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Enthalpy of fuel gas odorants on surrogate soil surfaces by gas chromatography[☆]

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Abstract

Heats of adsorption and heats of interaction for natural gas odorants on clay and organo-clay, respectively, were determined by means of wall-coated open-tubular (WCOT) column gas chromatography. The odorants studied are organic thiol and sulfide compounds. Clay stationary phases were created from the synthetic clay Laponite-RD. Subsequent coatings with octadecane created an organo-clay stationary phase. Experimental results show that, as a class, sulfide odorants have larger enthalpies on clay and organo-clay surfaces than thiol odorants. Therefore, we conclude that thiols are less likely to be sequestered on soil surfaces. The effect of hydrated clay surfaces on odorant enthalpies is also presented. Further, we demonstrate that Lewis acid–base chemistry on clay surfaces explains the significant difference in enthalpy magnitudes between the sulfide and thiol classes.

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Keywords: Clay; Enthalpy; Natural gas; Laponite; Thiol; Sulfide; Mercaptan

1. Introduction

Sulfur compounds, specifically thiols and alkylsulfides, are added in small quantities to fuel gas [natural gas and liquefied petroleum gas (LPG)] in the United States and Europe. These compounds have distinctive odors that alert individuals to gas leaks. Over time, however, the concentration of these added odorants in the fuel gases may decrease below olfactory thresholds. This phenomenon, referred to as

odorant fading, is often seasonal and occurs through various mechanisms. These mechanisms include odorant degradation by oxidation, and adsorption and absorption interactions of the odorants with various materials [1,2]. When natural gas and LPG leaks occur in transfer and service lines, adsorption and absorption processes between the odorants and the surrounding soil media often result in diminished odorant concentration in the fuel gas. As a result, the accumulation of explosive quantities of these gases may remain undetected. The consequences can be devastating, often resulting in the loss of life and property.

Chromatographic approaches to measuring enthalpies of adsorption and interaction have been applied successfully for many decades using packed columns

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[3–5]. Recently, the construction of wall-coated open-tubular (WCOT) columns with clay and organo-clay stationary phases has been reported [6,7]. We have shown that these WCOT columns provide the same thermodynamic results as the packed columns, but provide a lower uncertainty. Moreover, the measurements can be performed at lower temperatures.

In this work, we report enthalpies of adsorption, $-\Delta H_{\text{ads}}$, and interaction, $-\Delta H_{\text{int}}$, of common odorants used in the fuel gas industry on surrogate clay and organo-clay stationary phases, respectively, using WCOT columns. Specifically, we constructed the columns using Laponite-RD¹ clay (as the clay-soil surrogate) and an octadecane/Laponite-RD composite (as the organo-clay soil surrogate). Laponite-RD is synthetic clay that is frequently used in the research community to study clay systems, and as such, has been very well characterized [8–11]. We propose that these novel stationary phases serve as soil surrogates, representing a range of soil surfaces found throughout the world.

2. Theory

In gas–solid chromatography, the enthalpy of adsorption is determined by:

$$\ln\left(\frac{V_g}{T_c}\right) = -\frac{\Delta H_{\text{ads}}}{R} \cdot \left(\frac{1}{T_c}\right) + C \quad (1)$$

where ΔH_{ads} is the enthalpy of adsorption, V_g is the isothermal specific retention volume at column temperature T_c , R is the universal gas constant, and C is a constant that contains entropy information. This relationship assumes ideal-gas behavior and zero surface coverage (conditions of infinite dilution). When purely partitioning conditions exist, the enthalpy of dissolution (at solute infinite dilution) can also be determined with Eq. (1). When partitioning

and adsorption interactions occur, however, it is not always possible to distinguish the individual contributions of each interaction. Useful thermodynamic information is still obtained from these measurements, however, and is described here as an enthalpy of interaction. By measuring retention volumes at various temperatures, the appropriate enthalpy can be determined through the application of Eq. (1).

