University of Alberta

ADSORPTION OF SELECTED ORGANIC SOLVENTS ON CLAY & SAND BY INVERSE GAS CHROMATOGRAPHY

by

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ABSTRACT

The technique of Inverse Gas Chromatography (IGC) was employed for the study of the interactions between various organic solvents with various types of the major inorganic materials (clay minerals and sand) found in Alberta's oil sands. Heat of adsorption (-ΔH) was measured for each solvent with respect to each of the four studied inorganic materials. The calculation we used was based on the Infinite Dilution Thermodynamics approach used by Katsanos *et. al.* [*Journal of Chromatography A*. 795, 133-184 (1998)]. Retention time data is converted into Retention Volume; ΔH is then obtained by a plot vs. $1/T$. The solvents studied were straight chain, branched and cyclic alkanes, alkenes, aromatics, and ketones. The inorganic materials studied were kaolinite, illite, illite-smectite mixed layer, and sand. Our results show that solvents had significantly less affinity for sand when compared to the three types of clay studied. Additionally, solvent affinity to illite had appreciable difference when compared to kaolinite and the mixed layer of illite-smectite. Furthermore, increase in carbon number leads to increased adsorption to the clay. Branched or cyclic alkanes have slightly lower adsorption to clay when compared to straight chain alkane of the same carbon number. Double bonds significantly increase solvent affinity to clay, but have no effect on sand. Lastly, alcohols and ketones have very high affinity to clay that no elution occurred when either solvent was injected into the GC and only ketone eluted when sand was the stationary phase in the GC column.

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NOMENCLATURE

IGC	Inverse Gas Chromatography
ΔH	Enthalpy of Adsorption
ΔG	Gibbs Free Energy
ΔS	Entropy of Adsorption
V_n	Retention Volume
V_s	Volume of Solid Adsorbent
n_s	Moles of Adsorbed Solvent
t_n	Net Retention Time of Solvent
t_r	Retention Time of Probe
t_0	Retention Time of Marker
J	Correction Factor for Pressure Drop in the Column
p_i	Column Pressure at the Inlet
p_o	Column Pressure at the Outlet
μ_s	Chemical Potential in Adsorbed State
μ_G	Chemical Potential in the Gas Phase
μ^θ	Chemical Potential in the Standard State
T	Temperature in Kelvin
R	Universal Gas Constant
p	Pressure
c	Concentration of Adsorbed Solvent
q	Amount of Adsorbed Solvent
K	Equilibrium Constant of Adsorption
f	Flow Rate of Carrier Gas

CHAPTER 1

1.0 INTRODUCTION

Alberta's oil deposits exceed Saudi Arabia's proven oil reserves. Currently, most of the oil is actually bituminous sands which require a significant amount of water for extraction. For example, in 2005 Syncrude consumed a total of 18.5 barrels of water for every barrel of Sweet Blend produced. Water is drawn from Athabasca River and no re-discharge is allowed. From the supply-demand analysis, there is a possibility that the bottleneck for bitumen extraction will be the water availability. Tailing ponds are another concern since they take up a significant land area and take a long time to settle and be cleared [1]. Due to the worldwide depletion of energy resources and increasing demand, the pressure for finding ways to reduce dependency on water will continue to grow.

One possible route to explore is the use of an organic solvent. While factors which affect aqueous extraction have been extensively studied [2-11], non-aqueous extraction has not been studied as thoroughly. Vapour Extraction (VAPEX) method, which uses propane, butane, or carbon dioxide (or combination of) has drawn attention over the past few years. In this process, oil recovery depends on the transfer of solvent to the oil, governed by dispersion, and viscosity reduction of the oil (or bitumen) [12]. Consequently, studies related to viscosity reduction by numerous solvents have been carried out [13-15]. Many studies have dealt with the interaction between organic solvents and clay minerals in numerous fields. Inverse Gas Chromatography (IGC) technique, due to its simplicity, availability, and practicality, has become a popular method over the years in the study of clay-solvent interactions. Since clay minerals are generally good sorbents for organic solvents, clay (or modified clay) has been investigated as adsorbent of organic contaminants including chlorinated phenols and aromatic pesticides [16-18]. Bandosz *et al.* [19] studied n-alkane and alkene interactions with various types of smectites of varying chemical compositions due to their use as catalysts, adsorbents, and molecular sieves. Kubilay *et al.* [20] and Price *et al.* [21] studied organic solvent interactions with Kaolin and calcinated Kaolin since they are used as fillers to improve the physical properties of polymers. Yang *et al.* [22] studied the dispersive properties of untreated kaolinite and kaolinite surface-treated with titanate coupling agents. This treatment process is important for improving electrical properties and water resistance in plastic systems.

In the field of oil sands, in order to explore potential solvents, clay minerals have been studied in order to understand their surface properties and their interactions with organic solvents. Saada *et al.* [23] studied various types of alkanes and their interaction with illites and kaolinites. In their study, three types of material were studied for each clay mineral, which differed based on formation conditions (Heritage, Neoformation, and Agradation). They found that while the formation condition for illite did not affect the measured enthalpy of adsorption of alkanes, results for Kaolinite differed by up to 20% in few measurements.

There are two main types of IGC techniques and they differ by the amount of solvent probe injected. Each type leads to a different type of experiment to provide a different type of data. One approach is injecting finite amount of probe to obtain non-linear elution profiles; i.e. retention time depends on the quantity injected. This method allows for the determination of adsorption isotherms. The other approach, which is the one we used in this work and has been used by most of the authors quoted here, is to inject an infinitely small amount (~ 1 μL) of solvent probe. The purpose of this is to avoid saturating the solid surface so that we can study how the organic solvent interacts with an infinitely large amount of solid surface without competition for space from the solvent. When infinite dilution condition is met, retention time, and hence retention volume, is a constant for any given solvent at a fixed temperature. However, retention times can be obtained for various solvents at different temperatures. This approach is used in order to calculate the enthalpy of adsorption (ΔH) for each solvent on the selected solid surfaces. In our work, we used the approach Katsanos *et al*. [24] employed in order to obtain ΔH.

In the present work, we studied three types of clay: kaolinite, illite, and illite-smectite mixed layer. These three types of clays make up the majority of clay minerals found in Alberta's oil sands. Sand (SiO_2) was also studied. The organic solvents we used were normal, branched, and cyclo alkanes, 1-alkenes, aromatics, ketones, and alcohols. We also tried two column lengths for kaolinite and two mesh sizes for kaolinite. The objective of our work is to investigate how different functional groups in the organic solvents affect their interaction with inorganic minerals encountered in oil sands. The study of three different types of clay, and sand, is aimed to increase the understanding of how the structure of inorganic minerals can affect its interaction with organic solvents.

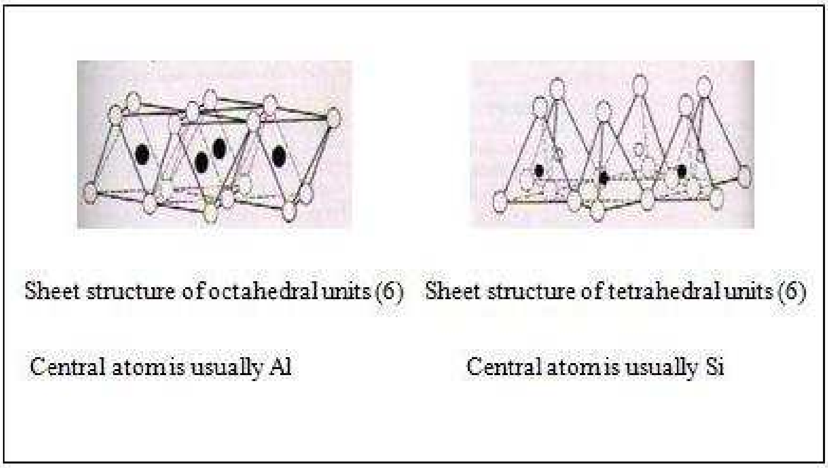
1.1 Adsorption Processes

There are two types of adsorption processes which involve a gas-solid interface. The first type is physi-sorption. In this process, the gas molecule interactions with the solid surface are mainly due to van der Waals forces. In chemi-sorption, the gas molecules form a chemical bond with the solid surface.

The effect of temperature on the two types of adsorption differs due to the type of interaction between the gas and the solid. An increase in temperature reduces physi-sorption. More energy in the system provides for kinetic energy which allows the gas to escape from the solid surface. As for chemi-sorption, an increase in temperature results in more energy in the system to overcome the activation energy required to break the gas chemical bonds in order to bind with the solid surface [25].

1.2 Inorganic Mineral Structures

Grim [26] described numerous types of clays in terms of basic structures and modifications. Most clay minerals contain two structural units as their building blocks. One such unit consists of Al, Fe, or Mg atoms embedded in the octahedral co-ordination with two sheets of closely packed oxygen atoms (or hydroxyl groups) such that the metal or Al atom is equidistant from the 6 oxygen atoms (or hydroxyl groups). When the centre atom is Al, only two-thirds of possible sites are filled [$Al_2(OH)_6$] or Al_2O_3. The other unit is a tetrahedral structure of silicon atoms at equal distance from four oxygen atoms (or hydroxyl groups). Figure 1-1 below shows the atomic structure of the two main building blocks. Different clay minerals are made up of different arrangements and/or substitutions of the above building blocks. The simplest and most common clay mineral, kaolinite, consists of a 1:1 ratio of the aforementioned structural units. The octahedral unit is mainly $Al_2(OH)_6$ while the tetrahedral structure is SiO_2, making the general formula of kaolinite $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$ [25]. With a very small amount of ionic substitution, kaolinite has negligible charge imbalance, caused mainly by broken bonds.



Sheet structure of octahedral units (6) Sheet structure of tetrahedral units (6)

Central atom is usually Al Central atom is usually Si

Figure 1-1. Building Blocks of Clay Minerals

Illite has a 2:1 unit structure. The two outer layers are silica sheets and in the middle is an alumina layer. The illite structure has considerable ionic substitution in the outer layers. Some Si atoms are substituted by atoms with fewer valence electrons, most commonly Al. Since Si has four valence electrons to Al’s three, substitution leads to charge imbalance. The layers are often negatively charged.

Smectite has a similar structure to illite. The difference is mainly in the ionic substitution. While for illites it’s mainly in the outer layers, for smectites it is within the middle layer, the alumina sheet. Some Al atoms are replaced by divalent atoms such as Mg and Fe II. Once again, due to the difference in the number of valence electrons, charge imbalance leads to negatively charged layers.

Sand has a simpler structure compared to clay. It consists only of a silica layer and has the chemical formula SiO_2.

