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Shaun Singh[a]; F. Handan Tezel[a]; Peter J. E. Harlick[a]
[a] Department of Chemical Engineering, University of Ottawa, Ottawa, Canada

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ADSORPTION OF TETRAFLUOROMETHANE AND NITROGEN BY VARIOUS ADSORBENTS

Shaun Singh, F. Handan Tezel,* and Peter J. E. Harlick

Department of Chemical Engineering, University of
Ottawa, 161 Louis-Pasteur, Ottawa, Ontario, Canada

ABSTRACT

Adsorption of tetrafluoromethane (CF_4) and nitrogen (N_2) was studied by various adsorbents for the possible separation of these gases by an adsorption process. Adsorbent screening was carried out for 13 different adsorbents by determining Henry's law constants at different temperatures and determining the adsorption selectivity for the separation of these gases. Heat of adsorption values were also determined for these adsorbents. This was accomplished by using the concentration pulse chromatographic technique. The adsorbents studied included one activated alumna, three different activated carbons, zeolites A, X, Y, and ZSM-5 at different SiO_2/Al_2O_3 ratios. Among them, three ZSM-5 zeolites and three activated carbon adsorbents were chosen for the determination of pure component isotherms at 23°C, since they showed the highest selectivity for CF_4–N_2 separation. Furthermore, activated carbon F-400, ZSM-5-30 (with a SiO_2/Al_2O_3 ratio of 30), and ZSM-5-280 (with a SiO_2/Al_2O_3 ratio of 280) were chosen to be studied further. Pure adsorption isotherms for CF_4

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*Corresponding author. E-mail: tezel@eng.uottawa.ca

and N_2 were determined for different temperatures between 23 and 100°C for these three adsorbents up to 140 kPa pressure. Standard volumetric technique was used for the determination of the adsorption isotherms. Freundlich isotherm equation was used to model the pure isotherms for N_2. Temperature dependent Toth isotherm model was used for the pure isotherms for CF_4 and using the parameters of the Toth isotherm, isosteres were determined for this adsorbate at different adsorption capacities. It was concluded that ZSM-5-280 was the best adsorbent for the separation of CF_4 from N_2 since it had the largest capacity for CF_4 and the lowest capacity for N_2 within the pressure and temperature range looked at in this study.

INTRODUCTION

The compound CF_4, commonly known as tetrafluoromethane, is a global warming gas, falling under the basket of perfluorocarbons (PFCs). It has an atmospheric lifetime of 50,000 years and its current atmospheric concentration is 72 pptv, up from a pre-industrial age concentration of zero. The global warming potential (GWP) of CF_4 is pegged at 6500 times greater than the carbon dioxide (CO_2) benchmark, based on a CO_2 lifetime of 100 years. Consequently, its emissions are to be limited by all industrialized nations as inscribed in the *1997 Kyoto Protocol*.[1]

The two major sources of CF_4 emissions are aluminum producers and semiconductor fabricators. The aluminum source of CF_4 is due to "anode effects" during the electrolytic reduction ("smelting") of alumina (Al_2O_3) to produce aluminum (Al). The smelter pot contains alumina dissolved in an electrolyte consisting of molten cryolite ($NaAlF_6$). The anode effect is triggered when alumina concentrations drop; excess voltages between the anode and alumina bath result in the formation of CF_4 from carbon in the anode and fluorine in the salts. In the semiconductor industry, CF_4 may be used as the primary gas for dry etching. For this process, known as reactive ion etching (RIE), the gas is heated into a plasma state in which CF_4 reacts with silicon dioxide (SiO_2) to yield gaseous silicon tetrafluoride (SiF_4) and CO_2. However, much of CF_4 remains intact and is eventually purged from the reaction chamber and released into the atmosphere. The CF_4 may be produced during PECVD (plasma enhanced chemical vapor deposition) chamber cleaning process in which PFCs are used to remove the residues after dielectric film deposition.

Several strategies are currently being investigated to mitigate CF_4 emissions. Aluminum smelters are developing technologies such as computerized alumina point feeders and anode gas monitors to limit the number and duration of anode effects. The semiconductor industry is trying to optimize PECVD cleaning processes by adjusting the operating conditions to achieve the highest consumption of influent PFC using the least amount of source gas, while at the same time maintaining a high tool throughput and clean effectiveness.[2] Other methods such as microwave plasma destruction,[3] thermal destruction,[4] and cryogenic recovery are energy intensive. Membrane separation may also be employed where the selectivity for inert gases in the effluent (He and N_2) over PFC is very high, and this process yields a retentate stream of concentrated CF_4.[5]

This study examines the feasibility of reducing CF_4 emissions by capturing the gas from nitrogen (N_2) rich streams through adsorption. The feed gas is assumed to be free of moisture. Adsorbent screening constitutes the first step in engineering an adsorption process. The optimal adsorbent should have a high capacity for CF_4 and a high selectivity for CF_4 over N_2 adsorption. Since adsorption is an exothermic process, it thermodynamically favors lower temperatures. The best adsorbent should exhibit a low heat of adsorption for N_2 while having at most a moderate heat of adsorption for CF_4.

Adsorbents Studied

The adsorbents chosen for this study are summarized in Table 1. These samples are commercially available, and encompass the wide spectrum of adsorbent families. The following sections describe the adsorbent families.

Activated Carbons

These are porous carbonaceous adsorbents containing pore diameters greater than about 20 Å. Activated carbons have greater surface areas than other adsorbents (over 1000 m^2/g). All the samples in this study were obtained from Calgon Carbon Corporation (Huntington, West Virginia, USA) and derived from bituminous coal. They were all activated using steam at high temperatures. APA carbon has a larger surface area compared to the other carbons due to the longer residence time in the activation furnace. It was also acid washed to remove acid soluble metals such as iron. This resulted in an increase in pore size and surface area.

Activated Alumina

This is a porous aluminum oxide with a small surface area (about 300 m^2/g) and large pore diameter of over 30 Å. The activated alumina adsorbent AA300 was obtained from Alcan Aluminium, Inc (Ontario, Canada).

