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Heat of Adsorption of Pure Sulfur Hexafluoride on Micro-Mesoporous Adsorbents

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Abstract. The isotherms and the isosteric heats of adsorption of pure SF_6 were measured on two microporous zeolites (NaX and Silicalite), one mesoporous alumina, and two activated carbons (BPL and PCB) at 305 K. The adsorption isotherms were Type I by Brunauer classification. The PCB carbon adsorbed SF_6 most strongly and the alumina adsorbed SF_6 most weakly. The adsorption of SF_6 on the other three materials were comparable in the low pressure region despite their drastic differences in the physicochemical properties. The heat of adsorption of SF_6 on the silicalite and the alumina remained practically constant over a large range of coverage. The heat of adsorption of SF_6 increased with increasing adsorbate loading on the NaX zeolite in the high coverage region. The heat of adsorption of SF_6 on the activated carbons decreased with increasing adsorbate loading before leveling off in the high coverage region.

Keywords: heat of adsorption, sulfur hexafluoride, micro-meso porous adsorbents, zeolites, alumina, activated carbons

Introduction

A large variety of micro-mesoporous adsorbents like zeolites, activated carbons, silica, and alumina gels are used for gas separation by adsorption technology. These adsorbents may behave like an energetically homogeneous material for adsorption of some gases. They may also exhibit different degrees of energetic heterogeneity for adsorption of other gases.

The most direct and quantitative measure of adsorbent heterogeneity for a gas-solid pair is given by the variation of the isosteric heat of adsorption of the gas with adsorbate loading. The adsorbent is energetically homogeneous for a gas if the isosteric heat of adsorption remains constant with increasing adsorbate loading. The adsorbent exhibits energetic heterogeneity for a gas if the isosteric heat of adsorption decreases with increasing adsorbate loading. The isosteric heat of adsorption may also increase with increasing adsorbate loading due to strong lateral interactions between the adsorbed molecules in the region of higher surface coverages (Sircar and Rao, 1999).

An energetically homogeneous adsorbent must be structurally and chemically uniform throughout its mass. Heterogeneity is introduced by the presence of a distribution (network) of micro-meso pores of different sizes and shapes within the adsorbent mass as well as by a distribution of chemically different adsorption sites within the pores. Most amorphous adsorbents like activated carbons and inorganic gels belong to this category. Most crystalline adsorbents like aluminosilicate zeolites are structurally uniform but energetic heterogeneity may be created by lattice defects, presence of a distributed silica-alumina ratio in the crystal framework, presence of different hydrated and nonhydrated cations at different locations within the framework, presence of trace amounts of moisture, nonuniform hydrolysis of framework during thermal regeneration, etc, (Sircar, 1994). Heterogeneity can also be introduced by the presence of a binder material

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used for pelletizing an otherwise homogeneous adsorbent (Cao and Sircar, 2001).

The structures of microporous crystalline adsorbents can generally be established from X-ray diffraction patterns but their chemical heterogeneity may not be quantified by today's technology. Today's technology also does not permit quantitative analysis of physico-chemical heterogeneity (distribution of pore size, shape, and surface chemistry) in micro-mesoporous amorphous adsorbents. Given this state of the art, it is apparent that realistic and accurate estimation of gas-solid molecular interactions within the pores of real adsorbents, which is needed for microscopic analysis of adsorbent heterogeneity, will be a very difficult, if not impossible, task. Consequently, experimental measurements of macroscopic isosteric heats of adsorption of gases on solids as functions of adsorbate loadings provide the only practical method for study of overall adsorbent heterogeneity. These properties can be very different for different gas-solid systems and they cannot be predicted a priori. The purpose of this note is to demonstrate this point by calorimetric measurement of isosteric heats of adsorption of pure SF_6 on various micro-meso porous adsorbents.