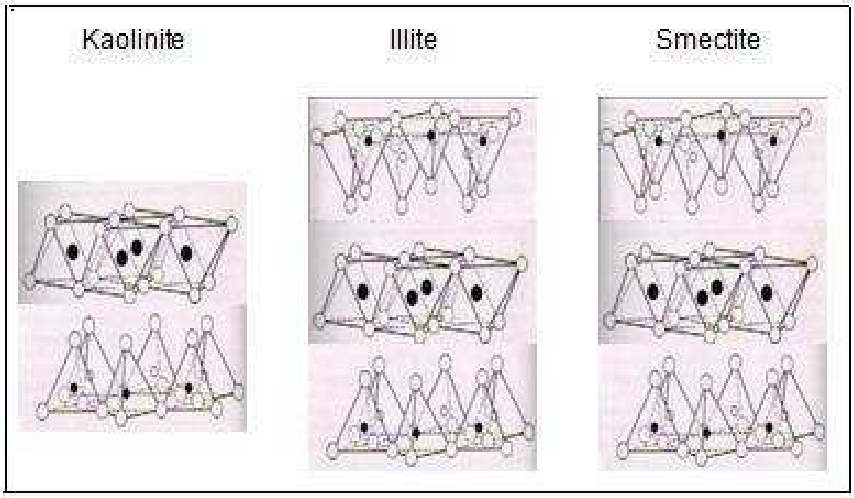


Figure 1-2. Structure of Clay Minerals

The three types of clays studied were kaolinite, illite, and a mixed layer of illite & smectite. A simple schematic of their atomic structure is shown above in figure 1-2. The choice was based on the make-up of Alberta's clay minerals in particular and the Earth crust in general. Illite is believed to make up 50% of clay in the Earth's crust [28]. As for Alberta's oilsands, estimates vary on composition but kaolinite is the dominant clay and illite is the 2nd largest component. Masliyah [1] reported that 2004 analysis estimates 69% of clay is kaolinite, 28% is illite, and 1.7% is mixed-layer clay. The three clays add up to more than 98% of clay minerals. Chalaturnyk *et al.* [27] reported that koalinite makes up 50-60% of clay while 30-50% consists of illite.

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CHAPTER 2

2.0 OIL SANDS EXTRACTION

Since our study is aimed at finding an alternative method to bitumen extraction from oil sands, it is important to understand the major steps involved in bitumen extraction. Presently, commercial methods utilize water for extraction. Aqueous processes have also been thoroughly studied and understanding their scientific background important when an alternative is explored.

2.1 Bitumen Liberation

The first step in bitumen extraction is the liberation of bitumen from the inorganic material (sand and clay). In the presence of bitumen, sand, and a solvent, the bitumen must first recede from the sand surface by establishing a three-phase contact point. An illustration is in figure 2-1 below.

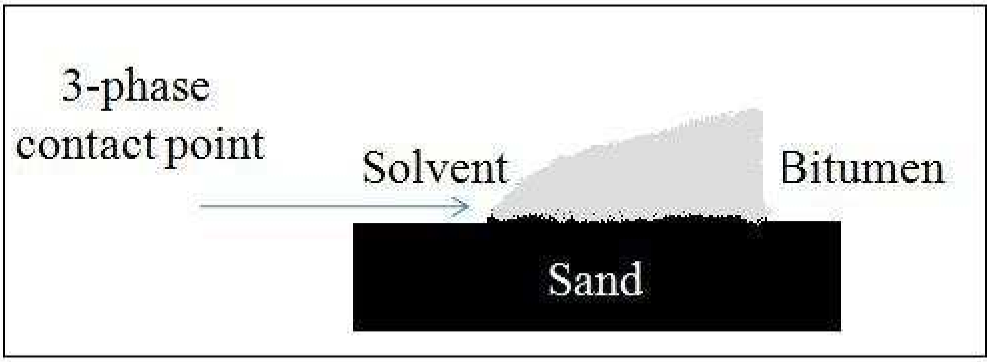

Figure 2-1. Three-phase contact point

Interfacial properties of the bitumen-sand, bitumen-solvent, and sand-solvent determine whether the bitumen will recede towards itself or not [1]. When the solvent is water, interfacial properties between the bitumen and the solvent are affected by the presence and activation of the amphiphilic compounds present in the bitumen [4]. Amphiphilic compounds are made up of a hydrophilic ionized head (such as COOH) and a hydrophobic hydrocarbon chain [5]. In the presence of water the ionized head will float at the water interface while the organic chains will remain in the bitumen. Such surface activity reduces surface tension of bitumen.

When organic solvent is used, the liberation process depends on the solvent removing bitumen from sand and clay. Since bitumen is very viscous, the solvent needs to reduce the viscosity in order for bitumen to flow. However, the solvent is not required to reach the surface of the inorganic solids in order to establish the three-phase contact point mentioned above. Solvent transfer in the bitumen is governed by dispersion, which is a combination of diffusion and convection [6]. Once the solvent reaches the solid surface and adsorb on it strongly, it would make the recovery process rather difficult. The focus of our work is the study of the adsorption of various organic solvents on sand and the dominant types of clay present in the Athabasca Oil Sands.

2.2 Bitumen Recovery

When the solvent is water, the liberated bitumen needs to be aerated (attached to air) in order to separate it from water. This is because water has the same density as bitumen up to a temperature of 120 °C, and density drops to only 95% that of bitumen at temperature of 220 °C [1-3]. Since bitumen is a mixture of heavy organic solvents, the use of an organic solvent does not require a bitumen/solvent separation process prior to processing/upgrading. On the flip side, the presence of fine minerals in the bitumen/solvent mixture can adversely affect bitumen transport and has the potential to damage upgrading facilities. Fine mineral attachment to the solvent depends on their interactions with the solvent. While our work sheds light on said interactions, our study and results do not touch on this subject.

2.3 Solvent Recovery

The last step in bitumen extraction is the recovery or management of the solvent. In the case of aqueous extraction, the utilized water will consist of fine minerals, sand, and a small amount of bitumen. This stable suspension is then pumped into tailing ponds until the fine minerals settle at the bottom. Tailings represent an environmental challenge since settling of fines is very slow; it has been estimated that few centuries are needed for de-watering [1]. The process of settling and recovery depends once again on the interactions between the solvent and inorganic solids. Therefore, our study of solvent interactions with clay and sand can provide an indication of the viability of solvent recovery at the end of the bitumen extraction process. The higher the affinity of the solvent for clay and sand, the more difficult it is to separate the inorganic minerals from the organic solvent.

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CHAPTER 3

3.0 INVERSE GAS CHROMATOGRAPHY

As mentioned in Chapter 1, Inverse Gas Chromatography (IGC) is a simple and popular method to study solid surfaces and their interaction with vapours of known composition. Figure 3-1 shows the schematic of an IGC setup. IGC differs from the traditional GC in that in the "inverse" technique, the injected probe is known while the stationary phase is the material being analyzed. In the traditional GC approach, the stationary phase is a standard packing while the injected fluid is the aim of analysis (generally in terms of composition). In IGC, the column is packed with the particles of interest (clay or sand in this study). The weight of material, column temperature, inlet and outlet pressures, and the flow rate of carrier gas are known. The retention time is measured for each (pure) injected solvent.

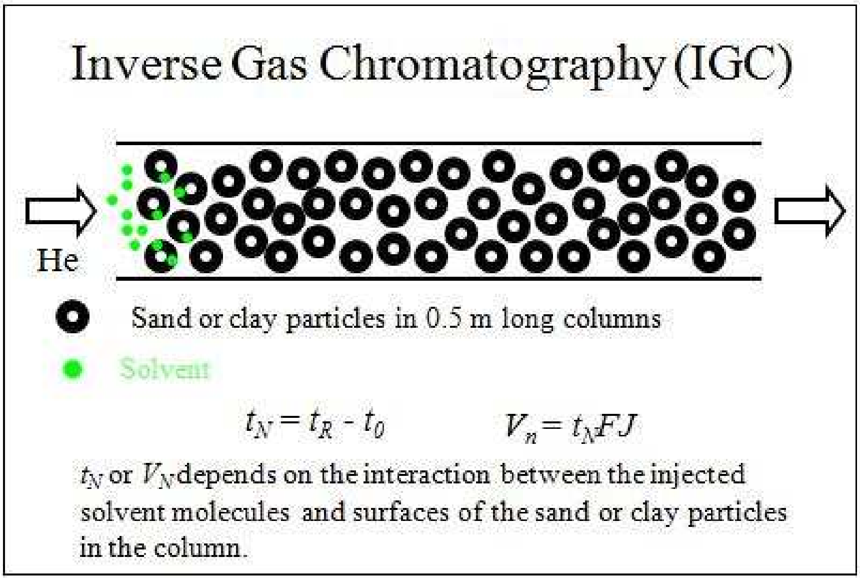

Figure. 3-1 Schematic Representation of IGC Column

3.1 Infinite Dilution Thermodynamics

Katsones *et al.* [1] used a simple relationship between retention volume (V_n) and adsorption enthalpy ($-\Delta H$) in order to utilize the data obtained from IGC experiments. The mobile phase (carrier gas and solvent probe in the vapour form) is assumed to be an ideal gas with a partial pressure, p (atm). The basic thermodynamic equation is:

$$\mu_s = \mu_G = \mu^\theta(T) + RT\ln(1/p) \tag{3-1}$$

where R is the universal gas constant, T is the temperature in K, μ_s is the chemical potential in the adsorbed state, μ_G is the chemical potential of the same solvent in the gas phase, and μ^θ is the chemical potential in the standard state of the pure solvent at 1 atm.

The Gibbs free energy of adsorption is

$$\Delta G = \mu_s - \mu^\theta(T) = RT\ln(1/p) \tag{3-2}$$

From the above equation, we can use the ideal gas law relationship to arrive at

$$\Delta G = RT\ln(cRT) \tag{3-3}$$

c is the concentration of the adsorbed solvent and can be expressed as q/K where q is the amount of solvent adsorbed per unit volume and K is the equilibrium constant, which is V_n/V_s where V_s is the volume of the solid adsorbent. Upon inserting these relationships into Equation (3) and solving for V_n, the equation becomes:

$$V_n = RTV_sq\exp(-\Delta G/RT) = RTn_s\exp(-\Delta G/RT) \tag{3-4}$$

where n_s is total amount of the solvent in the adsorbed state. Finally, taking the natural logarithm of both sides and using the relationship $\Delta G = \Delta H - T\Delta S$ gives us

$$\ln(V_n) = \ln(RTn_s) + \Delta S/R - \Delta H/RT \qquad (3\text{-}5)$$

Equation (3-5) is a very useful relationship for the IGC application being studied. Assuming that the vapour behaves like an ideal gas, and that ΔS and ΔH are independent of temperature, a plot of $\ln(V_n)$ vs. $1/T$ for each solvent on each solid surface would yield ΔH. The slope of the resultant line is $\Delta H/R$. At infinite dilution, n_s is assumed to be very small. For a narrow range of temperature, n_s is the dominating factor in the RTn_s in the first part of the equation, which means that $\ln(RTn_s)$ is a constant and the equation can be viewed as ($y = b + cx$). Since the value of $\ln(RTn_s)$ cannot be determined, ΔS cannot be accurately calculated from the y-intercept. However, if one assumes that $\ln(RTn_s)$ is negligible, ΔS can be determined.

