

COAL SURFACE THERMODYNAMICS BY INVERSE GAS CHROMATOGRAPHY*

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Introduction

Determination of coal surface interactions is important for the development of improved coal liquefaction and beneficiation methods. Knowledge of interactions at coal interfaces will aid the development of such technologically important coal reactions.

Although coals possess pores, they probably do not possess interconnected internal surfaces^{1,2}. Coals have the properties of adsorbents, including an external surface and the ability to absorb molecules in the bulk. A technique that determines coal surface interactions must be sensitive to interactions at the external coal surface.

Many techniques are available for studying interactions at surfaces, but most are not suitable for measuring interaction thermodynamics of complex coal surfaces. Static adsorption and calorimetric techniques measure coal-solute interactions, but they are plagued by diffusion of the solute into the coal³⁻⁵. In contrast, inverse gas chromatography (IGC) is a dynamic sorption technique. Only those interactions that occur during the time of travel of the solute contribute to the signal in IGC. Therefore, IGC is sensitive to coal-solute interactions that occur in the rapid uptake regime rather than those that occur during the slow approach to equilibrium that characterizes static sorption measurements of coals.

Theory

IGC is most straightforward in the regime of linear chromatography. In this regime, also called the "Henry's Law" or "infinite dilution" regime, the retention volume is most characteristic of the interaction between the solute and the stationary phase. For a single type of retention mechanism, i.e., surface adsorption, the Henry's Law constant, K_s , expresses the equilibrium thermodynamic interaction between the adsorbate and the stationary phase. K_s is the retention volume per accessible surface area of the stationary phase and per unit pressure of adsorbate in the gas phase⁶:

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

where V_N is the net retention volume, S is the surface area of the stationary phase that is accessible to the solute, R is the gas constant, T is the column temperature, and V_s is the specific

retention volume.

The dependence of retention volume on surface area has been used to determine S for stationary phases. If V_N is determined for a given probe molecule on a stationary phase of known S , then S can be calculated for a column of unknown S from⁶:

$$S = \frac{V_N}{V_g} \quad (2)$$

For polymers below T_g where adsorption occurs on the external geometrical surface, it has been shown that S is equivalent to the external geometrical surface, S_{geom} ⁷. For spherical particles of radius r and particle density ρ , S_{geom} is given by⁸

$$S_{geom} = \frac{3}{\rho r} \quad (3)$$

Since K_s is the equilibrium constant for surface adsorption, then

$$K_s = K_{s,o} e^{\frac{q_{st}}{RT}} \quad (4)$$

where q_{st} is the isosteric heat of adsorption. Substituting equation 1 and converting to natural logarithms gives

$$\ln(V_N/T) = \frac{q_{st}}{RT} + \ln K_{s,o} + \ln SR \quad (5)$$

The slope of a plot of $\ln(V_N/T)$ vs. $1/T$ gives q_{st} . The adsorption entropy, ΔS° , may be determined from^{9,10}

$$\Delta S^\circ = \frac{-q_{st}}{T} + 31.61 + R \ln V_g \quad (6)$$

Experimental

Experiments were conducted by injecting gas samples at pressures of 0.01 to 10.0 Torr from a glass manifold via an 8-port Valco GC valve with 0.015 and 0.100 ml sample loops. Pressures were measured with a 1 Torr Baratron gauge (MKS Instruments, Inc.) or a mercury manometer attached to the sample reservoir.

Gases were 99% purity or better. Liquids obtained from Aldrich in "sure-seal" bottles were subjected to at least three freeze-pump-thaw cycles before being introduced as gases at pressures below their vapor pressures.

Argon premium Illinois No. 6 coal was sieved to give the desired fraction (80/100, 60/70, or 40/60 mesh) and about 4g was packed into a 1/8 inch O.D., 2.1mm I.D. ss column about 1.5m in length. The particle density was 1.3 g/ml¹¹. The coal was degassed overnight at 150°C before each day's experiments. The

GC was a Hewlett-Packard 5890A equipped with both TCD and FID detectors. 0.03 inch I.D. ss tubing was used between the GC valve and the column inlet to minimize dead volume.

Data were collected over the range 30 to 150°C, with injector and detector temperatures at 180°C. The temperature of the chromatograph oven was accurate to $\pm 0.1^\circ\text{C}$ and was constant to within 0.2°C over different parts of the oven. Flow rates ranged from 5 to 35 ml/min. They were determined using a bubble meter and were corrected for the effect of water vapor. The pressure drop was determined using a pressure transducer (Omega Engineering, Inc.) on the column inlet and a barometer for measuring atmospheric pressure. Typical pressure drops were about 1 atm. Retention volumes were corrected using the pressure drop correction term, j^{12} .