Definition of Isosteric Heat of Adsorption

The Gibbsian Surface Excess (GSE) model of adsorption of a pure gas defines the isosteric heat of adsorption (q) as (Sircar, 1999):

$$q = -\left(\frac{\delta H^o}{\delta n^m}\right)_T \tag{1}$$

where H^o is the total enthalpy of a closed adsorption system containing a gas phase at pressure P in equilibrium with unit amount of an adsorbent and having a specific void volume of v^o (cm^3/g). The system temperature is T, and n^m is the equilibrium GSE of the pure gas (adsorbate loading) at P and T. It can be shown, that for an ideal gas (Sircar, 1999):

$$q = +RT^2 \cdot \left(\frac{\delta \ell n P}{\delta T}\right)_{n^m} \tag{2}$$

Eq. (2) is identical to the conventional definition of the isosteric heat of adsorption of a pure gas when n^m is replaced by the actual amount adsorbed (n^a) at P and T (Young and Crowell, 1962). Thus, Eqs. (1) and (2) provide a more general definition of the isosteric heat of adsorption since $n^m \sim n^a$ only at low gas pressures. It has been shown that this definition of q is very practical because it can be directly used to describe heat balance in adsorption columns (Sircar, 1999).

Equation (2) shows that q can be estimated as a function of n^m for pure gas adsorption by measuring GSE isotherms (n^m vs. P at constant T) at various temperatures. The isosteric heat as a function of n^m can also be directly obtained calorimetrically (Sircar et al., 1999). The latter method may be more accurate in many cases. Calorimetry is the only practical option for estimating multicomponent gas isosteric heats (Sircar and Rao, 1999). One type of calorimetry useful for this purpose is described below.

Calometric Measurement of Isosteric Heats

A Tian-Calvet type micro-calorimeter can be used to directly measure the isosteric heats of adsorption. Figure 1 shows a schematic drawing of such a calorimeter assembly. It consists of a calorimeter cell which is surrounded by thermopiles to collect and measure any heat generated within the cell during the ad(de)sorption process. The cell is connected to a gas dosage system through a valve. The entire assembly is thermostated at a constant temperature. A more detailed description of the apparatus, the experimental protocol, and the calibration of the thermopiles can be found elsewhere (Sircar et al., 1999).

The basic experiment consists of placing a known amount of the regenerated adsorbent inside the cell and measuring its specific void volume (v^o, cm^3/g) by helium expansion. The cell is then equilibrated with the adsorbate gas at pressure P^o and temperature T^o which is also the temperature of the thermostated bath. A known quantity of the pure adsorbate (ΔN, moles/gram of adsorbent) is then slowly transferred from the dosage side into the cell side by opening the interconnecting valve. A new equilibrium state is established in

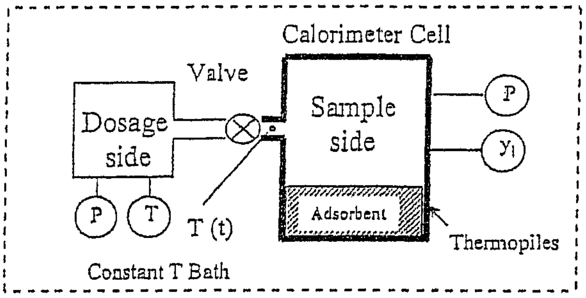

Figure 1. Schematic drawing of micro-calorimeter.

Table 1. Physical properties of sulfur hexafluoride.

				Permanent moments		Critical properties	
Molecular weight	Liquid molar volume[a] (cm^3/mole)	Kinetic diameter (Å)	Polarizability ($\times 10^{-25}$ cm^3)	Dipole ($\times 10^{18}$ esu-cm)	Quadrupole ($\times 10^{-26}$ esu-cm^2)	Pressure (KPa)	Temperature (K)
146.05	72.74	5.13	65.4	0.0	0.0	3.75	318.6

[a] At normal boiling point.

the cell side at pressure P^∞ and temperature T^o. The total amount of heat evolved during this process (ΔQ, cal/gram of adsorbent) is measured by integrating the precalibrated thermopile response curve (voltage vs. time).

