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Calorimetric Study of Phthalate Adsorption from Solution onto Silica Adsorbent and Correlation Between Energy and Adsorption Isotherms

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**Calorimetric Study of Phthalate Adsorption
from Solution onto Silica Adsorbent and
Correlation between Energy and Adsorption
Isotherms**

By:

Nasima Akter Goni

Thesis submitted to the Department of Chemistry & Biochemistry of Seton
Hall University in partial fulfillment of the requirements for the degree of

Master of Science

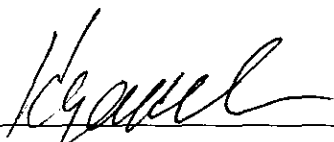
in

Chemistry

May, 2009
South Orange, New Jersey

We certify that we have read this Thesis and that, in our opinion, it is adequate in scientific scope and quality as a Thesis for the degree of Master of Science in Chemistry.

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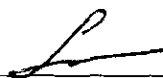
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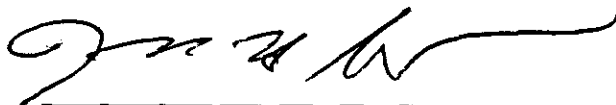
Nicholas H. Snow, Ph.D.

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Abstract

In separation science, the adsorption affinity of an analyte with an adsorption site (adsorbent) is the principle driving force for a separation process. To understand adsorption affinity we need to better understand the adsorption. Adsorption is a process through which an analyte accumulates on a surface under influence of the surface energy. In a liquid binary system, analyte accumulation can be accompanied by corresponding displacement of a solvent. As a consequence of analyte accumulation an adsorbed layer formed on the surface based on the amount of analyte adsorbed. To understand the adsorption process of phthalate esters from solution on the silica surface, a thorough knowledge of physicochemical properties of silica, phthalate and solvent (hexane) is required. Calorimetric measurement offers an opportunity for studying energy of analyte-surface interaction in an adsorption system. It is also possible to measure enthalpies covering a wide concentration range of analyte solutions from these types of interactions. Phthalate-silica interaction was studied from adsorption isotherm which was created using static and calorimetric experiments.

Chromatographic methods allow to measure adsorption from a low concentration region, which permits the estimation of adsorption equilibrium constant. The adsorption equilibrium constant is directly related to the energy isotherm, and the adsorption energy isotherm can be created using calorimetric experiments. Diethyl phthalate in hexane solutions were studied using a flow microcalorimeter. A matrix cartridge with a known amount of silica gel was placed in a calorimeter cell which was connected to an HPLC pump. An exothermic response was observed when diethyl phthalate adsorbed onto

silica, and enthalpy change was measured from that adsorption. A wide concentration range of diethyl phthalate solutions were studied and differential molar energies were measured. The differential molar energies were plotted over equilibrium concentrations and an energy isotherm was created. The energy isotherm then compared with adsorption isotherm, which was created from a static adsorption experiment with chromatography. The adsorption and energy isotherms from both experiments support the low coverage of diethyl phthalate onto silica, and are indicative of monomolecular layer adsorption.

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Chapter 1

Thermal Activity Monitor (TAM III)

1 Introduction

Microcalorimetry has been proven to be an invaluable tool for recognizing subtle differences in materials which are not apparent using any other technique. TAM III is an isothermal calorimeter system. Isothermal calorimeters occasionally referred to as heat conduction or as heat flow calorimeters. The measurement of heat conduction calorimeters is such way that a temperature gradient is propagated from the reaction ampoule to or from a surrounding heat sink. As a consequence the temperature of the reaction ampoule remains almost constant [1]. Isothermal microcalorimetry is recognized as a non-invasive, non-destructive, and non-specific technique that can be applied to study almost all kinds of physical and chemical processes in materials science [2].

Calorimetry measures the amount of heat produced or consumed in a chemical reaction, change of state, or formation of a solution. The measurement applies the 1st law of thermodynamics, which states that energy neither can be created nor destroyed, but can only change its form.

Thermal Activity Monitor, TAM III, the isothermal calorimeter system includes a heating source; a large oil bath (heat sink), a thermostat to maintain temperature, calorimeters and sample handling system. The calorimeters can be of single or twin design. In this research, twin channels (sample and reference) of a titration calorimeter have been used.

1.1 TAM III

A picture of TAM III housing, a calorimeter probe and a cartridge have been illustrated in Figure 1-1. The TAM III system is comprised of a large oil bath, a high precision thermostat, sample handling system (cartridge) and calorimeters. The calorimeter probe consists of a central shaft and outlet tubing. The cartridge consists of mesh screens and caps, and can be attached to the tip of the central shaft of the calorimeter probe.

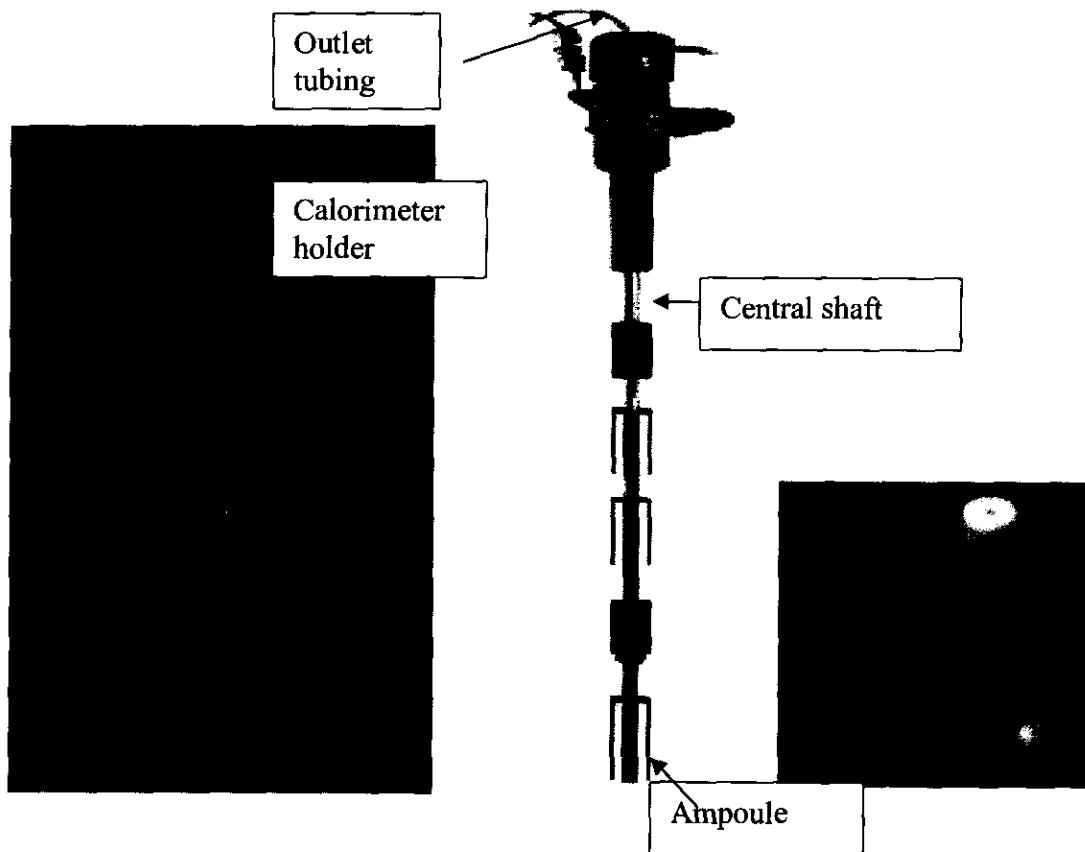


Figure 1-1: TAM III housing, a calorimeter probe, and a cartridge

Calorimeter holders are positioned inside the heat sink, and each holder is surrounded by individual heat detector e.g. thermocouples.

