



ELSEVIER

Journal of Chromatography A, 844 (1999) 191–199

JOURNAL OF  
CHROMATOGRAPHY A

# Determination of heats of adsorption of hydrocarbons on a synthetic clay by gas–solid chromatography using a wall coated open tubular column approach<sup>☆</sup>

T.J. Bruno<sup>a,\*</sup>, A. Lewandowska<sup>a</sup>, F. Tsvetkov<sup>b</sup>, H.J.M. Hanley<sup>a</sup>

<sup>a</sup>Physical and Chemical Properties Division, Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Boulder, CO 80303, USA

<sup>b</sup>Daren Laboratories and Scientific Consultants, Nes-Ziona, Israel

Received 4 December 1998; received in revised form 18 March 1999; accepted 18 March 1999

## Abstract

Heats of adsorption for a series of hydrocarbons on Laponite-RD clay were determined by two gas chromatographic methods. The first method was an extension of packed-column gas–solid chromatography. The second method employed a novel wall coated open tubular (WCOT) column that was prepared from clay aqueous suspensions. The two different methods of preparing chromatographic columns are discussed in this paper, and a comparison between the results obtained on the two systems is made. We conclude that the WCOT column method provides the same thermodynamic results as does the conventional packed-column method, while offering some definite improvements in the measurement process and data behavior. © 1999 Published by Elsevier Science B.V. All rights reserved.

**Keywords:** Adsorption; Clays; Heats of adsorption; Laponite-RD clay; Thermodynamic parameters; Hydrocarbons

## 1. Introduction

In this paper, we report a new method to measure the enthalpy of adsorption ( $\Delta H_{\text{ads}}$ ) of hydrocarbons on a clay matrix. Two separate approaches to the measurement were utilized, both of which were based upon gas chromatography. In the first method, clay was deposited on spherical glass beads to serve as the matrix of a packed chromatographic column.

This first method serves as a control, since the packed-column technique is well established. Although variations of this method have been used for many years for  $\Delta H_{\text{ads}}$  measurements, the approach suffers from poor efficiency and peak shape, the need for high column temperatures, and excessively long measurement times. The second method was based upon the construction of a wall coated open tubular (WCOT, capillary) column of clay on fused silica. The latter approach is novel and shows promise as an improvement over the conventional packed column procedure.

The hydrocarbons measured in this study were the *n*-alkanes C<sub>6</sub>–C<sub>12</sub>, 2,2-dimethylbutane, cyclohexane and quadricyclane. The adsorbent was synthetic

<sup>\*</sup>Contribution of the United States Government. Paper not subject to copyright in the United States.

\*Corresponding author. Tel.: +1-303-497-5158; fax: +1-303-497-5927.

E-mail address: bruno@boulder.nist.gov (T.J. Bruno)

Laponite-RD clay<sup>1</sup>. Laponite-RD is a research-grade artificial clay that has many points of similarity with natural clays, and it is commonly used as a replacement for clays in systematic studies. Moreover, the properties of Laponite-RD are very well characterized [1,2].

## 2. Theory

The enthalpy of adsorption may be obtained from the chromatographic experiment from [3–7]:

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

where  $\Delta H_{\text{ads}}$  is the enthalpy of adsorption,  $V_g$  is the isothermal specific retention volume (at column temperature  $T_c$ ),  $R$  is the gas constant and  $C$  is a constant containing entropy information. This equation assumes ideal gas behavior, and very low surface coverage of the adsorbate on the adsorbent (analogous to infinite dilution in gas–liquid chromatography). From this equation, a plot of  $\ln(V_g/T_c)$  against  $(1/T_c)$  will yield  $\Delta H_{\text{ads}}$  as the slope.

## 3. Experimental

The data presented in this paper were measured using two specially modified commercial gas chromatograph systems. One GC system was used for the packed columns, and the other for the WCOT columns. Both the packed columns and WCOT columns were prepared in the laboratory. A total of four columns were tested in this study: two packed and two WCOT columns. One column of each type was prepared as a control, containing no clay stationary phase. A packed column and a WCOT column

were prepared with the clay stationary phase for the enthalpy measurements.