By using a differential change in the cell side gas phase pressure $[\Delta P = (P^\infty - P^o) \rightarrow 0]$ during the experiment, and by introducing the gas into the cell side in such a way that its temperature remains equal to T^o during the process, it can be shown that the isosteric heat of adsorption (q^o) of a pure gas at P^o and T^o (or at the corresponding equilibrium GSE of n^{mo}) is given by (Sircar et al., 1999):

$$q^o = \frac{\left[\left(\frac{\Delta Q}{\Delta N}\right) - v^o\left(\frac{\Delta P}{\Delta N}\right)\right]}{\left[1 - \frac{v^o}{RT^o}\left(\frac{\Delta P}{\Delta N}\right)\right]} \quad (3)$$

The amount of gas introduced into the cell side (ΔN) can be obtained by measuring the pressure change of the dosage side during the process and its void volume. A mass balance for the cell side also yields (Sircar et al., 1999):

$$\Delta N = \Delta n^m + \frac{v^o \Delta P}{RT^o} \quad (4)$$

Equation (4) shows that the differential change in the adsorbate GSE (Δn^m) during the process can be easily calculated. Thus, the calorimeter can also be used as a conventional volumetric adsorption apparatus for obtaining the complete GSE isotherm for the gas at temperature T^o by carrying out a series of cumulative differential tests starting with the clean adsorbent $[P^o = 0,\ n^{mo} = 0]$ and then progressively increasing the value of P^o.

Experimental Systems

Sulfur hexafluoride was chosen as the gaseous adsorbate for this study because it is nonpolar and chemically inert which made the adsorption systems relatively simpler by ruling out specific pole-pole or acid-base type of gas-solid interactions. Furthermore, the SF_6 molecules are symmetric, large in size (octahedral in shape), and they possess high polarizabilities indicating that their interactions with the adsorption sites within the micropores of the adsorbents would be primarily dispersive (van der Waals) in nature and they would be very pronounced (large heats) and, thus, easier to measure (Young and Crowell, 1962). Table 1 lists some of the relevant properties of SF_6. The gas (99.99% pure) was supplied by Air Products and Chemicals, Inc.

Five different adsorbents were chosen for this study. They included two nanoporous zeolites (silicalite and NaX), one mesoporous alumina gel, and two micro-mesoporous activated carbons (coal and coconut shell based). The zeolites were pelletized using inorganic binders, the alumina was self-bonded, and the carbons were bonded using pitch. The adsorbents were used as received from their manufacturers after their thermal regeneration under vacuum ($10^{-3}\mu$m). The regeneration temperatures were, respectively, 350, 200, 200, and 130°C for the NaX zeolite, the silicalite, the alumina, and the carbons. Table 2 gives the source of these materials and their physical properties as reported in the manufacturer's data sheets. The materials provide a large spectrum of porosity and surface chemistry for adsorption of SF_6.

Experimental Results

Adsorption Isotherms

The adsorption isotherms of pure SF_6 were measured at 305 K on the adsorbents listed in Table 2 using the calorimeter as a volumetric adsorption apparatus. They are shown in Fig. 2. All isotherms are Type I in shape according to the Brunauer classification (Young and Crowell, 1962). The low pressure region isotherms (Henry's Law region) are shown in Fig. 3 as plots of $\ln n^m$ against $\ln P$. These plots are indeed linear verifying the Henry's Law. The Henry's Law

Table 2. Physical properties of adsorbents.