Thermostat: The temperature of the calorimeters is controlled by the thermostat with an accuracy of +/- 0.03°C. However, the temperature fluctuation (precision) is better than 0.0001°C, according to vendor (TA Instruments) paper [3]

Calorimeters: The principle of calorimeters is to record the thermal events of a reaction under study. The data gathered during a calorimetric experiment has within it much useful information about the reaction, including the reaction kinetics and the reaction thermodynamics, the reaction heat capacity change, the enthalpy change, the entropy change, the equilibrium constant and the reaction mechanism. In a heat flow calorimeter, a heat detector is used to continuously measure the heat flow associated with a thermal event due to physical or chemical processes.

Calorimetry measures:

Calorimetry measures heat, heat flow and/or heat capacity

$$\text{Heat Flow (rate)} \quad - \quad dQ/dt \quad [J \text{ s}^{-1}] = W \quad (1)$$

$$\text{Heat} \quad - \quad Q \quad [J] \quad (2)$$

$$\text{Heat Capacity} \quad - \quad C_p = dQ/dT \quad [JK^{-1}] \quad (3)$$

In these equations, Q=heat, dQ/dt is the rate of heat production, T=temperature, C_p= Heat capacity, t=time, J=joule, s=second, W= heat flow rate in watt. K= temperature in Kelvin.

Calorimetry refers to the measurements of the amount of heat produced or consumed in a chemical reaction. The rate at which heat is produced by a sample is turned to be the rate of heat production. This quantity is also commonly referred to as thermal power, heat generation or heat exchange. See details in section 1.5 “Heat Detection”.

Calorimeters record heat flow (as power) over the period of time in a reaction by a direct measurement or by conversion from temperature change, which offers access to the kinetics of the reaction. Integration of the power-time signal gives the extent of the reaction in terms of enthalpy change, which is a thermodynamic property of a reaction. Thus both kinetic and thermodynamic information are accessible from the same experiment and this can be explained as:

$$\frac{dQ}{dt} = \frac{dx}{dt} \Delta H \quad (4)$$

Where dQ/dt is power in W, dx/dt is the rate of increase of the amount reacted and ΔH is the enthalpy change. The integral of power with respect to time gives the cumulative enthalpy change (Q_t) at any time, so that

$$Q_t = x\Delta H \quad (5)$$

Where x is the amount of material reacted at time t .

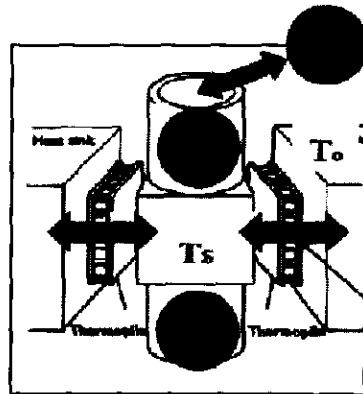
Thus thermodynamic properties, enthalpy change can be measured from a physical or chemical process to understand the mechanism of that process.

In isothermal calorimeters, the heat generated by the sample is exchanged with the surroundings. So, the rate of heat production for an isothermal calorimeter can be calculated by measuring the heat exchange through a heat detector which is positioned between the sample and a surrounding heat sink. So, the general heat balance equation for all types of calorimeter can be applied; $\frac{dQ}{dt} = \Phi + C \frac{dT}{dt}$

dQ/dt is the rate of heat production by a sample, Φ is the heat exchange with the surrounding, CdT/dt represents the rate of heat accumulation of the sample where C is the heat capacity of the sample, and dT is the change in temperature during the time dt .

Prior to understanding the heat flow balance equation of a twin channel calorimeter, it is necessary to understand the single channel calorimeter. The general heat balance equation of a calorimetric unit is illustrated in Figure 1-2.

Calorimetric Unit



General Heat Balance Equation

$$\frac{dQ}{dt} = \Phi + C \left(\frac{dT}{dt} \right)$$

Rate of Heat Production = Rate of Heat Exchange + Rate of Heat Accumulation
 The measured property

After calibration the following holds:

$$\blacksquare = \blacksquare$$

Figure 1-2: General Heat balance equation

Adapted from reference [2]

1.2 Single channel calorimeter:

A single channel calorimeter consists of a sample holder surrounded by an aluminum block (heat sink). The heat detector (thermocouples) is positioned in between the sample holder and the heat sink. The heat sink maintains the constant temperature (T_0) and measure by the thermostat. The schematic description of top view of a single calorimetric unit is illustrated in Figure 1-3.

In a thermal event, heat is formed by a sample is then exchanged with surrounding heat sink through heat detector, although a minor part is exchanged via irradiation.

Heat detectors consist of thermocouples which are made of semi-conducting materials that have a unique feature that a voltage will develop when these materials are exposed to different temperature. The heat that passes through the heat detectors toward heat sink will exchange with the media of the surrounding thermostat. Thus, the heat sink maintains a constant temperature. The heat exchange between the sample and the heat sink is determined by the heat exchange coefficient (k) and the heat capacity(C), describing the thermal inertia of the calorimeter (including the sample and the heat detector).

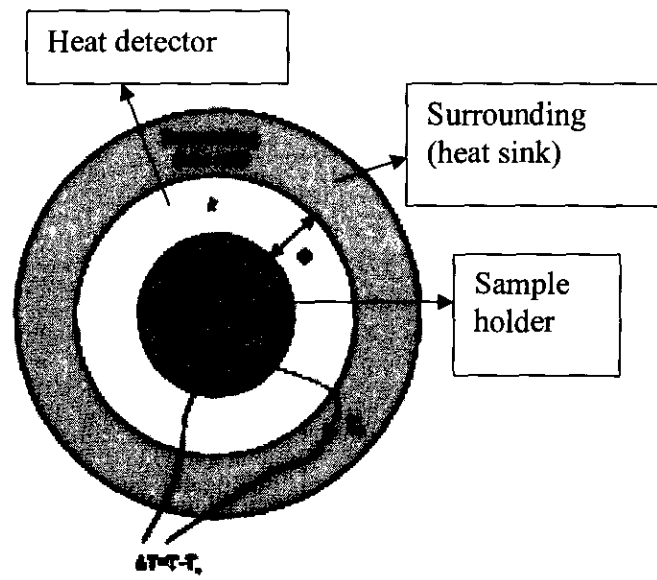


Figure 1-3: Schematic of top view of a single channel calorimeter

Adapted from reference [3]

1.2.1 Heat balance equation of a single calorimeter:

The temperature of the surrounding heat sink is T_0 , the sample and the sample holder are considered a uniform unit with temperature T , and the average heat capacity is C . The rate of heat production by the sample is defined as dQ/dt and the rate of heat transfer to the surrounding is Φ . The area between the sample and the surroundings represents the thermal resistance R of the heat transfer between the sample and the surrounding, which is characterized by the heat transfer coefficient $k=1/R$ (units W/K).

The heat formed by a sample positioned inside a single calorimeter must either be exchanged with the surrounding or used to heat up the sample. Thus, a heat balance analysis gives the rate of heat production by the sample, which has to be balanced with the rate of heat loss to the surrounding, and the rate of heat accumulation. Thus, the following heat balance equation holds.

$$\frac{dQ}{dt} = \Phi + C \frac{dT}{dt} \quad (6)$$

According to Newton's cooling law, the rate of heat transfer between the sample and the surrounding is proportional to the temperature difference between the sample and the surrounding,

$$\Phi = k\Delta T = k(T-T_0) \quad (7)$$

The term Φ represents the heat exchange with the surroundings. Due to the design of the calorimeter with the heat detector positioned in between the sample

ampoule and the surrounding heat sink, most of the heat produced by a sample will flow through the heat detector. In addition, the heat loss via irradiation is considered by calibration. Thus, Φ represents the measured heat flow.

Combining two equations (6 and 7)

$$\frac{dQ}{dt} = k(T - T_0) + C \frac{dT}{dt} \quad (8)$$

This is the general heat balance equation for all single calorimeters.

The equation tells us that the rate of heat production by a sample can be obtained by measuring the temperature difference over the heat detector and by considering the change of the sample temperature (time derivative).