The gas chromatograph that was used with packed columns was a modified commercial instrument equipped with a hot wire thermal conductivity detection (TCD) system and a flash vaporization injector. The temperature of the column oven was measured with a thermocouple, and had an uncertainty of  $\pm 0.5^\circ\text{C}$ . For the experiments in which the column temperature had to be below  $70^\circ\text{C}$ , the oven was cooled to the desired temperature with a Ranque–Hilsch vortex tube [8]. Inlet pressures were predetermined with mass-flow controllers, and measured with calibrated Bourdon tube gauges. This pressure was typically 100 kPa, and had an uncertainty of 0.5%. The Bourdon tube gauges were calibrated against a transfer standard that was itself calibrated against a dead mass pressure balance primary standard. The outlet pressure (taken to be the atmospheric pressure) was measured with a fixed cistern mercury barometer. The readings from the barometer were corrected for the effect of temperature on the density of mercury, and for the expansion of the brass scale. Column outlet flow-rates were measured with a thermostatted soap film flow meter. The flow-rate was corrected for the column temperature, and the water vapor pressure,  $P_{\text{H}_2\text{O}}$ , of the soap solution was corrected for the flowmeter temperature. The measured volumetric flow-rates ranged from 25 to 30 ml/min, and showed an uncertainty of 0.5% for the entire course of the measurements. Research-grade helium was used as the carrier gas for the measurements performed on this instrument.

The GC system used for the measurements on the WCOT columns was a commercial instrument modified for providing precision retention data [9,10]. This instrument was equipped with a flame ionization detector, a split/splitless injector, and an automatic sampler. The oven temperature for this instrument was measured with a quartz crystal oscillator thermometer that had an uncertainty of  $\pm 0.03^\circ\text{C}$ . Temperature stability was enhanced in this instrument by adding additional thermal mass in the form of copper plates, strategically located in the column oven. The column head pressure was controlled with an electronic pressure regulator. The pressure was typically maintained at 33 kPa, and had an uncertainty of 0.5%. An electronic barometer that had an

<sup>1</sup>Certain 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.

uncertainty of  $\pm 1.3$  Pa was used to measure the outlet pressures for this instrument.

The volumetric flow-rates from the outlet of the WCOT column were measured (with the column connected to the flame ionization detector) with an anemometric flow meter calibrated for the carrier gas, which for measurements on this instrument was research-grade nitrogen. In this case the flow-rate was obtained from the best-fitted line of the flow-rate against column temperature. The flow-rates from this instrument ranged from 0.9 to 1.5 ml/min, and had an uncertainty of 3%. Peak retention data for both the packed and WCOT column instruments were logged with a commercial electronic integrator.

### 3.1. Column preparation

The preparation of both the packed column and the WCOT column is based upon the longstanding observation that clays (of nearly all types) have a very high affinity for glasses, especially when deposited on a glass surface from an aqueous suspension. Also well known is the fact that many clays form stable suspensions in a variety of polar solvents, especially aqueous solvents. The procedure of stationary phase preparation will be described in detail for both the packed and WCOT columns. Some preliminary, general comments about the coating process are in order, however.

The desire to coat clay on the inside of the capillary is obvious; it provides the most convenient method for producing a capillary-based stationary phase. In the case of the packed column, it may not be immediately obvious to the reader why coating on glass beads was desirable, rather than directly packing clay into a column. The particles of the refined Laponite-RD are actually platelets 25–30 nm in diameter, with a thickness of 1 nm. It would clearly be impossible to directly pack a usable chromatographic column with this fine material, although it is possible to spray-dry the material into larger agglomerates or macrostructures [11–13]. The spray-drying option was unavailable to us, thus coating the clay on a support in a fashion similar to the preparation of gas–liquid chromatography packings was chosen as the best alternative approach.