Table 1. List of Adsorbents Studied

Adsorbent	Supplier	Pore Diameter (Å)	Description
AA300	Alcan	>30	Activated alumina, small surface area—300 m^2/g
APA	Calgon	>20	Activated carbon, bituminous acid washed, surface area of 1,400 m^2/g
BPL	Calgon	≈ 20	Activated carbon, bituminous, surface area of 1,260 m^2/g
F400	Calgon	≈ 20	Activated carbon, bituminous, surface area of 1,000 m^2/g
5A	Linde	4.3	Zeolite A with small apertures and fair amount of Ca^{2+} Si/Al $= 1$
NaX	Linde	7.4	Zeolite X with a high amount of Na^+ $SiO_2/Al_2O_3 = 3$
HiSiv1000	UOP	7.4	Zeolite Y with a small amount of H^+ $SiO_2/Al_2O_3 < 20$
HiSiv3000	UOP	6.0	Zeolite ZSM-5 zeolite with very few Na^+ cations $SiO_2/Al_2O_3 > 1000$
NaY	UOP	7.4	Zeolite Y with a high amount of Na^+ $SiO_2/Al_2O_3 \approx 5$
H-Y-5.1	Zeolyst	7.4	Faujasite with a high amount of H^+ $SiO_2/Al_2O_3 = 5.1$
H-Y-80	Zeolyst	7.4	Faujasite with a fair amount of H^+ $SiO_2/Al_2O_3 = 80$
ZSM-5-30	Zeolyst	6.0	Pentasil zeolite with a fair amount of NH_4^+ $SiO_2/Al_2O_3 = 30$
ZSM-5-280	Zeolyst	6.0	Pentasil zeolite with a small amount of NH_4^+ $SiO_2/Al_2O_3 = 280$

ZSM-5 Zeolites

These are synthetic zeolites, or porous crystalline aluminosilicates, which consist of a framework of channels (pores with definite sizes) with diameters of 6 Å. Commonly known as the ZSM-5 structure, the channels are constructed from 10-member rings [10 oxygen atoms together with 10 aluminum (Al) and/or silicon (Si) atoms]. They also include cations for ionic charge balance, whose abundance increases as the SiO_2/Al_2O_3 ratio decreases. The pentasil zeolites in this study include ZSM-5-30 and ZSM-5-280 from Zeolyst (Valley Forge, Pennsylvania, USA) and HiSiv3000 from UOP (Mount Laurel, NJ, USA). Both of the Zeolyst samples contained ammonium (NH_4^+) cations and the UOP sample contained sodium (Na^+) cations. The number following ZSM-5 describes the SiO_2/Al_2O_3 ratio with each of the adsorbents.

Faujasites and Linde Type A Zeolites

The faujasite zeolites consist of channels built with large 12-member rings (known as X or Y structures), while the type A zeolites contain small 8-member rings.[7] Like pentasil zeolites, these adsorbents contain cations whose number depends on the SiO_2/Al_2O_3 ratio. The NaY and HiSiv1000 were obtained from UOP, while NaX and 5A were provided by Linde. Zeolyst produced H-Y-5.1 and H-Y-80. The surface areas for these adsorbents are approximately 400 m^2/g.

EXPERIMENTAL METHODS

Adsorption Measurements with a Gas Chromatograph

The concentration pulse method (CPM) was used for initial screening of adsorbents.[8–10] This method allows the quickest screening of the adsorbents. The experimental apparatus includes a modified HP (Hewlett Packard) 5730A Gas Chromatograph fitted with a 40 Series Gow-Mac thermal conductivity detector. A calibrated MKS 1179 mass flow controller regulated the carrier gas flow rate. The adsorbate, CF_4 or N_2, is injected into a gas stream of nonadsorbing carrier gas (helium in this case) flowing through an adsorption column filled with the adsorbent of study. The concentration, c (measured as voltage), of the adsorbate leaving the column is measured as a function of time, t. The mean retention time, μ, is then defined by:

$$\mu = \frac{\int_0^\infty ct\,dt}{\int_0^\infty c\,dt} \tag{1}$$

The mean retention time is a function of the length of the column L, interstitial velocity v, column porosity ε, adsorbent true density ρ, temperature T, and the Henry's law constant, K:

$$\mu = \frac{L}{v}\left[1 + \frac{(1-\varepsilon)}{\varepsilon} K\rho RT\right] \tag{2}$$

where R represents the Ideal Gas law constant. For low pressures, the Henry's law constant relates the amount of gas adsorbed per unit mass of adsorbent, q, to the adsorbate pressure, P, at constant temperature:

$$q = KP \tag{3}$$

Generally, $\mathrm{d}q/\mathrm{d}P$ is the greatest in the Henry's law region. Therefore, the evaluation of K for each adsorbent provides a quick measure of adsorbent performance.

The heat of adsorption can be found by determining K at different temperatures. The heat of adsorption $-\Delta H$ can then be determined by fitting the $K(T)$ data to the equation

$$K = K_0 \exp\left[\frac{-\Delta H}{RT}\right] \tag{4}$$

where K_0 is the pre-exponential constant. A plot of the K vs. $1/T$ data in a semi-log domain (Van't Hoff plot) would show a linear relationship.

Adsorption Measurements with a Volumetric Unit

The volumetric method was used to determine the adsorption isotherm (the relation between q and P) outside of the Henry's law region for screened adsorbents. A modified Micromeritics Accusorb 2100E constant volume unit was used to admit known volumes of either CF_4 or N_2 into the adsorbent at various pressures. The difference between the initial and equilibrium pressures determines the amount of gas adsorbed at equilibrium pressure through the Ideal Gas law.

RESULTS AND DISCUSSION

CF_4 Henry's Law Constants for Adsorption

The Van't Hoff plots of CF_4 for various adsorbents studied are shown in Fig. 1. The adsorbents AA300, H-Y-5.1, and HiSiv1000 are not included since negligible adsorption occurred with these adsorbents.

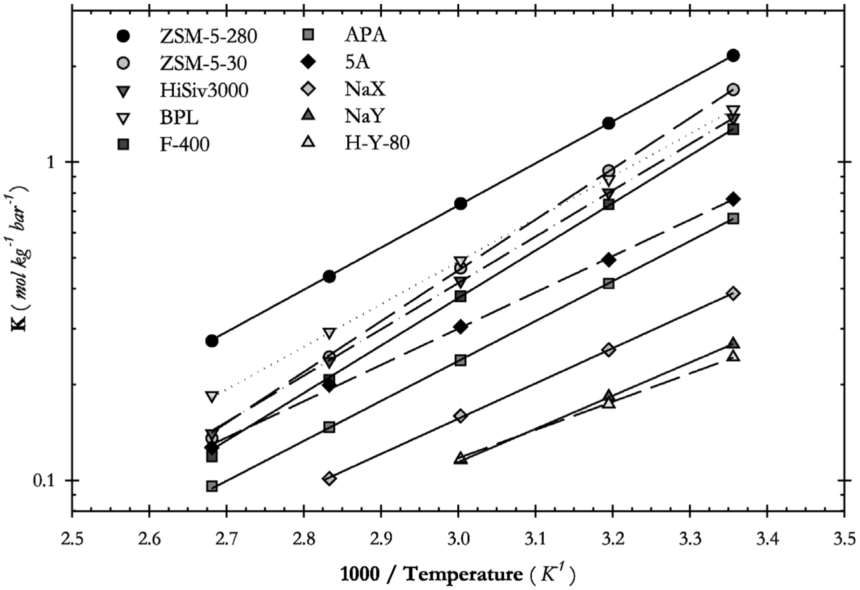

Figure 1. Henry's law constants for CF_4 adsorption as a function of temperature for all the adsorbents studied.