3. Experimental

Previously, we have reported the preparation of clay-coated WCOT columns, integration of the columns into modified gas chromatographs, measurement procedures, and data and error analysis [6,7]. Thus, complete descriptions of these experimental aspects will not be provided here. Modifications to the clay coating procedure and the preparation of the organo-clay column, however, are discussed. In addition, the specific experimental conditions under which these data were collected are also reported.

3.1. Materials

A listing of the solutes used in this study is provided in Table 1. Stationary phase material used in the construction of the WCOT columns included octadecane and Laponite-RD. Laponite-RD is a synthetic hectorite with an empirical formula of $\text{Na}_{0.7}^+[(\text{Si}_8\text{Mg}_{5.5}\text{Li}_{0.3})\text{O}_{20}(\text{OH})_4]^{-0.7}$. At the concentrations used in this study, Laponite-RD completely disperses in aqueous solutions resulting in primary particle sizes with approximate dimensions of 25×1 nm [8–11]. In addition, pentane, methylene chloride, ethanol, and acetone were used as rinsing or coating solvents. All solutes, stationary phase material, and reagents were obtained from commercial sources, and were used without further purification. The reported purity of all solutes ranged from 97 to 99.5% (w/w). Distilled/de-mineralized water (de-mineralized to greater than 18 M Ω) was used in the preparation of all aqueous solutions. Each solute is listed by the IUPAC name in Tables 1 and 2. Throughout the natural gas industry, however, 2-methyl-2-propanethiol (**4**) is generally referred to as *tert.*-butyl mercaptan (or TBM). Flexible fused-silica capillary tubing (320 μm I.D. \times 435 μm O.D.) was

¹Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Table 1
Heat of adsorption, $-\Delta H_{\text{ads}}$, and interaction, $-\Delta H_{\text{int}}$, values for selected odorants and *n*-alkanes using WCOT columns

Solute	Laponite-RD	Hydrated	Octadecane/ Laponite-RD
	$-\Delta H_{\text{ads}}$ (kJ/mol) ^{a,b}	Laponite-RD $-\Delta H_{\text{ads}}$ (kJ/mol) ^b	$-\Delta H_{\text{int}}$ (kJ/mol) ^b
Ethanethiol (1)	58.5±3.0 (5.1%)	34.6±2.3 (6.5%)	42.4±0.9 (2.1%)
1-Propanethiol (2)	64.5±3.2 (5.0%)	36.2±2.3 (6.4%)	48.4±0.9 (1.8%)
2-Propanethiol (3)	62.0±2.7 (4.4%)	–	48.6±1.8 (3.7%)
2-Methyl-2-propanethiol (4)	68.9±2.5 (3.6%)	46.4±1.7 (3.6%)	53.4±1.0 (1.8%)
1-Methyl-1-propanethiol (5)	67.3±2.7 (4.0%)	–	–
Tetrahydrothiophene (6)	84.2±1.0 (1.2%)	77.2±1.4 (1.8%)	58.5±1.4 (2.3%)
Methyl sulfide (7)	70.0±1.0 (1.4%)	63.1±0.6 (0.9%)	51.0±0.9 (1.8%)
Ethylmethyl sulfide (8)	77.7±0.7 (0.9%)	76.3±1.5 (2.0%)	59.3±1.0 (2.8%)
Ethyl sulfide (9)	85.5±0.7 (0.9%)	83.9±0.7 (0.8%)	–
<i>n</i> -Pentane	–	–	32.7±2.8 (8.5%)
<i>n</i> -Hexane	55.1±1.2 (2.2%)	–	39.5±1.7 (4.3%)
<i>n</i> -Heptane	60.3±3.8 (6.3%)	–	46.4±0.7 (1.5%)
<i>n</i> -Octane	73.8±2.6 (3.5%)	–	52.7±0.7 (1.2%)
<i>n</i> -Nonane	78.5±1.2 (1.5%)	–	59.7±0.4 (0.7%)
<i>n</i> -Decane	82.7±1.0 (1.2%)	–	61.8±0.9 (1.4%)

^a Values for *n*-alkanes from Ref. [6].

