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Adsorption Equilibrium Parameters of Trace Impurities

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Abstract: Atmospheric air contains various trace impurities which include oxides of nitrogen, carbon, sulphur, and light hydrocarbons. Prior to cryogenic distillation of air to produce oxygen, nitrogen, and argon, these trace impurities have to be removed since many of these compounds constitute a safety hazard in the plant. In this study, adsorption has been considered for their removal and adsorption behavior of ethylene, acetylene, nitrous oxide, acetonitrile, methyl tert-butyl ether, methyl sulfoxide, dimethyl sulfoxide, and methanol have been studied in the Henry's Law low concentration region with several different adsorbents. Adsorption equilibrium parameters have been determined with samples of Alcan pure alumina, Alcan alumina/13X composites Actiguard 600/650PC, CABSORB Chabazite, Ceca13X, and Clinoptilolite by using the concentration pulse chromatographic technique. Heat of adsorption values and van't Hoff plots have been presented.

Keywords: Activated alumina, adsorption of trace impurities, chabazite, clinoptilolite, Henry's Law constants, Zeolite 13X

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INTRODUCTION

The use of adsorption for separation processes is a growing trend in industry. Determination of equilibrium parameters and fluid solid adsorption equilibria is a crucial step in designing gas separation units. One key aspect for adsorption research is the development of new adsorbents. In this study, various adsorbents like activated alumina and zeolites were tested for a wide range of adsorbates. In addition, composite adsorbents that consist of a mixture of zeolites and alumina were also tested. Activated alumina does not possess an ordered crystal structure and consequently, the pores are nonuniform. Zeolites, on the other hand, are crystalline aluminosilicates that consist of well-defined uniform intra-crystalline pore structures in the crystal and macropores in the binder system of the formed particle (1).

The study included adsorption of commonly found impurities in the atmospheric air, feed streams for carbon dioxide purification, and cracked gas streams in refineries. Most of the problem components in the cryogenic air separation process (carbon dioxide, nitrous oxide, acetylene, ethylene etc.) boil at temperatures above oxygen. Therefore, these concentrate in the oxygen product at the bottom of the low pressure column. The trace contaminants in the oxygen cause problems ranging from operability issues (fouling, plugging, and contamination) to equipment damage, and safety incidents, caused by the reaction of hydrocarbon compounds with high purity oxygen. For these reasons, care must be taken in both the design and operation of an air separation unit to prevent the accumulation of trace components (2,3). The adsorbates are examined for Henry's Law constants since they are separated at very low concentrations. Activated alumina/zeolite composites were characterized for acetylene, ethylene, carbon dioxide, and nitrous oxide adsorption. Previous work has suggested that alumina/zeolite composites are useful for the removal of trace impurities from air (4). The composite adsorbents were further characterized for the adsorption of acetonitrile, methyl tert-butyl ether, methyl sulfoxide, dimethyl sulfoxide, and methanol as adsorbates. These tests were conducted to evaluate the efficacy of composite adsorbents for application in oxygenated species removal from various gas streams (e.g. carbon dioxide).

THEORY

A dynamic method of analysis was used to characterize and study the adsorbents based on adsorption equilibria. The chromatographic method can be used in several ways: step change, tracer gas, and pulse

chromatography. The concentration pulse chromatographic technique is an attractive adsorbent screening method since it is relatively fast and requires an inexpensive set up. This method was used in the present study to determine the Henry's Law constants and heats of adsorption of the systems studied. It is less cumbersome than other unsteady state techniques commonly used, namely gravimetric and volumetric methods (5–17).

Equilibrium parameters are derived by matching the first moment of the response peak of the column packed with the adsorbent to an impulse change in concentration, at the inlet of the column. To ensure the validity of these calculations, the process has to be governed by physical adsorption (i.e. no chemisorption); else the column containing the adsorbent cannot be considered for concentration pulse chromatography technique. Under these circumstances, the signal of the detector is proportional to the adsorbate concentration which is recorded against time at the exit of the column. From this response peak, the first moment of the chromatogram μ, is determined experimentally using the Simpson's approximation (6). The first moment is directly related to the Henry's Law constant and determined knowing the experimental set up values. Dimensionless Henry's Law constants can be calculated from the corrected first moments of the response peaks (corrected with respect to the dead time of the system, μ_D) as shown in Equation 1 (10,15):

$$\mu = \frac{\int_0^\infty c(t-\mu_D)dt}{\int_0^\infty cdt} = \frac{L}{v}\left[1 + \frac{(1-\varepsilon)K}{\varepsilon}\right] \tag{1}$$

where t is the time, c is the adsorbate concentration measured at the outlet of the column, L is the column length, ε is the bed porosity, v is the interstitial fluid velocity, K is the dimensionless Henry's Law adsorption equilibrium constant, and μ_D is the system dead time.