Adsorbent	Manufacturer	Pore volume (cm^3/g)		Density (g/cm^3)		Micropore structure
		Micropore (<20 Å)[a]	Total (<1000 Å)[a]	Helium	Bulk	
NaX zeolite (Beads: 2.1 mm dia.)	UOP (Type 13X)	0.17[b]	0.54	2.46	0.62	Channel and cavity
Silicalite (Pellets: 8.0 mm long × 1.5 mm dia.)	UOP (Type SP115)	0.10[b]	0.45	2.50	0.75	Elliptical and circular channels
Alumina (Beads: 1.9 mm dia.)	Alcan (Type AA300)	Negligible	0.38	2.62	1.34	Network
Coconut shell based carbon (Granules: 6–16 mesh)	Calgon (Type PCB)	0.40	0.72	2.2	0.44	Network
Coal based carbon (Granules: 6–16 mesh)	Calgon (Type BPL)	0.35	0.70	2.1	0.48	Network

[a] Pore diameter.
[b] Intracrystalline pore volume.

Table 3. Henry's law constants for SF_6 adsorption.

Adsorbents:	PCB carbon	BPL carbon	Silicalite	NaX zeolite	Alumina
Henry's law constant: (mol/kg/atm)	46.0	18.0	17.5	14.2	0.17

constants reported in Table 3 indicate that SF_6 is very weakly adsorbed on the alumina and it is very strongly adsorbed on the PCB carbon. On the other hand, the strengths of SF_6 adsorption are similar on the NaX zeolite, the silicalite and the BPL carbon. Furthermore, Fig. 2 shows that the saturation capacities for SF_6 adsorption on these materials increase in the order PCB carbon > BPL carbon > NaX zeolite > silicalite > alumina. This is consistent with the relative sizes of the micropore volumes of these materials (primary adsorption space) given in Table 2.

The NaX zeolite is a highly polar crystalline adsorbent with sodium cations providing the charged adsorption sites inside its cavities (∼13A in diameter). The silicalite is a nonpolar crystalline adsorbent with very little or no ion exchange capacity within its elliptical straight (5.7 × 5.1 Å) and near-circular zigzag channels (5.4 Å diameter). The activated carbons are moderately polar amorphous adsorbents with networks of micro-mesopores of unknown sizes and shapes. Despite such drastic differences between the pore structure (shape and size) and the surface chemistry of these materials, the low pressure adsorption isotherms of SF_6 on some of these materials (NaX zeolite, silicalite, and BPL carbon) were surprisingly similar. This demonstrated the complexity and unpredictability of adsorption of SF_6 on these materials.

The adsorption of SF_6 on the alumina was very weak because the adsorbent was primarily a mesoporous solid (mean pore diameter = 65Å). The PCB carbon adsorbed SF_6 more strongly than the BPL carbon because it has relatively smaller micropores.

Isosteric Heat of Adsorption

The isosteric heats of adsorption of pure SF_6 were calorimetrically measured at 305 K as functions of adsorbate loadings (GSE) on the adsorbents of Table 2. They are shown in Fig. 4(a, b, c). The heat on the silicalite sample remained constant (∼9.4 Kcal/mole) over a very large range of surface coverage ($0 \leq n^m \leq 1.5$ mmoles/g) and then it rapidly decreased as the adsorption of SF_6 approached its saturation capacity ($n^m \sim 1.6$ mmoles/g). The heat on the NaX zeolite sample was constant (∼7.0 Kcal/mole) in the low surface coverage region ($0 \leq n^m \leq 0.2$ mmoles/g) and then it gradually increased as the adsorbate loading was increased. The heat on the alumina was the lowest among all systems studied and it remained constant (∼4.8 Kcal/mole) over the range of the data ($0 \leq n^m \leq 0.6$ mmoles/g). The heats on both carbons were fairly high at the limits of zero surface coverage (∼10.0 Kcal/mole for PCB carbon and ∼8.5 Kcal/mole for BPL carbon) and then they decreased substantially as the