1.3 Twin Channel Calorimeter:

A twin channel calorimeter consists of two single calorimeters, one holding a sample and the other one holding an inert reference. Each calorimeter is surrounded by an individual heat detector. For each of the calorimeters, the general heat balance equation can be applied. The signal that is reported by a twin calorimeter is a differential signal, i.e. the difference in heat flow between the sample and the reference side. The reference calorimeter contains inert substances with same heat capacity as the sample, so the differential signal can directly measure the heat exchange of the sample via heat detector, which in turn is the rate of heat production by the sample.

The differential signal of a twin calorimeter is independent of the fluctuations of the thermostat. Furthermore, the noise of the differential signal can be reduced by balancing the time constants of the sample and reference sides. The time constant depends on the heat capacity, and thus it is possible to balance the time constant of sample and reference side by adjusting (balancing) the heat capacity of the reference side to match the heat capacity of the sample side. This can be achieved by using a suitable amount of an inert reference material e.g. water or sea sand, in the reference ampoule.

1.3.1 Heat balance equation of a twin calorimeter:

The general heat balance equation for the sample and reference side respectively can be written as;

$$\frac{dQ_S}{dt} = \Phi_s + C_s \frac{dT_S}{dt} \quad \text{sample side} \quad (9)$$

$$\frac{dQ_R}{dt} = \Phi_R + C_R \frac{dT_R}{dt} \quad \text{reference side} \quad (10)$$

The index S and R are used to denote the sample and reference side respectively.

Rewriting these equations:

$$\frac{dQ_S}{dt} = k_s(T_s - T_0) + C_s \frac{dT_S}{dt} \quad \text{sample side} \quad (11)$$

$$\frac{dQ_R}{dt} = 0 = k_R(T_R - T_0) + C_R \frac{dT_R}{dt} \quad \text{reference side} \quad (12)$$

Taking the difference (subtraction) between these (11 and 12) equations gives;

$$\frac{dQ_S}{dt} - \frac{dQ_R}{dt} = \frac{dQ_S}{dt} - 0 = \frac{dQ_S}{dt} = k_s(T_s - T_0) + C_s \frac{dT_s}{dt} - k_R(T_R - T_0) - C_R \frac{dT_R}{dt} \quad (13)$$

If the reference cell is designed to be similar to the sample cell, the resistance of the heat transfer between the sample and the surrounding can be considered to be identical, thus;

$$k = k_R = k_S \quad (14)$$

In addition, as the reference material is selected to have the same heat capacity as the sample, the sample and reference cells will be identical;

$$C = C_R = C_S \quad (15)$$

The equation can be simplified to;

$$\frac{dQ_S}{dt} = k(T_s - T_R) + C \frac{d(T_s - T_R)}{dt} \quad (16)$$

$$\frac{dQ_S}{dt} = k(T_s - T_R) + C \left(\frac{dT_s}{dt} - \frac{dT_R}{dt} \right) \quad (17)$$

$$\frac{dQ_S}{dt} = k(T_s - T_R) + C \frac{dT_s}{dt} \quad (18)$$

Note: $dT_R/dt = 0$ as the reference ampoule contain inert material.

Equation 18, tells the rate of heat production of sample in a twin calorimeter can be obtained from the difference in temperature between the sample and the reference side. This eliminates the external noise, thus the twin channel calorimeter is sensitive.

1.3.2 Top View of twin calorimeter:

The schematic of top view of twin calorimeter is illustrated in Figure 1-4. Channel /cell 1 used as sample (S) and channel /cell 2 used as reference (R).

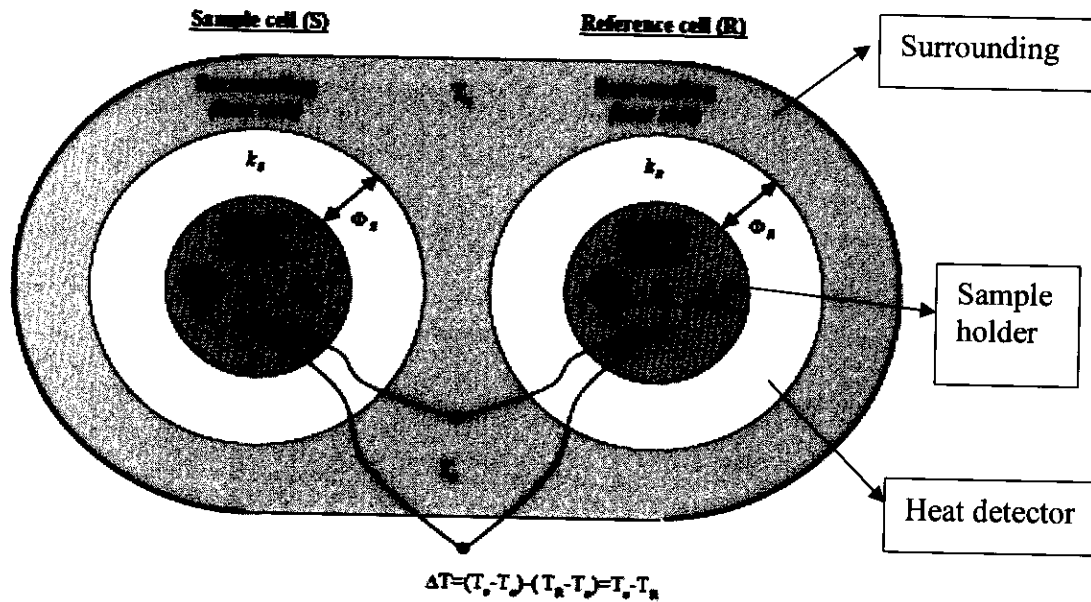


Figure 1-4: A schematic (top view) of Twin channel calorimeter

Adapted from reference [3]

1.3.3 Measuring procedure of twin channel calorimeters:

A representation of a twin channel calorimeter in TAM III system is illustrated in Figure 1-5. This includes the ampoule (sample, reference) holder, heat detectors (thermocouples), calibration heater, and heat sink (oil bath) as a heating source. Both sample and reference holders are surrounded by heat detectors and placed in a common heat sink. Calorimeter probes are placed in the sample and reference holder.

In twin channel calorimeter, the reference side (cell) contains an inert reference substance with the same heat capacity as the sample cell. During a thermal event, a temperature gradient will be imposed across the heat detectors; this produces a proportional voltage. This in turn is the heat flow signal that we monitor through TAM software. The signal from the reference side will be almost zero. Thus the signal generated by a twin calorimeter is a differential signal [3].

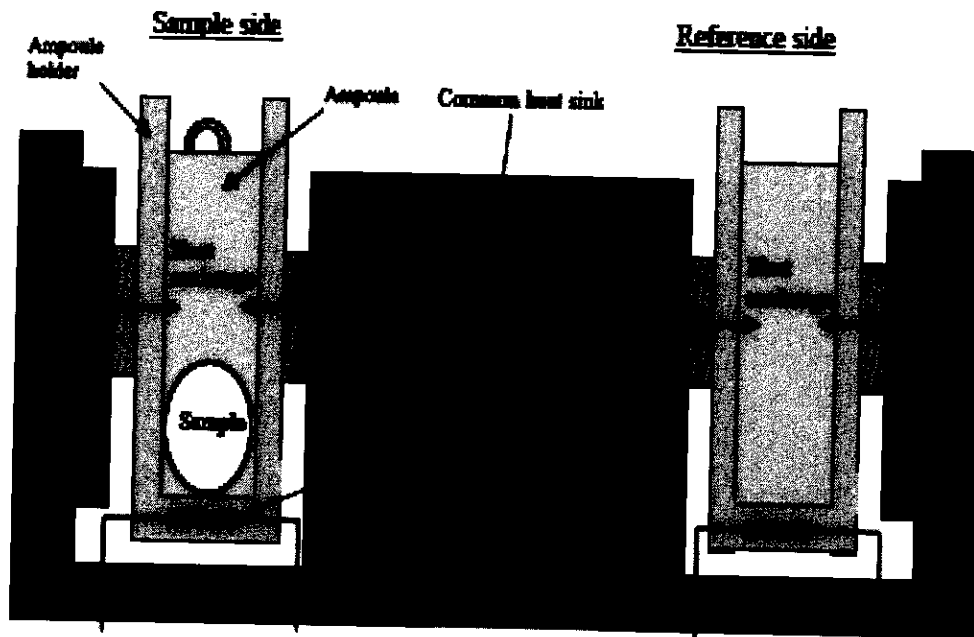


Figure 1-5: Schematic of twin channel calorimeters with sample and reference side
Adapted from reference [3]

1.4 Sign conventions:

From a thermodynamic point of view heat flow caused by an exothermic event are assigned negative values (energy lost by system). However, Thermometric/TA instruments assigned heat flow values corresponding to exothermic reactions as positive; therefore the data values corresponding to exothermic reactions are also reported as positive.