^b Expanded uncertainties (two standard deviations) and the relative standard deviation (RSDs, %) are reported for each value.

obtained from a commercial source, and cut to length in the laboratory.

3.2. Column preparation

Each fused-silica capillary was first washed with a series of solvents and distilled/de-mineralized water prior to coating [6,7]. To coat the capillaries with clay, a 1.5% (w/w) Laponite-RD suspension was passed through the column under a nominal nitrogen

head pressure of 2.8 bar. After flushing the columns for approximately 6 h, the columns were conditioned at 150 °C overnight with a nitrogen purge. This coating procedure was repeated twice. The presence of a clay coating was confirmed by measuring the retention of an *n*-alkane probe (hexane or octane). Column lengths of 8.3 and 24 m were constructed with pure Laponite-RD, while the Laponite-RD/octadecane column was 10 m.

The organo-clay stationary phase was prepared

Table 2
Physical property and solute hydrogen-bond basicity data for odorants

Compound		V_c^a	T_b^a	M_r^b	$\beta_2^{\text{H}^c}$
Name	CAS	(m ³ /kmol)	(K)		
Ethanethiol (1)	75-08-1	0.207	308.153	62.136	0.16
1-Propanethiol (2)	107-03-9	0.254	340.87	76.163	0.16
2-Propanethiol (3)	75-33-2	0.254 ^d	325.71	76.163	0.16
2-Methyl-2-propanethiol (4)	75-66-1	0.307	337.37	90.189	0.16
1-Methyl-1-propanethiol (5)	513-53-1	0.307 ^d	358.13	90.189	0.16
Tetrahydrothiophene (6)	110-01-0	0.249	394.267	88.174	0.26
Methyl sulfide (7)	75-18-3	0.201	310.48	62.136	0.29
Ethylmethyl sulfide (8)	624-89-5	0.254 ^d	339.8	76.163	0.29
Ethyl sulfide (9)	352-93-2	0.318	365.252	90.189	0.29

^a Experimental values for critical volume, V_c , and normal boiling temperature, T_b , taken from Ref. [18].

^b Values for relative molecular mass, M_r , taken from Ref. [18].

^c Solute hydrogen-bond basicity values, β_2^{H} , obtained from Ref. [17].

^d Calculated values taken from Ref. [18].

using a dynamic coating method [12]. After coating the column with clay, a second fused-silica capillary (10 m×200 μm I.D.) was connected to one end of the clay column. The other end of the column was connected to a solvent washing reservoir that contained a 13% (w/w) octadecane/pentane solution. Approximately 8 ml of the coating solution were passed through the column under a nominal nitrogen head pressure of 1.4 bar. The second column serves as a restrictor that minimizes the buildup of stationary phase near the end of the column [12]. This facilitates the formation of a uniform stationary phase coating along the entire capillary length. After this coating, the column was conditioned in a GC oven at 50 °C with a nitrogen gas purge (nominally, 0.3 bar head pressure) until the flame ionization detection (FID) signal stabilized. Prior to commencing the enthalpy measurements, the flow characteristics for the organo-clay column were determined by varying the column temperature between 28 and 75 °C, and measuring the flow-rate of the carrier gas at each of the different column temperatures. Flow rates were measured from the column outlet with a soap film flow meter.

3.3. Measurement conditions

The retention volume for each solute was measured by injecting 1 μl vapor samples. Retention volumes were measured between four to seven temperatures over a temperature range of 130 to 250 °C on the clay column and 35 to 75 °C on the organo-clay column. On average, five vapor injections were made at each column temperature. A split/splitless injector was used with the split ratio set at 150:1 to approximate zero surface coverage. FID was used on all columns. The injector and FID system were maintained at 250 °C. Research-grade nitrogen was used as a carrier gas for all experiments. To create a partially hydrated clay surface, the carrier gas was not dried prior to use. Retention time data were collected on a commercial computer equipped with peak processing software.