It is very difficult to directly verify that a clay coating is indeed present on the glass surface be-

cause many clays, including Laponite-RD, form a transparent film on glass. In this work, we employed two indirect tests in an attempt to ensure that a coating was indeed produced. First, we compared the chromatographic behavior of both the packed and capillary (that is, the uncoated WCOT) columns with and without the clay treatment. The results of these tests are discussed later in this section. Second, we added a small quantity of methylene blue to the clay suspension (0.1 CEC, that is, 10% of the cation-exchange capacity, which for Laponite-RD is 0.06 mequiv./g), and coated several small slabs of fused silica and glass which were similar in composition to the materials used for the column and support. Upon drying the slabs, a very discernible blue tint was seen on the surface that is indicative of the presence of a clay–methylene blue coating. This procedure with methylene blue is a common test used by clay chemists to trace the presence and fate of clay samples on glass, and to measure the surface areas of clay coatings on glass [14].

### 3.2. Packed column preparation

The stationary phase for the packed columns was prepared by coating the clay onto the surface of spherical glass beads (80–100 mesh, 149–177  $\mu\text{m}$ , commercially available chromatographic grade, washed and oven-dried). The Laponite-RD clay was obtained from a commercial source and used without further purification. A 1% (m/m) clay suspension was prepared from oven-dried Laponite-RD mixed with HPLC-grade water. An appropriate amount of the clay suspension needed to produce approximately 30 layers of coating was mixed with glass beads in a fluted flask. Additional water was added in order to cover completely the glass beads. The coating process was accomplished with a rotary vacuum evaporator, with the temperature of the slurry maintained at 120°C. The coating process was performed relatively quickly, in approximately 1 h, to avoid damage to the friable particles. After the evaporation was completed, the clay-coated glass beads were dried in an oven maintained at 110°C for 12 h in order to drive off any residual water. The oven-dried, coated beads were sieved, and the particles passing 80–100 mesh were used for the column packing.

The columns were constructed from 1.98 m (0.635

cm O.D.) copper tubing plugged at the ends with small wads of silanized Pyrex wool. Prior to packing, the empty column was washed three times with acetone and toluene and left to dry overnight under a flow of filtered air. The coated beads were packed into the column under gentle agitation and vacuum. The packed column was coiled and then installed in the chromatograph. The column packing was conditioned for 1 h, under a flow of helium (30 ml/min), at a temperature of 250°C.

### 3.3. WCOT column preparation

The clay stationary phase for the WCOT column was prepared from a 1% (mass/mass) Laponite-RD suspension in HPLC-grade water prepared 24 h before the column coating was to be performed. An empty 30-m fused-silica capillary column was washed (prior to coating) with methylene chloride, a mixture of ethanol and acetone, and finally HPLC-grade water under nitrogen pressurization. The coating of the capillary was accomplished by flowing the Laponite-RD suspension under a head pressure of nitrogen at the rate of 4 ml/h for 6 h. The column was then conditioned at 100°C for 2 h, at 200°C for an additional 1 h and for 72 h at 250°C with nitrogen flow at approximately 2 ml/min. The coating procedure described above was repeated three times.

### 3.4. Chromatographic measurement procedures

For the packed column, samples were introduced into the carrier gas with a flash vaporization injector maintained at 300°C; injection was done manually with a 10- $\mu$ l chromatographic syringe. To obtain injections in which the sample was at zero surface coverage, a heated vial holder was constructed and used to generate a controlled headspace, and the headspace was sampled. At each column temperature, we made five to 10 injections of each fluid, depending upon the sample chromatographic behavior. For example, rapidly eluting fluids required more measurements because of somewhat higher uncertainties in the retention times. Air was injected with each fluid to approximate the gas hold-up time of the column (see Eq. (3)). At the beginning and end of each series of injections, the column and flowmeter temperatures, the column flow-rate, the

column head pressure, and the atmospheric pressure were measured.

The TCD temperature was set to 200°C, a moderate setting intended to prevent any sample condensation on the hot wires, and at the same time maintain good sensitivity. The helium carrier gas was passed through molecular sieve 5A and an oxygen trap prior to entering the chromatograph. Retention times were recorded on a commercial integrator.