The dimensionless Henry's Law constant, K can be converted to a dimensional constant, K_p using Equation 2:

$$K_p(Dimensional) = \frac{K(Dimensionless)}{RT_\rho} \tag{2}$$

where T is the absolute temperature, ρ is the density of the adsorbent, and K_p is the dimensional Henry's Law adsorption equilibrium constant. By determining K_p values at different temperatures, a van't Hoff plot can be constructed and the heat of adsorption, ΔH can be determined based on equation 3:

$$\ln K_p = \ln K_o - \frac{\Delta H}{RT} \tag{3}$$

The heat of adsorption values for these systems can be used as a pre-screening tool. For bulk separation applications using pressure swing adsorption, adsorbents that exhibit high heat of adsorption are less suitable. The bulk gas separation has significant heat effects associated with the exothermic physical adsorption due to large amount of the feed being adsorbed, which could lead to significant rise in temperature within the PSA column. Since the adsorption capacity of an adsorbent decreases with the rise in temperature for a physical adsorption process, this temperature rise decreases the efficiency of the overall process. However, for trace removal applications, since the percentage of the feed that is adsorbed is very low, heat effects are minimal even with high heat of adsorption systems. Also, if a temperature swing adsorption (TSA) process is used, the regeneration can be complete even for systems with high heat of adsorption.

EXPERIMENTAL METHOD AND MATERIALS

A schematic diagram of the experimental apparatus is given in Fig. 1. Measurements were made in a Varian 1400 series Gas Chromatograph equipped with a thermal conductivity detector and a sample injection valve. Column specifications and operating conditions are given in Table 1. The dead volumes between the sample injection valve, column and detector were minimized by using stainless steel piping of minimum volume (1/16″). The dead time, μ_D between the sample injection valve

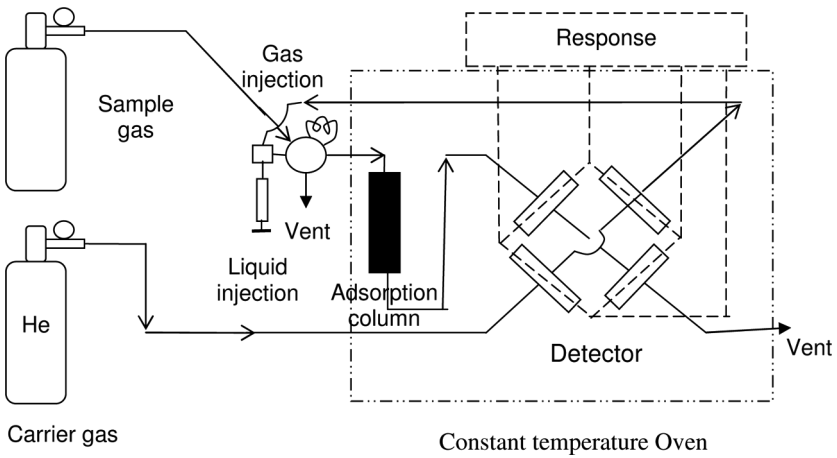


Figure 1. Apparatus used in the study of adsorption of pure gases.

and detector was calculated at room temperature under fixed carrier gas flow rate by measuring the mean of the response peak produced when a gas sample pulse was passed through the column containing glass beads of the same size as the adsorbent. All experimental means of the response curves were corrected by subtracting the corresponding system dead time.

A sample pulse at atmospheric pressure was injected into the helium carrier gas stream and sent to the adsorption column packed with the adsorbent. The column was fully contained in the chromatographic oven for accurate temperature control. Two injection ports were used, one for gas injection and the second for liquid injection. The column temperature was maintained at a constant temperature higher than the liquid adsorbate boiling temperature in order to ensure gas phase adsorption and isothermal operation. Henry's Law constants and heat of adsorption values were determined using Equations 1–3. Gas sampling, monitoring, and analysis of response peaks were carried out through LABVIEW data acquisition system which ensured accurate detection of the sample introduction time. Carrier gas velocities were controlled with an MKS digital mass flow controller followed by verification with bubble meter measurements at the column exit. The bed porosity was determined using a constant volume system, by measuring the volume of a packed chromatographic column of glass beads of same size with helium gas.

Before starting the experiments, the packed column was regenerated under helium purge for 24 hours. This ensured that any impurities or moisture adsorbed from air did not hinder the adsorption capacity of the adsorbent. With the same reasoning, a carrier gas of helium flowed continuously through the system for purging between experimental runs. The experimental details are outlined in Table 1. Table 2 gives details on adsorbents used in this study while carrier and sample gases are listed in

Table 1. Experimental specifications used with concentration pulse method

Carrier gas:	Helium
Column length:	13.19 cm
Column inner diameter:	0.45 cm
Carrier gas flow rate:	8–75 cc/min
Regeneration temperature:	548–573 K (275–300°C)
Regeneration time with He purge:	24 Hours
Column Temperature	323–573 K (50–300°C)
Detector Temperature	Column temperature + 40°C
Particle size:	20–60 mesh (0.0246–0.0833 cm)
Bed porosity:	0.35
Total Pressure	1 atm
Thermal Conductivity Bridge Power	100 mA

