



Enthalpy of adsorption for hydrocarbons on concrete by inverse gas chromatography[☆]

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ABSTRACT

Enthalpies of adsorption, ΔH_a , are reported for several light hydrocarbons on normal construction concrete. ΔH_a , which are a measure of the adhesion strength of a molecule on a surface, were determined by gas–solid chromatography with a packed column containing 60–80 mesh concrete particles. With this approach, the specific retention volume for a compound is measured as a function of temperature, and these data are used to calculate ΔH_a . For the hydrocarbons studied, we found that ΔH_a was relatively large for unsaturated hydrocarbons. These are the first determinations of ΔH_a of hydrocarbons on construction concrete, but useful comparisons with other ionic solids such as clays can be made.

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1. Introduction

In this study, we report the initial results of a program to study the interaction of energetic materials (e.g., fuels and explosives) with common construction materials (e.g., concrete). The goal of the program is to generate data that will facilitate the forensic analysis of events such as fires and bombings.

The enthalpy of adsorption, ΔH_a , is a thermodynamic measure of the strength of interaction between an adsorbate and the surface of an adsorbent. Gas–solid chromatography, in which the adsorbent serves as the matrix of a packed chromatographic column, is a well established method for the measurement of ΔH_a [1–6]. In this type of experiment, specific retention volumes are determined at multiple temperatures under isothermal conditions. ΔH_a is then obtained by use of Eq. (1),

$$\ln V_g = -\frac{\Delta H_a}{RT} + C, \quad (1)$$

where V_g is the specific retention volume, T is the column temperature, R is the gas constant, and C is a constant containing entropy information [1,3]. A plot of $\ln V_g$ versus $1/RT$ yields $-\Delta H_a$ as the slope. This equation assumes ideal-gas behavior and very low surface coverage of the adsorbate on the adsorbent [1–3,5,6].

The adsorbates used in this study were primarily linear, branched and cyclic alkanes from C3–C8, but we also measured the unsaturated compounds propene and benzene for comparison. These compounds are components in many light fuels. The adsorbent in this study was ordinary construction concrete. Such concrete is produced from a mixture of Portland cement, water, and aggregate (sand and gravel). Portland cement is a complex substance that is made by heating a mixture of limestone and clay to about 1450 °C [7]. The composition of the cement varies, but it typically contains 50–70% Ca_3SiO_5 , 15–30% Ca_2SiO_4 , 5–10% $\text{Ca}_3\text{Al}_2\text{O}_6$, 5–15% $\text{Ca}_2\text{AlFeO}_5$, a few percent CaSO_4 , and various admixtures in small amounts [7].

Some important related studies have been reported for hardened cement pastes (model systems) [8–12]. In that work, similar methods were used, but with the primary goal of determining the surface free energy of the cement pastes.

2. Materials and methods

2.1. Materials

The compounds used as adsorbates in these measurements were all obtained from commercial sources. They had purities of at least 98% and were used without further purification. The sample of concrete was cast two years prior to the beginning of this study (which lasted for about six months). This is important because it takes at least a year for the cement to harden [7]. The concrete was made with Portland cement (Type I-II, ASTM C150), with a water/cement

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mass ratio of 0.338, a coarse aggregate (rock)/cement ratio of 2.27, and a fine aggregate (sand)/cement ratio of 1.69. Various admixtures totaled less than 1% by mass. This formulation is considered a “normal” construction concrete.

2.2. Preparing the packed columns

The concrete was broken into small pieces with hammers, and the coarse aggregate was removed by hand. A ball mill was used to grind the remaining concrete into small particles. The milled concrete was separated with a set of standard sieves, and the 60–80 mesh (180–250 μm) fraction was collected. This mesh size is typical for stationary phases [13,14]. Two columns were constructed; each was made from a 1 m length of copper tubing (0.635 cm O.D., 0.476 cm I.D.) that had been washed with acetone and toluene. A 1 cm plug of glass wool was inserted into one end of the copper tube. The tube was then clamped in a vertical position with the glass wool on the bottom. House vacuum was attached to the bottom of the tube and the 60–80 mesh particles were packed into the column under gentle agitation. Approximately 25 g of concrete was used for each column (the exact masses were determined on an analytical balance with a standard uncertainty of 0.0001 g). A 1 cm plug of glass wool was inserted into the other end of the copper tube, and then the column was coiled and installed in the chromatograph. The column was thermally insulated from both the inlet and the detector by the installation of ~ 3 cm of stainless steel tubing on each end. The stainless steel has a relatively low thermal conductivity when compared to copper, which limits any temperature gradients in the column that are due to differences between oven temperature and inlet/detector temperature. Before any measurements were made, the column was conditioned for about 24 h at 150 $^{\circ}\text{C}$ with a constant flow of helium carrier gas.