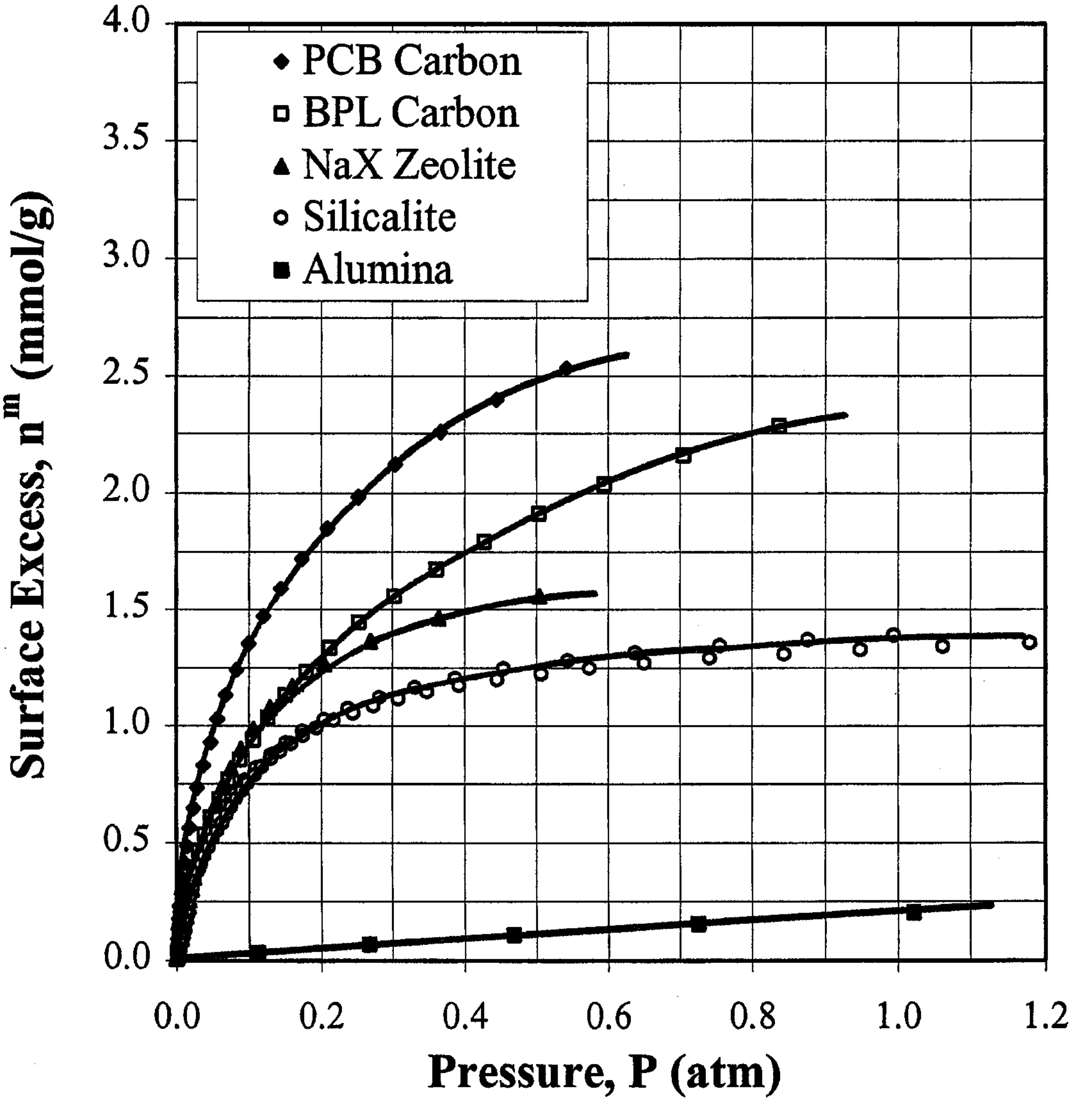

Figure 2. Adsorption isotherms of SF_6 on various adsorbents at 305 K.

SF_6 loading was increased. Finally, they leveled off (~7.8 Kcal/mole for PCB carbon and ~7.0 Kcal/mole for the BPL carbon) at higher coverages of SF_6.

Our calorimetrically measured data on the isosteric heats of adsorption of SF_6 on silicalite and NaX zeolite compare fairly well with those reported by others (MacDougall et al., 1999; Ruthven and Doetsch, 1975) using non-calorimetric methods as shown in Table 4.