Table 2. Adsorbent specifications

Commercial name	Commercial number	Shape	Size	Supplier
Alcan Activated Alumina	AA-300	Spherical	20 × 60 mesh	RioTinto Alcan, Brockville, Canada
Alcan Activated Alumina composites	Actiguard 600PC (x% 13X and y*% activated alumina) x < y*	Spherical	20 × 60 mesh	RioTinto Alcan, Brockville, Canada
	Actiguard 650PC (x%13X and y % activated alumina) x < y	Spherical	20 × 60 mesh	RioTinto Alcan, Brockville, Canada
Zeolite X (Si/Al = 1.25)	Ceca G5-13 X	Spherical	20 × 60 mesh	CECA Specialty Chemicals Inc., Honfleur, France
Chabazite (Si/Al = 0.15)	CABSORB	Spherical	20 × 60 mesh	GSA Resources Inc., Cortaro, Arizona, USA
Clinoptilolite (Si/Al = 0.2)	Ash Meadows Clinoptilolite	Spherical	20 × 60 mesh	American Resource Corp, Amargosa Valley, Nevada, USA

*More 13X when compared to Actiguard 600PC (i.e. $y^* < y$).

Table 3. Carrier and sample gas specifications (18)

Name	Purity	Dipole moment (Debye)	Polarizibility $\times 10^{24}$ cm^3	Quadrupole moment (cm^2)	Supplier
Helium (Carrier)	99.999%	0	0.20	–	Praxair Inc., Ottawa, Canada
Carbon dioxide	99.9%	0	2.91	-14.9×10^{-40}	Praxair Inc., Ottawa, Canada
Acetylene	99.9%	0	3.93	4.87×10^{-40}	Praxair Inc., Ottawa, Canada
Ethylene	99.97%	0	4.25	4.37×10^{-40}	Praxair Inc., Ottawa, Canada
Nitrous oxide	99.9%	0.16	3.03	1.6×10^{-34}	Praxair Inc., Ottawa, Canada
Methyl sulfoxide	99.9%	—	—	—	Fisher Scientific Company, Ottawa, Canada
Acetonitrile	99.8%	3.92	4.40	—	Sigma Aldrich Canada Ltd., Oakville, Canada
Dimethyl sulfoxide	99.3%	3.96	—	—	Fisher Scientific Company, Ottawa, Canada
Methyl tert-butyl ether	99.0%	—	10.68	—	Commercial alcohols Inc., Toronto, Canada
Methanol	99.8%	1.70	3.29	—	Fisher Scientific Company, Ottawa, Canada

Table 3. Henry's Law constants were determined for acetylene, ethylene, carbon dioxide, and nitrous oxide with all the adsorbents studied. Alcan Actiguard 600PC and Alcan Actiguard 650PC adsorbents were further characterized with acetonitrile, methanol, methyl tert-butyl ether, dimethyl sulfoxide, and methyl sulfoxide.

RESULTS AND DISCUSSIONS

Equilibrium Data

Henry's Law constants were calculated based on Equations 1 and 2 using the first moment of the response peaks for all the adsorbents studied at various temperatures. These results are summarized in Figs. 2a–c as van't Hoff plots. From the slope of these plots the heat of adsorption values were calculated using the van't Hoff equation (Equation 3).

Alcan AA-300 Activated Alumina Adsorbent

This adsorbent is the base activated alumina obtained from RioTinto Alcan. The Henry's Law constants obtained for acetylene, ethylene, and nitrous oxide for Alcan AA-300 alumina adsorbent in the temperature range of 50–150°C (323–423 K) are plotted against inverse temperature in Fig. 2a–c, respectively. Results showed that as the temperature of the column increased, the first moment and the Henry's Law constant decreased as expected, since physical adsorption is an exothermic process. Acetylene was much more strongly adsorbed compared to ethylene and nitrous oxide which was due to the highly active triple bond structure of the acetylene molecule. Acetylene is an air impurity that must be removed prior to cryogenic distillation owing to its low solubility in liquid oxygen. When present in sufficient quantities, it can plug the equipment and pipes. Also, acetylene is a flammable component and its presence in oxygen constitutes a safety hazard within the cryogenic plant. Acetylene results were not plotted in Fig. 2a at the low temperatures of 50 °C and 75°C (323 K and 348 K) since the peaks obtained were too wide to have an accurate first moment determination. The heat of adsorption values, van't Hoff parameters and corresponding R^2 values for Alcan AA-300 Activated Alumina are given in Table 4 for acetylene, ethylene, and nitrous oxide. The heat of adsorption value for acetylene was much higher than that of the double-bonded ethylene followed by nitrous oxide. This is due to the dual effect of a triple bond and a quadrupole