Adsorbents zeolite X and Y exhibited the lowest Henry's law constants. The CF_4 molecule is spherical with a kinetic diameter of 4.66 Å.[11] Relative to CF_4, the pore sizes of zeolites X and Y and activated alumna are quite large. This fact, coupled with their small surface areas, explains why these adsorbents are unable to capture much of the CF_4 gas molecules. The ranking of the faujasites in descending order of K values are NaX $>$ NaY $>$ H-Y-80. This trend may be attributed to the amount and type of cations in each of the adsorbents. Despite having the same structure, NaX contains a higher amount of Na^+ ions than NaY because of smaller SiO_2/Al_2O_3 ratio. Both of these adsorb much better than H-Y-80, which contains a relatively small amount of H^+ ions. Since there is a charge difference between Si^{+4} and Al^{+3}, the more Al there is in the structure of an adsorbent, the more cations will be needed to neutralize this charge difference.

The adsorbent 5A performed better than zeolites X and Y. For 5A, the Ca^{2+} cation takes advantage of the polarizability of CF_4 (3.84×10^{-24} cm^3) to retain some of the gas molecules.[12] As discussed with zeolites X and Y, CF_4 adsorption favors adsorbents containing many cations. Although the pore opening of this adsorbent is slightly smaller than CF_4, the polarizability of this component makes it possible for CF_4 to enter the pores.

The activated carbons have moderately high K values. The weakest is the APA, which has the largest pore opening of the three samples. Due to their large surface areas and slightly polar nature,[6] activated carbons have high capacity for CF_4 gas molecules.

The ZSM-5 zeolites exhibited the highest Henry's law constants. Their pore sizes are optimal since they are slightly larger than the size of the CF_4 molecule. In addition their specific cations and SiO_2/Al_2O_3 ratio influence the adsorption. The ZSM-5-280 and ZSM-5-30 adsorbents with NH_4^+ ions perform better than HiSiv3000, which contains Na^+ ions. Since ZSM-5-280 gives higher K values than ZSM-5-30, an increase in the number of NH_4^+ ions causes an increase in adsorption. This may be the result of less pore blockage by cations. It looks like there may be an optimum SiO_2/Al_2O_3 ratio for adsorption of CF_4 among the ZSM-5 family of zeolites.

Heat of Adsorption

Van't Hoff plots for CF_4 with all the adsorbents studied are shown in Fig. 1. As predicted by Eq. (4), these plots are linear. From the Henry's law constant data, the heats of adsorption and pre-exponential constants for CF_4 and N_2 are calculated and given in Table 2. The heat of adsorption is a measure of interaction between the adsorbate gas and the solid adsorbent. The higher the heat of adsorption, the stronger is the interaction between the adsorbate and the adsorbent. For the adsorbents studied, the value of heat of adsorption, in general, follows the order of the Henry's law constant, K. The heat of adsorption is a measure of the amount of energy required to regenerate (degas) the adsorbent. For a cyclic process in which the adsorbent is reused, a high ΔH value would cause the process to be slower and more costly. The ideal adsorbent for the separation of CF_4 would have a high capacity and low heat of adsorption.

Selectivity

The selectivity indicates the ease of adsorption separation for using an adsorbent to separate one component from another. Using K values obtained for both CF_4 and N_2, the selectivity, α, is defined as:

$$\alpha = \frac{K_{CF_4}}{K_{N_2}} \tag{5}$$

The selectivity of each adsorbent as a function of inverse temperature is shown in Fig. 2. Depending on the relative values of ΔH for CF_4 and N_2, the

Table 2. Heats of Adsorption and Henry's Law Pre-exponential Constants for CF_4 and N_2 with Various Adsorbents

Adsorbent	CF_4		N_2	
	$-\Delta H$ (kJ mol^{-1})	K_0 (mol kg^{-1} bar^{-1})	$-\Delta H$ (kJ mol^{-1})	K_0 (mol kg^{-1} bar^{-1})
AA300	N/A	N/A	N/A	N/A
APA	24.0	4.04×10^{-5}	18.8	3.70×10^{-5}
BPL	25.6	4.66×10^{-5}	19.5	5.60×10^{-5}
F400	25.6	3.92×10^{-5}	19.7	4.11×10^{-5}
5A	21.8	1.13×10^{-4}	24.5	1.19×10^{-5}
NaX	21.2	7.39×10^{-5}	21.4	1.40×10^{-5}
HiSiv1000	N/A	N/A	N/A	N/A
HiSiv3000	27.9	1.78×10^{-5}	24.3	5.16×10^{-6}
NaY	19.7	9.41×10^{-5}	22.2	7.43×10^{-6}
H-Y-5.1	N/A	N/A	N/A	N/A
H-Y-80	17.4	2.18×10^{-4}	10.0	6.80×10^{-4}
ZSM-5-30	30.6	7.41×10^{-6}	22.8	1.11×10^{-5}
ZSM-5-280	25.4	7.75×10^{-5}	15.9	2.24×10^{-4}

selectivity could increase or decrease with temperature, as can be seen from this figure. An interesting observation is that adsorbents belonging to the same family perform similarly and there is no overlap between families within the temperature range studied.

Zeolites X, Y and 5A give the lowest selectivity values. For this group of adsorbents, selectivity decreases with decreasing temperature except for H-Y-80. As mentioned before, the effect of temperature on the selectivity depends on relative values of ΔH for CF_4 and N_2.

The activated carbons fall into the middle for selectivity values. Despite their high K values for CF_4, activated carbons also adsorb N_2. This results in smaller selectivity values than expected for this group of adsorbents.

The ZSM-5 zeolites have the highest selectivity values. They have high K values for CF_4 and do not readily adsorb N_2 because of its lower polarizability (1.74×10^{-24} cm^3).

Pure Component Isotherms

The pure component N_2 and CF_4 isotherms were determined outside of the Henry's law region for the three ZSM-5 zeolites and the three activated carbon adsorbents, which showed the highest selectivities among the adsorbents studied.