2.3. Chromatographic measurements

A gas chromatograph with a thermal conductivity detector (TCD) was used for this study. UHP grade helium was used as the carrier gas. The injector port and the TCD were maintained at 210 $^{\circ}\text{C}$. For the measurements reported herein, the oven (i.e., column) temperature ranged from 30 $^{\circ}\text{C}$ to 190 $^{\circ}\text{C}$. Oven temperatures above ~ 200 $^{\circ}\text{C}$ were found to irreversibly change the chromatographic behavior of the column packing, so those data (and any subsequent data collected on the same column) are not reported. The number of temperatures used to determine ΔH_a for a given compound varied from four to nine, depending on the chromatographic behavior of the compound and the temperature limitations of the stationary phase.

The carrier gas flow-rate was determined with a soap-film flowmeter. The flowmeter consisted of a 50 mL graduated cylinder (with an attached mercury-in-glass thermometer) inside a larger glass cylinder filled with water. The water bath dampens variations in room temperature and improves temperature uniformity in the flowmeter. The corrected flow-rate (F_c) was determined in the following way [1,3]. First, the flowmeter temperature was measured with a standard uncertainty of 0.1 $^{\circ}\text{C}$ with the attached thermometer. Ambient pressure, which was assumed to be the same as flowmeter pressure (p_{fm}), was measured with a standard uncertainty of 15 Pa (i.e., $\pm 0.02\%$) with an electronic pressure gauge. Then, with a stopwatch, the period for 20 mL of flow was measured at least three times in the flowmeter, and the results were averaged (typical flow periods were between 30 s and 60 s). Based on the repeatability, the estimated standard uncertainty in the time measurement is 0.2 s. The average measured flow-rate (F) was then corrected for the vapor pressure of water at the temperature of the flowmeter (p_w), and the difference between the flowmeter tem-

perature (T_{fm}) and the column temperature (T). The mathematical form of these corrections is

$$F_c = F \left(1 - \frac{p_w}{p_{\text{fm}}} \right) \frac{T}{T_{\text{fm}}} \quad (2)$$

The flow-rate was determined before and after each series of injections, and the average of the two determinations was used to calculate the net retention volume (typically, the “before” and “after” values of F_c differed by $\leq 0.3\%$). Corrected helium flow rates between 22 mL/min and 83 mL/min were used. The desired flow rates were obtained by setting the column inlet pressure between 34 kPa (5 psi) and 138 kPa (20 psi). To correct for the pressure drop along the column, the Martin–James compressibility factor (j) was used, Eq. (3), where p_i is the column inlet pressure and p_o is the atmospheric pressure at the column outlet:

$$j = 1.5 \left\{ \frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1} \right\} \quad (3)$$

The adjusted retention time, t'_R , is the retention time of the adsorbate minus the retention time of a non-retained substance (for this work the air peak was used). For this type of thermodynamic measurement, the surface coverage of the stationary phase during chromatography must be small; hence, the amount of adsorbate injected onto the column must be small. For liquid samples, it is difficult to make a small enough injection to approach the zero-surface-coverage limit. To solve this problem, glass bulbs were used to generate a controlled vapor space above the liquids. A small amount of the liquid was placed in a glass bulb (which was then sealed with a septum) and allowed to equilibrate with its vapor phase. The vapor (plus residual air) was then manually sampled through the septum with a 10 μL chromatographic syringe. The gases, such as propane, were handled similarly – the air inside a glass bulb was partially replaced by the gas and then sealed with a septum. Injections of ~ 1 μL of such air–vapor mixtures resulted in small chromatographic peaks with negligible tailing. For any case in which t'_R was found to depend on the size of the injection, the data were rejected. Typically, the t'_R from 6 or 7 injections were averaged for each determination of specific retention volumes (V_g), although as many as 18 injections were done in some cases and as few as 4 were done in others. The relative standard deviations of the replicate values of t'_R were always $\leq 1\%$. V_g was calculated by use of Eq. (4), where w_s is the mass of the adsorbent phase:

$$V_g = \frac{F_c \cdot j \cdot t'_R}{w_s} \quad (4)$$

3. Results and discussion

The value of $-\Delta H_a$ for each hydrocarbon is shown in Table 1, along with the expanded uncertainty (U) in $-\Delta H_a$ (we used a coverage factor [15,16] of $k = 2$). Table 1 also shows the temperature range over which measurements of V_g were made for each compound. Values of V_g for more highly retained compounds were measured at relatively high temperatures in order to achieve narrow, symmetric, chromatographic peaks. However, the maximum column temperature was limited to ~ 473 K by the stability of the concrete adsorbant, as discussed below. Therefore, the temperature range for the chromatographic measurements was limited by necessity, and does not represent the temperatures expected for a fire.

For these hydrocarbons, plots of $\ln V_g$ versus $1/RT$ displayed excellent linearity over the temperature ranges used for these measurements. In fact, all of the R^2 values for linear fits to the plots were ≥ 0.992 , and half of the R^2 values were ≥ 0.999 . Fig. 1 shows the data for all of the n -alkanes and for propene and benzene. As expected, at a given temperature, larger values of V_g were obtained for larger alkanes. Fig. 1 also shows the steady increase in the slope

Table 1
Enthalpy of adsorption (ΔH_a) data for a variety of light hydrocarbons on concrete.

Compound	Carbon #	$-\Delta H_a$ (kJ mol ⁻¹)	U (kJ mol ⁻¹) ^a	T range (K) ^b
Propane	3	24.2	0.3	303.15–343.15
Propene	3	39.3	1.9	323.15–373.15
Butane	4	29.4	0.6	313.15–373.15
2-Methylpropane	4	28.4	0.6	313.15–373.15
<i>n</i> -Pentane	5	31.1	1.0	333.15–413.15
2-Methylbutane	5	30.9	1.6	333.15–393.15
2,2-Dimethylpropane	5	31.7	1.7	323.15–383.15
Cyclopentane	5	30.4	1.4	333.15–393.15
<i>n</i> -Hexane	6	34.3	1.5	373.15–433.15
Cyclohexane	6	31.6	1.2	363.15–423.15
Benzene	6	51.1	4.8	423.15–463.15
<i>n</i> -Heptane	7	36.5	0.9	403.15–453.15
2,3-Dimethylpentane	7	33.8	0.8	403.15–453.15
<i>n</i> -Octane	8	42.0	1.1	413.15–453.15

^a This is the expanded uncertainty in $-\Delta H_a$.

^b This is the temperature range over which measurements of V_g were made.

of such plots (i.e., the steady increase in $-\Delta H_a$) as the molar mass of the alkanes increases. Finally, Fig. 1 illustrates the difference in the behavior of the unsaturated compounds, compared to that of the alkanes.

Fig. 2 shows a plot of carbon number versus $-\Delta H_a$. Generally, branched and cyclic isomers are expected to exhibit a smaller values of $-\Delta H_a$, because they cannot contact a surface as fully as a linear alkane [17,18]. We do observe this trend, but in some cases it is not large enough to be statistically significant. Consequently, for the alkanes, there is a fairly steady increase in $-\Delta H_a$ with carbon number. On the other hand, propene and benzene do not fit the trend exhibited by the alkanes; in fact, they have much larger values of $-\Delta H_a$ compared to those of C3 or C6 alkanes, respectively. Presumably this stronger interaction is due to coordination of the Lewis-basic π -electrons to Ca^{2+} (or other Lewis acid sites such as hydroxyl groups on the surface of the concrete) in the concrete [19].

The current study with concrete makes an interesting comparison to earlier studies with clay, another ionic solid [17,19–23]. Some reported values of $-\Delta H_a^0$ for hydrocarbons on the synthetic clay Laponite-RD are 56.0 ± 0.2 kJ/mol for *n*-hexane, 47.2 ± 1.2 kJ/mol for cyclohexane, 61.6 ± 1.4 kJ/mol for *n*-heptane, and 65.2 ± 1.6 kJ/mol for *n*-octane [20]. Some reported values of $-\Delta H_a^0$ for hydrocarbons on high-purity kaolin clay are 48 ± 3 kJ/mol

for *n*-pentane, 59 ± 4 kJ/mol for *n*-hexane, 69 ± 4 kJ/mol for *n*-heptane, and 81 ± 5 kJ/mol for *n*-octane [22]. In general, the values of $-\Delta H_a^0$ for alkanes on concrete are smaller than those reported for clays, although there is quite a bit of variation in $-\Delta H_a^0$ among the clays [17,19–23].