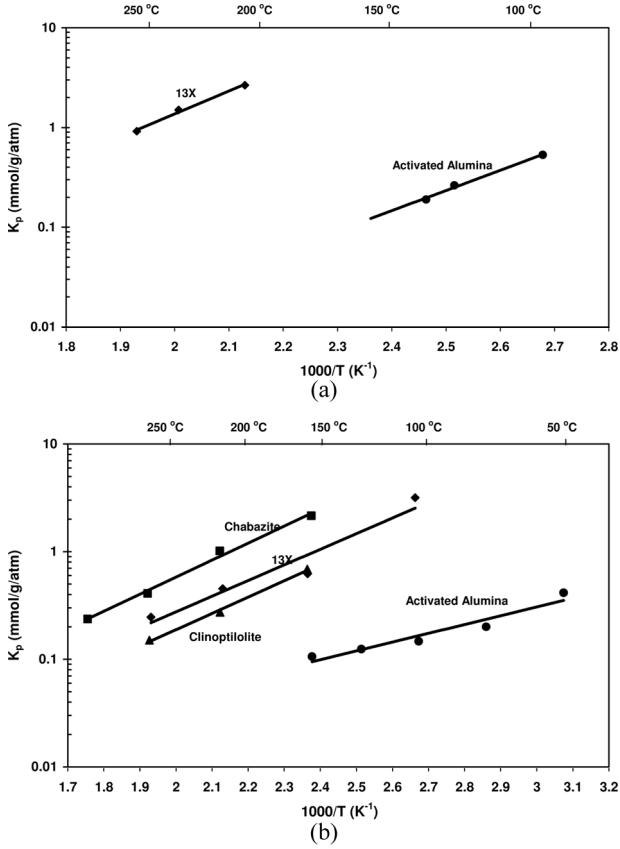
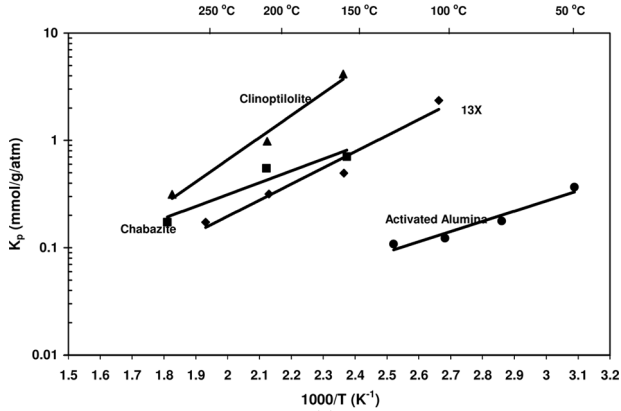


Figure 2. (a) Henry's Law constants as van't Hoff plots for Acetylene with Alcan AA-300 activated alumina and Ceca G5-13X adsorbents; (b) Henry's Law constants as van't Hoff plots for Ethylene with Alcan AA-300 activated alumina, CABSORB Chabazite, Ceca G5-13X and Ash Meadows Clinoptilolite adsorbents; (c) Henry's Law constants as van't Hoff plots for nitrous oxide with Alcan AA-300 activated alumina, CABSORB Chabazite, Ceca G5-13X and Ash Meadows Clinoptilolite adsorbents.

moment that acetylene has, which causes it to be much more interactive with the adsorbents (induced dipole between the alumina surface and the π electron system of acetylene).

A carbon dioxide peak was not present for any of the temperatures tested. This comes from the fact that carbon dioxide is very strongly adsorbed in pure activated alumina (19,20). Since the peak widens as the adsorption capacity increases for the concentration pulse chromatographic technique, it was impossible to quantify the carbon dioxide peaks.



(c)

Figure 2. Continued.

Table 4. Heat of adsorption, van't Hoff parameter and sum of squares data for all adsorbents

Adsorbent	Adsorbate	ΔH (cal/mol)	R^2
Alcan AA-300	Acetylene	7846	0.9518
	Ethylene	5180	0.9650
	Nitrous oxide	4322	0.9416
CABSORB Chabazite	Ethylene	7236	0.9929
	Nitrous Oxide	5050	0.9152
Ceca G5-13X	Acetylene	10600	1
	Ethylene	7203	0.9202
	Nitrous oxide	6880	0.9565
Alcan Actiguard 600PC	Acetylene	10666	1
	Ethylene	5838	0.9997
	Nitrous oxide	4721	0.9894
	Methyl sulfoxide	9325	0.9259
	Dimethyl sulfoxide	7783	0.8209
	Methanol	9679	0.9901
	Methyl t-Butyl ether	5558	0.9706
	Acetonitrile	9657	0.9513
Alcan Actiguard 650PC	Acetylene	12353	1
	Ethylene	6501	0.9996
	Nitrous oxide	5902	0.9541
	Methyl t-Butyl ether ether	18194	1
Ash Meadows Clinoptilolite	Ethylene	6930	0.9961
	Nitrous oxide	9471	0.9833

CABSORB CHABAZITE ADSORBENT

This adsorbent was obtained from GSA Resources Inc. and was tested with acetylene, nitrous oxide, and ethylene in the temperature range 150 to 300°C (423–573K). The corresponding van't Hoff plots and parameters for ethylene and nitrous oxide for CABSORB Chabazite are shown in Figs. 2b, 2c and Table 4.