V_n can be obtained from IGC by using the approach employed by Price *et al.* [2] in order to convert net retention time, t_n, into V_n. The equation is

$$V_n = J*f*t_n \qquad (3\text{-}6)$$

The net retention time is obtained from the retention time of the probe, t_r, by subtracting the zero retention time ($t_n = t_r - t_0$) and the retention volume is calculated as below:

$$V_n = Jf(t_r - t_0) \qquad (3\text{-}7)$$

where f is the carrier gas flow rate (helium), t_0 is the retention time of a non-interacting probe, also known as the zero retention time. Methane was used as the non-interacting marker in our experiments. J is the correction factor for the pressure drop across the column as calculated by

$$J = 1.5\,[(p_i/p_o)^2 - 1]/[\,(p_i/p_o)^3 - 1] \qquad (3\text{-}8)$$

where p_i and p_o are the inlet and outlet pressures of the column, respectively. p_o is in the range of 13 psi whereas p_i varies temperature and depends on the material in the column. In this study, p_i was close to 22 psi for sand for the range of temperature tested. As for illite and illite-smectite, p_i was slightly above the outlet pressure and varied with increasing temperature from 14 to 18 psi. As for kaolinite, p_i was higher and varied with increasing temperature from 25 to 32 psi.

It is interesting to note that from the above relationships, the particle size distribution, mass, and surface area of inorganic minerals, and the column length should not affect ΔH. Our results which will be presented in Chapters 4 and 5 will support these assumptions as results comparable to literature values were obtained even though different column lengths (i.e., different mass) and mesh size in the work of other researchers. Since the use of Equation (3-5) relies on the infinite dilution conditions, the injected solvent would not affect the resultant ΔH for a particular solvent/surface system. In fact, this condition was verified in the present study.

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CHAPTER 4

4.0 EXPERIMENTAL

4.1 Sample Preparation

Clay minerals were in the fine form. In order to increase their size, we compressed the clay under a pressure of ~ 4 tonnes to form large chucks of clay. Then we grinded and sieved them into the intended mesh size of 35 – 40 (425 – 500 μm). The sand sample obtained had a mesh size of 40 – 100 (152 – 425 μm), therefore there was no need for compression and grinding. It is worth noting that when the particles are too small, it would create a large pressure drop, ($p_i - p_o$), which makes Equation (2-8) not applicable. Although the intention was to have a mesh size the same as clay, compression/crumbling cycle was not possible. After compression, sand immediately forms small fines under the least crumbling, so we decided to sieve the original sample into mesh size 40 – 70 (215 – 425 μm) in order to have a particle size range narrower than in which it was supplied.

4.2 Column Preparation

⅛ inches outer diameter stainless steel tubes were washed with acetone in the lab and then dried with vacuum for 6 hours. One end was plugged with inert glass wool, and then the inorganic solid was filled from the other side. Once filled, the other end is also plugged with inert glass wool. To ensure even packing throughout the column, it was constantly shaken during filling. The column was then placed in the gas chromatograph and conditioned with Helium for 48 hours at 60ºC to ensure that any residual solvent is removed before data is collected. Additionally, the column was then conditioned for 12 hours at each temperature setting for data collection in order to achieve pressure drop and moisture equilibrium. Helium was used as carrier gas for all experiments. The flow rate was in the range of 25 ml/min to 30 ml/min and was measured with the use of a soap bubble flow-meter. The selected flow rate was based on the GC manual [HP 4890D Gas Chromatograph Operating Manual, Hewlett Packard Company (1997)] recommendation. For a source pressure of 60 psi, the optimal flow rate is 28 ml/min.

Column length used was 50 cm. The choice was based on the fact that both 50 cm and 100 cm columns yield comparable ΔH, as discussed in Chapter 3. Retention time decreases with decreasing column length; consequently, run time is reduced. This allowed us to carry more experiments at a wide range of temperatures. The mass of inorganic material was roughly around 1 g used in each column.

4.3 Instrumentation

A Hewlett Packard 4890 gas chromatograph equipped with a flame ionization detector (FID) was used. Hamilton syringes were used for injecting vapour probes. Infinite dilution was achieved when 0.1-1 μL of probe was injected. To verify infinite dilution conditions, varying amounts of each probe were injected. Measured retention times were within experimental uncertainty. At least 3 retention times were taken at the infinite dilution condition; the average was used for our calculations. For most solvents, retention time was reproducible within 5% of their average retention times, which was the value used for subsequent calculations. For polar solvents, retention time sometimes differed by more than 5%, and more frequently so at very low and very high temperatures. If a change in the volume of injected solvent results in significantly different retention time, infinite dilution condition is not met. In such cases, experiments were repeated with smaller injections until infinite dilution condition was established.

4.4 Materials

Sand, pure SiO_2 (99.80%), was obtained from Acros Organics while kaolinite was obtained from Ward Minerals (in the powder form). Illite and illite-smectite source clays (in wide range of particle sizes, from fine power to large pieces) were purchased from the Source Clays Repository, of the Clay Minerals Society at Purdue University. The origin of the illite sample was Montana, USA, while the origin of the illite-smectite (70/30) mixed layer clay was Czechoslovakia. At the time of purchase, that was the source clay available at the Repository. According to supplier-provided information, source clays have been carefully selected from the source deposits by professionals to minimize in situ variations and pre-treatment involved only low-temperature, steam-fired tray drying, and imp or Raymond mill pulverization. Chemical composition of illite and illite-smectite is given in the table below:

Table 4-1: Chemical Composition of Illite and Illite-Smectite as Provided by the Supplier

Clay	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5
Illite	49.3	24.25	0.55	7.32	0.55	0.03	2.56	0.43	0	7.83	0.08
Illite-Smec	51.6	25.6	0.039	1.11	<.1	0.04	2.46	0.67	0.32	5.36	0.04

The charges on the layers are provided by the supplier as follows:

Table 4-2: Layer Charges for Clays

Clay	Octahedral layer	Tetrahedral layer	Interlayer
Kaolinite	0.11	-0.17	-0.06
Illite	-0.44	-1.23	-1.68
Illite-Smec	-0.48	-0.81	-1.29

Due to porosity differences, the mass of sample in the column differed slightly despite the same column length. Inlet pressure was also different for the same reason. Temperature range for tests also differed due to the change in affinity of solvents to each type of clay. Summary of sample mass, temperature range, and inlet pressure is given below:

Table 4-3: Sample mass, pressure drop, temperature range for experiments, and incremental increase of temperature

Solid	mass (g)	temp. range (ºC)	temp. increment (ºC)	pre-heat (ºC)	ΔP (atm)
Kaolinite	1.357	100 – 320 (373 – 593 K)	10	100 (373 K)	0.8 – 1.2
Illite	1.526	110 – 365 (383 – 638 K)	10 (5 above 340 ºC)	110 (383 K)	0.1 – 0.3
Illite-Smectite	1.119	120 – 300 (393 – 573 K)	10	120 (393 K)	0.1 – 0.2
Sand	1.3	40 – 80 (313 – 253 K)	10	80 (253 K)	0.6 – 0.7

The solvents were purchased from Fisher Scientific and Sigma Aldrich (depending on the availability at the time of purchase). They were reagent or HPLC grade and were used without further purification since the experimental technique is chromatography. The retention time is different for each chemical and the intensity of the peak depends on concentration. The solvents used were n-pentane, hexane isomers, cyclohexane, 1-hexene, n-heptane, n-octane, n-nonane, n-decane, n-dodecane, toluene, propyl benzene, dichloromethane, butanone (a ketone), methanol, and ethanol. The non-interacting solvent used to determine the zero retention time was methane.

IGC studies involving clay often included the non-polar alkanes to determine dispersive component of the surface energy. Polar solvents exhibit dispersive and specific interactions with clay. Specific interactions depend on the acid-base of the clay/sand surface [1-5]. Previous studies of other researchers also indicated that clay has strong acidic properties due to OH^- groups and oxygen atoms in the silica layer, which means that basic solvents do not elute from the column [5] and hence no data can be obtained. We tried to get results with alcohol probes but there was no elution at all. Butanone, commonly known as methyl ethyl ketone (MEK), only eluted the column when the stationary phase contained sand. No elution was detected with clay samples. Halogenated hydrocarbons were not tested due to the expected lack of interest in its utility due to environmental concerns. Ethers are flammable gases; tests at high temperatures in a gas chromatograph can be hazardous; therefore no tests were carried out with ethers.

4.5 References

1. Bandosz, T.J., Jagiello, J., Andersen, B., and Schwarz, J.A., *Inverse Gas Chromatography Study of Modified Smectite Surfaces,* Clays and Clay Minerals, 40 (3), pp. 306-310 (1992)

2. Kubilay, S., Gurkan, R., Savran, A., and Yalcinkaya, Z., *Determination of the Surface Properties of Untreated and Chemically Treated Kaolinites by Inverse Gas Chromatography*, Colloid Journal 68, pp. 274-284 (2006)

3. Price, G.J. and Ansari D.M., *An Inverse Gas Chromatography Study of Calcination and Surface Modification of Kaolinite Clay,* Physical Chemistry Chemical Physics 5, pp. 5552-5557 (2003)

4. Yang, Y.C. and Yoon, P.R., *Examination of the Surface Properties of Kaolinites by Inverse Gas Chromatography: Dispersive Properties*, Korean Journal of Chemical Engineering 24 (1), pp. 165-169 (2007)

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CHAPTER 5

5.0 RESULTS AND DISCUSSION

5.1 Measurement of the Net Retention Volume

Figures 5-1 to 5-4 show retention volume plots of selected solvents for the four types of inorganic materials as a function of temperature. Solvent affinity for the inorganic materials decreased with increasing temperature. This is mainly due to increased thermal energy available in the system which allows organic solvents to desorb from the clay or sand surface, a feature of physi-sorption as discussed in Section 1.1. Since no chemi-sorption occurred with any solvent/solid system used in the experiment, it can be safely assumed that minimal surface modification took place during the course of experiments. In fact, this assumption was experimentally verified. Solvents were injected in random order and also before and after non-eluting solvents were injected. Retention time was within the experimental error for each solvent/clay system regardless of the order of the runs.

Solvents with seven or more carbons exhibited much higher retention volumes (i.e., higher affinity) to clay even at elevated temperatures (150 – 300 °C) than those with six or less carbons (100 – 180 °C). 1-Hexene and toluene were the exception as they exhibited affinity which exceeded that of n-octane with the three types of clay used in experiments. As suggested by Bandosz et al. [1], specific interactions of the clay surface with π-bonds of alkenes significantly increase their affinity for clay surfaces due to the presence of strong acidic centres (Lewis acids) in the clay. In their study, smectite was studied. The presence of the π-bond in 1-hexene increased the magnitude of ΔH by 10 kJ/mol compared to n-hexane. Aromatic compound such as toluene only exhibited measurable retention volumes at extremely high temperatures. The three π-bonds in aromatic solvents, as with 1-hexene, significantly increase solvent affinity to clay surfaces.