Column dead volumes were determined from geometrical considerations for the different mesh fraction particle sizes and checked using columns of the same length and diameter packed with the same mesh fraction of nonporous glass beads. Retention times for various solutes on the glass bead columns were characteristic of the dead volume.

Data were collected using Lab Calc software (Galactic Industries Corp.) at rates of one point per second. Retention times were determined as first moments of the peaks using Simpson's rule. Adsorption entropies were calculated using de Boer's approach⁹, assuming a standard gaseous state with a pressure of 1.01×10^6 dyne/cm² and a standard adsorbed state with a pressure of 0.338 dyne/cm.

Results and Discussion

I. Technique

With injection sizes greater than about 10^{-4} μmole of adsorbate, peak tailing increased greatly. With injection sizes below this saturation limit, peak shapes and retention times were independent of injection size. This behavior resembles that seen with column overload¹³. Assuming close packing of adsorbates on the coal surface, the injection sizes corresponding to the onset of column saturation gave specific surface areas of about 0.02 m²/g, similar to the geometrical surface area of coal in the column. This indicates that the accessible surface of coal in the column was equal to the external surface of the coal. All thermodynamic data were obtained using injection sizes below the saturation limit.

Table I shows accessible and geometrical surface areas calculated using equations 2 and 3 for columns containing different particle sizes of coal using three different adsorbates. From the table it is seen that the agreement between S and S_{geom} for methane and *n*-butane is good. The agreement for neopentane is worse and this will be discussed in the next section. These results show that the accessible surface is equal to the external surface of the coal, and provide further support for the idea that coal behaves as an adsorbent in IGC.

The surface areas in Table I, when corrected for the amount

of coal in the column, give specific surface areas on the order of $0.05 \text{ m}^2/\text{g}$. Assuming coal particle sizes of $25 \mu\text{m}$, typical of those used in static sorption experiments, gives an external geometrical specific surface area of $0.10 \text{ m}^2/\text{g}$. This value is smaller than specific surface areas determined by static sorption by at least 1 to 2 orders of magnitude^{1,4}. This provides evidence that static sorption determines a "coal surface area" which contains a contribution from absorption. In contrast, IGC measures a coal surface area that is due to surface adsorption only.

II. Thermodynamics

Figure 1 is a plot of q_{st} vs. polarizability, α , for linear alkanes, neopentane, and cyclopropane on Illinois No. 6 coal determined by IGC. In plot 1A, it is seen that the strength of interaction with the coal surface increases linearly with the polarizability of the adsorbate. The increase in q_{st} from methane to ethane is 3.2 kcal/mol , while that between ethane and propane is 2.8 kcal/mol . Between propane and *n*-hexane, the increase in q_{st} per CH_2 group of the adsorbate levels off to a constant value of about 2.1 kcal/mol . On carbon surfaces, the increase in q_{st} per CH_2 group of the adsorbate varies between about 1.0 and 3.0 kcal/mol , depending on the history of the carbon^{10,14}. Our values for Illinois No. 6 coal are higher than for graphitized carbon black surfaces and fall within the range for non-graphitized and oxidized surfaces.

While the adsorption enthalpies for the linear alkanes scale with polarizability, neopentane does not fall on the line. The effect of increased branching of the adsorbate on retention is well known for graphitized carbon surfaces¹⁵. This effect is probably responsible for the relatively low adsorption enthalpy of neopentane on Illinois No. 6 coal. In this context, it is interesting to reconsider the data in Table I. The data for neopentane show larger errors than those for methane and *n*-butane. This is probably due to the smaller coal surface area accessed by neopentane.

Plot 1B corresponds to adsorption heats on Illinois No. 6 coal extracted with tetrahydrofuran. The linear hydrocarbons show the linear relation between q_{st} and α , while neopentane falls slightly below the line. The decrease in the values of q_{st} for Plot 1B compared to 1A are greatest at high values of α , corresponding to the larger hydrocarbons. This indicates a decrease in carbon atom density as a result of extraction. For polyethylene glycol vs. carbon black, a decrease in the slope of a plot of q_{st} vs. carbon number was ascribed to a decrease in the energy of nonspecific interaction due to a decrease in the density of carbon atoms at the surface¹⁶.

Figure 2 is a plot of q_{st} vs. ΔS° for linear hydrocarbons and neopentane on both the extracted and original Illinois No. 6 coal. The linear relationship is an example of the well-known isokinetic effect¹⁷. The fact that the isokinetic effect holds supports the existence of a common surface adsorption interaction of these molecules with the coal.