The measurement procedure used for the WCOT columns differed in some respects from the procedure used for the packed columns. A split/splitless injector set for a 200:1 split was used to obtain solute injected for zero surface coverage. Liquid samples were transferred to the injector with an automatic sampler set to deliver 1  $\mu$ l. Methane was injected with each of the fluids to approximate the carrier gas hold-up time [15].

The fluids used as adsorbates in these measurements were all obtained from commercial sources. The purity of these materials (which varied from 98 to 99.5%, m/m) was verified by gas chromatography–mass spectrometry, and they were used without any further purification. A listing of the fluids is provided in the left-hand column of Table 1. All of these are familiar compounds, except perhaps quadricyclane (quadricycloheptane, relative molecular mass=92.14, CAS No. 278-06-8). This compound is of interest as an alternative gas turbine fuel.

Before any experiments were done with the clay columns, we verified that our adsorbates did not interact with the glass beads of the packed columns, or the fused silica of the WCOT columns. This was done by performing chromatographic measurements with a packed column containing uncoated beads, and a capillary column that had not been treated with clay. No measurable retention was observed on these control columns. By this we mean that samples injected into the uncoated columns coeluted with unretained compounds (air in the case of the packed columns, methane in the case of the WCOT columns). Hence, any subsequent heats of adsorption on the clay stationary phases were considered to be due solely to solute–clay interactions.

The chromatographic peaks from which the retention times were calculated generally had Gaussian-like shapes with only minimal tailing. There was no evidence of column overload. In the case of

Table 1  
Measurement of the enthalpy of adsorption,  $\Delta H_{\text{ads}}$ , on Laponite-RD, measured on the packed and WCOT columns, for the fluids studied<sup>a</sup>

Fluid	Laponite-RD packed column $-\Delta H_{\text{ads}}$ (kJ/mol)	Laponite-RD WCOT column $-\Delta H_{\text{ads}}$ (kJ/mol)	Difference with respect to packed column
<i>n</i> -Hexane	56±0.2 (0.4%)	55.1±1.2 (2.2%)	1.0
<i>n</i> -Heptane	61.6±1.4 (2.3%)	60.3±3.8 (6.3%)	1.3
<i>n</i> -Octane	65.2±1.6 (2.5%)	73.8±2.6 (3.5%)	−8.6
<i>n</i> -Nonane	71.3±1.8 (2.5%)	78.5±1.2 (1.5%)	−7.2
<i>n</i> -Decane	80.0±1.0 (1.3%)	82.7±1.0 (1.2%)	−2.7
Undecane	84.5±7.4 (8.8%)	91.7±2.4 (2.6%)	−7.2
Dodecane	–	96.3±2.7 (2.8%)	–
Cyclohexane	47.2±1.2 (2.5%)	48.5±1.4 (2.9%)	−1.3
2,2-Dimethylbutane	48.3±0.8 (1.66%)	47.9±0.8 (1.7%)	0.4
Quadricyclane	51.5±3.2 (6.2%)	57.3±0.4 (0.7%)	−5.8

<sup>a</sup> The expanded uncertainties (two standard deviations) and the RSD (%) are provided with each value. The difference in enthalpy value from both techniques (with respect to the packed column) is provided in the right-most column.

dodecane (the highest molecular mass hydrocarbon measured), some moderate tailing and difficulties with obtaining reproducible peaks occurred on the packed columns.

The number of temperatures chosen for a given series of experiments varied from 4 to 7, depending on the chromatographic behavior of the compound on the stationary phase. For the packed column measurements, the temperatures ranged from 60 to 225°C. For the WCOT columns, temperatures ranged from 50 to 150°C. In general, more isotherms were measured for the compounds with the lowest and highest relative molecular masses. The very light compounds typically had very short retention times, and the very heavy compounds sometimes exhibited poor peak shape. Both of these situations led to higher uncertainties in the measured retention times.