Measurements were conducted at a constant head pressure for each analyte, with temperature-dependent flow-rates varying between 3.0 and 11 ml/min. The net retention volumes for the odorants typically ranged from 1 to 19 ml. For the sulfide class on all

columns and the thiol class on the organo-clay column, the eluting chromatographic peaks were nearly symmetrical and retention time did not vary at the vapor concentrations injected. Asymmetric peaks, however, were obtained from the thiol compounds on the two clay columns. To approximate conditions of infinite dilution for these measurements, only those retention times with a signal-to-noise ratio of less than 10 were used in the enthalpy calculations. Over the temperature range of these measurements, the Van 't Hoff plots yielded constant slopes.

For measurements made on the clay columns, methane was used to determine the hold-up volume at each temperature. Since methane is slightly retained on organic surfaces, the hold-up volume for the organo-clay column was determined by injecting a series of *n*-alkanes on the column. This was accomplished by injecting a dilute vapor obtained from the headspace of a sample solution containing pentane, hexane, and heptane, and calculating the hold-up volume by the method of Peterson and Hirsch [13]. In both cases, the hold-up volume markers were injected with each solute sample. All injections were performed manually.

Due to the volatility and stench of the odorants, modified sample vials were prepared in a fume-hood prior to use. These sample vials were fitted with a permeation tube that permits the sampling of dilute vapor for each of the odorants. The permeation sample vials were heated to 60 °C to “charge” the vapor space prior to use. Details for the construction of the permeation tube sample vials are provided elsewhere [14,15]. Vapor samples for the *n*-alkanes were obtained by sampling the headspace above the fluid in a sample vial.

4. Results and discussion

The measured enthalpy values for the odorants on the WCOT columns are presented in Table 1. These values were obtained after applying the necessary corrections factors described previously [6,7]. The uncertainties for each measured enthalpy represent the standard error of the slope obtained from Eq. (1). These uncertainties are included in Table 1 with a coverage factor of $k=2$ (that is, two standard deviations) [16]. In addition, enthalpy values for

selected *n*-alkanes on the clay and organo-clay stationary phases are also included for reference purposes.

Both physical and chemical property data were used to evaluate the enthalpy data sets for correlation, and are summarized in Table 2 [17,18]. Correlations were performed between the physical properties listed in Table 2 and each odorant class (i.e., thiols and sulfides), and are presented in Table 3. When each odorant class is treated separately, the measured enthalpy values and individual physical properties are well correlated, with relative molecular mass (M_r) and critical volume exhibiting higher degrees of correlation than normal boiling point. Hence, throughout this work, enthalpy values are plotted against M_r , with the understanding that similar figures would be obtained using critical volumes.

The $-\Delta H_{\text{ads}}$ for the odorants and *n*-alkanes on Laponite-RD are plotted as a function of M_r in Fig. 1. The numerical labels for individual solutes in Fig. 1 are included in Tables 1 and 2. The cyclic sulfide, tetrahydrothiophene, has enthalpy characteristics similar to the *n*-alkyl sulfides; thus, it is grouped with them for discussion and presentation purposes throughout this work. As expected from the results presented in Table 3, the individual odorant classes show a high degree of correlation between enthalpy and M_r . If, however, the odorants are treated collectively (i.e., thiols and sulfides combined), it is clear from Fig. 1 that this would result in a poor correlation. Thus, further analyses were needed to explain the offset between the two classes of odorants. To accomplish this, the enthalpy values for both classes were combined and evaluated. The remainder of this work discusses the analysis of these combined data.