Conclusion

Thermodynamic data for adsorption at the external surface of Illinois No. 6 coal have been determined by IGC. The behavior of Illinois No. 6 coal in these experiments fits with the view that coals are crosslinked macromolecular networks capable of taking up molecules into their bulk^{18,19}. This supports the position that coals do not contain interconnected pore networks^{1,2}.

The surface thermodynamic data are reasonable as they fall within the limits of those for non-graphitized carbon surfaces. The determination of surface thermodynamics for various coals and modified coals by IGC will enable the creation of a coal surface interaction database. This will aid the development of improved coal reaction strategies.

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- *A full paper on this topic has been submitted to The Journal of Physical Chemistry.

Table I. Geometrical and Accessible Surface Areas for Columns Containing 4 grams of Illinois No. 6 Coal of Different Particle Sizes.

Column	1	2	3
Mesh Fraction	80/100	60/70	40/60
r (μm) [†]	82.5	115.5	169.0
S_{geom} (m^2) [*]	0.110	0.080	0.055
S^a (m^2) [‡]	--	0.091	0.061
S^b (m^2) [‡]	--	0.150	0.038
S^c (m^2) [‡]	--	0.078	0.051
Diff S^a-S_{geom} , %	--	13.8	10.9
Diff S^b-S_{geom} , %	--	87.5	-32.7
Diff S^c-S_{geom} , %	--	-1.25	-7.27

[†]particle radius for the average particle size of the given mesh fraction.

^{*}Calculated from equation 3 assuming spherical particles.

[‡]Determined using equation 2 by setting the accessible surface area of column 1 to its geometrical surface area.

^a CH_4 from data at 90°C; ^bneo- C_3H_{12} from data at 115°C; ^c $\text{n-C}_4\text{H}_{10}$ from data at 120°C.

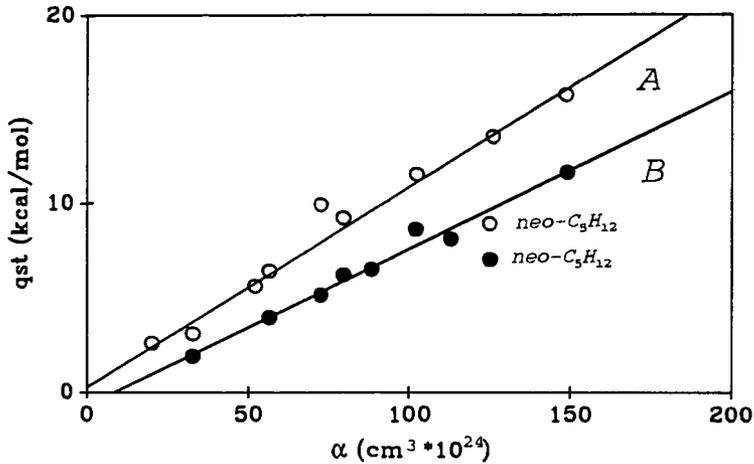


Figure 1. Heats of adsorption vs. polarizability for hydrocarbons on Illinois No. 6 coal. A, Original coal, o. B, Coal extracted with tetrahydrofuran, •.

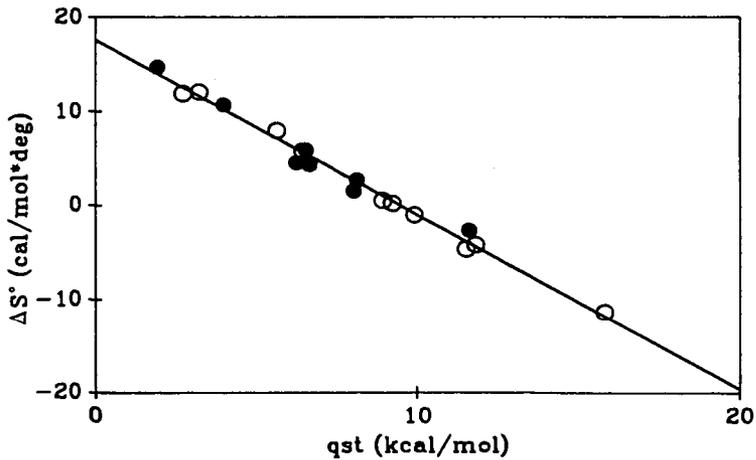


Figure 2. Heats of adsorption vs. entropies of adsorption for hydrocarbons on original and THF-extracted Illinois No. 6 coal. o, Original Coal; •, THF-extracted Coal.