We believe that values of V_g will be especially useful for the forensic analysis of fires because V_g is a direct measure of how strongly a compound is retained on a concrete surface. We found that V_g shows a clear, but relatively small, dependence on the extent of branching. (See Table S1 of the electronic supplementary material for a complete list of the values of V_g that were determined.) For example, for the four pentane isomers at 373.15 K, V_g was 0.413 L kg^{-1} for pentane, 0.355 L kg^{-1} for 2-methylbutane, 0.357 L kg^{-1} for cyclopentane, and 0.280 L kg^{-1} for 2,2-dimethylpropane. For *n*-hexane and cyclohexane at 423.15 K, V_g was 0.293 L kg^{-1} and 0.254 L kg^{-1} , respectively. By contrast, for benzene at 423.15 K, V_g was 2.87 L kg^{-1} , which is an order of magnitude higher than the six-carbon alkanes. Similarly, at 323.15 K, V_g was almost seven times higher for propene than for propane (1.23 L kg^{-1} and 0.183 L kg^{-1} , respectively). Based on repeatability over time (see Table S1), we estimate that our measurements of V_g have a relative standard uncertainty (u_r) of $\leq 9\%$. The values of V_g suggest that when a hydrocarbon fuel comes in contact with concrete, larger alkanes will remain on the surface longer (as expected),

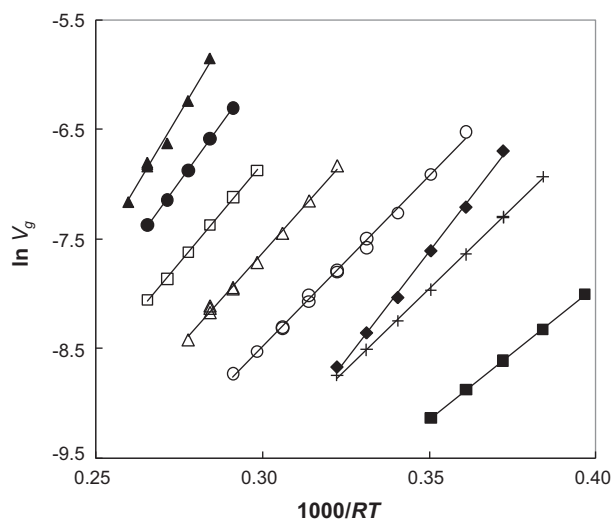


Fig. 1. Plots from which $-\Delta H_a$ was obtained for benzene (\blacktriangle), octane (\bullet), heptane (\square), hexane (\triangle), pentane (\circ), propene (\blacklozenge), butane ($+$), and propane (\blacksquare). Error bars have been omitted for clarity, but the uncertainty of the data is discussed in the text.

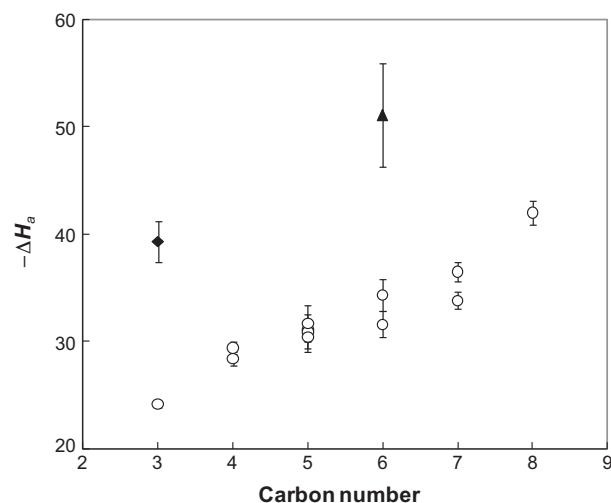


Fig. 2. Plot of $-\Delta H_a$ as a function of carbon number. The values of $-\Delta H_a$ for propene (\blacklozenge) and benzene (\blacktriangle) are much higher than the trend for alkanes (\circ).

with some dependence on the specific skeletal isomer. More interestingly, we expect that unsaturated compounds will remain on concrete surfaces much longer than alkanes with similar molar masses.