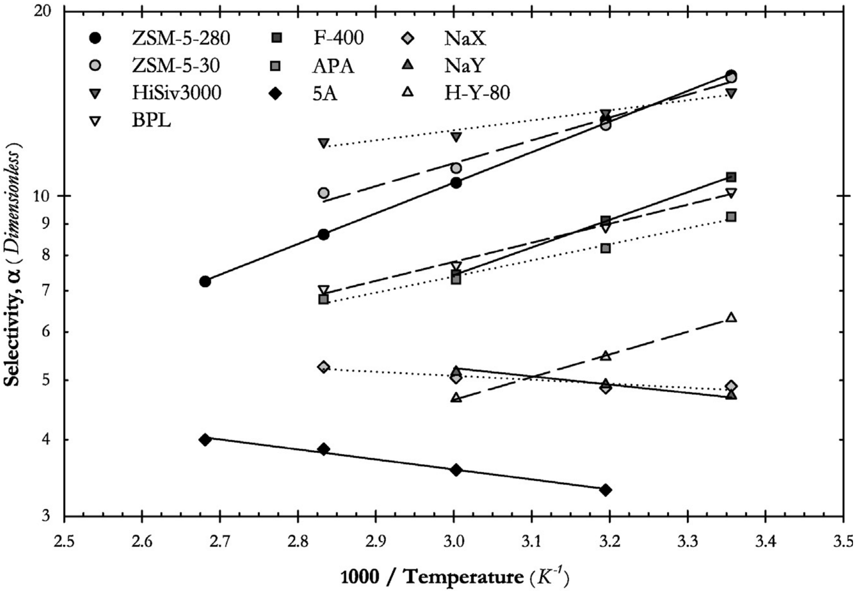

Figure 2. The selectivity of various adsorbents for $CF_4 \neq N_2$.

Using the volumetric method, isotherms for each of these top six adsorbents were determined at 23°C and are shown in Fig. 3a and b for CF_4 and N_2, respectively.

The CF_4 data were fitted to the Toth isotherm equation, which contains three parameters:

$$q = \frac{q_m BP}{[1 + (BP)^n]^{(1/n)}} \tag{6}$$

The regressed parameters (q_m, B, and n) are given in Table 3. These values were obtained at pressures up to 130 kPa. As can be seen from Fig. 3a, all the adsorbents tend to perform similarly for CF_4 adsorption, except HiSiv3000 whose capacity is relatively small at higher pressures. The ZSM-5-280 zeolite, which has the highest Henry's law constant for CF_4, has the highest capacity for this gas up to 120 kPa. At pressures up to 100 kPa, the ZSM-5-30 and ZSM-5-280 adsorbents are the best. The top adsorbent in this range is ZSM-5-280. From 110 to 130 kPa, the activated carbon F-400 isotherm approaches and intersects the ZSM-5 isotherms. The best adsorbent at pressures higher than 120 kPa is F-400 for CF_4.

The N_2 data were fitted to the two-parameter Freundlich equation:

$$q = BP^{1/n} \tag{7}$$

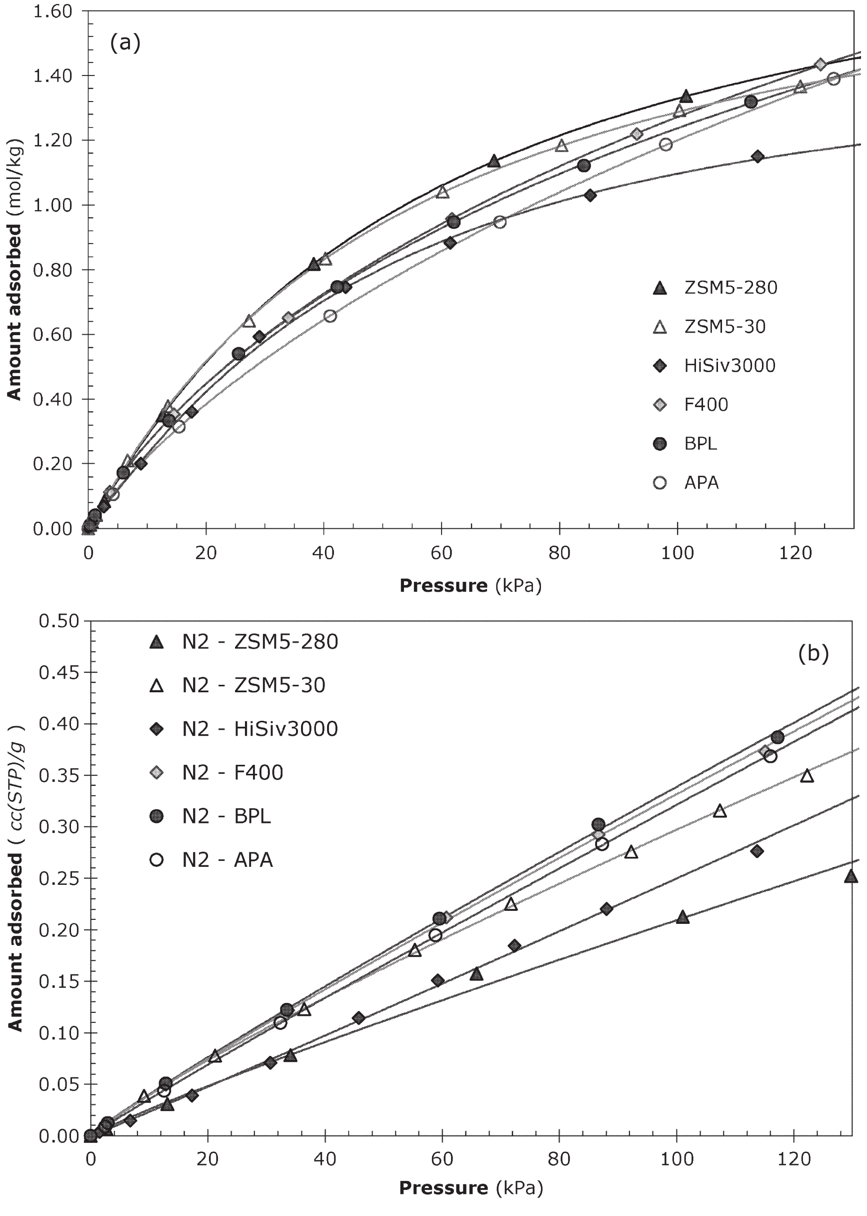

Figure 3. Experimental adsorption isotherms at 23°C: a) for CF_4, fitted to the Toth equation, b) for N_2, fitted to the Freundlich equation.

Table 3. CF_4 and N_2 Adsorption Isotherm Parameters for Pressures up to 130 kPa at 23°C

	Toth Parameters (CF_4)			Freundlich Parameters (N_2)	
Adsorbent	q_m (mol kg^{-1})	B (kPa^{-1})	n	B (mol kg^{-1} kPa$^{-1/n}$)	$1/n$
ZSM-5-280	2.01	0.0158	1.13	0.00318	0.909
ZSM-5-30	1.86	0.0173	1.16	0.00545	0.868
HiSiv3000	1.47	0.0166	1.38	0.00219	1.028
APA	12.3	0.00282	0.431	0.00395	0.955
BPL	4.85	0.00821	0.548	0.00478	0.925
F400	6.92	0.00616	0.482	0.00470	0.924

This equation is better suited than the Toth equation to fit the N_2 data, which are almost linear. The values for the Freundlich parameters (B, $1/n$) are also tabulated in Table 3 for N_2. From Fig. 3b, it can be seen that activated carbons and ZSM-5-30 adsorb N_2 to a higher degree than ZSM-5-280 and HiSiv3000.