Figure 4(a) suggests that the silicalite sample behaves like a homogeneous adsorbent for SF_6 adsorption over a large range of coverage. Previous calorimetric heat measurements for SF_6 adsorption on silicalite crystals showed that the adsorbent behaved like a homogeneous material with some lateral interactions (Dunne et al., 1996). The reported heat of adsorption of ~8.3 Kcal/mol at the limit of zero coverage compares well with our data of 9.4 Kcal/mol. The present pelletized sample contains ~19% alumina binder and thus, the material should actually be heterogeneous (Cao and Sircar, 2001). However, the heterogeneity for SF_6 adsorption is masked except at very high pressures (large SF_6 coverage) because the adsorption of SF_6 on the alumina binder is very weak as shown by Fig. 2. This behavior can be described by a thermodynamic model of heat of adsorption of a gas on a composite adsorbent consisting of a binder

Table 4. Literature comparison of heats of SF_6 adsorption (kcal/mol) in Henry's law region.

Adsorbent	This work[a] (calorimetric)	Dunne et al. (1996)[b] (calorimetric)	MacDougall et al. (1999)[b] (ZLC)	Ruthven and Doetsch (1975)[b] (gravimetric)
Silicalite	9.4	8.3	7.9	–
NaX zeolite	7.0	–	–	6.9

[a] zeolites with binders.
[b] crystals.