One difficulty in this study is that concrete dehydrates at temperatures above ambient [7], which changes its chromatographic behavior. Before the initiation of the measurements of ΔH_a that are reported herein, we found it necessary to condition the chromatographic column in a flow of dry helium at 423 K in order to remove loosely bound water from the concrete [7] and thereby stabilize its chromatographic behavior. This conditioning lasted for about 24 h, over which period the detector baseline stabilized. This type of conditioning was done in the studies on clays as well [19–22]. Over the course of our measurements, the column stability was tested by occasionally repeating measurements of V_g for hexane and pentane. These repeated measurements can be seen in Fig. 1. After conditioning, the column performance was found to be quite stable until it experienced temperatures greater than ~ 473 K, after which the values of V_g increased significantly. This is consistent with the earlier work on clay in which removal of moisture had a similar effect [19]. It is also consistent with earlier observations of higher surface energies in dehydrated cement pastes [8,9,11].

We also did an experiment to estimate the extent of dehydration caused by the conditioning of the chromatographic column at 423 K. A 5.000 g portion of the 80–100 mesh concrete was placed in an aluminum pan and then put in an oven maintained at 423 K. After 1 h, the mass of the concrete was 4.791 g (a loss of 4.2%); after a total 16.5 h at 423 K, the mass of concrete was 4.780 g; and after a total of 5 days at 423 K, the mass of concrete was 4.777 g (for a total loss of 4.5%). Then the concrete was removed from the oven and kept on the bench for a time to see if the dehydration is reversible; after a week at ambient conditions the mass of the concrete was 4.859 g. Hence, it appears that most of the dehydration at 423 K occurs within the first hour, and that some of the dehydration is irreversible, as expected [7].

A recent review [4] recommends checking the reliability of chromatographically determined enthalpies of adsorption with measurements from a second column prepared with the same packing material, which we have done. The second column was used to re-measure ΔH_a for *n*-pentane and *n*-hexane. For *n*-pentane, $-\Delta H_a$ was found to be 34.6 kJ/mol, with an expanded uncertainty of 1.0 kJ/mol. For *n*-hexane, $-\Delta H_a$ was found to be 42.3 kJ/mol, with an expanded uncertainty of 2.4 kJ/mol. Comparing these repeat values to those in Table 1, it is clear that the uncertainty intervals for the two repeat measurements do not overlap the values in Table 1. In fact, the uncertainty intervals would have to be about doubled in order to achieve overlap. For *n*-pentane, a relative uncertainty of 6% in both values of ΔH_a would be just large enough for the two measurements to overlap. For *n*-hexane, a relative uncertainty of just over 10% in both values of ΔH_a would be large enough for the two measurements to overlap. Therefore, the uncertainties given in Table 1 are valid only for comparison of measurements made on that same column. The actual uncertainties appear to be substantially larger – the results for *n*-pentane and *n*-hexane suggest a relative uncertainty of $\sim 10\%$ for the values of ΔH_a . One contribution to the larger uncertainty is presumably the complexity of the concrete itself, and the difficulty in separating the cement from the aggregate.

As discussed above, we were able to achieve narrow, symmetric, chromatographic peaks with hydrocarbons by adjusting the column temperature and inlet pressure. However, we were not able to achieve acceptable peak shapes for more polar adsorbates. For example, hydrogen bond donors and acceptors (such as methanol and acetone) displayed very broad and asymmetric peaks, so data are not reported for such compounds.

4. Conclusions

The enthalpy data reported herein represent a first step in quantifying and understanding the interactions of energetic materials on construction concrete. We have found that unsaturated hydrocarbons interact much more strongly with the surface of concrete than do saturated hydrocarbons. Consequently, we expect unsaturated compounds to be preferentially retained on this type of surface. In addition, our results suggest that the moisture content of the concrete impacts ΔH_a and V_g ; therefore, it must be reiterated that the data reported herein are for partially dehydrated concrete. The issue of concrete dehydration also put limits on the upper column temperature, and therefore, on the types of adsorbates that one can study with this type of packed column. Another complexity in working with such “real world” materials is the difficulty in obtaining repeatable samples. Higher uncertainties must be accepted for such measurements, as illustrated by our comparison of results from two different columns. In this case we believe there is merit in the use of model systems [8–11] that contains only Portland cement, with no aggregate or additives.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2011.04.075.

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