As can be seen from these results, the heat of adsorption values and Henry's Law constants for this adsorbent are much higher than those for Alcan AA-300. The experiments had to be carried out at higher temperatures compared to the AA-300 Alcan Activated Alumina adsorbent to get accurate values of the Henry's Law constants. When the adsorption capacity is very high, (i.e. when the adsorbate is very strongly adsorbed, especially at low temperatures for the adsorbates studied), the first moment of the peak, μ, becomes very large (see equation 1) and the peak widens quite a bit, making it impossible to accurately identify the peak separately from the baseline. Acetylene peaks were not observed even at these high temperatures and was likely very strongly adsorbed. Ethylene had a higher K_p value at all temperatures tested and a higher ΔH value than nitrous oxide with this adsorbent due to its double bond structure which showed more interaction with the adsorbent.

CECA G5-13X ADSORBENT

This is the base 13X zeolite adsorbent obtained from CECA Specialty Chemicals Inc. The Henry's Law constant values obtained for this adsorbent with acetylene, ethylene and nitrous oxide in the temperature range of 100 to 250°C (373–523 K) are plotted as a function of inverse absolute temperature in Figs. 2a–c respectively. The corresponding van't Hoff parameters are given in Table 4. Acetylene peaks were only included at temperatures greater than 200°C (473 K), due to much stronger adsorption at lower temperatures. Acetylene had the highest Henry's Law constants and the heat of adsorption values among the adsorbates studied for this adsorbent, due to the dual effect of its triple bond and its quadrupole moment. Due to the more interactive nature of the 13X adsorbent, the K_p values for acetylene, ethylene, and nitrous oxide were higher when compared to Alcan Activated Alumina. The heat of adsorption values, van't Hoff plot parameters and the R^2 values for each of the adsorbates are given in Table 4. Ethylene had a slightly higher heat of adsorption value when compared to nitrous oxide due to the presence of double bond in its structure.

ASH MEADOWS CLINOPTILOLITE

This is the base adsorbent obtained from the American Resource Corp. The Henry's Law constant plots for Ash Meadows Clinoptilolite with ethylene and nitrous oxide are shown in Figs. 2b and 2c for the temperature range of 150–250°C (423–523 K). Results indicated that as the temperature of the column increased, Henry's Law constants decreased, which is consistent with exothermic physical adsorption. Carbon dioxide and acetylene peaks were not observed at the temperatures tested for reasons of very strong adsorption. When the results for nitrous oxide and ethylene are compared with this adsorbent, it was observed that Henry's Law constants as well as the heat of adsorption values for ethylene were much smaller than those for nitrous oxide for all the temperatures tested. ICP analysis on the Ash Meadows Clinoptilolite, showed that a large number of divalent Ca^{++} ions were present within the structure. When the zeolite has divalent cations in its structure, rather than monovalent cations, its surface becomes more heterogeneous, since the positive and negative ion pockets on the surface are less frequent and are more concentrated. This heterogeneity of the surface makes it more attractive to polar molecules. Since nitrous oxide has a much higher quadrupole moment compared to ethylene, as well as a dipole moment, it is not surprising to see higher K_p and heat of adsorption values for this adsorbate. Higher K_p values for nitrous oxide at low temperatures make Clinoptilolite a possibly useful adsorbent for nitrous oxide trace impurity removal from ambient air. The heat of adsorption for ethylene with Clinoptilolite was not very different than that for other adsorbents as can be seen in Table 4.

ALCAN ACTIGUARD 600PC ADSORBENT

This is a composite of Alcan activated alumina and Ceca 13X adsorbent obtained from Rio Tinto Alcan. For all temperatures tested, a carbon dioxide peak was not observed at all, since this adsorbent contained some activated alumina in which carbon dioxide is known to be chemisorbed. The results for Alcan Actiguard 600PC with all the other adsorbates studied for temperature range of 150–300°C (423–573 K) are shown as van't Hoff plots in Fig. 3. Corresponding heat of adsorption data are given in Table 4. Henry's Law constants could not be obtained at low temperatures studied, since some of the adsorbates were very strongly adsorbed. This caused an unusual widening of the response peak at lower temperatures, decreasing the precision of the calculations to unacceptable levels.