As shown, poor correlations between the measured enthalpy data and a single physical property (i.e., $-\Delta H_{\text{ads}}$ vs. M_r) are obtained. Since the cross-corre-

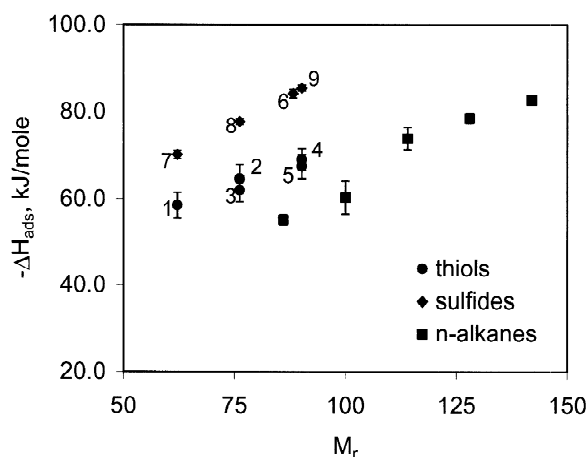


Fig. 1. Plot of $-\Delta H_{\text{ads}}$ against relative molecular mass, M_r , for odorants on WCOT column coated with Laponite-RD (clay soil surrogate). Odorant numerical labels correspond to those listed in Tables 1 and 2.

lation between various physical properties is large, it would not be appropriate to simultaneously model the enthalpy data with more than one physical property. Thus, chemical property descriptors that represent chemical characteristics of odorants were selected for use in multi-linear models. Sulfur compounds are known to behave as Lewis bases [19]. Therefore, a value was needed to quantify the basicity of each of the odorants. For this study, we choose solute hydrogen-bond basicity, β_2^{H} , values reported by Abraham et al. [17]. These β_2^{H} values are scaled values, derived from Gibbs energies of complexation for a set of bases measured against a series of reference acids in tetrachloromethane [17]. These values, in conjunction with other parameters, have been used in linear solvation energy relationships (LSERs) to predict chromatographic retention behavior [20]. Additional solute descriptors that are used in LSERs include solute hydrogen-bond acidity, α_2^{H} , and solute dipolarity/polarizability, π_2^{H} . These

Table 3
Correlation coefficients of $-\Delta H_{\text{ads}}$ and $-\Delta H_{\text{int}}$ with physical variables for each odorant class

	Laponite-RD		Hydrated Laponite-RD		Octadecane/Laponite-RD	
	Thiols	Sulfides	Thiols	Sulfides	Thiols	Sulfides
Relative molecular mass	0.9676	0.9999	0.9217	0.9378	0.9969	0.8438
Normal boiling point	0.8370	0.9117	0.5238	0.7380	0.8303	0.7090
Critical volume	0.9671	0.8447	0.9346	0.9476	0.9927	1.0000

descriptors, however, were excluded in the evaluation of the enthalpy data presented here because they were either statistically identical (π_2^H) or zero (α_2^H). While most gas chromatographic research using LSERs has focused on gas–liquid chromatography, recent application to gas–solid chromatographic data indicate that LSERs provide valuable insights into vapor–solid interactions [21].

As before, correlations between each combined data set and the physical properties listed in Table 2 were performed and are presented in Table 4. While there is marginal correlation between the measured enthalpy values and the physical properties of the sulfur compounds, the correlations improved dramatically when the basicity of the individual solutes is also taken into account. Multi-linear regression was determined by:

$$H_X = aP + b\beta_2^H + c \quad (2)$$

where the subscript X represents either adsorption or interaction, P corresponds to the specific physical parameter being used in the regression, and a , b , c are coefficients from the regression. Using β_2^H as a second independent variable in a multi-linear regression, the correlation coefficients obtained between the measured enthalpies and individual physical property variables all increased, as shown in Table 4. The correlation of the measured enthalpies with relative molecular mass (M_r) and β_2^H as the two independent variables is highest on two of the columns. While this high degree of correlation with M_r is similar to our previous observations with hydrocarbons on Laponite-RD surfaces [6], it is important to note that the high degree of correlation is only observed when the chemical characteristic (namely, basicity) of the compounds is also consid-

ered. The improved correlation between solute enthalpy and a physical property, by incorporating solute basicity into the regression analysis, is in agreement with recent studies of polar organic molecules on mineral and clay surfaces [22]. The correlations between the enthalpy data and β_2^H were also determined, and are included in Table 4.