1.5 Heat detection:

The heat detectors used in twin calorimeters are referred to see beck modules; when a sample generates heat, a temperature gradient is developed over the heat detectors with heat flowing from warm to cold side. The semi-conducting materials used in the thermocouples develop a voltage when these materials are exposed to different temperatures. The voltage produced is proportional to the temperature gradient. This in turn is proportional to the heat flow signal and we monitor through sensor.

1.6 Isothermal Titration Calorimeter:

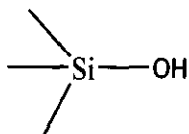
A twin channel Isothermal Titration Calorimeter (ITC) was used for all experiments. This consists of two nanocalorimeters with a reference (B) and a sample side (A) and 4ml stainless ampoules. The experiments were conducted in closed ampoules and sealed by cir-clips [4]. The sample side calorimeter has a central shaft (stainless steel) through which the solvent is delivered. The central shaft contains inlet

and outlet openings bored throughout its length and connected to the ampoule. The inlet is connected by peek tubing to HPLC pump which delivers solvent into the ampoule at a controlled flow rate. The outlet line is connected to the waste container. This configuration will act as a flow calorimeter, maintaining the solvent delivery with accurate and continuous flow in the experiment.

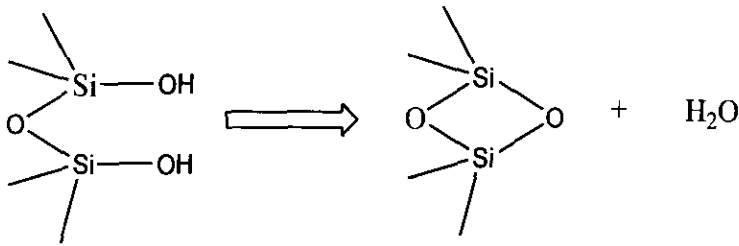
1.7 Adsorbent: Silica

Davisil Chromatographic silica Grade 636 was used in all experiments. This is amorphous silica with particle size of 250-500 μm , surface area of 480 m^2/g and pore volume 0.75 cm^3/g . (sigma-Aldrich)

Surface silanols: The surface of amorphous silica is constructed of several different terminal groups. The major portion of the silica surface is covered with single (isolated or free) silanols. Free silanols contain a silicon atom that has three bonds in the bulk structure, and the fourth bond is attached to a single hydroxyl group.



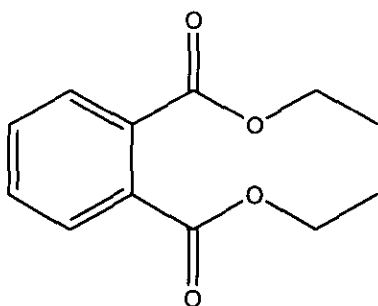
The calcination process at high temperature often removes the water molecules from adjacent silanols, leading to a formation of a siloxane bond. This dehydroxylated silica is very inert, but can slowly absorb water and rehydroxylate [5].



The properties of amorphous silica with high specific surface area depend largely on the chemistry of the surface of the solid phase as expressed by Iler. et.al [6] , where there is a strong chemical interaction between the adsorbed molecule and the atoms in the surface, a complete monomolecular layer is formed even when there is only a relatively low concentration of adsorbate in the liquid phase adjacent to the surface. Further adsorption of a second layer can occur only through the interaction of weaker secondary forces extending from the surface beyond the first adsorption layer. In such cases, the formation of the first layer is termed “chemisorption” and follows the Langmuir adsorption isotherm, and the formation of a second layer, if it occurs, is termed “physical adsorption”.

The key characteristic of the siloxane (SiOSi) surface of SiO₂ is that the so called “residual valences” react with water so that at ordinary temperature the surface becomes covered with silanol (SiOH) groups. Chemisorptions of molecules on the silanol surfaces of silica occur when a single layer of molecules is adsorbed by either covalent or ionic binding with surface atoms. Hydrogen bonds are also formed between polar atoms, such as oxygen atom of the molecules and the hydrogen atom of silanol groups on the surface. In these cases there is a binding force between a specific atom of the adsorbate and an atom the surface so that once the silica surface becomes covered, no second layer is adsorbed [6].

1.8 Analyte: Diethyl Phthalate (DEP)



Diethyl phthalate (C₁₂H₁₄O₄): molar mass 222.24 g/mol, a colorless liquid with a slight aromatic odor. Diethyl phthalate is produced industrially by the reaction of phthalaic anhydride with ethanol in the presence of concentrated sulfuric acid catalyst. The purity of manufactured phthalate esters is reportedly between 99.7% to 99.97%, and the main impurities being isophthalaic acid, terephthalaic acid, and maleic anhydride [7]

Diethyl phthalate is used as a plasticizer for cellulose ester plastic films. There is a wide variety of consumer products that contain diethyl phthalate or are covered by diethyl phthalate-containing plastic packaging.

1.9 Gas Chromatography (GC) Techniques

Gas chromatography (GC) is the premier technique and most used technique for separation and analysis of volatile compounds. The sample is injected, becomes vaporized, and is transported through a column via the carrier gas, usually helium or hydrogen [8]. The heart of this chromatography is the column; today the most popular columns are made of fused silica and are open tubes with capillary dimensions. The stationary liquid phase (column) is coated on the inside surface of the capillary wall.

A detector senses the effluents from the column and provides a record of the chromatography in the form of chromatogram. The detector signals are proportionate to the quantity of each analyte making possible quantitative analysis. The most common detectors are the flame ionization detectors with high sensitivity.

1.9.1 Principles of GC:

Gas chromatography is a separation method in which the components of a sample partition between two phases: one of these phases is a stationary bed with a large surface area, and the other is a gas which percolates through the stationary bed. The sample is vaporized and carried by the mobile gas phase (the carrier gas) through the column. Samples partition into the stationary liquid phase and this is based on their solubilities at the given temperature. The components of the sample separate from one another based on their relative vapor pressure and affinities for the stationary bed [9]. A GC system is comprised of a gas, an oven holding the column, an injector, detector and data acquisition system (e.g. recorder). The schematic of GC system is illustrated in Figure 1-6 [10].