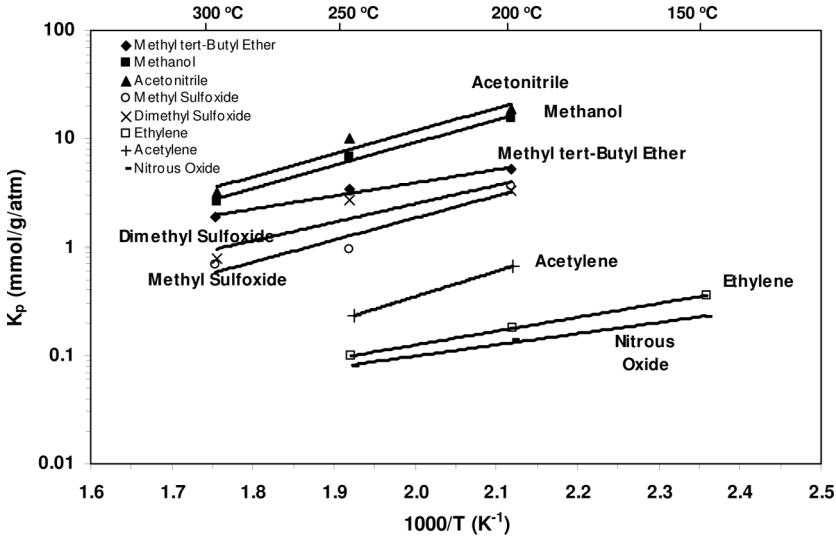


Figure 3. Henry's Law constants for acetonitrile, methanol, methyl tert-butyl ether, methyl sulfoxide, dimethyl sulfoxide, acetylene, ethylene, and nitrous oxide impurities for Alcan Actiguard 600PC adsorbent.

Acetonitrile had the largest K_p values among the adsorbates studied, owing to its triple bond structure and a higher dipole moment of 3.92 Debye. Methanol being a polar molecule (dipole moment of 1.7 Debye) had greater attraction to the heterogeneous polar composites followed by the double bonded methyl tert-butyl ether, dimethyl sulfoxide, and methyl sulfoxide. The Henry's Law constant values were inversely proportional to the column temperatures as mentioned earlier for other adsorbents. Acetylene was more strongly adsorbed than ethylene and nitrous oxide by Alcan Actiguard 600PC and CECA G5-13X adsorbents.

Based on the results from Table 4, acetylene had the highest and nitrous oxide had the lowest heat of adsorption values for Alcan Actiguard 600PC. Methanol, acetonitrile, and methyl sulfoxide had similar ΔH values in the range of 9300–9600 cal/mol, followed by lower ΔH values for dimethyl sulfoxide, ethylene, and methyl tert-butyl ether in decreasing order.

ALCAN ACTIGUARD 650PC ADSORBENT

This is a composite adsorbent obtained from Rio Tinto Alcan which contains a higher composition of Ceca 13X within the Alcan activated

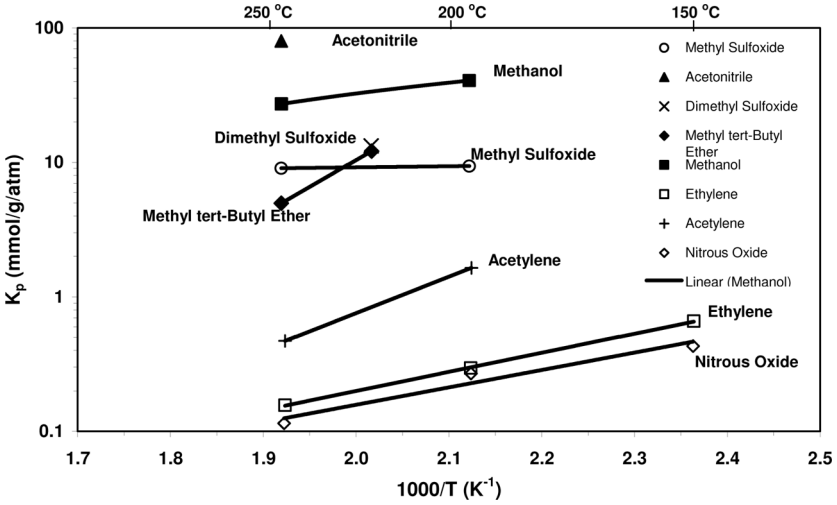


Figure 4. Henry's Law constant results for acetonitrile, methanol, methyl tert-butyl ether, methyl sulfoxide, dimethyl sulfoxide, acetylene, ethylene and nitrous oxide impurities for Alcan Actiguard 650PC adsorbent.

alumina adsorbent compared to Alcan Actiguard 600PC. Carbon dioxide peaks for this adsorbent were not observed at the temperatures tested for the same reasons mentioned with the discussion of the Alcan Actiguard 600PC adsorbent. The corresponding van't Hoff plots and their parameters in the temperature range of 150–250°C (423–523 K) are given in Fig. 4 and Table 4, respectively. Alcan Actiguard 650PC was a much better adsorbent compared to Alcan Actiguard 600PC, as well as Alcan AA-300 with much higher Henry's Law constants for all the adsorbates studied. This is expected, since Alcan Actiguard 650PC contains more 13X than Alcan Actiguard 600PC. As listed in Table 2, both of the Actiguard adsorbents contain 13X zeolite as well as regular activated alumina. Since 13X showed higher Henry's Law constant values compared to Alcan AA-300 alumina, the higher the composition of 13X in the structure of the adsorbent, the higher would be the Henry's Law constant. The order of the Henry's Law constants for all the adsorbates was the same as Alcan Actiguard 600PC, except for methyl tert-butyl ether which had a higher ΔH than acetylene.