As expected from the correlation presented in Table 4 and the difference in β_2^H between the groups, the $-\Delta H_{\text{ads}}$ for the sulfides are remarkably different from that of the thiols. This is readily shown in Fig. 1 and explained by the surface chemistry of the clay. On pure clay surfaces, Lewis acid sites are associated with the broken edges of the clay platelets, while the Lewis base sites are associated with the lone-pair electrons of the oxygen atoms on the 001 surface of the platelets [23]. The counter ions associated with the clay surface (in this case, sodium) are also considered Lewis acids [10]. Thus, as the solutes interact with the clay surfaces, the sulfides are more strongly adsorbed to the Lewis acid sites since they are stronger Lewis bases. As a result, the sulfides have larger $-\Delta H_{\text{ads}}$.

When the interactions of the odorants with the octadecane/Laponite-RD surface are examined, one must consider the contributions from the $-\Delta H_{\text{ads}}$ as well as enthalpies of solutions when interpreting $-\Delta H_{\text{int}}$. In Fig. 2, the measured values for $-\Delta H_{\text{int}}$ are given as a function of M_r . As with the $-\Delta H_{\text{ads}}$ values on Laponite-RD, the sulfide and the thiol compounds are readily grouped together. In this case, however, the average enthalpy difference between the two groups has decreased. This can be explained, again, by considering the surface chemistry of the clay. When the octadecane is applied to the clay surface, it will likely preferentially adsorb to areas with surface defects (Lewis acid sites). This results

Table 4
Correlation coefficients of $-\Delta H_{\text{ads}}$ and $-\Delta H_{\text{int}}$ with physical variables for entire odorant set

	Laponite-RD		Hydrated Laponite-RD		Octadecane/Laponite-RD	
	Linear	Multi-linear ^a	Linear	Multi-linear ^a	Linear	Multi-linear ^a
Relative molecular mass	0.5382	0.9785	0.4393	0.9903	0.6195	0.9837
Normal boiling point	0.7540	0.9764	0.6114	0.9798	0.6982	0.8754
Critical volume	0.3715	0.9250	0.3192	0.9699	0.4174	0.9747
Solute hydrogen-bond basicity	0.7973	–	0.9174	–	0.6840	–

^a Correlation coefficient obtained from a fit of the respective enthalpy with the physical variable in column 1 and the solute hydrogen-bond basicity, β_2^H .

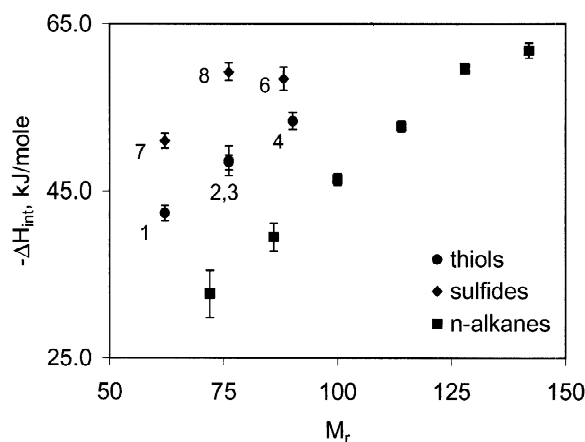


Fig. 2. Plot of $-\Delta H_{\text{int}}$ against M_r for odorants on WCOT column coated with octadecane and Laponite-RD (organo-clay soil surrogate). Odorant numerical labels correspond to those listed in Tables 1 and 2.

in a diminished number of Lewis acid sites in which the solutes can interact. Thus, the relative magnitude of the difference between enthalpy values between the odorant groups decreases. Further, odorant interactions with the octadecane fraction of the organo-clay composite material should be governed by partition mechanisms. These processes are characterized by an enthalpy of solution, ΔH_S . Therefore, the net solute interaction with the organo-clay stationary phase is controlled by a combination of both adsorption (ΔH_{ads}) and partitioning (ΔH_S) processes. As with the *n*-alkanes, the overall effect of these combined interactions results in a measured decrease in enthalpy for each odorant on the organo-clay substrate with respect to pure clay.