#### 4. Results and discussion

The measured values of the enthalpies of adsorption,  $\Delta H_{\text{ads}}$ , on Laponite-RD of the fluids studied in this work are tabulated in Table 1. In each case, the  $\Delta H_{\text{ads}}$  value has been determined from the application of Eq. (1), after the appropriate corrections (described earlier) were applied to the retention measurements.

The  $\Delta H_{\text{ads}}$  for dodecane on Laponite-RD for the packed column is not included because the chromatographic behavior was poor (poor peak shape,

very high retention). This fluid required the use of much higher temperatures than did the other fluids. Included with each enthalpy datum is the expanded uncertainty (with the coverage factor  $k=2$ ). These uncertainties have been determined by a propagation of errors from all of the experimental quantities.

Both sets of measurements, from the packed column and from the WCOT column, independently correlate very well with physical variables known to affect adsorption: carbon number (for the *n*-alkanes), relative molecular mass, normal boiling temperature, and critical (or molar) volumes. The Pearson correlation coefficients for these correlations are provided in Table 2, and, as an example, a plot showing  $\Delta H_{\text{ads}}$  against relative molecular mass (RMM) for the fluids is shown in Fig. 1. The question that must be answered is: do the two approaches (packed vs. WCOT) measure the same quantity?

##### 4.1. Comparison of packed column and WCOT laponite-RD measurements

The uncertainties in the measurements are typical

Table 2  
Pearson correlation coefficients of  $\Delta H_{\text{ads}}$  with physical variables

	Packed column	WCOT column
Carbon number	0.9781	0.9798
Relative molecular mass	0.9806	0.9798
Normal boiling temperature	0.9659	0.9832
Critical volume	0.9886	0.9896

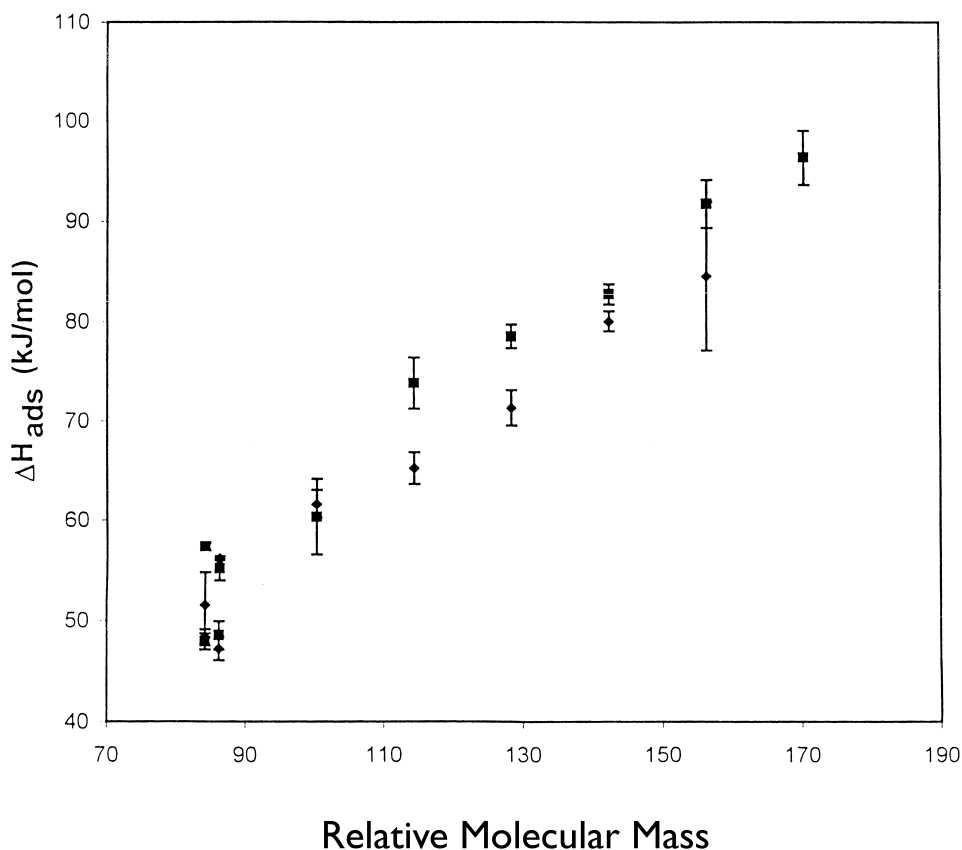


Fig. 1. A plot of  $\Delta H_{ads}$  against relative molecular mass of each of the fluids measured in this study, on the packed column and on the WCOT column.

