

ADSORPTION ENTHALPIES FOR HYDROCARBONS ON WYODAK COAL SURFACES BY INVERSE GAS CHROMATOGRAPHY

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(Keywords: Wyodak coal, coal surfaces, inverse gas chromatography)

Introduction

Studies of coal surface interactions are important for understanding how technologically important reagents interact with coal. Thermodynamic data provide a quantitative means to assess the interactions between reagents and coal. Knowledge of interaction strengths for solutes with coal surfaces should enable the design of more effective coal reaction strategies and lead to better utilization of coal as fuel and chemical feedstock.

In addition, studies of coal surface thermodynamics provide information about the structure and chemistry of coal. An important advantage with surface thermodynamic data is that they are not complicated by processes in bulk coal. For example, surface data are free of mass transport effects and intermolecular coal-coal associations which may exist in the bulk. Surface interaction data therefore provide a direct measure of the interaction between the solute and coal for a single specific type of chemical or physical property of the coal.

We recently developed the technique of inverse gas chromatography (IGC) for obtaining coal surface thermodynamics.¹ Solute molecules are carried past coal packed into a stainless steel tube. IGC provides a means to discriminate against the diffusion of solutes into bulk coal and thus enables the measurement of surface adsorption thermodynamics for polar and nonpolar molecules with coal surfaces. Coal IGC data are collected in the Henry's Law region of the adsorption isotherm, so the data represent interactions with the coal at infinite dilution surface coverage.

The present paper reports surface thermodynamic data for Wyodak coal surfaces. Because the coal is from the Argonne Premium Coal Sample Bank, it is intended that the interactions at this surface provide a benchmark for interactions of solutes with a low rank, high oxygen content coal. In the present work, it has been found that the Wyodak surface has relatively weak (low exothermicity) adsorption enthalpies with saturated hydrocarbons (alkanes) but quite strong (highly exothermic) interactions with alkenes and aromatic adsorbates. Recently, Ahsan et al. reported calorimetric data for aromatics with original and with citric acid washed (CAW) Wyodak coal.² These workers observed that citric acid washing of Wyodak coal caused heats of immersion (ΔH_{imm}) for the coal in aliphatic acids to decrease while ΔH_{imm} in aryl sulfonic acids increased. In contrast, CAW caused no changes in the ΔH_{imm} of Illinois No. 6 coal in these acids. Nishioka observed that alkylation or washing in 2N HCl caused a drastic increase in the swelling ratio of the pyridine insoluble portion of a Wyoming subbituminous coal.³ These changes were not observed for a higher rank Illinois No. 6 coal. He ascribed the changes in the Wyoming coal to the reduction of strong ionic forces in the coal by HCl or by the tetrabutyl ammonium salt which acts as a catalyst in the alkylation procedure. The existence of strong ionic forces in low rank coal is supported by the results of the present work. These forces make themselves felt in the unusually exothermic interactions of unsaturated hydrocarbon adsorbates with the Wyodak coal surface.

Theory

IGC differs from analytical GC in that in IGC the emphasis is on stationary phase properties as opposed to properties of the injected solute. In IGC, the retention volume serves as a measure

of the interaction strength between the single, pure injected solute and the stationary phase. The interaction is most straightforward in the regime of linear chromatography. In this regime, the retention volume represents the Henry's Law constant for the solute-stationary phase interaction. If the retention volume is sensitive to the surface of the stationary phase, then the Henry's Law constant expresses the equilibrium interaction between the injected solute and the stationary phase and gives the equilibrium constant for surface adsorption, K_s . This relationship is expressed by equation 1.

$$K_s = \frac{V_s}{RT} \quad (1)$$

where V_s is the retention volume per unit adsorbate gas pressure and per unit accessible surface area, S , of the stationary phase ($V_s = V_N/SRT$ where R is the ideal gas constant, T is the column temperature, and V_N is the retention volume corrected for pressure drop across the column.) The van't Hoff equation gives the enthalpy from the temperature dependence of the equilibrium constant. For equilibrium surface adsorption at infinite dilution surface coverage, the van't Hoff equation gives the isosteric adsorption enthalpy, q_{st} , as the slope of a plot of the natural logarithm of the retention volume over temperature vs. inverse temperature. Equation 2 is the defining equation:

$$\frac{d(\ln V_N/T)}{d(1/T)} = \frac{-q_{st}}{R} \quad (2)$$

Plots of $\ln(V_N/T)$ vs. $1/T$ were used to determine the isosteric adsorption enthalpies for saturated and unsaturated hydrocarbons on Wyodak coal surfaces.