COMPARISON OF ALL ADSORBENTS TESTED

The comparison of all the six different adsorbents studied in this paper can be seen in Fig. 5. Based on their Henry's Law constant values at

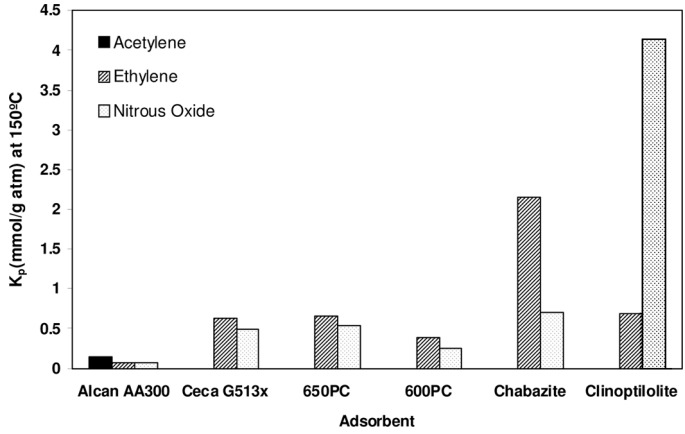


Figure 5. Comparison of Henry's Law constant results for acetylene, ethylene and nitrous oxide impurities at 150°C for adsorbents, Alcan AA-300, Alcan Actiguard 600PC, 650PC, Ceca G5-13X, CABSORB Chabazite, and Ash Meadows Clinoptilolite.

423 K (150°C), at which temperature we were able to get the most data, CABSORB Chabazite had the highest Henry's Law constant for ethylene and nitrous oxide adsorption except for Ash Meadows Clinoptilolite. The adsorbent Alcan AA-300 alumina showed the lowest Henry's Law constant values for these gases.

The order of heat of adsorption for ethylene, nitrous oxide, and acetylene for tested adsorbents is shown below:

Ethylene: CABSORB Chabazite > Ceca G5-13X > Ash Meadows Clinoptilolite > Alcan Actiguard 650PC > Alcan Actiguard 600PC > Alcan AA-300 alumina

Nitrous oxide: Clinoptilolite > Ceca G5-13X > Alcan Actiguard 650PC > CABSORB Chabazite > Alcan Actiguard 600PC > Alcan AA-300 alumina

Acetylene: Alcan Actiguard 650PC > Alcan Actiguard 600PC > Ceca G5-13X > Alcan AA-300 alumina

In this study, composite adsorbents were also tested to determine the effect of the zeolite percentage in activated alumina, on the Henry's Law constants for the gas adsorbates. The results observed on Alcan Alumina, Ceca G5-13X zeolite, Alcan Actiguard 600PC and 650PC are shown in Fig. 6 at 150°C (423 K). As can be seen from this figure, the composite with a higher percentage of zeolite in its structure gave the highest

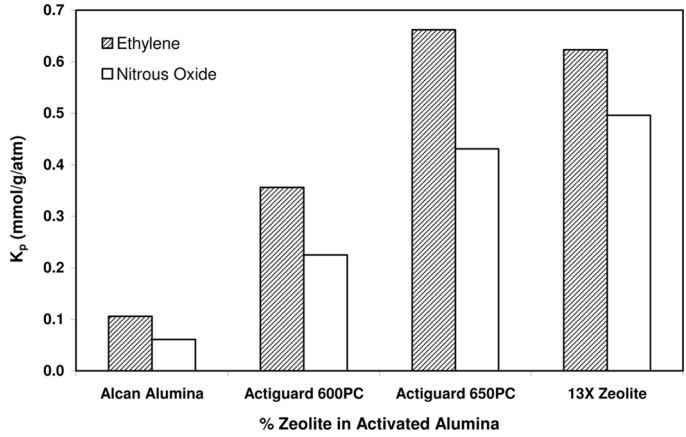


Figure 6. The affect of zeolite in activated alumina adsorbent for ethylene and nitrous oxide Henry's Law constants for adsorption at 150°C (423 K).

Henry's Law constant values for ethylene, even compared to the pure zeolite. These results suggest that there is a linear relationship between the amount of zeolite in the composite adsorbent and the Henry's Law constant for the composites, but when the pure zeolite is taken into account, the relationship is non-linear. For nitrous oxide adsorption, this relationship is linear, even when the pure zeolite is included.