of those expected from a chromatographic measurement of  $\Delta H_{ads}$ , which are usually between 500 and 4000 J/mol (with  $k=2$ ) [6,7]. For the packed column measurements, the average coefficient of variation was 3.1%, while that for the WCOT column measurements was 2.5%. The average deviation in  $\Delta H_{ads}$  between the two methods is  $-3.3$  kJ/mol (vis á vis the packed column), and the average absolute deviation is 3.9 kJ/mol. Thus, within experimental uncertainty, the overall agreement (on a fluid by fluid basis) between the measurements obtained from both techniques is not unreasonable. We believe that the higher relative uncertainty obtained with the packed column is due to its inherently lower chromatographic efficiency. This problem becomes more severe as the size of the adsorbate molecule increases. The uncertainties from other instrumental factors, such as temperatures,

pressures and flow-rates, cannot account for the higher uncertainty in  $\Delta H_{ads}$  for the packed column.

Inspection of the measurements in Table 1 indicates that for six of the fluids measured (*n*-hexane, *n*-heptane, *n*-decane, undecane, cyclohexane, 2,2-dimethylbutane), the results from the two methods are the same within experimental uncertainty. The agreement between the  $\Delta H_{ads}$  of undecane on the two columns must be interpreted cautiously because of the high relative uncertainty of the value measured on the packed column. For four of the fluids, the results are outside the combined experimental uncertainties (*n*-octane, *n*-nonane, undecane, and quadricyclane), but are essentially within a factor of 2 of the combined uncertainties.

It can be seen in the right-most column of Table 1 that the enthalpies measured on the packed column tend to be somewhat lower (by 3.3 kJ/mol, on

average) than those measured on the WCOT column. We believe that this difference is the result of abrading clay from the surface of the glass beads of the packed column during the packing process. The surface of the WCOT column maintains its integrity and coverage better than the packed column because of the column preparation is far less invasive.

The correlation of the enthalpy measurements with relative molecular mass was examined to explore further the agreement between the measurements from the packed and WCOT columns. While we could have used any of the correlated variables discussed earlier, relative molecular mass was chosen as the least ambiguous. Two weighted fits were performed, of the form:

$$\Delta H_{\text{ads}}^{\text{P}} = \alpha^{\text{P}} + \beta^{\text{P}} \cdot \text{RMM} \quad (2)$$

and

$$\Delta H_{\text{ads}}^{\text{WCOT}} = \alpha^{\text{WCOT}} + \beta^{\text{WCOT}} \cdot \text{RMM} \quad (3)$$

where RMM is the fluid relative molecular mass, and  $\alpha$  and  $\beta$  are fitting coefficients. The superscripts P and WCOT denote the respective columns. The weighting factors were taken as the reciprocals of the individual uncertainties. We then tested the null hypothesis:  $H_0: \alpha^{\text{P}} = \alpha^{\text{WCOT}}, \beta^{\text{P}} = \beta^{\text{WCOT}}$ . The null hypothesis is the mathematical statement asserting that the coefficients from the two fits are statistically the same and, therefore, the two data sets are, in fact, statistically the same. Disproving the null hypothesis is an assertion that the two data sets, from the packed column and the WCOT column, are in fact statistically different. The two coefficients are tested simultaneously; both of the coefficient equalities expressed in the null hypothesis must be true in order to affirm (or rather, fail to reject) the null hypothesis. The  $F$ -test was performed on the weighted fits described above. We calculated our test statistic  $F=0.37$  at the 95% significance level, with a  $P$  value of 0.7. Since 0.7 is far greater than the threshold  $P$  value of 0.05, we fail to reject the null hypothesis and, therefore, must conclude that, statistically, the two data sets are in fact not different [16]. This test, combined with the observation of good overall agreement and close agreement among many of the fluids, leads us to conclude that, in fact, the packed column and the WCOT column are measuring the same  $\Delta H_{\text{ads}}$ . This

is evidence that the physical structures of the clay surfaces on both columns are the same in terms of pore sizes, pore spacings, and platelet spacings.