Comparing the N_2 data with CF_4 adsorption at pressures up to 120 kPa, ZSM-5-280 zeolite has the highest capacity for CF_4 and the lowest capacity for N_2, therefore offers the best adsorption separation among the adsorbents studied under these conditions.

Adsorption Isotherms at Different Temperatures

The temperature dependence of CF_4 and N_2 adsorption isotherms was investigated for ZSM-5-30, ZSM-5-280 zeolites, and activated carbon F-400 and the results are shown in Figs. 4–6. The symbols represent the experimental data. As expected, adsorption capacity decreases as temperature is increased due to the exothermic nature of adsorption. Most of the N_2 isotherms are almost linear for all of these adsorbents. The CF_4 isotherms tend to be linear as temperature increases due to decreasing adsorption capacity.

For CF_4 gas with each adsorbent, the set of multiple temperature isotherms were fitted to the Toth equation (6) where temperature dependency of the parameters are given as:[13]

$$q_{\mathrm{m}} = q_{\mathrm{m},0} \exp\left[\chi\left(1 - \frac{T}{T_0}\right)\right] \tag{8}$$

$$B = B_0 \exp\left[\frac{Q}{RT_0}\left(\frac{T_0}{T} - 1\right)\right] \tag{9}$$

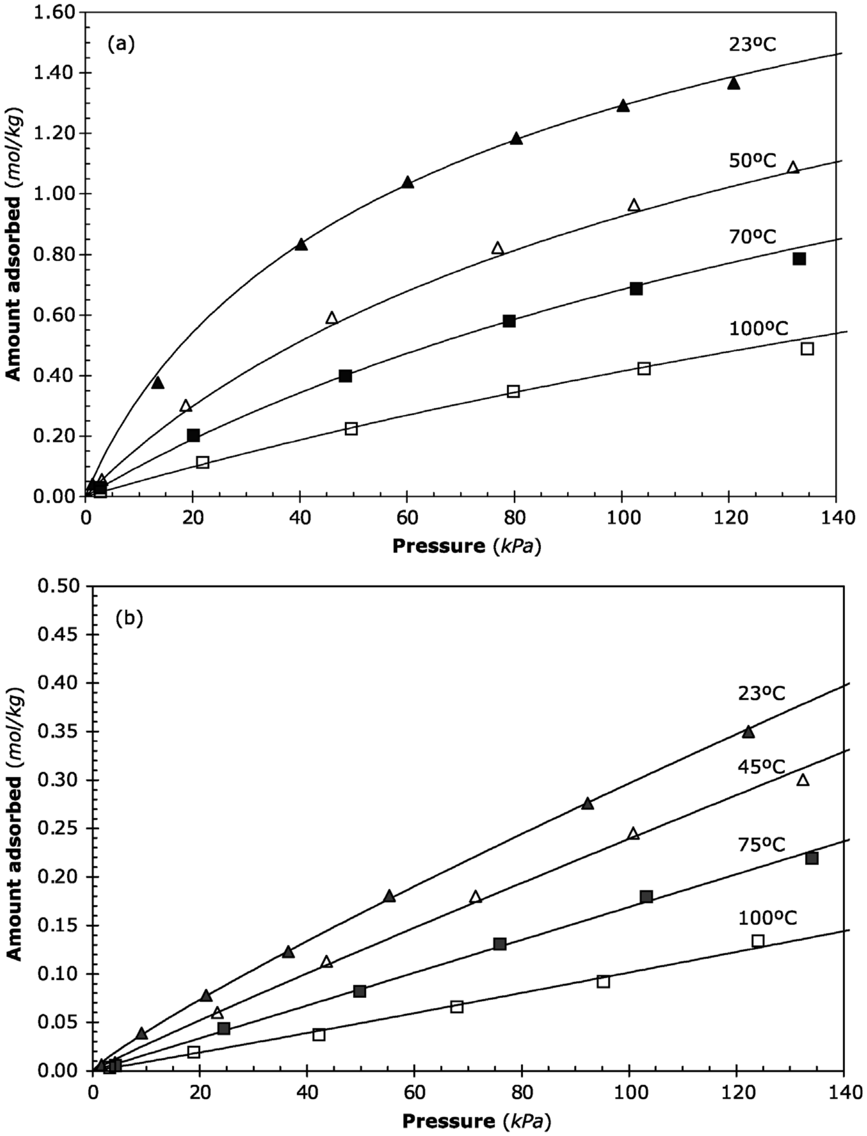

Figure 4. Experimental adsorption isotherms at various temperatures for ZSM-5-30: a) for CF_4, fitted to the temperature dependent Toth equation, b) for N_2, fitted to the Freundlich equation.