While experiments for clay were carried out at temperatures higher than 100 ºC, experiments for sand were carried out between 40 and 80 ºC. Organic solvents with eight carbons or less, including toluene, exhibited negligible affinity for sand. Retention time was very close to the zero retention time (that of methane). No reliable data could be obtained, even at low temperatures. Furthermore, the presence of π-bonds in solvents did not lead to increased affinity for the sand. Propyl benzene (which has 9 carbons) exhibited affinity comparable to n-nonane and n-decane despite having three π-bonds. This can be attributed to the negligible presence of Lewis acid centres in sand, which was verified with a weak base. Butanone (methyl ethyl ketone) was used in all experiments. No elution occurred when the stationary phase was clay, but with sand retention volume was comparable to n-nonane. Basic solvents (methanol, ethanol, and butanol) were also injected but no peaks were detected with clay or sand as the stationary phase.

5.2 Determination of Heat of Adsorption

Figures 5-5 to 5-8 are the plots of $\ln(V_n)$ vs. $1/T$ for clays and sand. As demonstrated by Equation 3-5, the slope obtained from such a plot can be used to calculate the enthalpy of adsorption, ΔH.

For the kaolinite and illite samples, straight lines ($R^2 > 0.99$) were obtained for all solvents with the exception of 1-hexene. This trend indicates that ΔH is independent of temperature for non-polar solvents and there is temperature dependence for 1-hexene. For illite-smectite mixed layer, no data was obtained for any polar solvent. Non-polar solvents had linear slopes, indicating that ΔH is independent of temperature in the range used for our experiments. As for sand, pressure drop was very high due to the small size of particles and low porosity, causing variance in retention time up to 10% for many measurements. Straight line was obtained by dropping out measurements taken at the lowest and highest temperatures.

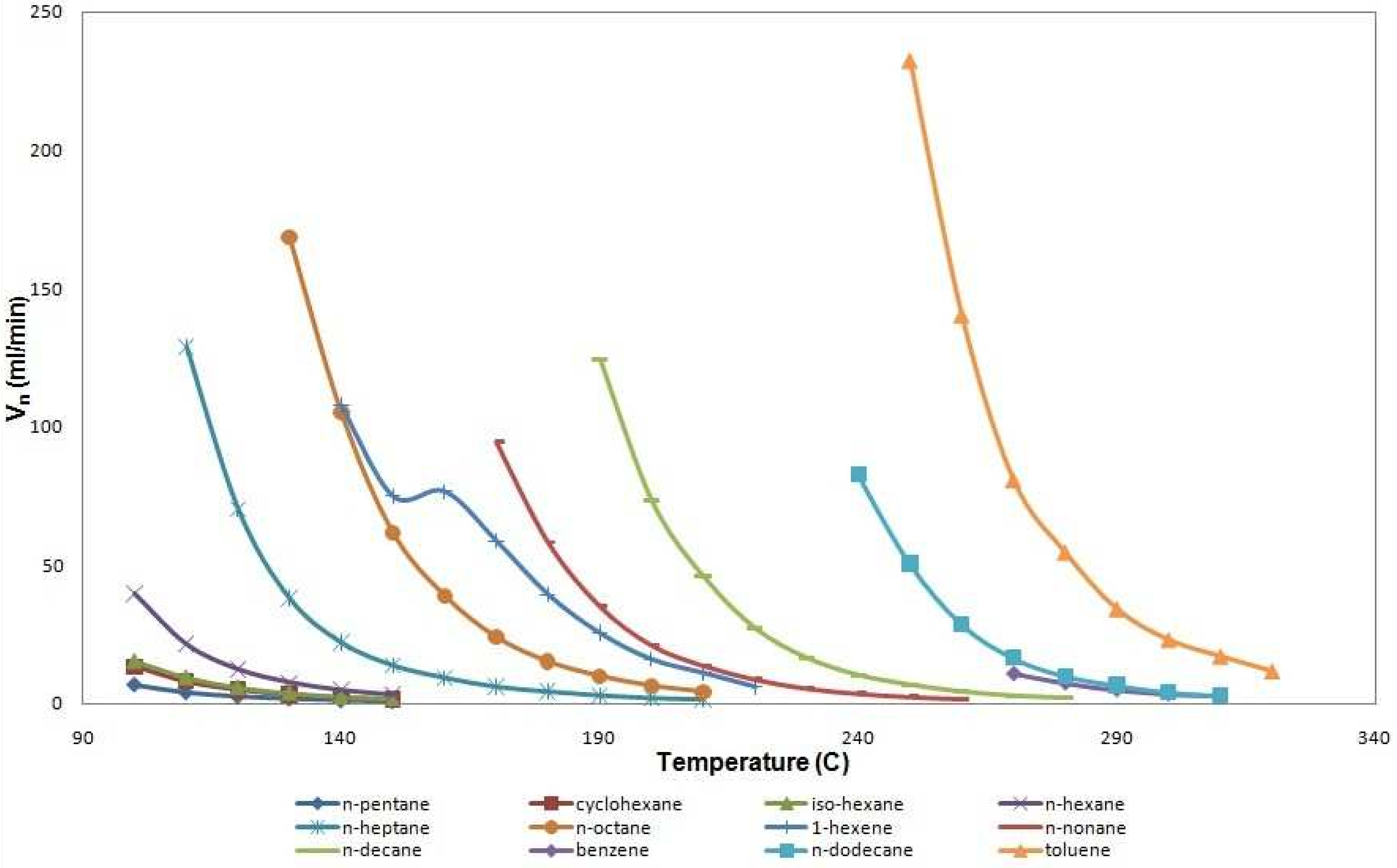

Figure 5-1: Retention Volume, V_n, of selected Organic Solvents with Kaolinite Clay