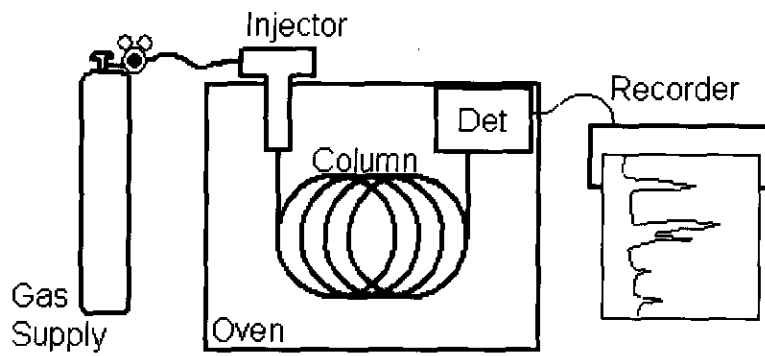


Figure 1-6: Schematic of GC instrument

Adapted from reference [10]

Research Goal

Diethyl phthalate has been widely used in the chemical and pharmaceutical industry. For example, a number of studies have been conducted for phthalate adsorption onto a silica stationary phase, in order to better understand separation mechanisms; however the adsorbate-adsorbent interaction has not been fully demonstrated. The use of thermal technique can be an effective way of studying phthalate-silica adsorption process. The adsorption experiments can be conducted using microcalorimetry under isothermal conditions. Energy required (enthalpy change) by the adsorption process helps understanding of the basic adsorption mechanism [11]. The adsorption process can take place in two steps, firstly displacement of the solvent from silica surface followed by the adsorption of analyte on the surface. The stoichiometry and the energetic process depends on both solute/silica interface in terms of surface area, porosity, nature and energy of adsorbing sites as well as and the type of analyte [12]. Calorimetry offers an opportunity for directly studying adsorbate-adsorbent interactions in the system. It is possible to obtain calorimetric data which covers a wide concentration range of sample solutions, and the relationship between the enthalpy change and the amount of analyte adsorbed help studying the type of interaction [13]. In particular, this investigation may aid the understanding of the interaction between diethyl phthalate and silica through a hydrogen bonding interaction.

In a flow calorimetric experiment, the surface coverage of silica surface by diethyl phthalate can be estimated based on the energy that required for diethyl phthalate (DEP)

to be adsorbed onto silica, and the energy (enthalpy change) can be directly measured from the experiment. An energy isotherm can be created by plotting the molar energy value for these adsorbed DEP against their concentration.

The amount of adsorbed diethyl phthalate can also be measured using a static adsorption experiment from solutions covering a wide concentration range. DEP saturated solutions from the adsorption experiments can be analyzed through GC for equilibrium concentration. An adsorption isotherm can be created by plotting the adsorption value against the equilibrium concentration of DEP.

The adsorption isotherm can be correlated with the energy isotherm that was measured through the calorimetric experiment. This correlation leads to an understanding of the phthalate-silica interaction for the adsorption process.

Chapter 2

2 Experimental

2.1 Chemicals:

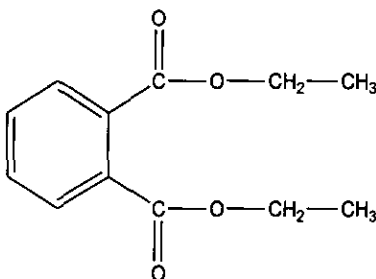


Figure 2-1: Molecular structure of Diethyl phthalate

2.1.1 Diethyl phthalate: C₁₂H₁₄O₄

Diethyl phthalate is an Eastman product supplied by Sigma-Aldrich (St. Louis, Mo, USA), a clear, low odor liquid, having good stability to heat combination and UV light and excellent resistance to hydrolysis. CAS No 84-66-2, batch # 09621MD.

Table 2-1: Diethyl phthalate parameters:

| | |
|--------------------------|----------------|
| Density @20°C | 9.32ib/gal |
| Acidity as phthalic acid | 0.007 wt % max |
| Boiling point | 298°C |
| Freezing point | <-50°C |
| Assay | 99.5 wt% min |
| Molecular wt | 222.24 g/mol |

Reported from reference [14]

2.1.2 Silica gel (SiOH):

Silica gel, Davisil grade 636, Sigma –Aldrich, CAS 112926-00-8, ID # 236802-100G,
batch # 07515EH,

Table 2-2: Silica Gel parameters

| | |
|----------------|-----------------------------|
| Purity | 99% |
| Particle size: | 35-60 mesh, 250-500 μ m |
| Pore volume | 0.75cm ³ /g |
| Pore size | 60 Å , |
| Surface area | 480m ² /g |

Reported from reference [14]

2.1.3 Hexane:

Hexane, (C₆H₁₄), Mallinckrodt, purity 95%, Lot # C27E09

2.2 Instrumentation:

2.2.1 Gas chromatography (GC):

Agilent Technology, 6890N GC system with FID, Serial # US10524060, Agilent Technology 7683B series injector.

Column: HP-5, 10m length, 0.53mm internal diameter, 2.65 μ m film thickness. Serial number: US4856323A, lot # 19095J-121. The stationary phase of a non polar column used 5% diphenyl and 95% dimethylpolysiloxane, Agilent Technology. Temperature limit: -60°C to 280°C.

Nitrogen gas (zero grade), ultra pure helium gas, ultra pure hydrogen gas.

20ml glass vials with stainless steel crimp cap, volumetric flasks with plastic caps, shaker, crimper, de-crimper and a calibrated balance.

2.2.2 Calorimeters:

Thermal Activity Monitor, (TAM III) system with thermostat set up at 23°C , Serial no 53, Thermometric /TA instruments, titration calorimeter (sample and reference channel), 4ml stainless steel ampoules with Teflon septa, Agilent HPLC pump, volumetric flasks as sample solution reservoir, peek tubing, TAM assistance software for data analysis.

2.3 Static Adsorption Experiments:

2.3.1 Sample preparation:

Several concentrations of diethyl phthalate solutions were prepared using hexane in glass volumetric flasks. DEP was weighed accurately into tared glass volumetric flasks. DEP solutions were prepared for 0.1%, 0.2%, 0.5%, 1.0%, 1.3%, 1.5%, 1.7% wt/vol in hexane. These were the DEP solutions and used within 24 hours of preparation.

A known amount, (100 -300mg) of silica gel was weighed and transferred to a 20mL glass vial. Several glass vials were thusly prepared and 5mL of each DEP solution was accurately transferred into each glass vial containing silica gel. The glass vials were then crimped with stainless steel cap and shaken until the adsorption process reached equilibrium approximately 24 hours at a constant (23°C) temperature at a moderate speed. The supernatant was collected carefully and analyzed through GC. A control solution experiment was conducted similarly but no silica gel for assessing loss of solutes to the vial during adsorption process.

2.3.2 GC Analysis:

The supernatant from the static experiment was diluted (1/100ml) in hexane and the equilibrium concentration of DEP was determined using Agilent 5890 GC with FID. A calibration curve was prepared using three standard solutions prior to each analysis of sample solutions. The initial temperature for oven was 100°C, with a rate of 10°C/min to the final temperature of 225°C. The injection port was prepared at 300°C with a split-less

injection of 1ul. The FID temperature was 300° C. The column used was an HP5 (5%-phenyl)-95% methylpolysiloxane, 10m long and 2.65um film thickness. The carrier gas was helium at 10.5ml/min, the run time was 15minutes.

The data acquisition was conducted using Atlas ThermoFisher software. The calibration curve was determined using Excel. The equilibrium sample concentrations were calculated using sample area responses. DEP adsorption amount, Γ , was calculated for each sample using the following equation [15]:

$$\Gamma = \frac{(C_0 - C_e)V}{mS}$$

Where C_0 and C_e , are the initial and equilibrium concentration, V is the volume of DEP stock solution transferred into the vial, m is mass of silica which was weighed into the vial, S is the surface area of silica gel. The resulting molar adsorption values per surface area were then plotted against the equilibrium concentrations. Thus the adsorption isotherm was created from chromatographic experiments.