Experimental

The procedure and apparatus for IGC of coal surfaces have been described previously.¹

Adsorbate liquids were obtained from Aldrich at the highest purities available and were used without further purification. They were admitted to the vacuum manifold for injection after at least 3 freeze-pump-thaw cycles. Adsorbate gases were obtained from Aldrich or from Matheson in the highest purities available and were admitted to the vacuum manifold directly. Wyodak coal (-20 mesh) was obtained from the Argonne Premium Coal Sample bank. The coal was sieved to 40/60 mesh and packed into 1/8 inch O.D. stainless steel tubes about 100 cm in length. The columns were heated in helium at 150°C or at 250°C for at least a week until the GC baseline stabilized. Significant weight loss (~30%) was observed. In order to eliminate the large dead volume these columns were repacked using coal which had been previously heated at 115°C in vacuum.

Retention volumes were determined from the first moments of the GC peaks. Van't Hoff plots were constructed using data obtained at temperature intervals of 5 to 10° over at least a 30° temperature range. At least 5 retention volumes were obtained at every temperature. The errors in the adsorption enthalpies were 7% or lower. Data for Illinois No. 6 coal are taken from reference 1.

Results and Discussion

Figure 1 shows plots of the isosteric adsorption heat, q_{st} , vs. the electronic volume polarizability of the adsorbates, α' , for *n*-alkane adsorbates on two different rank coals, an Illinois No. 6 bituminous coal and a Wyodak subbituminous coal.¹ Data for propene and 1-butene are also shown for the Illinois No. 6 coal. The lower plot is for alkanes on Wyodak coal and the upper plot is for alkanes on Illinois No. 6 coal. Both coals were heated at 150°C in helium. These plots demonstrate that these two coals have different dispersive surface interactions with alkanes. The Illinois No. 6 coal has more exothermic adsorption heats with alkanes, demonstrating that it has a more polarizable surface than

the Wyodak coal. Dispersive surface tensions, γ_s^d , have also been determined for the two coals, and are $\gamma_s^d=104 \text{ mJ/m}^2$ for Illinois No. 6 and $\gamma_s^d=25.2 \text{ mJ/m}^2$ for Wyodak.^{1,5} These data demonstrate that Wyodak coal possesses a relatively low energy surface, similar to those found for polymers such as polyethylene.⁶ This conclusion supports the idea that Wyodak coal has surface properties which are similar to those of its precursor, a polymeric cellulosic type of material. On the other hand, Illinois No. 6 coal possesses a higher energy surface, similar to those found for carbonaceous materials.⁴ As seen from the center plots, heating to 250°C or extracting either of the coals results in a surface with similar adsorption heats for alkanes. The adsorption heats for n-alkanes on both of these modified surfaces are similar to heats for alkanes on graphitized carbon black.⁴ The plot for Illinois No. 6 coal also shows data for two alkenes, propene and 1-butene. On Illinois No. 6 coal, alkene adsorbates have interactions which depend on adsorbate electronic polarizability (α') in the same way as the alkanes.

In Figure 2, adsorption heats for alkanes on Wyodak coal heated at 150°C and at 250°C are replotted. However, in Figure 2, these data are plotted vs. (total) volume polarizability, α' , whereas in Figure 1, they are plotted against electronic volume polarizability, α'_e . For alkanes, $\alpha'=\alpha'_e$, because these adsorbates only interact with the surface via induced dipole-induced dipole (London dispersion) forces. Also plotted in Figure 2 are adsorption heats for alkene and aromatic adsorbates on Wyodak coal. For alkenes, there is an additional induction contribution to α' . This contribution may make itself felt if there exists a dipole or Coulomb force at the surface which is capable of inducing a dipole in the adsorbate (Debye force).

Interpretation of the data for alkenes on the 250°C-heated coal appears relatively straightforward (Figure 2). The alkene adsorbates on this surface have q_s 's which depend on the total volume polarizability, α' , in the same way as the alkanes. (Alkenes on the 250°C-heated Wyodak surface have ~1.5-2.0 kcal/mol additional interaction with this surface over that expected from electronic polarizability (α'_e) alone.) Apparently, alkenes interact with this surface according to their total volume polarizabilities, α' . As seen from Figure 2, benzene has a somewhat stronger interaction with the 250°C-heated Wyodak coal surface than expected based on α' .

The data for alkenes on the 150°C-heated Wyodak surface appear to be more complex. (See Figure 2.) Propene and 1-butene have higher adsorption heats by ~3-4 kcal/mol with this surface than expected based on α' . It may be fortuitous that these adsorbates give adsorption heats on the 150°C-heated coal surface which equal those expected based on α' for the 250°C-heated coal surface.

Comparing the adsorption heats for alkenes on Illinois No. 6 coal (Figure 1) with those for alkenes on Wyodak coal (Figure 2) shows that there is an additional type of force operating at the Wyodak surface which produces more exothermic interactions with alkenes and aromatics. Ionic forces exist in low rank coals.³ At a surface, the presence of small cationic charges augments the adsorption heats with molecules that contain additional electron density in double, triple, or aromatic bonds.⁴ Such effects are observed for hydroxylated silica and for zeolite surfaces.⁴ Silica contains a cationic proton while zeolites contain Na^+ , Ca^{2+} , etc. ions. The existence of ionic forces at the Wyodak coal surface would explain the more exothermic adsorption heats with alkene and aromatic compared to alkane adsorbates. Studies are underway to explore the nature of these forces at the surfaces of original and modified Wyodak coal surfaces.