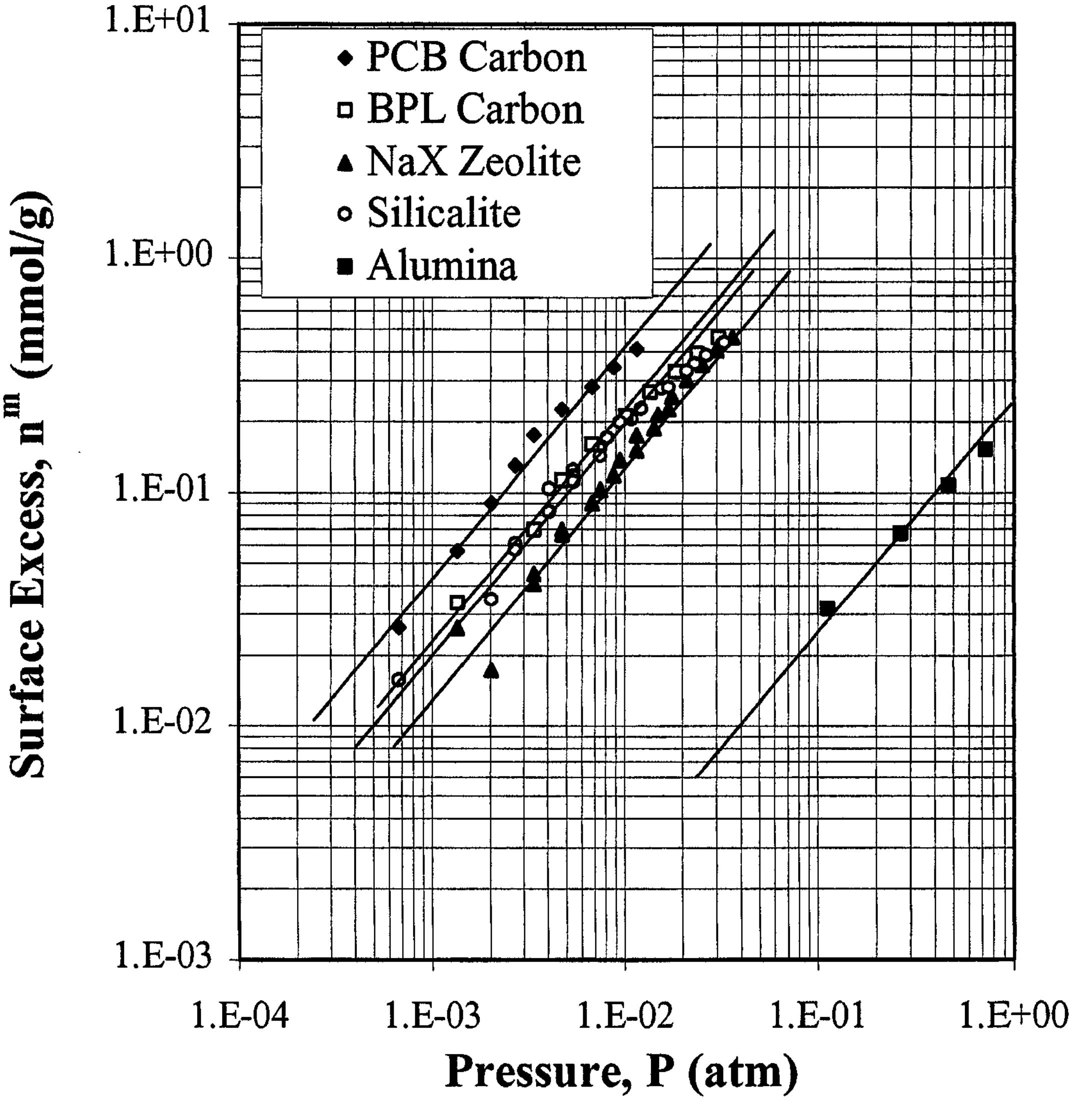

Figure 3. Adsorption isotherms of SF_6 on various adsorbents in the Henry's law region at 305 K.

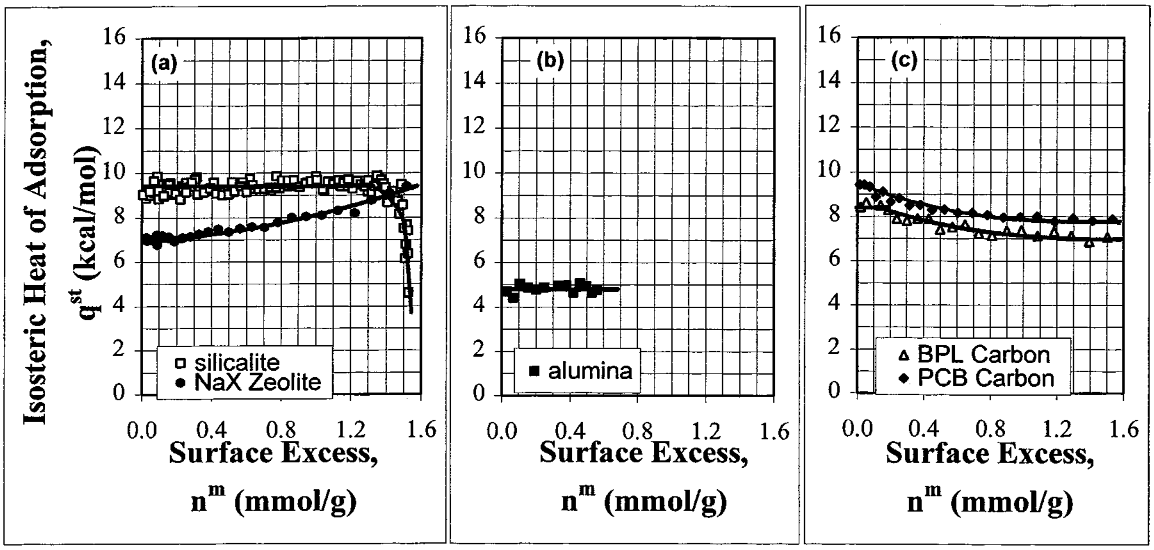

Figure 4. Isosteric heats of adsorption of SF_6 on various adsorbents at 305 K: (a) silicalite, NaX zeolite, (b) alumina, (c) BPL and PCB carbons.

material and a homogeneous adsorbent (Cao and Sircar, 2001).