2.4 Calorimetric Experiments:

Calorimetric experiments were performed at 23°C using flow calorimeter. A known amount of silica gel (0.15g) was placed in a matrix cartridge, and fitted with 250 mesh screen at both ends, and closed. Cartridge was attached to the tip of the central shaft of the calorimeter. A 4 ml stainless steel ampoule was fixed around the cartridge connected and closed to the central shaft. The continuous solvent flow provided by HPLC pump will pass through the inlet tubing in the central shaft, enter to the cartridge and adsorb onto the silica. When the cartridge is filled, excess solvent will be collected into the

ampoule, which will drain to waste through the outlet tubing. This configuration will keep the silica saturated. A reference calorimeter cell was prepared with same amount (0.15g) of silica gel. The sample and the reference ampoules were placed in TAM III instrument. Hence this experiment was conducted in the closed ampoule system with constant volume, pressure and temperature. The system was equilibrated with hexane at 0.3ml/min until a stable baseline was achieved. Several concentrations of DEP (0.01%-2.0%) in hexane (prepared in 200ml volumetric flask) were introduced thru the solvent line into the silica. The heat flow signal for each concentration was monitored and recorded by the TAM software. The enthalpy change, ΔH , for each concentration was determined by the integration of the corresponding exothermic peak. Adsorption enthalpies or energies were determined as mJ and this was calculated as energy per gram of silica adsorbent, mJ/g. This was further expressed as molar energy, kJ/mol. The molar energies were plotted against the corresponding concentrations and an isotherm was created.

Chapter 3

3 Result and Discussions

3.1 Results: Static Adsorption Experiments (with GC analysis):

The supernatant liquid from the static adsorption experiments was analyzed for diethyl phthalate equilibrium concentration by GC. A calibration curve was prepared from three dilutions of lowest concentration (0.1%) of DEP standard solution. The least squares regression line for the calibration curve had a R^2 value of 1.000, and an example calibration plot is shown in Figure 3-1. Thus a calibration curve was determined prior to each analysis. The sample response from GC and the slope of the calibration curve was used to calculate the equilibrium concentration of DEP. See Figure 3-2 for an example chromatogram of 1.0% concentration from GC using Atlas software.

The equilibrium concentration (C_e) was calculated as mg/ml and further expressed as molar concentration, $\mu\text{mol/mL}$. See Table 3-1 for the initial and equilibrium concentration for all sample solutions.

The molar adsorption value (Γ) for each solution was calculated using the following equation;

$$\Gamma = \frac{(C_0 - C_e)V}{mS}$$

Where V (5mL) is the volume of DEP solution transferred into the vial, m is mass of silica which was weighed into the vial (silica weights are listed in Table 3-2). S , ($480\text{m}^2/\text{g}$) is the surface area of silica gel. Molar adsorption values were calculated for all

sample solutions. The resulting molar adsorption values per surface area were plotted against the equilibrium concentrations. Adsorption isotherm is illustrated in Figure 3-3.

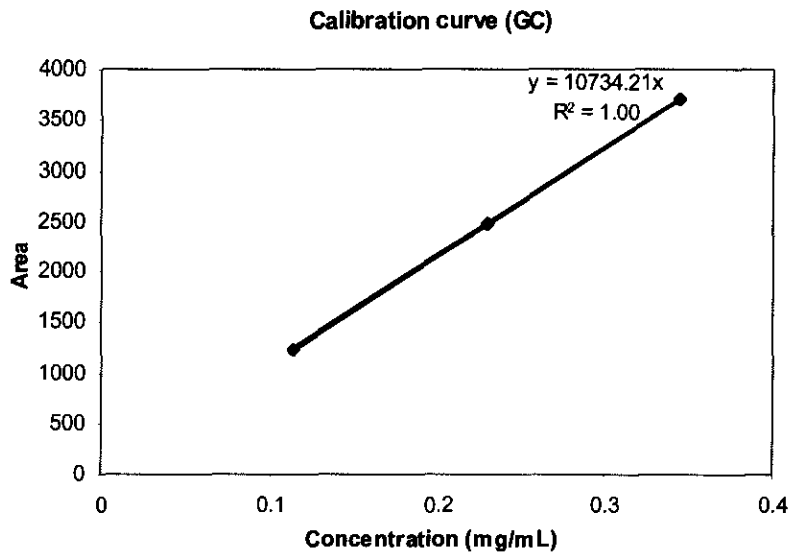


Figure 3-1: GC Calibration plot

Calibration curve was prepared using three dilutions of 0.1% diethyl phthalate solutions. Plot shows a linear regression with correlation coefficient value of 1.000

Table 3-1: Equilibrium concentration calculation from static adsorption experiments:

| DEP | DEP | | DEP | |
|------|------------------------------|--------------------|----------------------------------|--------------------|
| | Initial Concentration, C_0 | | Equilibrium Concentration, C_e | |
| wt% | mg/mL | $\mu\text{mol/mL}$ | mg/mL | $\mu\text{mol/mL}$ |
| 0.1% | 1.15 | 5.17 | 0.0354 | 0.160 |
| 0.2% | 2.12 | 9.55 | 0.172 | 0.774 |
| 0.5% | 5.08 | 22.9 | 0.117 | 0.525 |
| 1.0% | 10.3 | 46.4 | 1.60 | 7.20 |
| 1.3% | 13.0 | 58.6 | 7.64 | 34.4 |
| 1.5% | 15.1 | 68.1 | 9.71 | 43.7 |
| 1.7% | 17.2 | 77.5 | 11.9 | 53.3 |

Table 3-2: Molar adsorption value calculation:

| DEP | DEP | | Wt of silica | DEP |
|------|----------------------------|----------------------------|--------------|--------------------------------|
| | Initial concentration | Equilibrium concentration | | Adsorption value |
| wt% | C_0 , $\mu\text{mol/mL}$ | C_e , $\mu\text{mol/mL}$ | mg | Γ , $\mu\text{mol/m}^2$ |
| 0.1% | 5.17 | 0.160 | 101.25 | 0.516 |
| 0.2% | 9.55 | 0.774 | 107.39 | 0.852 |
| 0.5% | 22.9 | 0.525 | 307.90 | 0.756 |
| 1.0% | 46.4 | 7.20 | 306.28 | 1.33 |
| 1.3% | 58.6 | 34.4 | 154.30 | 1.64 |
| 1.5% | 68.1 | 43.7 | 155.01 | 1.64 |
| 1.7% | 77.5 | 53.3 | 149.82 | 1.68 |

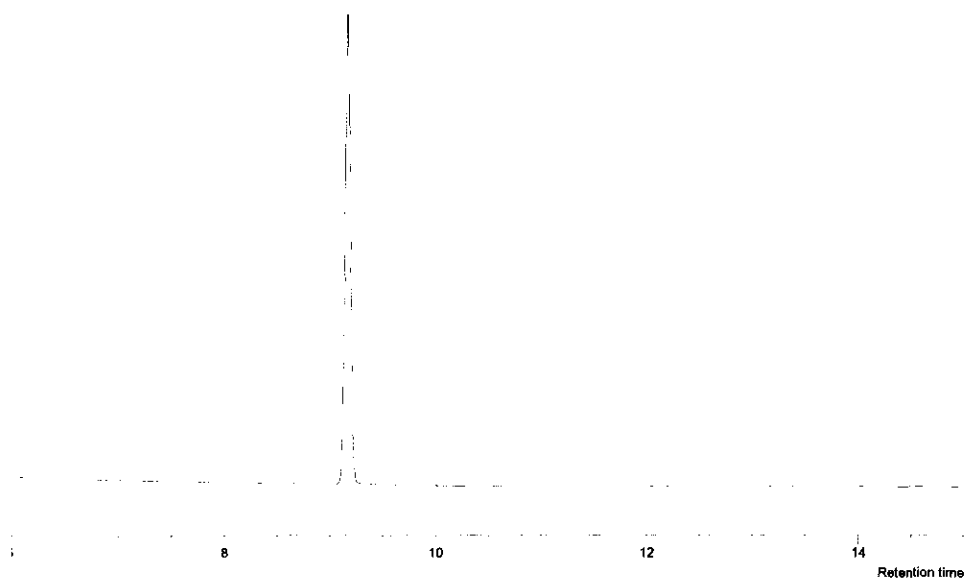


Figure 3-2: GC Sample solution chromatogram (1.0%)