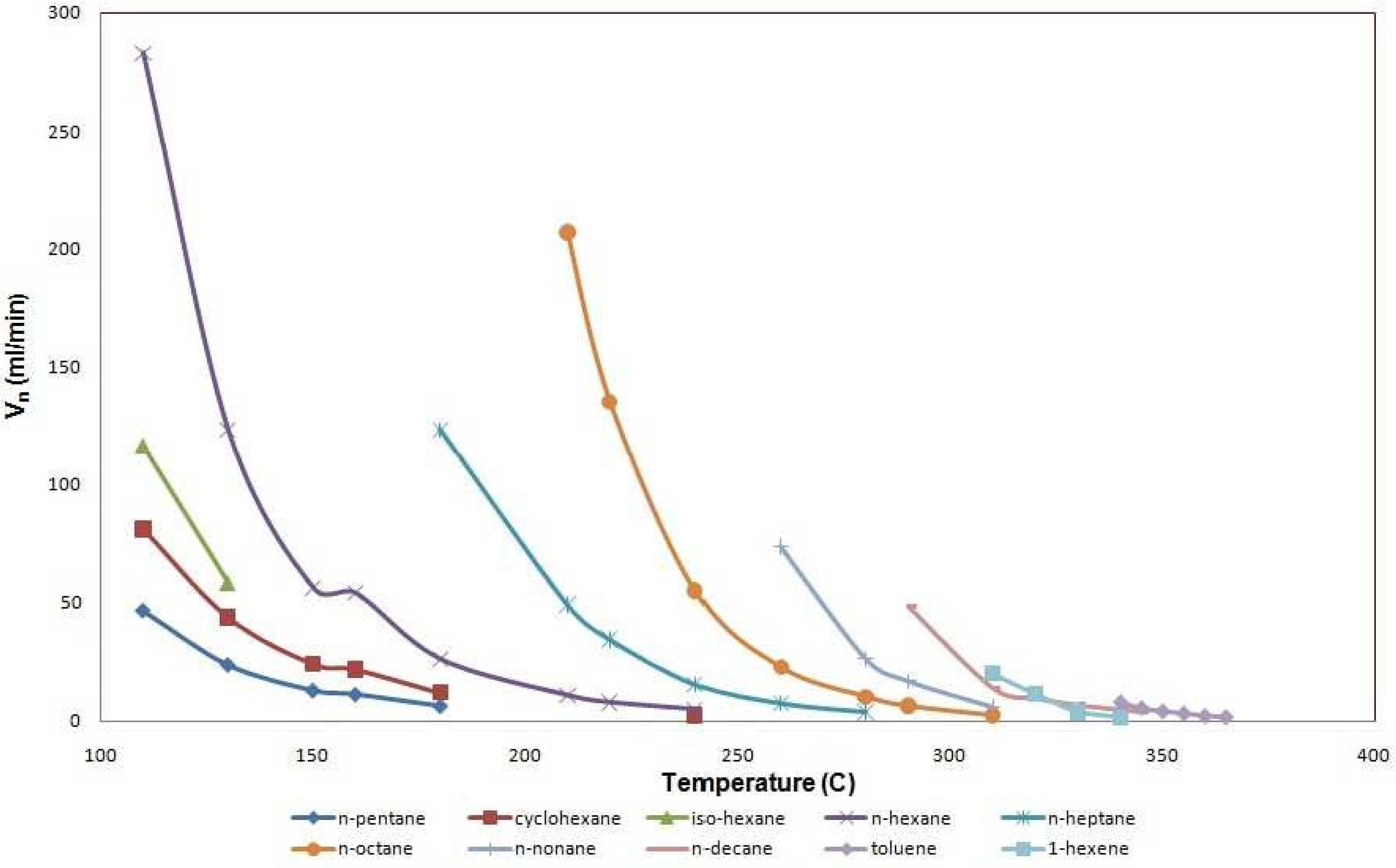

Figure 5-2: Retention Volume, V_n, of selected Organic Solvents with Illite Clay

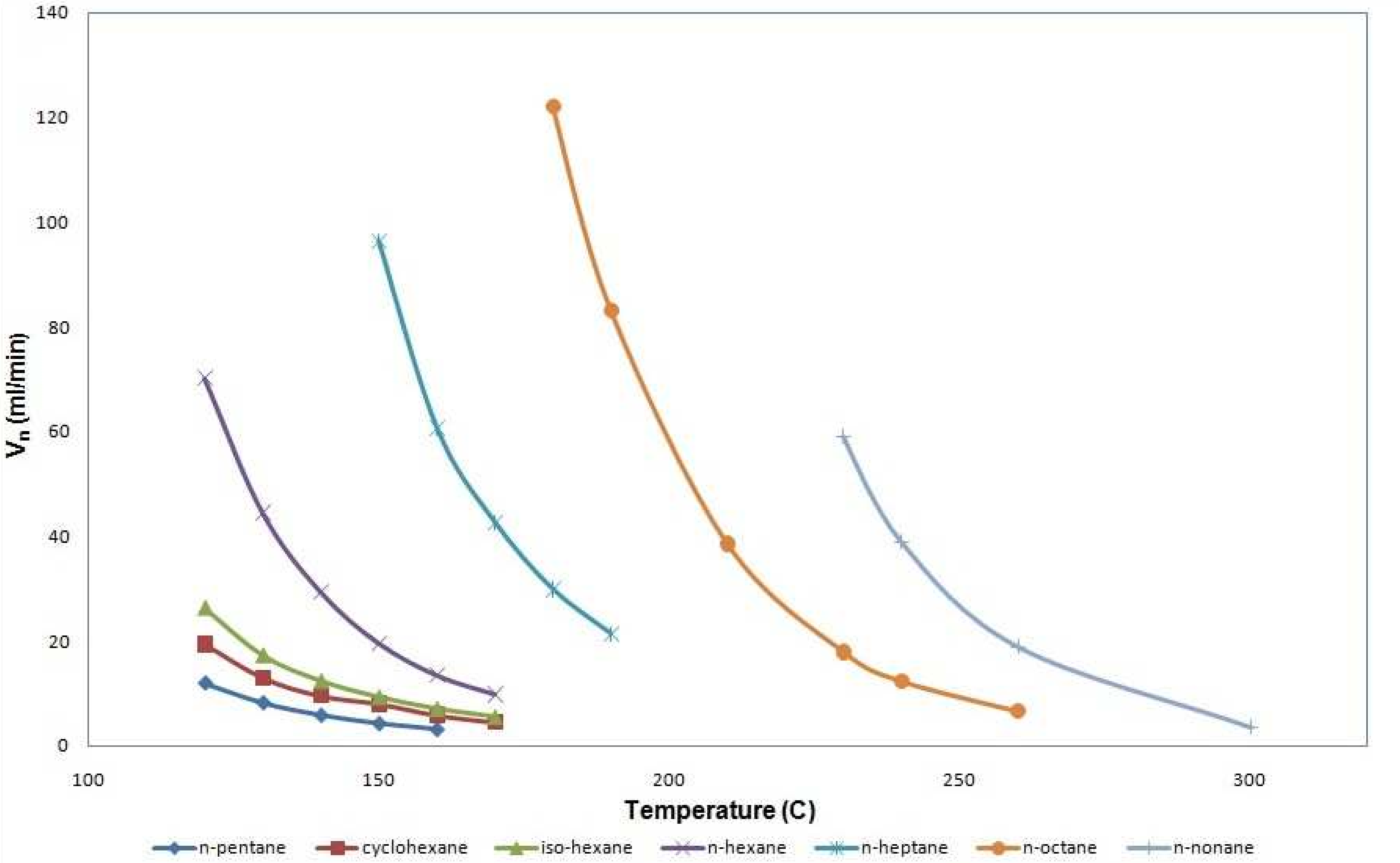

Figure 5-3: Retention Volume, V_n, of selected Organic Solvents with Illite-Smectite Clay

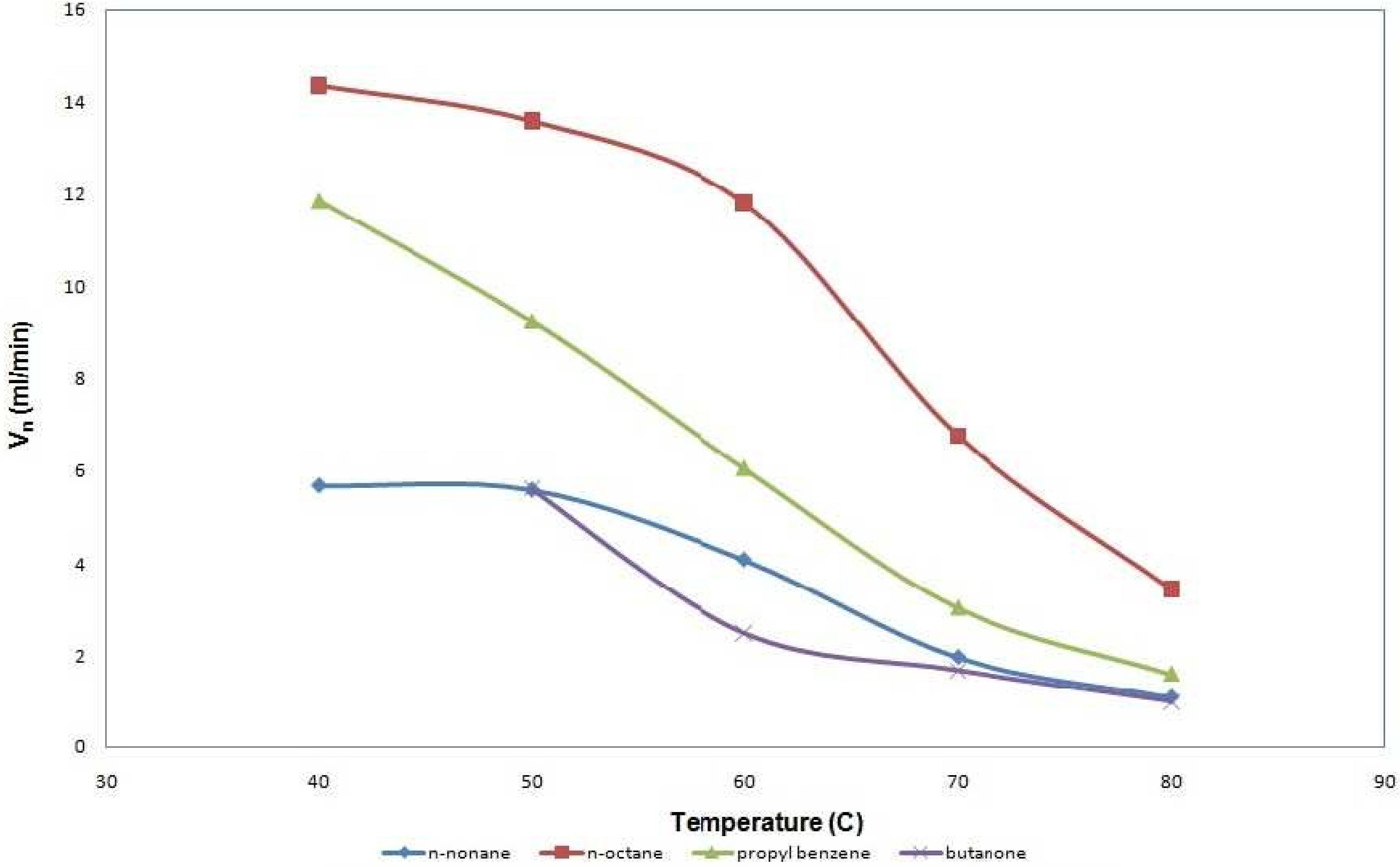

Figure 5-4: Retention Volume, V_n, of selected Organic Solvents with Sand

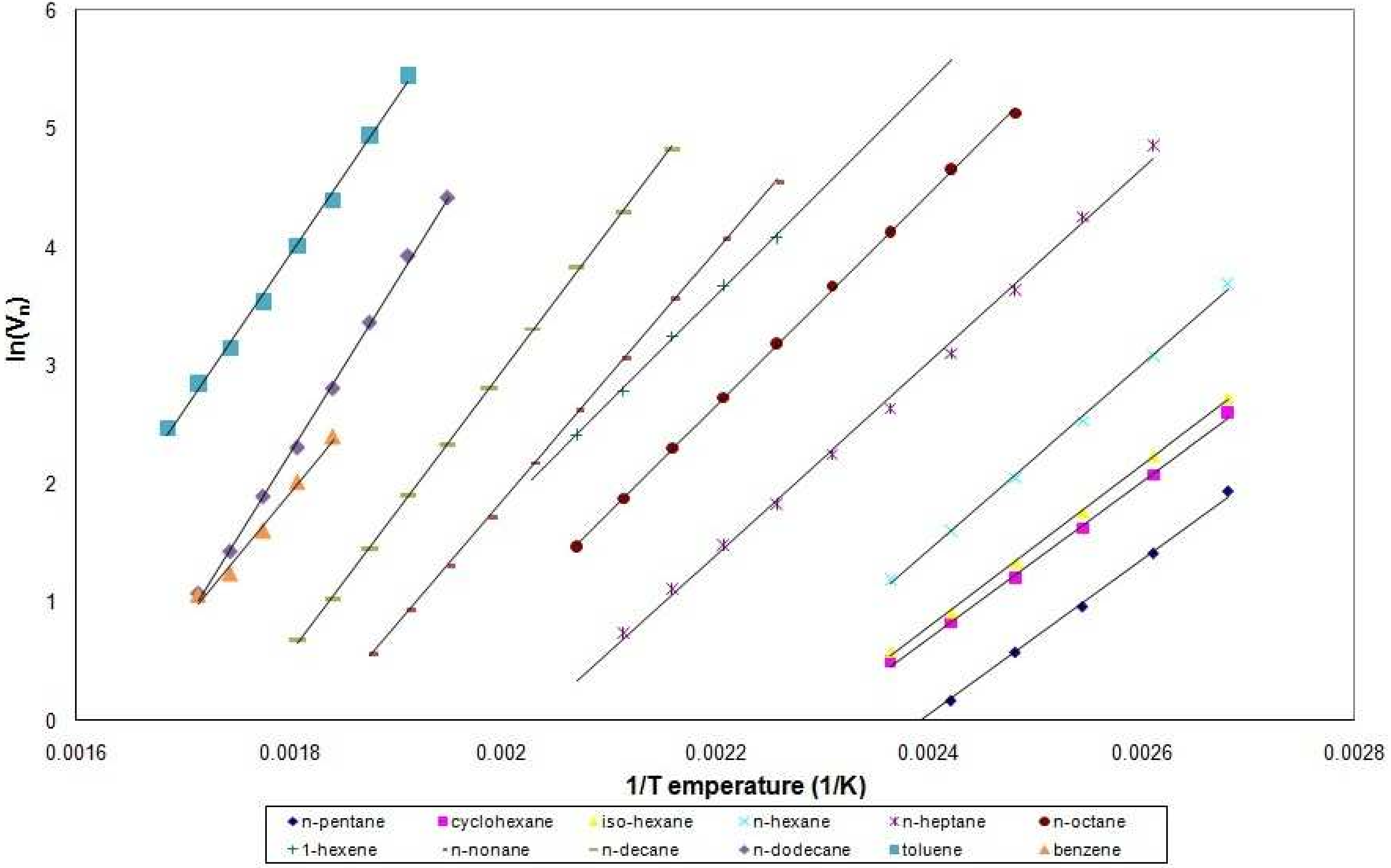

Figure 5-5: ln(V_n) vs. 1/T plot of selected Organic Solvents with Kaolinite Clay