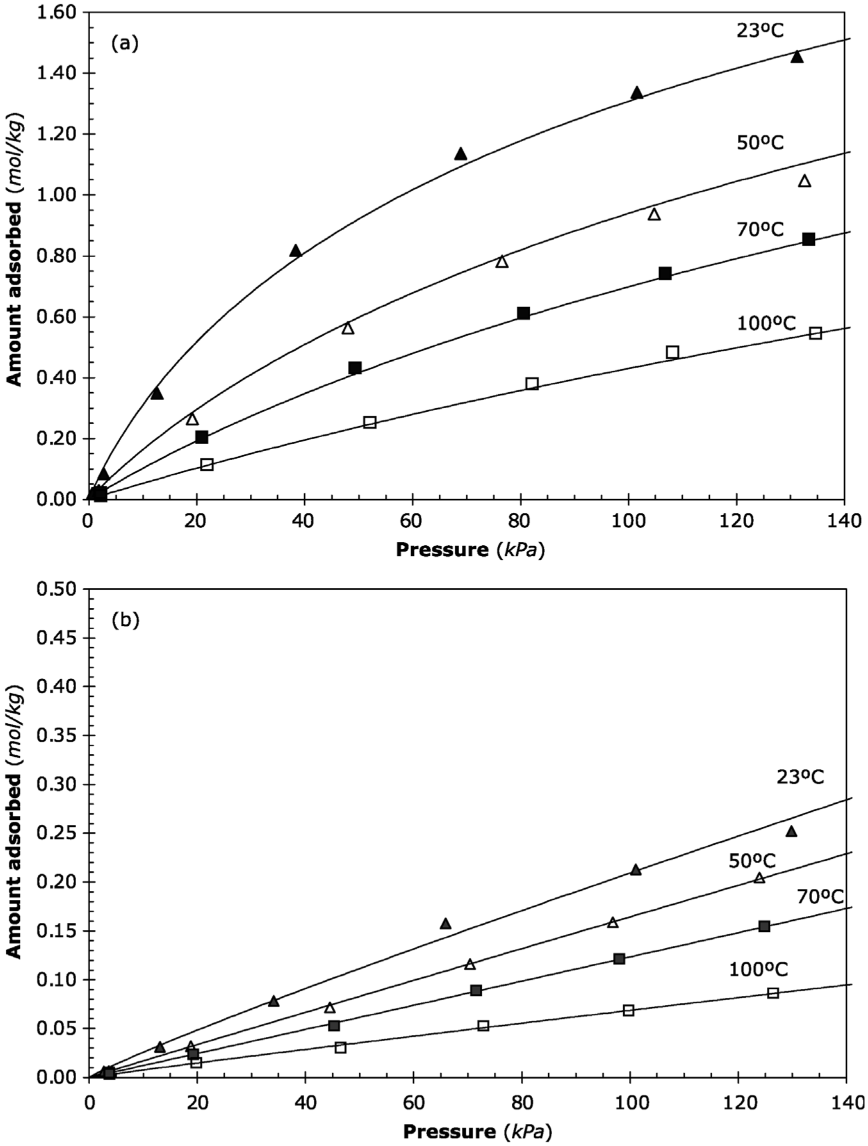

Figure 5. Experimental adsorption isotherms at various temperatures for ZSM-5-280: a) for CF_4, fitted to the temperature dependent Toth equation, b) for N_2, fitted to the Freundlich equation.

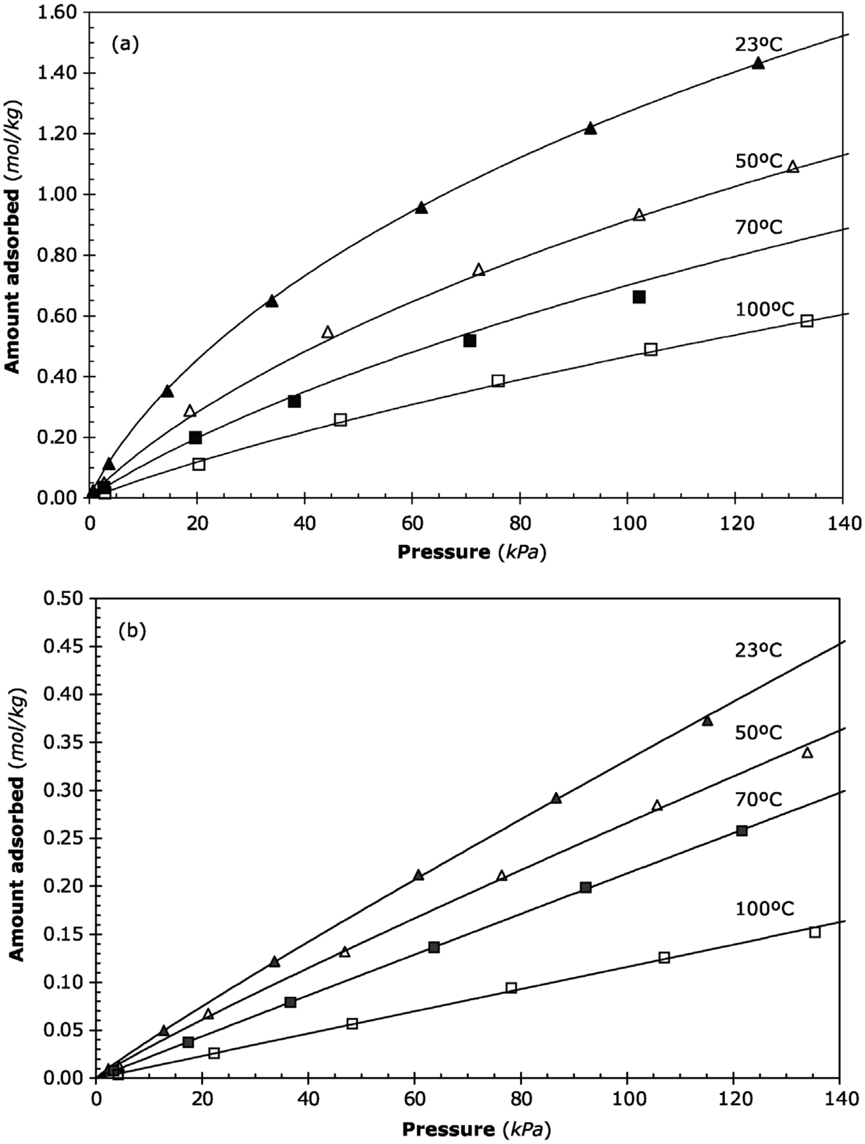

Figure 6. Experimental adsorption isotherms at various temperatures for F400: a) for CF_4, fitted to the temperature dependent Toth equation, b) for N_2, fitted to the Freundlich equation.

$$n = n_0 + \alpha\left(1 - \frac{T_0}{T}\right) \tag{10}$$

and regressed isotherms are shown in Figs. 4–6 as solid lines. The regressed values for the parameters in above equations are given in Table 4.

The CF_4 multiple temperature isotherms were well correlated by the Toth equation for ZSM-5-30, ZSM-5-280, and F-400. The regressed parameters obtained for each adsorbent were used to predict isosteres (relationship between pressure and temperature at constant amount adsorbed) that are shown in Figs. 7–9.

A comparison of three isosteres in the low-temperature region demonstrates that F-400 offers slightly higher capacity for CF_4 over the ZSM-5 adsorbents at high pressures while the reverse is true at medium pressures. All the three adsorbents demonstrate a steady decline in the amount adsorbed as the temperature is increased in the high-pressure region.

The multiple temperature isotherms were not well correlated by the Toth equation for N_2 isotherms since data are too close to the Henry's law region. Therefore, no isosteres were obtained with N_2. For this gas, the multiple temperature isotherms were each fitted to a constant temperature Freundlich equation (7). The values obtained for the parameters of this equation are given in Table 5.

When adsorption isotherms of CF_4 and N_2 are compared with ZSM-5-30, ZSM-5-280, and F-400 at different temperatures, it can be seen that CF_4 isotherms are more or less similar to each other for all these adsorbents at all the temperatures studied. On the other hand, N_2 isotherms are quite different with ZSM-5-280 having the lowest capacity, followed by ZSM-5-30 and F-400 having the highest capacity for N_2 at all the temperatures. Therefore for the adsorption separation of CF_4 from N_2, ZSM-5-280 would be the best performing one among these three adsorbents.