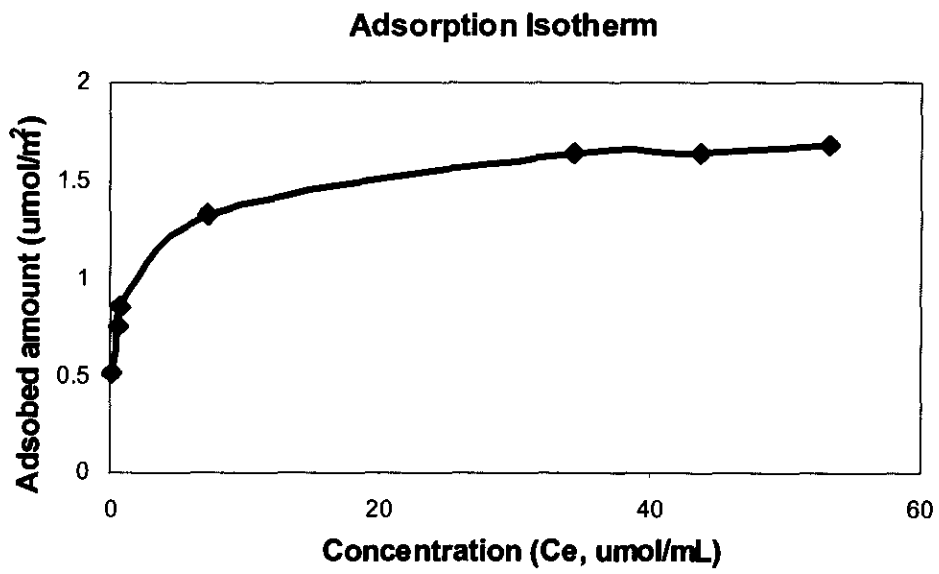


Figure 3-3: Adsorption isotherm from static adsorption experiments

3.2 Discussion: Static Adsorption Experiments:

Arthur et al [16] noted that the surface chemistry and reactivity of silica gels are mainly determined by surface hydroxyl groups. Hydrophilic silica surfaces (characterized by silanol, Si-OH) can interact with other compounds through the adsorption process. The adsorption capacity is one of the important factors used in evaluating silica materials as adsorbents [17]

Figure 3-3 demonstrates the adsorbed amounts as a function of their equilibrium molar concentrations. The adsorption equilibrium constant agrees with the Langmuir type isotherm. The adsorption value of diethyl phthalate reaches a plateau near $1 \mu\text{mol}/\text{m}^2$, which demonstrates the maximum amount of DEP adsorbed approximately $1 \mu\text{mol}/\text{m}^2$.

The size of the DEP molecule can be calculated approximately $166 \text{ \AA}^2/\text{molecules}$ based on the maximum adsorption value.

The adsorption isotherm suggests a low surface coverage with one step mechanism. This mechanism displays the adsorption process is of a monomolecular fashion by forming a complete monolayer.

According to R.Iler et al., where there is a strong interaction between the adsorbed molecule and the surface, a complete monomolecular layer is formed even when there is only a relatively low concentration of adsorbate in the liquid phase adjacent to the surface. This statement points to a strong affinity between DEP and silica gel in this adsorption process. This can be explained by the driving force being either a polar-polar interaction or a hydrogen bonding interaction between DEP and silica gel. Thus, the

hydrogen atom of the hydroxyl group from the silanol, Si-OH can directly act as hydrogen-bonding acceptor to form a hydrogen bond with the oxygen atom of the ester group of the DEP molecule. [11],[18]. Therefore, the DEP-silica adsorption driving force can be explained possibly through O-H bonding interaction, and the structure is illustrated in Figure 3-4

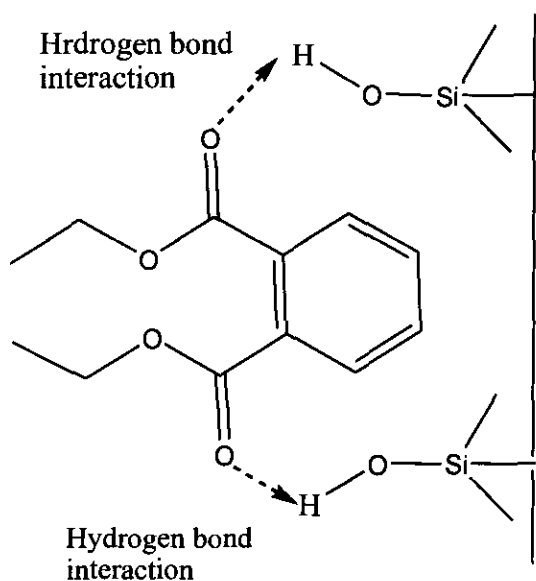


Figure 3-4: One of the possible interactions (O-H bonding) between Diethyl phthalate and Silica gel

3.3 Results: Microcalorimetric Experiment:

The differential adsorption enthalpy, ΔH , was measured as the thermal effects of various concentrations of DEP (0.01-2.0%) adsorption onto silica surface. See Table 3-3 for the calculation of these concentrations of DEP solutions. The power/time response of each sample returned to the base line approximately within 1 hour; see Figure 3-5 for a heat flow signal over the period of time. This indicates the observed response was generated by the heat released when the DEP molecule adsorbed onto the silica surface [19]. The differential enthalpies were calculated as per gram of silica (mJ/g) and further expressed as molar energy (kJ/mol). See Table 3-4 for accumulative values of molar energy. The molar energies were plotted against the equilibrium concentrations of DEP solutions to create an isotherm. See Figure 3-6 for the energy isotherm.

3.4 Discussion: Microcalorimetric Experiments:

The heat flow signal of DEP molecule adsorption on the silica adsorbent at a constant temperature indicates the adsorption process is of an exothermic nature, which is driven by the enthalpy change [20]. The enthalpy change for this adsorption process was calculated by integrating the exothermic peak of the solutions at each concentration level. According to the energy isotherm (Figure 3-6), adsorption energy increases until the surface active sites have been occupied. The maximum energy required by the DEP molecule is approximately 7kJ/mol, which is indicative of low adsorbate loading capacity on the silica surface. This isotherm also suggests a monomolecular layer adsorption with Langmuir-type behavior.