The measured $-\Delta H_{\text{ads}}$ values for the odorants on the clay and the hydrated-clay surfaces are compared in Fig. 3. It is interesting to note that the impact of hydration of the clay surface dramatically changes the measured enthalpy of the thiols while having little impact on the sulfides. Since the humidity of the carrier gas was not precisely controlled, it is difficult to elucidate the exact mechanism for these observations. One possible explanation for the difference, however, is presented. On dry clay surfaces, the Lewis acid sites significantly contribute to the retention of the sulfur compounds. When moisture in the carrier gas is present, the clay surface is hydrated. Specifically, water molecules associate with

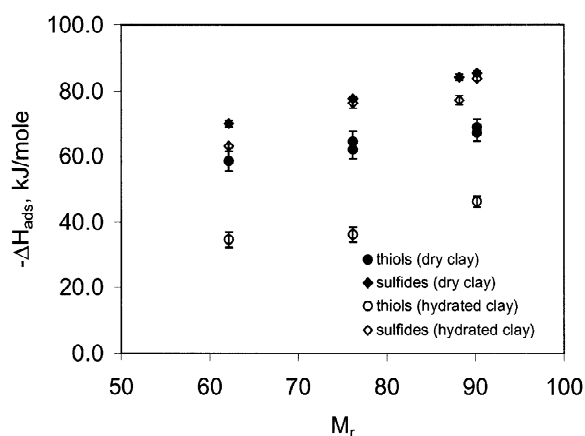


Fig. 3. Plot of $-\Delta H_{\text{ads}}$ against relative molecular mass, M_r , for odorants on WCOT column coated with dry and hydrated Laponite-RD (clay soil surrogate).

counter-ions on the surface of the clay and the Lewis acid sites on the platelet edges [10]. Since water molecules behave as stronger Lewis bases than the sulfides and thiols ($\beta_2^{\text{H}}=0.38$ [17]), the number of Lewis acid sites available on the clay surface decreases. It is apparent that this decrease in the number of available Lewis acid sites results in a decrease in the measured interactions between the thiols and the hydrated clay. Further investigation, however, is required to validate this hypothesis.

5. Conclusions

While adsorption and absorption interactions with soil media have long been suspected as potential mechanisms of odorant fading in the fuel gas industry, the magnitude of these interactions have previously been unknown. The enthalpy data measured by gas chromatography that are reported here represent a significant step in quantifying and understanding the contribution of adsorption and absorption interactions that occur in natural soils. We have demonstrated that Lewis acid–base chemistry on the synthetic-clay surfaces significantly influences the enthalpy magnitude between odorant compounds and soil surfaces. In addition, our results show that, as a class, the sulfide odorants have larger $-\Delta H_{\text{ads}}$ and $-\Delta H_{\text{int}}$ on clay and organo-clay surfaces, respectively, than the thiol class. In addition, the results

presented suggest that moisture content in soils significantly impact $-\Delta H_{\text{ads}}$ values for thiols. Therefore, thiols are less likely to be sequestered on soil surfaces. This implies, for example, that the natural gas odorant most commonly used in the United States, TBM, is less likely to be sequestered on soil surfaces than the odorant tetrahydrothiophene (an odorant more commonly used in many European nations). Readers should be cautioned, however, that all odorants have enthalpies of adsorption and interaction on soil surfaces that are greater than the hydrocarbon gases to which they are added. Thus, all odorants are susceptible to this mechanism of odorant fading.

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