Table 4. Temperature Dependent Toth Equation Parameters for CF_4 Adsorption

	Adsorbents		
Parameters	ZSM-5-30	ZSM-5-280	F400
T_0 (K)	296	296	296
B_0 (kPa^{-1})	0.0179	0.0137	0.00625
Q/RT_0 (dimensionless)	10.6	10.3	9.14
$q_{m,0}$ ($mol\,kg^{-1}$)	2.56	3.42	7.53
χ (dimensionless)	0	0	0
n_0 (dimensionless)	0.734	0.625	0.453
α (dimensionless)	0.876	0.904	0.509

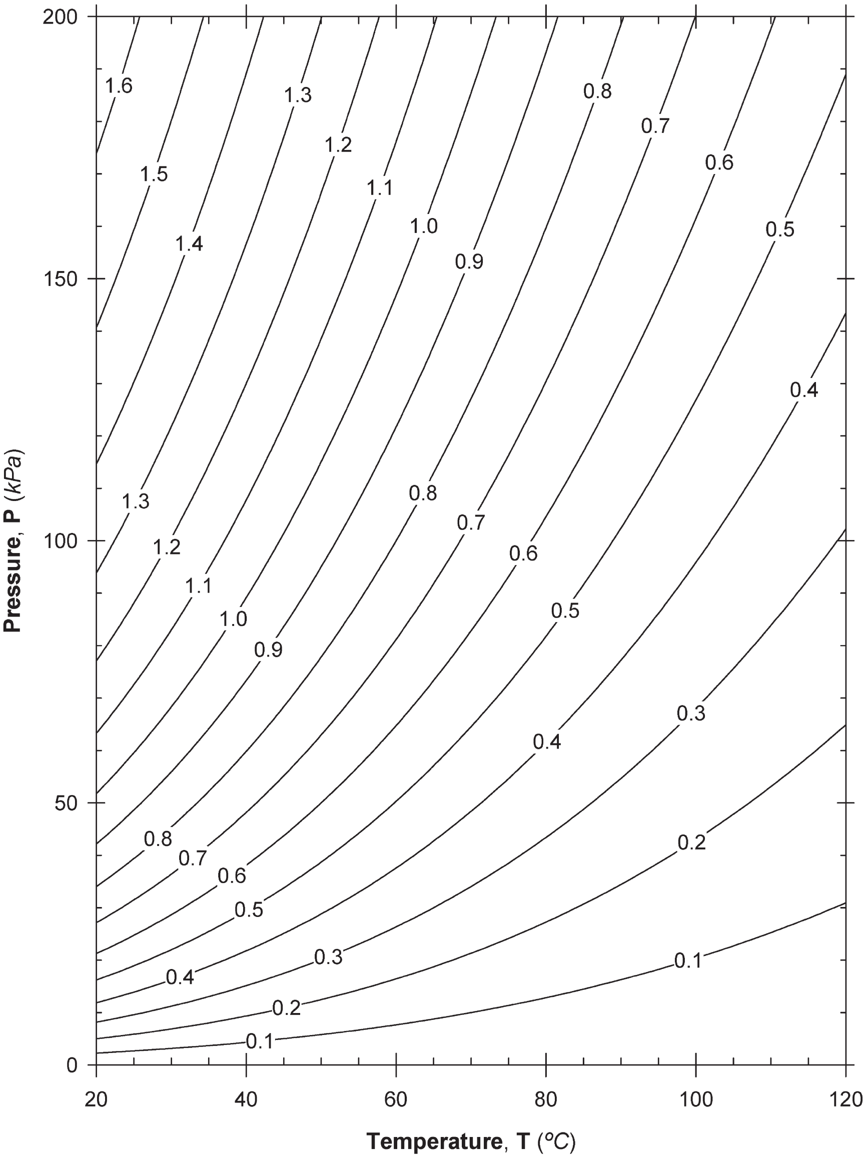

Figure 7. Adsorption isosteres for CF_4 with ZSM-5-30. Numbers on the curves indicate different amount adsorbed in *mol/kg*.

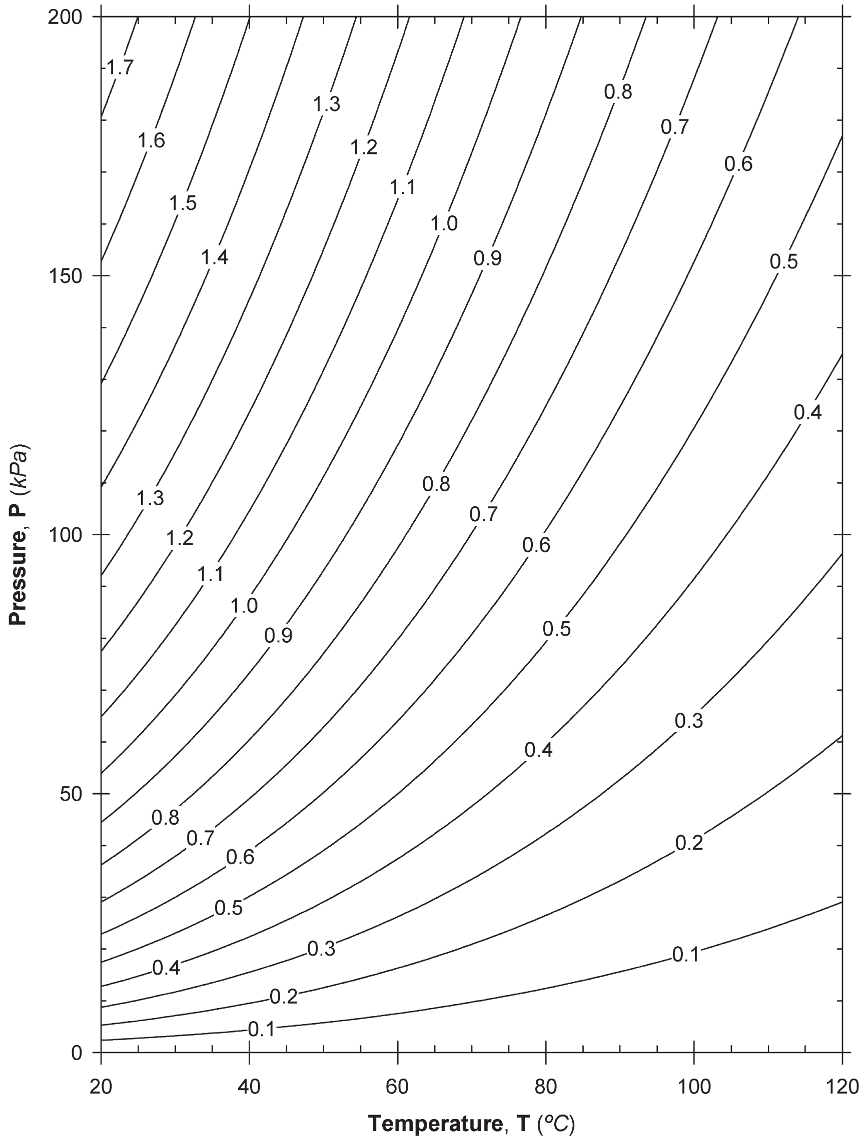

Figure 8. Adsorption isosteres for CF_4 with ZSM-5-280. Numbers on the curves indicate different amount adsorbed in *mol/kg*.