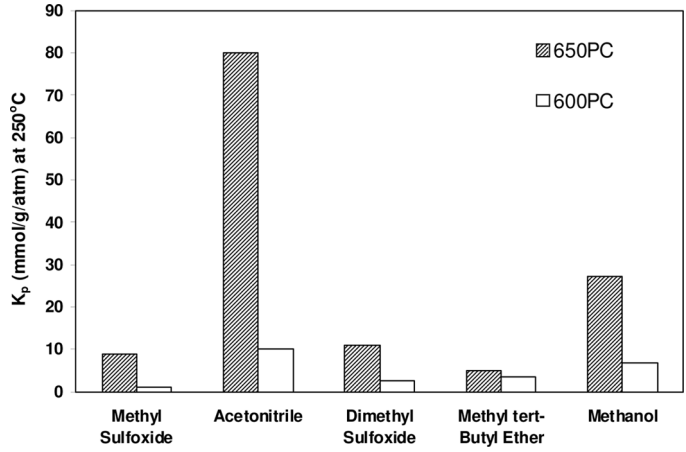


Figure 7. Comparison of the adsorption Henry's Law constants at 250°C for Alcan Actiguard 650PC and 600PC for five trace impurities studied.

A comparison of Alcan Actiguard 600PC and 650PC adsorbents for methyl sulfoxide, acetonitrile, dimethyl sulfoxide, methyl tert-butyl ether and methanol impurities at 250°C (523 K) are given in Fig. 7. Results suggested that Alcan Actiguard 650PC which has a higher ratio of 13X zeolite to activated alumina in the adsorbent structure showed greater affinity for adsorption and thus higher K_p values for all these adsorbates, compared to Alcan Actiguard 600 PC. The difference between these two adsorbents was much higher for the triple bonded acetonitrile and the highly polar methanol.

CONCLUSIONS

This study showed the order of Henry's Law constants and heats of adsorption for six different adsorbents and for various impurity gases. The adsorbents screened included Alcan AA-300 activated alumina, activated alumina/13X zeolite composites (Alcan Actiguard 600PC and 650PC), CABSORB Chabazite, 13X zeolite (CECA G5-13X), and Ash Meadows Clinoptilolite adsorbent. Henry's Law constants measured were inversely proportional to the absolute temperature of the system, which validated the application of the van't Hoff equation. Based on K_p and heat of adsorption values, Chabazite had the highest capacity and interaction with ethylene and Clinoptilolite had the highest capacity and interaction with for nitrous oxide. Alcan AA-300 alumina had the lowest K_p values and heat of adsorption for nitrous oxide and ethylene. For acetylene adsorbate, the value of heat of adsorption was the highest for the composite Alcan Actiguard 650PC, and the lowest for the Alcan AA-300 alumina. All these tested adsorbents find applications in the trace impurity removal from air. The present work gives basic guidelines on adsorbents that can be used to target specific impurities present in air.

The study on the effect of 13X zeolite addition into activated alumina composite adsorbent showed that a higher ratio of 13X zeolite to activated alumina present in the Alcan Actiguard 650PC adsorbent structure gave higher K_p values for ethylene. It was also observed that a higher composition of 13X zeolite in the composite exhibits a higher adsorption capacity, compared to both pure 13X zeolite and pure activated alumina adsorbents which indicated a combined effect between these adsorbents for the adsorption of ethylene.

The results with other impurities, acetonitrile, methanol, dimethyl sulfoxide, methyl sulfoxide, and methyl tert-butyl ether also showed that Alcan Actiguard 650PC was also better than Alcan Actiguard 600PC in removing them. This observation can be tied to the compositions of the hybrid adsorbents.

For Alcan AA-300 alumina, Alcan Actiguard 650PC and 600PC, carbon dioxide peaks were not observed at the temperatures tested since they contained activated alumina, which is known to chemisorb carbon dioxide.

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NOMENCLATURE

c	Sorbate Concentration in bulk phase (mol/cm^3)
K	Average Henry's Law adsorption equilibrium constant (dimensionless)
K_0	Pre-exponential factor (mol/g/atm)
K_p	Average Henry's Law adsorption equilibrium constant (mol/g/atm),
L	Length of the chromatographic column (cm)
R	Gas constant (cal/mol/K)
R^2	Coefficient of determination
t	time (s)
T	Absolute Temperature (K)
v	Interstitial fluid velocity (cm/s)
Greek Letters	
ΔH	Heat of adsorption at low coverage (cal/mol)
ε	Porosity of the bed (dimensionless)
μ	First moment (s)
μ_D	System dead time (s)
ρ	Density of the adsorbent (g/cc).
Abbreviations	
GC	Gas Chromatograph
He	Helium gas
ICP	Inductively Coupled plasma spectrometry
PSA	Pressure swing adsorption

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