Upon a more detailed examination of the  $n$ -alkane  $\Delta H_{\text{ads}}$  data, we found that for the packed column, the experimental uncertainty (of the measurements in Table 1) was highly correlated with the measured  $\Delta H_{\text{ads}}$  (Pearson correlation coefficient = 0.707). For the WCOT column, however, the correlation with experimental uncertainty was much smaller (Pearson correlation coefficient = -0.20). There is clearly a systematic error associated with the measurements on the (less efficient) packed column that is not present in the measurements on the WCOT column. This is probably associated with the relatively lower efficiency of the packed column as compared with the capillary column. Unfortunately, individual uncertainties are seldom reported in previous studies reported in the literature. For this reason, we are unable to determine if this is a general problem that is encountered with packed column measurements.

To summarize, the WCOT column yielded  $\Delta H_{\text{ads}}$  values that, overall, are statistically not different from those obtained with the packed column. The WCOT measurements showed a lower experimental uncertainty, and the uncertainty was not correlated with the measurements. By contrast, the  $\Delta H_{\text{ads}}$  measured from the packed column was statistically correlated with the uncertainty.

#### 4.2. $\Delta H_{\text{ads}}$ on Laponite-RD

Examination of the data for the fluids on Laponite-RD reveals an increase in  $\Delta H_{\text{ads}}$  with carbon number and relative molecular mass. This observation is consistent with those of other authors who have studied clays and modified clays [17]. This behavior is expected because the larger molecules have more potential points of interaction with the surface. Moreover, there is an entropic constraint. If a larger molecule is adsorbed on a surface with more than one point of interaction, any point of interaction that is temporarily broken is more likely to be reestablished if other points remain intact.

While this paper documents the first chromatographic study of  $\Delta H_{\text{ads}}$  for Laponite-RD, it is nonetheless useful to compare the values measured here with those obtained by other authors on other clay

Table 3  
Experimental measurements of  $\Delta H_{\text{ads}}$  on clays, from Refs. [17,18]

Compound	$-\Delta H_{\text{ads}}^{\text{a}}$ (kJ/mol)	$-\Delta H_{\text{ads}}^{\text{a}}$ (kJ/mol)	$-\Delta H_{\text{ads}}^{\text{b}}$ (kJ/mol)
Cyclohexane	53.3	–	–
Hexane	64	53.5	41.8
Heptane	72.7	54.8	49.8
Octane	83.2	–	53.1
Nonane	90.7	–	54.8
Decane	99.1	–	59.8

<sup>a</sup> Chromatographic determination of  $\Delta H_{\text{ads}}$  on montmorillonite.

<sup>b</sup> Thermogravimetric determination of  $\Delta H_{\text{ads}}$  on aluminum oxide intercalated montmorillonite.

systems [18,19]. Some representative comparisons are provided in Table 3. Here, we present two chromatographic measurements of  $\Delta H_{\text{ads}}$  on natural montmorillonite (columns 1 and 2 in Table 3), and a thermogravimetric measurement of  $\Delta H_{\text{ads}}$  on aluminum oxide intercalated montmorillonite (column 3). As the data in this table show,  $\Delta H_{\text{ads}}$  increases with carbon number and relative molecular mass of the adsorbate on montmorillonite. The wide variability in measured values of  $\Delta H_{\text{ads}}$  is also apparent, due primarily to variability in the composition and history of the adsorbent. This serves to point out the importance of performing measurements on refined, well-characterized adsorbents. The magnitudes of the  $\Delta H_{\text{ads}}$  values presented in the table clearly indicate that our measurements presented in this study are of reasonable magnitude for clays.