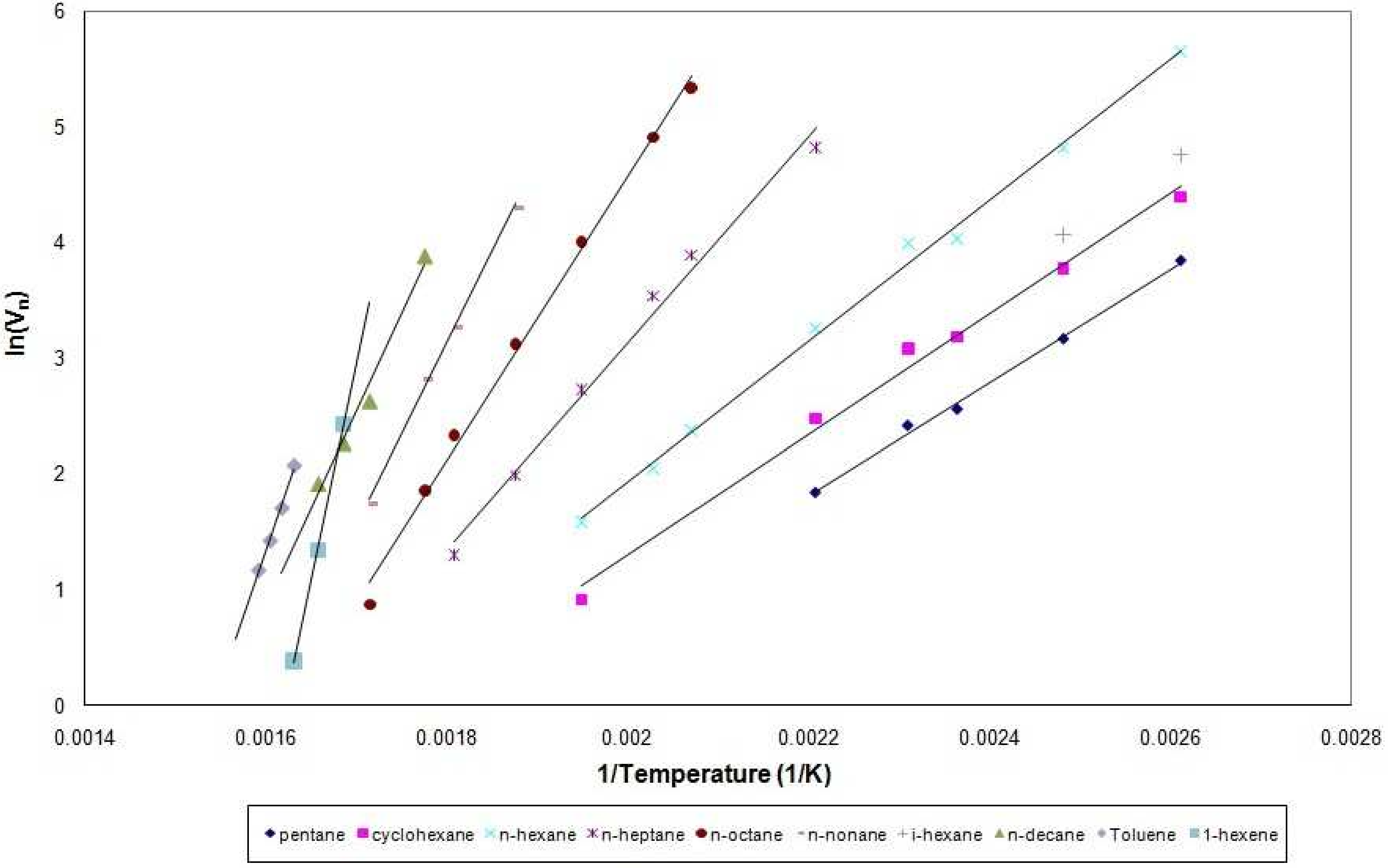

Figure 5-6: ln(V_n) vs. 1/T plot of selected Organic Solvents with Illite Clay

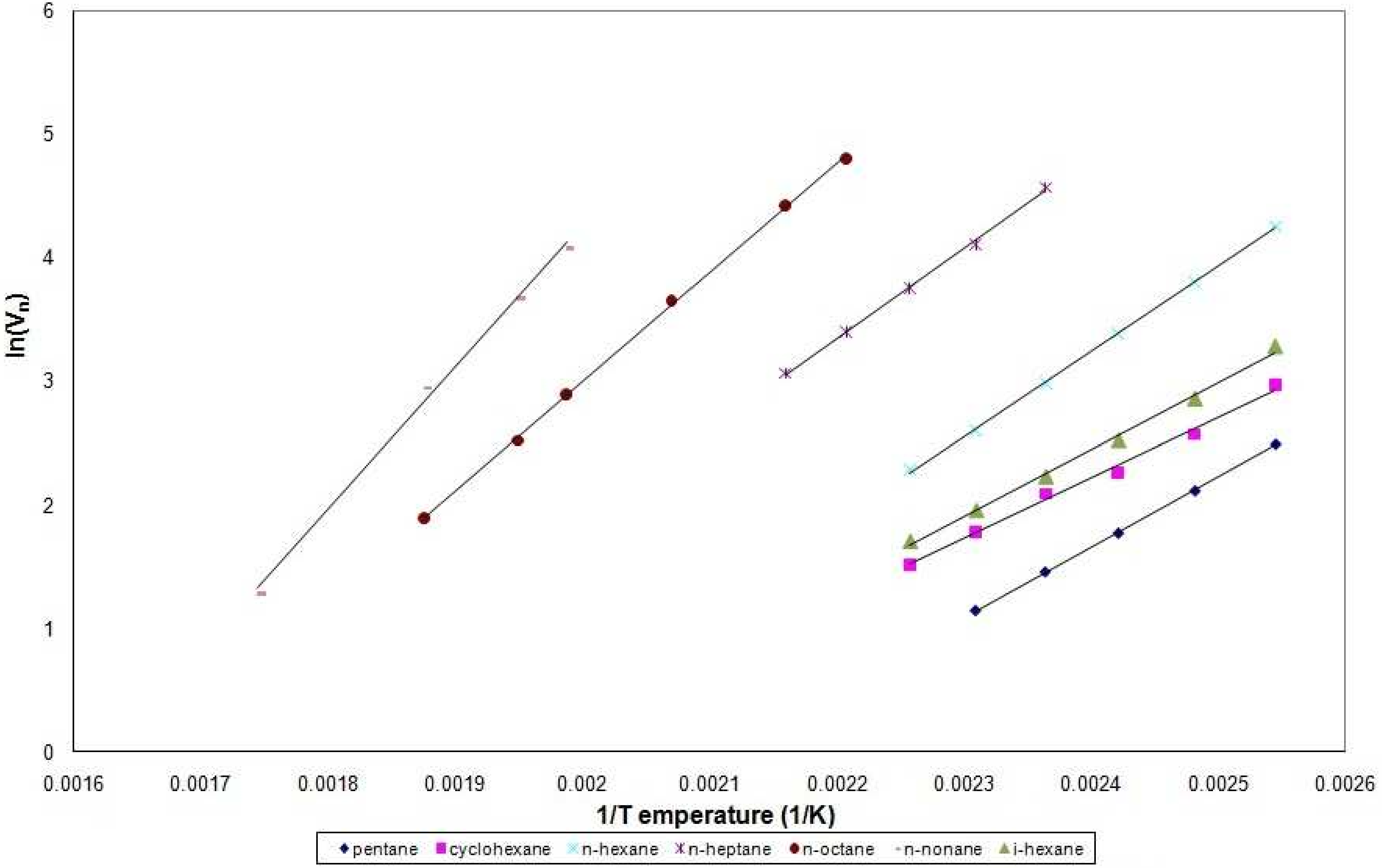

Figure 5-7: ln(V_n) vs. 1/T plot of selected Organic Solvents with Illite-Smectite Clay

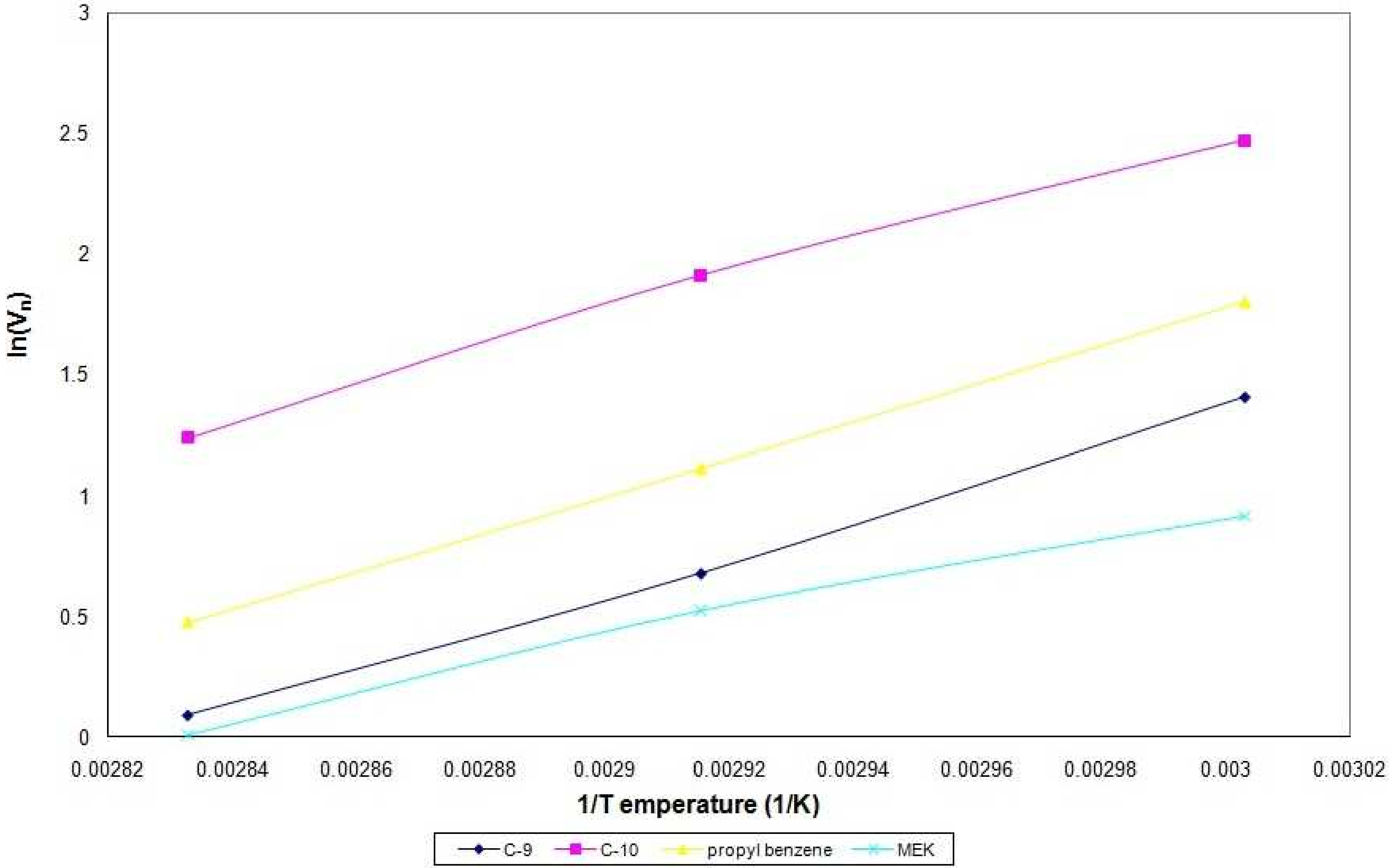

Figure 5-8: ln(V_n) vs. 1/T plot of selected Organic Solvents with Sand

5.3 Experimental Error

Sources of errors come from the measured inlet and outlet column pressures, carrier flow rate measurements, and retention times of probes and the non-interacting marker. Since the above quantities are used for the calculation of the retention volume, V_n, which is then plotted against $1/T$ to obtain ΔH, the sources of errors would lead to deviations in the resultant slope (and hence ΔH). Retention time measurements were repeated three times for each data point, and same was done with the flow rate of the carrier gas. Data was generally within 5% of the average for most solvents. When the plot was completed, only one value of ΔH for each solvent (on each inorganic surface) was obtained. However, since 5% was generally the deviation for measurements obtained directly from experimentation, the error margin in ΔH is expected to be the same for most solvents. However, there were few exceptions. For polar and high molecular weight solvents, peaks were very broad and heavily skewed. A precise retention time was therefore very difficult to determine. When a straight line was not obtained from the plot of ln V_n vs. $1/T$ for the entire range of temperatures used in experiments, data points at the extremes were omitted in order to obtain a straight line. In the case of 1-hexene with kaolinite, measurements used for determination of ΔH were taken for the temperature range 170 to 210 ºC. Data obtained outside this range was omitted. As shown in Figure 5-5 above, the $\ln(V_n)$ vs. $1/T$ plot did not produce a straight line for 1-hexene. This can be due to two reasons: significant errors in retention time determination; or non-linear temperature dependence of ΔH outside the temperature range 170 to 210 ºC. Clays have Lewis acid centers ($AlOH_2^+$) which can donate a proton to a monomer such as 1-hexene. A possible polymerization process is as follows [2]. The initiation reaction is the proton-donating Lewis acid site and the monomer:

$$(AlOH)^- H^+ + CH_2{=}CHCH_2CH_2CH_2CH_3 \leftrightarrow H\text{-}(CH_2C^+HCH_2CH_2CH_2CH_3)AlOH^- \quad (5\text{-}1)$$