Figure 3-5: Heat flow signal over time from calorimetric experiment

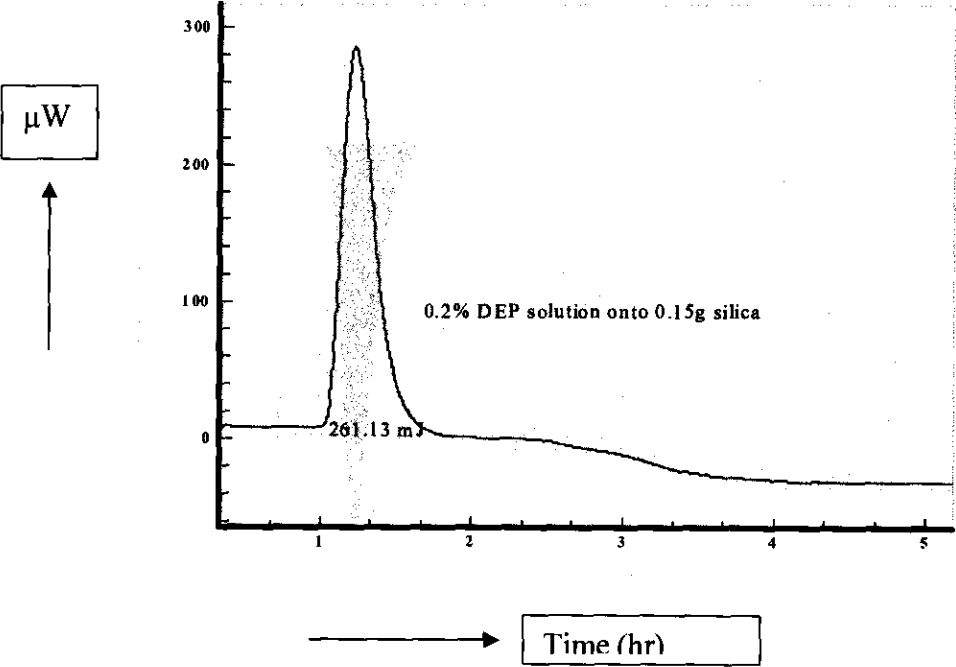
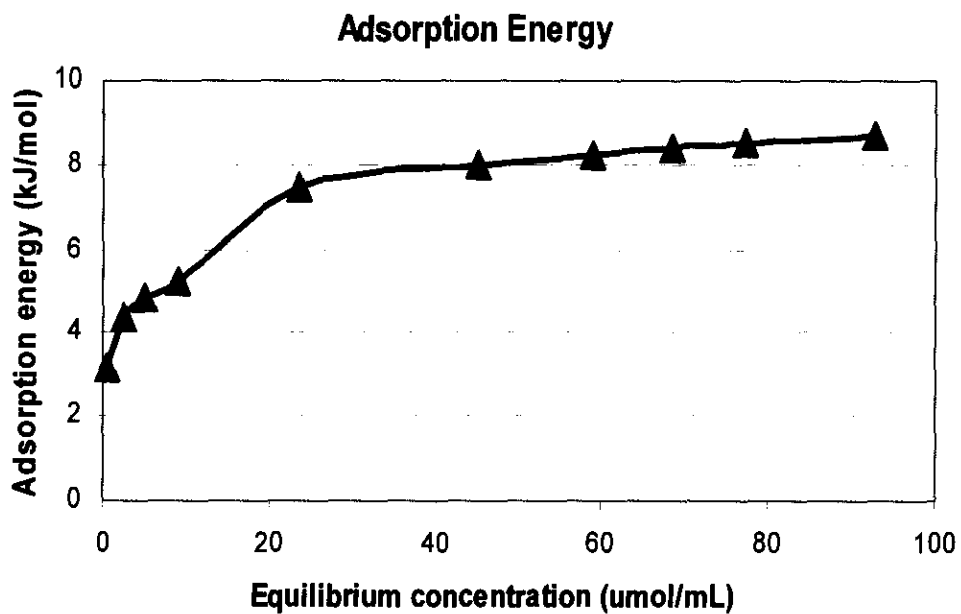


Table 3-3: DEP Concentration calculation -Microcalorimetric experiments:

| DEP | DEP | | |
|-------|---------|---------------|---------|
| | Wt | Concentration | |
| wt% | g | mg/mL | umol/mL |
| 0.01% | 0.02084 | 0.104 | 0.469 |
| 0.05% | 0.1139 | 0.570 | 2.56 |
| 0.1% | 0.2278 | 1.14 | 5.12 |
| 0.2% | 0.4050 | 2.03 | 9.11 |
| 0.5% | 1.042 | 5.21 | 23.4 |
| 1.0% | 2.006 | 10.0 | 45.1 |
| 1.3% | 2.622 | 13.1 | 59.0 |
| 1.5% | 3.040 | 15.2 | 68.4 |
| 1.7% | 3.426 | 17.1 | 77.1 |
| 2.0% | 4.121 | 20.6 | 92.7 |

Table 3-4: Molar energy calculation-Microcalorimetric experiments:

| DEP | DEP | | Wt of silica | DEP |
|-------|-----------------|--------------------------|--------------|--------------|
| | Enthapy | Enthalpy /gram of silica | | Molar Energy |
| wt% | ΔH , mJ | ΔH , mJ/g | g | kJ/mol |
| 0.01% | 2110 | 14100 | 0.1495 | 3.14 |
| 0.05% | 2930 | 19600 | 0.1495 | 4.36 |
| 0.1% | 3250 | 21700 | 0.1495 | 4.830 |
| 0.2% | 3510 | 23500 | 0.1495 | 5.22 |
| 0.5% | 5040 | 33700 | 0.1495 | 7.50 |
| 1.0% | 5380 | 36000 | 0.1495 | 8.00 |
| 1.3% | 5540 | 37000 | 0.1495 | 8.23 |
| 1.5% | 5620 | 37600 | 0.1495 | 8.36 |
| 1.7% | 5710 | 38200 | 0.1495 | 8.49 |
| 2.0% | 5830 | 39000 | 0.1495 | 8.67 |



Accumulated value of ΔH was used in this plot

Figure 3-6: Adsorption energy isotherm of DEP from Microcalorimetric experiments

Therefore, the energy isotherm from the Microcalorimetric experiments agrees with the adsorption isotherm from the static experiments, in terms of the adsorption process. Hence the adsorption process is driven by the adsorbate-adsorbent affinity which is either a polar-polar interaction, or a hydrogen (O-H) bonding interaction between DEP molecule and silica gel, Si-OH.

3.5 Comparison of Adsorption Isotherm and Energy Isotherm:

The adsorption isotherm from the static adsorption experiments was compared with the energy isotherm created from the Microcalorimetric experiments. Both isotherms are supportive of similar adsorption behaviour. The low adsorbate loading capacity on the silica adsorbent has been confirmed by both experiments.

The saturation of surface loading capacity from both adsorption and energy isotherms demonstrates the complete monomolecular layer adsorption. The isotherms from both experiments also support the strong affinity between the adsorbate and the adsorbent. This adsorbate-adsorbent affinity can be explained either from a polar-polar interaction or a hydrogen bonding interaction of DEP molecules with the polar site of SiOH. Figure 3-7 has been illustrated for the comparison plot of adsorption and energy isotherms with the left axis related to energy [kJ/mol] and right axis related to adsorption [$\mu\text{mol}/\text{m}^2$].

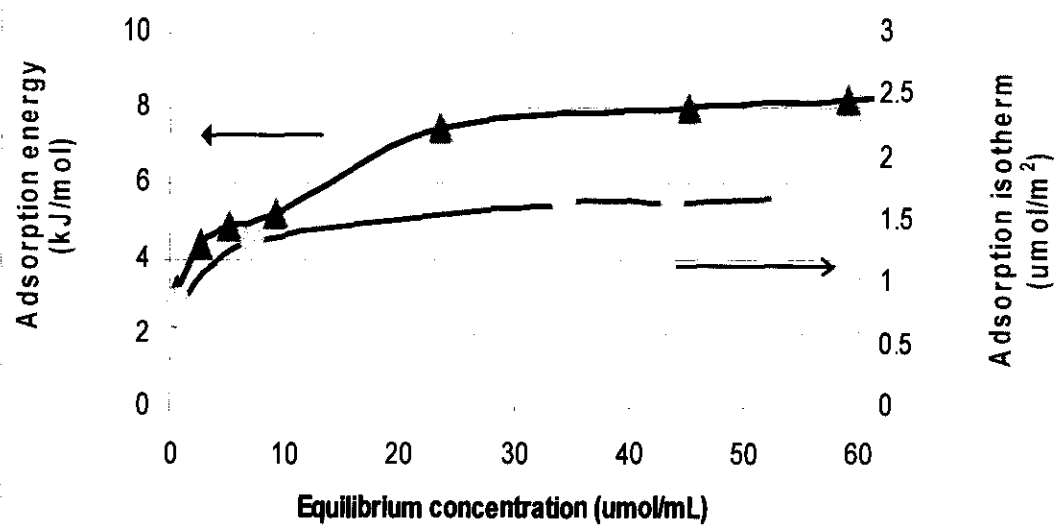


Figure 3-7: Comparison of Adsorption Isotherm (right axis) and Energy Isotherm (left axis) from static and Microcalorimetric adsorption experiments.

Conclusion

The experimental data from static adsorption experiments establish the correlation between adsorption isotherm and the energy isotherm, which was extracted from Microcalorimetric experiments.

Both static and Microcalorimetric experimental data are supportive of the complete monomolecular adsorption with a relatively low surface coverage. Experimental data using both techniques are in the agreement that the primary driving force for diethyl phthalate-silica adsorption is either polar-polar interaction or hydrogen bonding interaction between DEP molecules and silica gel (silanol, Si-OH).

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