## 5. Conclusions

In this paper, we have presented chromatographic measurements of the enthalpy of adsorption of 10 hydrocarbon fluids on the surface of a clay (Laponite-RD). Two measurement methods have been employed: a standard packed-column method, and a newly developed WCOT method. For the measurements on the clay surface, we have demonstrated that the two methods give the same value for  $\Delta H_{\text{ads}}$  within experimental uncertainty. The experimental uncertainty is lower for the measurements done on the WCOT column. Moreover, we have noted that the older, packed-column approach produces  $\Delta H_{\text{ads}}$  values that have a surprisingly high

correlation coefficient with their corresponding uncertainties, indicating that the uncertainties may not be entirely random. By contrast, this correlation is absent with the WCOT approach. The measurements made on the WCOT column are in general somewhat higher than those produced on the packed column, indicating a higher degree of surface integrity in the WCOT column. We, therefore, believe that the WCOT approach has a great deal of promise for becoming a standard measurement protocol, especially when applied to clays. The behavior of  $\Delta H_{\text{ads}}$  with physical variables follows our expectations based on previous studies and physical intuition.

## Acknowledgements

The financial support of the United States Air Force, Contract No. AFOSR-MIPR-94-0027, is gratefully acknowledged. The authors would like to acknowledge the assistance of Dominic Vecchia and Jolene Splett of the Statistical Engineering Division of NIST. One of us (AL) acknowledges the financial support of the NIST Professional Research Experience Program.

## References

- [1] B.S. Neumann, K.G. Sansom, *Israel J. Chem.* 8 (1970) 315.
- [2] Laponite Technical Bulletin, L104/90/A, Laporte Industries, Eversholt, Bedfordshire, UK.
- [3] D. Atkinson, G. Curthoys, *J. Chem. Educ.* 55 (1978) 564–566.
- [4] D. Atkinson, G. Curthoys, *J. Chem. Educ.* 56 (12) (1979) 802–804.
- [5] S.A. Greene, H. Pust, *J. Phys. Chem.* 62 (1958) 55–58.
- [6] R.J. Laub, R.L. Pecsok, in: *Physicochemical Applications of Gas Chromatography*, Wiley, New York, 1978.
- [7] J.R. Conder, C.L. Young, in: *Physicochemical Measurement by Gas Chromatography*, Wiley, Chichester, 1979.
- [8] T.J. Bruno, *Anal. Chem.* 58 (1986) 1596.
- [9] T.J. Bruno, K.H. Wertz, *J. Chromatogr. A* 736 (1996) 175–184.
- [10] T.J. Bruno, K.H. Wertz, M. Caciari, *Anal. Chem.* 68 (8) (1996) 1347–1359.
- [11] U. Mingelgrin, F. Tsvetkov, *Clays Clay Miner.* 33 (1985) 285–294.
- [12] F. Tsvetkov, U. Mingelgrin, *Clays Clay Miner.* 35 (1987) 391–399.



- [13] F. Tsvetkov, U. Mingelgrin, N. Lahav, *Clays Clay Miner.* 38 (1990) 380–390.
- [14] P.T. Hang, G.W. Brindley, *Clays Clay Miner.* 18 (1970) 203–212.
- [15] T.J. Bruno, *J. Chromatogr. A* 721 (1996) 157–164.
- [16] D. Vecchia, J. Splett, Statistical Engineering Division, National Institute of Standards and Technology, Boulder, CO, personal communication, 1998.
- [17] H. Lao, C. Detellier, *Clays Clay Miner.* 42 (4) (1994) 477–481.
- [18] M.L. Occelli, R.A. Innes, *Appl. Catal.* 14 (1985) 69–82.
- [19] G.L. Keldsen, J.B. Nichalas, K.A. Carrado, R.E. Winans, *J. Phys. Chem.* 98 (1994) 279–284.