Acknowledgement

This work was supported by a Fellowship from the University of Dayton Research Council.

References

1. Glass, A. S.; Larsen, J. W. *Energy Fuels* 1994, 8, 629-636.
2. Ahsan, T.; Wu, J. H.; Arnett, E. M. *Fuel* 1994, 73, 417-422.
3. Nishioka, M. *Fuel* 1993, 72, 1725-1731.
4. Kiselev, A. V.; Yashin, Y. I. *Gas-Adsorption Chromatography*; Plenum: New York, 1969.
5. Glass, A. S., unpublished data.
6. Zisman, W. A. *Contact Angle, Wettability, and Adhesion*, ACS Adv. Chem. Ser. No. 43; American Chemical Society: Washington, DC, 1964; pp. 1-51.

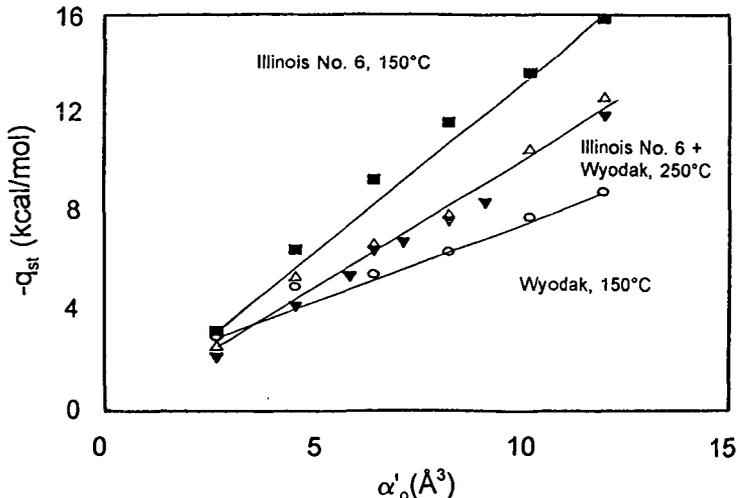


Figure 1. Isosteric adsorption heat (q_{st}) vs. electronic volume polarizability (α'_o) for hydrocarbons on Wyodak and Illinois No. 6 coal surfaces. ■=alkanes on Illinois No. 6 heated at 150°C. ▲=alkanes on Wyodak heated at 250°C. ○=alkanes on Wyodak heated at 150°C. For ■, ▲, ○ adsorbates are (from left to right): methane, ethane, propane, *n*-butane, *n*-pentane, *n*-hexane; ▽=alkanes and alkenes on Illinois No. 6 coal extracted in tetrahydrofuran and heated at 150°C. For ▽ adsorbates are: methane, ethane, cyclopropane, propane, propene, 1-butene, *n*-pentane, *n*-hexane. All coals heated in helium.

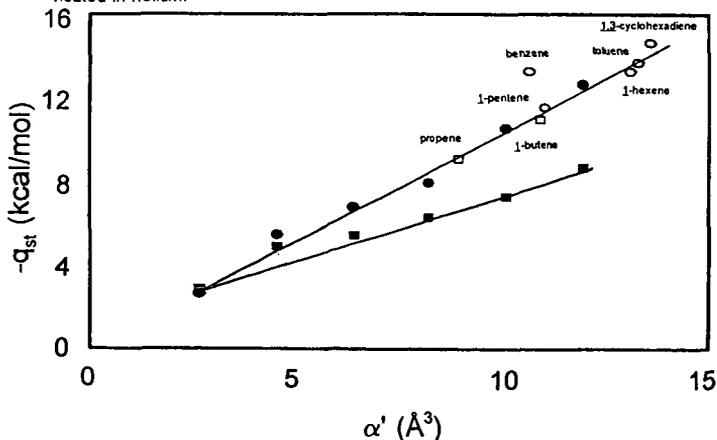


Figure 2. Isosteric adsorption heat (q_{st}) vs. volume polarizability (α') for hydrocarbons on Wyodak coal surfaces. ■=alkanes on Wyodak heated at 150°C. ●=alkanes on Wyodak heated at 250°C. □=alkenes on Wyodak heated at 150°C. ○=alkenes and aromatics on Wyodak heated at 250°C. For ■ and ● adsorbates are: methane, ethane, propane, *n*-butane, *n*-pentane, *n*-hexane. For □ adsorbates are propene and 1-butene. For ○ adsorbates are 1-pentene, 1-hexene, 1,3-cyclohexadiene, benzene, and toluene.