC) were determined by an on-line RI Monitor (6).

Results and Discussion

Sequential adsorptions of urea and thiourea from aqueous solutions as a function of solute concentration are shown in Figures 1 and 2. Computer graphics shown in the figures represent consecutive heat effects produced as the concentration of the solutes increases in steps from 0.01 to 0.10 milimoles. The resulting adsorption peaks are obtained from the reduction of the solute concentrations following the percolation of the solutions through the adsorbent. The shape of the peaks is related to the adsorption rate. The peaks show a distinct difference between the kinetics of adsorption on the imcroporous carbon BPL as compared with non-microporous Graphon, the adsoprtion process being completed much faster on the latter adsorbent. Figures 3, 4 show the adsorption isotherms and figures 5, 6 give the corresponding heats of adsorption for Carbon BPL and Graphon respectively.

It is immediately clear that the adsorption of thiourea is higher and stronger on both carbons than that of urea. There are no adsorption plateaux. As the adsorptions per unit basal plane are similar for carbon BPL and Graphon they probably occur exclusively on that surface.

Similar results have been obtained with Na_2S and NaCl. The latter salt is hardly adsorbed at all on both carbons from aqueous solutions, but Na_2S gives very high heats of adsorption, higher than those of thiourea, as shown below, for adsorption from 0.01M solutions.

Adsorbent	Adsorption umol g^{-1}		Heat of Adsorption, Jg^{-1}	
	Thio-urea	Na_2S	Thiourea	Na_2S
Graphon	62	12.5	0.43	8.1
Chemviron BPL	604	383	26.00	63.4

It is concluded that the graphitic basal planes have strong affinity for S, both in ionic and non ionic forms, suggesting that the Π electronic system of the basal plane interacts intensely with the polarisable sulphur atom.

References

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6. A.J. Groszek & S. Partyka, Langmuir, 9, pp 2721-2725, 1993.

Figure 1 Sequential Heats of Adsoprtion of Thiourea from Water on 0.0704g of Graphon

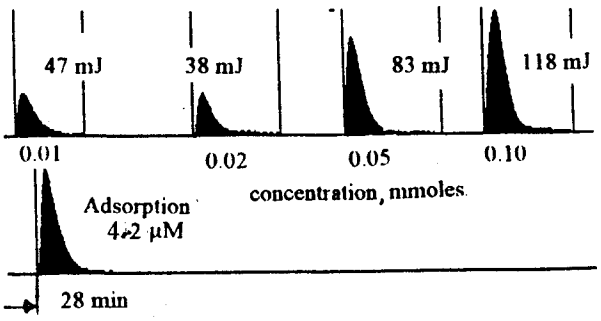

Figure 2 Sequential Heats of Adsorption of Thiourea from Water on 0.0067g of Active Carbon BPL.

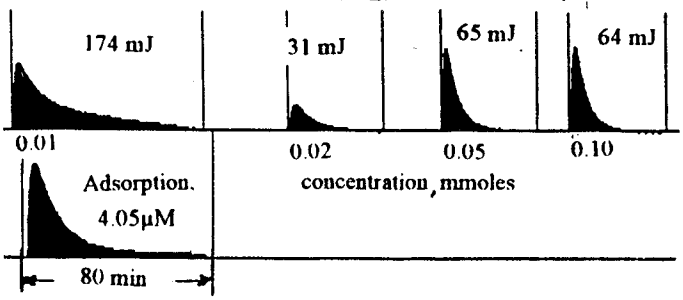

Figure 3: Adsorption of Thiourea and Urea on Active Carbon BPL

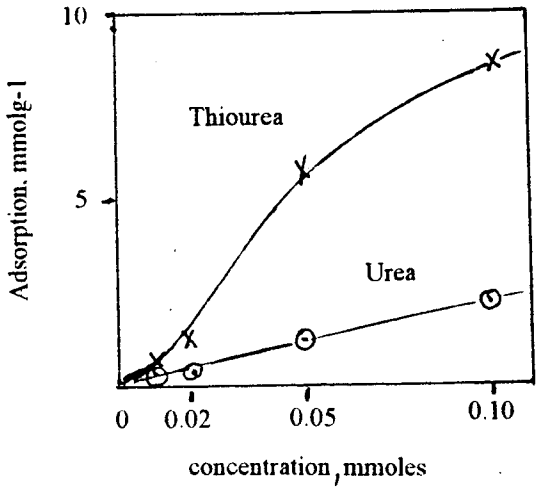

Figure 4 Adsorption of Thiourea and Urea on Graphon

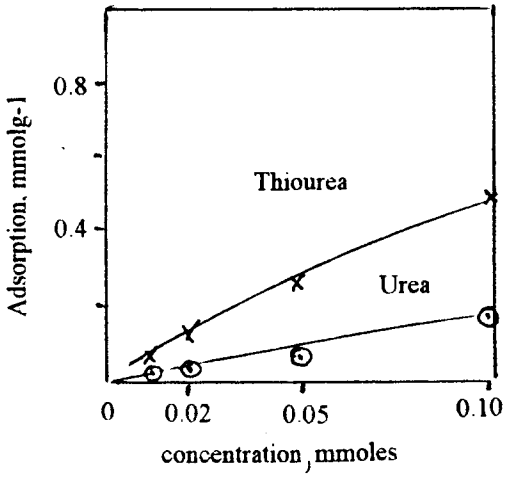

Figure 5 Cummulative Heats of Adsoprtion of Thiourea and Urea on Active Carbon BPL

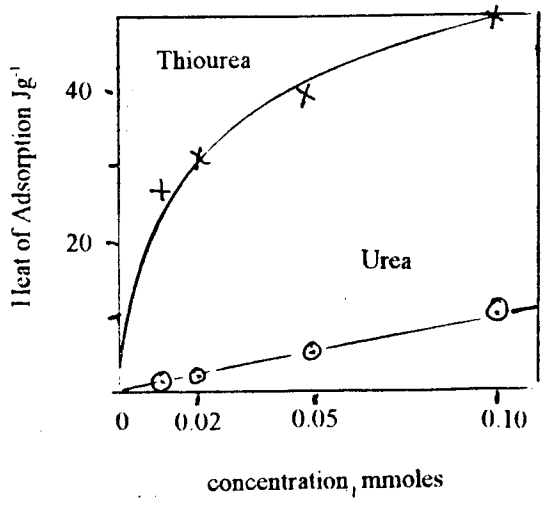

Figure 6 Cummulative Heats of Adsoprtion on Graphon