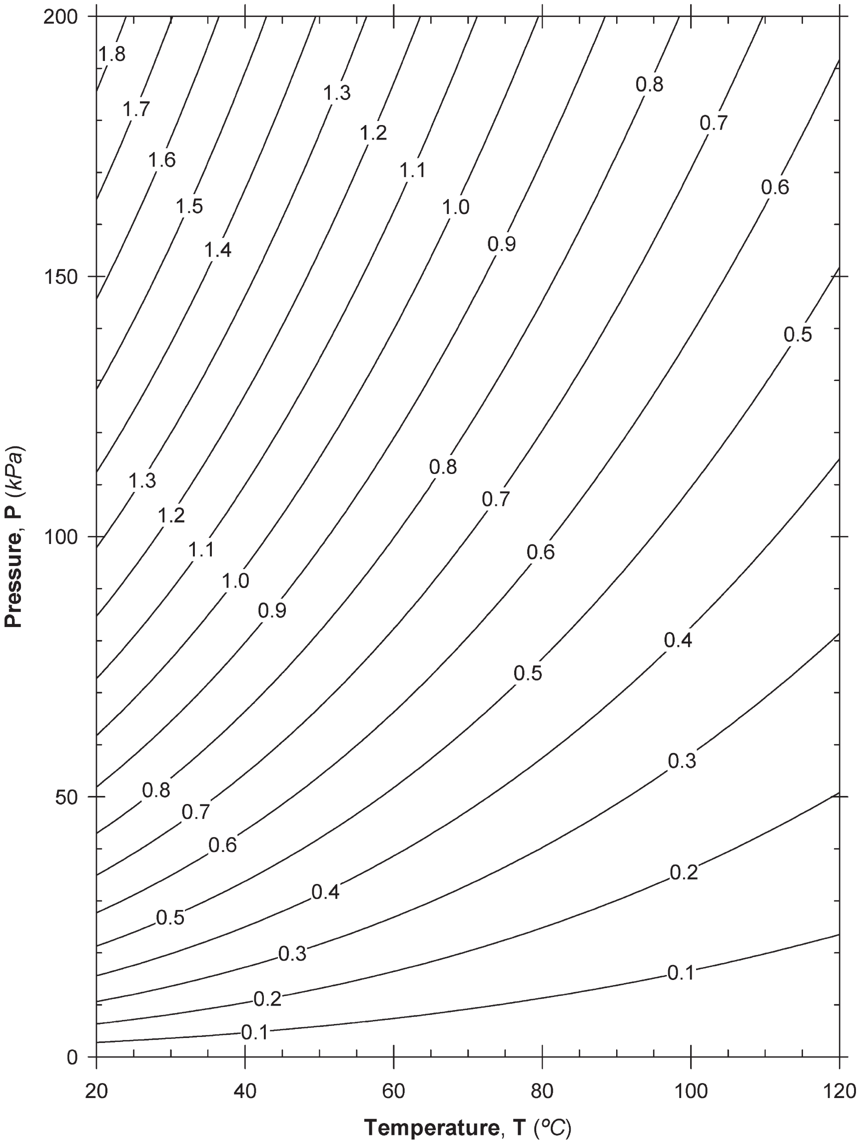

Figure 9. Adsorption isosteres for CF_4 with F-400. Numbers on the curves indicate different amount adsorbed in *mol/kg*.

Table 5. Freundlich Isotherm Parameters for N_2 Adsorption at Different Temperatures

Temperature (°C)	Adsorbents		
	ZSM-5-30	ZSM-5-280	F-400
23	$K = 0.00545\ \text{mol kg}^{-1}\ \text{kPa}^{-1/n}$	0.00318	0.00470
	$1/n = 0.868$	0.909	0.924
45	0.00306	—	—
	0.947	—	—
50	—	0.00176	0.00390
	—	0.985	0.917
70	—	0.00121	0.00227
	—	1.004	0.986
75	0.00167	—	—
	1.003	—	—
100	0.000834	0.000854	0.00117
	1.043	0.953	0.998

CONCLUSIONS

Following conclusions could be drawn from this study.

- Although activated carbons have high adsorption capacities for CF_4, their selectivities in the Henry's law region are not very good for $CF_4{-}N_2$ separation, since they also have relatively high adsorption capacities for N_2.
- The ZSM-5 zeolite adsorbents have the highest selectivities among the adsorbents studied in the Henry's law region. The ZSM-5-280 shows the highest selectivity in this region among the ZSM-5's.
- The CF_4 adsorption depends on the SiO_2/Al_2O_3 ratio for most of the adsorbents studied. For the ZSM-5 zeolites, there might be an optimum ratio for CF_4 adsorption.
- At pressures higher than the Henry's law region, adsorption capacities of ZSM-5-30, ZSM-5-280, and F-400 are quite similar for CF_4 for different temperatures that are looked at in this study. The ZSM-5-280 has the lowest adsorption capacity for N_2, among these three adsorbents, for all the pressure and temperature regions studied in this work.
- Considering the adsorption separation application of CF_4 and N_2 gases, ZSM-5-280 would be the best adsorbent to be used.

NOMENCLATURE

B	constant in Eq. (6) (kPa^{-1}) and Eq. (7) ($mol\,kg^{-1}\,kPa^{-1/n}$)
c	adsorbate concentration at column exit, measured as voltage (mV)
CPM	concentration pulse method
$-\Delta H$	heat of adsorption (kJ)
K	Henry's law constant ($mol\,kg^{-1}\,bar^{-1}$)
K_0	pre-exponential constant in Eq. (4) ($mol\,kg^{-1}\,bar^{-1}$)
L	adsorption column length (m)
n	constant in Eqs. (6) and (7) (dimensionless)
P	gas pressure (bar or kPa)
PECVD	plasma enhanced chemical vapor deposition
q	amount of gas adsorbed per unit mass of adsorbent ($mol\,kg^{-1}$)
q_m	constant in Eq. (6) ($mol\,kg^{-1}$)
R	ideal gas law constant ($8.314 \times 10^{-5}\,m^3\,bar\,mol^{-1}\,K^{-1}$ or $8.314 \times 10^{-3}\,kJ\,mol^{-1}\,K^{-1}$)
T	absolute temperature (K)
T_0	reference temperature in Eqs. (8)–(10) (K)
t	time (sec)
v	interstitial velocity ($m\,sec^{-1}$)
Greek letters	
α	selectivity ratio from Eq. (5) (dimensionless)
χ	constant in Eq. (10) (dimensionless)
ε	column porosity (dimensionless)
μ	mean retention time (sec)
ρ	adsorbent true density ($kg\,m^{-3}$)

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