The propagation reaction is between the protonated monomer with another 1-hexene monomer, hence denoted as M:

$$H\text{-}M^{+}_{n}AlOH^{-} + M \leftrightarrow H\text{-}M^{+}_{n+1}AlOH^{-} \qquad (5\text{-}2)$$

Since polymerization of 1-hexene with clay acting as catalyst is a plausible occurrence, the experimental error is then due to the formation of higher molecular weight alkanes, which have different heats of enthalpy. This is not a foregone conclusion since cationic polymerization is usually carried out at low temperatures. For example, Lewis acid polymerization of butyl rubber is carried out at – 100 ºC [3]. This is because the degree of polymerization decreases with increasing temperature [2].

Due to the strong affinity of 1-hexene for illite, no elution was observed for temperatures below 300 ºC. Above that temperature, retention time varied by 5 to 10% from the average. Retention time was comparable to n-nonane and n-decane and lower than that of toluene. ΔH for 1-hexene was expected to be close to that of the two alkanes, and lower than that of toluene, but was found to be higher than even toluene. As for n-decane and toluene, the temperature range was 290 to 345 ºC. At the highest temperatures, the change in retention time became negligible as temperature was increased. This led to a reduced magnitude of ΔH (even smaller than that of n-nonane), so the calculation was based on data obtained from 290 to 330 ºC experiments.

As for n-dodecane with illite, no elution was observed when vapour was injected. Small amount of liquid was injected instead. The peaks were very broad and skewed and the magnitude of ΔH was lower than either of n-nonane and n-decane even though retention time/volume was higher than both and even higher than toluene. Since the data was obtained by injecting the probe in the liquid form, the infinite dilution condition was not met. Therefore, the result reported in this study is that no elution occurred (since no peak was detected with probe in the vapour form).

For experiments with sand, the range of temperature used was 40 to 80 ºC. No straight line was obtained when ln(V_n) was plotted vs. 1/*T*. Data obtained at 40 and 80 ºC were omitted in order to obtain straight lines for the four solvents used in that set of experiments. While ΔH for solvents with sand is not accurate, and may carry significant errors, it was observed that retention volume and ΔH was significantly lower than those of clay.

5.4 Measured Heat of Adsorption

Using the slope for all solvents from the ln(V_n) vs. 1/*T* plot, -ΔH values were calculated and are shown in Table 5-1 below. All selected solvents had lower affinity for sand when compared to clay.

Table 5-1: Calculated -ΔH (kJ/mol) values for selected solvents on the four inorganic materials

Solvent	Kaolinite	Illite	Illite-Smectite	Sand
n-pentane	45.2	40.6	47.5	~0
Cyclohexane	46.3	43.4	40.6	~0
iso-hexane	48.4	44.2	45.0	~0
n-hexane	56.5	50.5	57.2	~0
n-heptane	65.9	74.6	60.6	~0
n-octane	74.5	102.4	73.6	~0
1-hexene	75.1	241.0	No Elute	~0
n-nonane	88.3	131.5	95.9	64.4
n-decane	99.3	139.9	No Elute	60.0
Toluene	109.7	191.1	No Elute	~0
Benzene	90.0	No Run	No Run	~0
n-dodecane	120.9	No Elute	No Elute	No Run
butanone	No Elute	No Elute	No Elute	44.3
propyl benzene	No Elute	No Elute	No Elute	64.7
Methanol	No Elute	No Elute	No Elute	No Elute

For n-pentane and hexanes, affinity for illite was lower than for kaolinite and the illite-smectite mixed layer while n-heptane and heavier hydrocarbons exhibited higher affinity for illite. For the three types of clay, n-hexane exhibited higher affinity than branched or cyclo-hexane. A similar trend was also observed by Saada *et al.* [4] for illite and kaolinite, which were the two types of clay studied. The reason was attributed to nanorugosity due to structural defects. For a perfectly smooth surface, alkanes of the same molecular weight are expected to exhibit the same affinity. For molecularly rough surfaces, only straight chains have the maximum interaction with the solid surface. For branched or cyclic alkanes, not all methyl groups are able to fully interact with the solid surface. This caused reduced affinity for the solid surface.

The difference in ΔH between n-hexane and 1-hexene on kaolinite is 18.6 kJ/mol. Comparison between benzene and cyclohexane (same structure but benzene has the equivalent of 3 π-bonds) shows a difference of ~ 44 kJ/mol, which translates to 14.6 kJ/mol for each π-bond. For sand, propyl benzene and n-nonane (both with 9 carbons) have similar magnitude of ΔH, which means the π-bonds have negligible effect on sand.

Figure 5-9 shows the effect of the number of carbons in n-alkanes on ΔH. A linear relationship between the carbon number and enthalpy of adsorption was established for the entire range of alkanes used for kaolinite only. For illite, it is linear for C-6 to C-9 whereas for illite-smectite, it is linear for C-7 to C-9. The increase of affinity as the chain length increases is due to the van der Waals interactions between the gas molecule and the solid surface. The presence of additional methyl groups leads to additional gas-solid interactions and consequently increased adsorption.

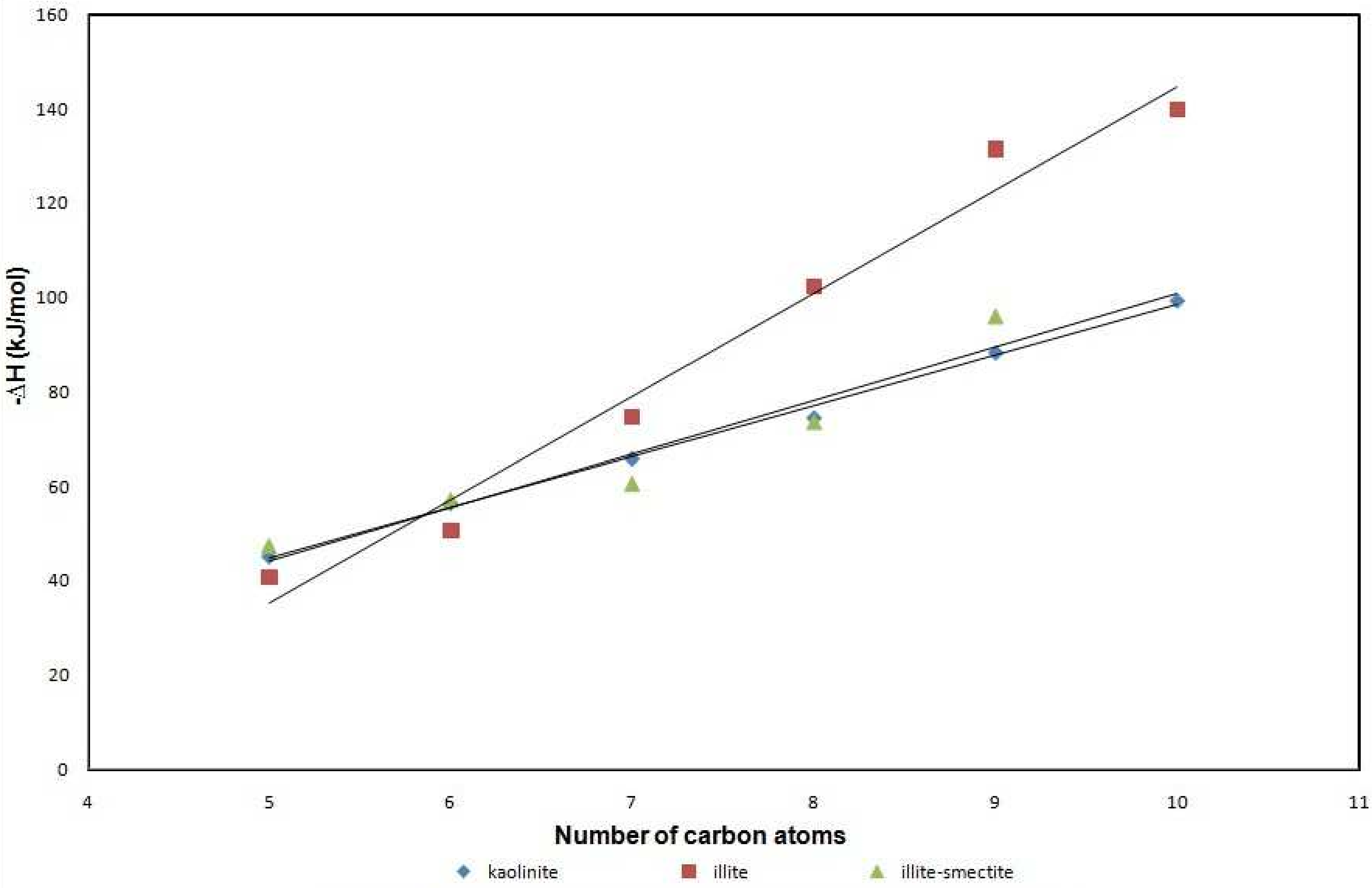

Figure 5-9: Plot of -ΔH versus the number of carbons in n-alkanes for clays

Saada *et al.* also studied the effect of clay formation. Three types of illite and three types of kaolinite were used as pairs from three types of formations: Agradation, Neoformation, and Heritage. All samples were sourced from France with the exception of illite formed by Neoformation which was sourced from Hungary. The ΔH values for the solvents they used (pentanes and hexanes) with the three types of illite were within 5% of their average. Such a small difference can be attributed to experimental error. For kaolinite, results differed by more than 10% from the average, with Heritage formation having the greatest magnitude of ΔH and Agradation having the smallest. While the formation of clays we used is not known (not disclosed by suppliers), results were closest to what was obtained by Saada *et al.* for clays in Neoformation (which was also equivalent to the average of the three types of formations). It's also important to note that they used 30 cm columns and the particle size was 250 – 400 μm in diameter whereas we used 50 cm columns and 425 – 500 μm particles. This confirms the assumptions we made in Chapter 2 that column length and particle size do not affect calculations for ΔH.