The heat of adsorption of SF_6 on the NaX zeolite increases with increased loading at higher coverages presumably because of lateral interactions between the adsorbed SF_6 molecules. This is consistent with previously measured data on similar systems (Dunne et al., 1996). However, it is surprising that the lateral interactions are absent or not very pronounced at higher SF_6 coverages in the silicalite sample whose micro pore sizes are closer to the adsorbate size. The heat data does not indicate any heterogeneity exhibited by the NaX sample for adsorption of SF_6.

The heat of adsorption of SF_6 on the mesoporous alumina sample is relatively low (Fig. 4b) due to the absence of micropores. The material also behaves like a homogeneous adsorbent in the range of the data. Both PCB and BPL carbons exhibit substantial heterogeneity for SF_6 adsorption (Fig. 4c). However, the isosteric heat-adsorbate loading variations for these two carbons are qualitatively similar.

These data clearly demonstrate the complexity of interactions between the adsorbate and the porous substrate which cannot generally be predicted a priori. Experimental measurement of isosteric heat and their variations with adsorbate loadings must be carried out for study of energetic heterogeneity.

Isosteric Heat in the Henry's Law Region

According to the Henry's Law, all gas adsorption isotherms should be linear at the very low pressure region (Young and Crowell, 1962; Ross and Olivier, 1964):

$$n^m = KP \qquad 0 \le P \le P^* \tag{5}$$

where $K(T)$ is the Henry's Law constant at temperature T. The pressure P^* represents the upper bound of the Henry's Law region. It follows from Eqs. (2) and (5) that:

$$q_{\mathrm{H}} = -RT^2 \cdot \left[\frac{d\ell nK}{dT}\right] \qquad 0 \le P < P^* \tag{6}$$

where q_{H} is the isosteric heat of adsorption of a pure gas in the Henry's Law region. Equation (6) shows that q_{H} should be a constant (independent of adsorbate loading) in that region.

The calorimetric heat data of Fig. 4 for adsorption of SF_6 on the alumina, the silicalite, the NaX zeolite, and the BPL carbon indeed show that the isosteric heats of adsorption of SF_6 are constants in the very low pressure regions (low adsorbate loadings). In fact, they remain constants over a relatively large range of adsorbate loadings for the alumina, the NaX zeolite, the BPL carbon and the silicalite samples. It may, however, not be possible to experimentally observe a region of constant q_{H}, as in the case of the PCB carbon, where the Henry's Law region stops at a very low value of P^*. This behavior is expected when the adsorbent is highly heterogeneous for adsorption of a gas (Ross and Olivier, 1964).

Summary

The isotherms for adsorption of pure SF_6 and the corresponding isosteric heats of adsorption as functions of adsorbate loadings on various micro-mesoporous adsorbents were measured at 305 K using a differential microcalorimeter. Two pelletized crystalline zeolites (NaX and silicalite), one mesoporous alumina, and two activated carbons (coal and coconut shell based) were used as adsorbents. The SF_6 was most strongly adsorbed on the coconut shell carbon and it was most weakly adsorbed on the alumina. The SF_6 adsorption isotherms on the other three adsorbents were similar in the low pressure region despite drastic differences in the structures and chemical natures of these materials.

The alumina and the silicalite samples behaved like homogeneous adsorbents for SF_6 adsorption (isosteric heats of adsorption were constants with increasing adsorbate loadings) except at very high surface coverages for the silicalite where the heat decreased very rapidly. The NaX zeolite was also homogeneous for SF_6 adsorption but it exhibited significant lateral interaction between adsorbed molecules at higher coverages (isosteric heat of adsorption increased with increasing adsorbate loading). Both activated carbons exhibited significant energetic heterogeneity for adsorption of SF_6 (isosteric heat decreased with increasing adsorbate loading).

This study shows that the interactions of SF_6 with the adsorbent materials of this work are complex and they cannot be predicted a priori. Experimental measurements of isosteric heats of adsorption are required to establish the heterogeneity of adsorption of a gas-solid pair.

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