5.5 Measured Entropy of Adsorption

Entropy of adsorption, ΔS, was also calculated for all selected solvents with respect to the four inorganic materials used in this work. As discussed in Chapter 3, while the values are not accurate due to the non-zero term $\ln(RTn_s)$, it was assumed to be zero and the ΔS was obtained from the y-intercept in the $\ln(V_n)$ vs. $1/T$ plots. The purpose here is to compare ΔS for the selected organic solvents. Values are shown below in Table 5-2:

*Table 5-2: Calculated -ΔS (J/mol*K) values for selected solvents on the four inorganic materials*

Solvent	Kaolinite	Illite	Illite-Smectite	Sand
n-pentane	130.2	74.3	100.6	~0
Cyclohexane	126.3	76	79.3	~0
iso-hexane	129.8	65.9	88	~0
n-hexane	144.6	85.4	110.7	~0
n-heptane	137.9	123.1	105.8	~0
n-octane	141.8	166.9	122.7	~0
1-hexene	135.7	387.8	No Elute	~0
n-nonane	160.1	210.7	156.6	182
n-decane	174.1	195.6	No Elute	159.8
Toluene	164.9	294.8	No Elute	~0
Benzene	147.3	No Run	No Run	~0
n-dodecane	198.9	No Elute	No Elute	No Run
butanone	No Elute	No Elute	No Elute	125.4
propyl benzene	No Elute	No Elute	No Elute	179.6
Methanol	No Elute	No Elute	No Elute	No Elute

Trends for entropy of adsorption are similar to those for enthalpy of adsorption. The magnitude of ΔS increases with increasing number of carbons in alkanes. Sand does not deviate from clay while for illite the magnitude of ΔS is small compared to other clays when the solvent is hexane o pentane, but for higher carbon number solvents the change in enthalpy for illite increases significantly and becomes higher than for the other clays for heavier solvents. As discussed earlier, the values for ΔS cannot be accurately obtained from the y-intercepts of $\ln(V_n)$ vs. $1/T$ plots. Consequently, only a relative comparison in general terms can be speculated but further discussion can lead to making erroneous conclusions.

5.6 Effect of Column Pre-Conditioning Temperature

We also wished to explore the effect of the column pre-conditioning procedure. Various groups chose the pre-conditioning temperature as the highest temperature at which experiments were conducted [5-7] or at an intermediate temperature [1]. We chose to pre-condition the columns at the lowest temperature used for the clays we tested. The main reason behind our approach is to avoid irreversibly changing the properties of clay (such as moisture content and atomic spacing) by heating and cooling cycles; i.e., the aim is to determine retention volume at, say 150 ºC, without having heated the sample to 200 ºC previously in order to maintain a pristine form at the time of the experiment. It is also for practical considerations due to the aim of our work. In the oil sands industry, it is not practical or feasible to heat the ore to temperatures higher than the aimed extraction temperature. However, due to the lack of justification in literature as to why pre-conditioning is chosen at a specific temperature, we also explored the effect of pre-conditioning at a high temperature to study its effect. For kaolinite, after carrying out experiments at 170 ºC, the column was cooled to 100 ºC and experiments were repeated. Then again after completing experiments at 230 ºC, experiments were repeated for hexanes and n-heptane.

Table 5-3: Comparison of calculated -ΔH (kJ/mol) values for selected solvents on kaolinite at different pre-conditioning temperatures

Solvent	100 ºC	170 ºC	230 ºC
n-pentane	45.2	54.4	No Run
Cyclohexane	46.3	55.1	No Run
iso-hexane	48.4	56.8	57.3
n-hexane	56.5	65.2	64.5
n-heptane	65.9	67.9	70.7

Table 5-3 above shows the calculated ΔH values for solvents on the same kaolinite sample but each set of data were obtained after pre-conditioning the column at three different pre-conditioning temperatures. Results show that pre-conditioning at higher temperatures leads to increased affinity of solvents for koalinite. An earlier study by Saada *et al.* [8] on the wetting behaviour of clay concluded that 25% of the kaolinite surface is hydrophilic, which means it is generally oleophilic and is wetted by oil. This conclusion may indicate that additional heating of kaolinite, which has the potential to remove moisture off the surface, causes the kaolinite to become even more oleophilic, as indicated by the increased magnitude of ΔH when the pre-conditioning temperature is increased.

5.7 Intention of Study and Implication of Results

The study was carried out to explore all possible functional groups in a potential organic solvent, provided they are environmentally acceptable. Many criteria need to be met in order for a solvent to be considered in a non-aqueous bitumen extraction. This work studied the criterion related to adsorption to the surface of inorganic minerals. The importance of this criterion is two-fold: first, the solvent must exhibit appreciable affinity for the inorganic minerals in order to compete with bitumen (and hence peel it off). Secondly, the solvent must be easily recoverable from the inorganic compounds once the extraction process is completed.

Measured enthalpies of adsorption indicate that a significant amount of energy is needed in order to recover the organic solvent from clay. This is specially the case for solvents containing polar groups (such as toluene and benzene). Toluene is a strong diluent of bitumen. However, the enthalpy of adsorption for toluene on clay is significantly higher than the enthalpy of adsorption of non-polar alkanes of similar molecular weight, which means the energy required to recover toluene is significantly more. On the other hand, cycloalkanes exhibit lower affinity for clay when compared to straight-chain alkanes of similar molecular weight. Additionally, cycloalkanes dissolve bitumen better than straight-chain alkanes and ashphaltene precipitation is lower.

Ashphaltene precipitation occurs when the solvent/bitumen ratio exceeds a specific threshold and the amount of ashphaltene which precipitates depends on the amount and type of solvent used. This phenomenon restricts the amount of solvent which can be used. The lower the threshold ratio, the lower amount of solvent which can be used, hence viscosity reduction is negatively affected. Precipitation is also an issue for the transport of bitumen.

Since cylcoalkanes, compared to normal alkanes, have smaller affinity to clay and are better diluents, the results obtained from this work imply a potential for further exploration of cycloalkanes.

5.8 References

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CHAPTER 6

6.0 Conclusions and Future Work

The measured values for the retention volume indicate that solvents have higher affinity to clay at low temperatures. Affinity is reduced with increasing temperature. This observation implies that solvent extraction of bitumen can potentially be carried out at a low temperature and solvent recovery from the inorganic minerals is attained by increasing the temperature, i.e. adding energy to the system.

The amount of energy needed to recover the solvent is deduced from the enthalpy of adsorption. The measured enthalpies of adsorption indicate a significant amount of energy is needed to recover organic solvents from clay. The amount of energy is directly proportional to the molecular weight of straight-chain alkanes and increases with the presence of double bonds. Each additional methyl group increases ΔH by ~ 5 kJ/mol whereas each double bond contributes to ~ 15 kJ/mol. The enthalpy of adsorption is slightly decreased when the solvent is branched or cyclic alkane.

Results obtained from this work indicate that using an organic solvent for bitumen extraction needs further study and consideration. Cycloalkanes need to be explored further due to better favorability in terms of recovery, solvation, and ashphaltene precipitation. Due to the large magnitude of enthalpies of adsorption for organic solvent/clay systems, solvent recovery by thermal processes may prove costly. An alternative method must be considered. The utilization of a bio-degradable polymer, as an additive, can be used in order to compete with the organic solvent for adsorption on the clay surface. Our work shows that an increase in molecular weight of alkanes leads to higher affinity of the solvent for clay. This means that a polymer will have considerably higher affinity for clay and prevent the solvent from adsorbing on the sand and clay surfaces. Future work in the area of non-aqueous bitumen extraction from oil sands will be focusing on cycloalkanes, toluene, and bio-degradable polymers.

APPENDIX A

Sample Calculations

Choosing data for pentane probe with illite at 110 ºC, below are the calculations.

- average retention time, t_r, of pentane: 1.728 min
- zero retention time, t_0: 0.038 min
- column outlet pressure, p_o, (atmospheric pressure in the laboratory): 13.5 psi
- column inlet pressure, p_i: 14.5 psi
- carrier gas flow rate, f: 27.9 ml/min

The net retention time for pentane is:

$t_n = t_r - t_0 = 1.690$ min

Using inlet and outlet pressures, J is obtained from Equation (3-8), as follows:

$J = 1.5\, [(p_i/p_o)^2 - 1]/[\, (p_i/p_o)^3 - 1] = 0.964$

From Equation (3-7), retention volume is calculated:

$V_n = Jf(t_r - t_0) = 46.5$ ml

Retention volume for the same solvent is calculated similarly for each temperature. The natural log of retention volume is plotted against 1/T (in Kelvin units).

For $\ln(V_n)$ plot vs. 1/T, the slope obtained was 4884.7

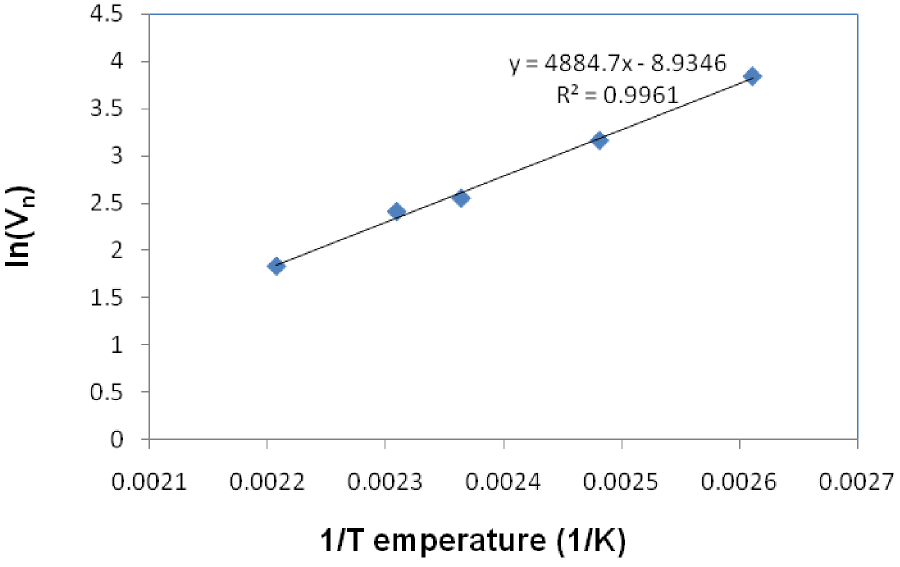

Figure A-1: $\ln(V_n)$ vs. 1/T plot of pentane with illite

From Equation (3-5), this corresponds to $-\Delta H/R$. For R = 8.314 J/mol K, $-\Delta H$ is:

$-\Delta H = 4884.7R = 40{,}614$ J/mol = 40.6 kJ/mol

From the y-intercept,

$-\Delta S = -8.9346R = 74.3$ J/mol*K