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TRACE CONTAMINANT STUDIES OF HSC ADSORBENT

by

DENNIS TZYY-NIAN YIEH

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DENNIS TZYY-NIAN YIEH

A THESIS SUBMITTED IN PARTIAL
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Houston, Texas

December, 1978

ABSTRACT

TRACE CONTAMINANT STUDIES OF HSC ADSORBENT

by

Dennis Tzyy-nian Yieh

The adsorption and desorption of fifteen trace contaminants on HSC (polyethylenimine coated acrylic ester) adsorbent have been experimentally investigated with the following two objectives: 1) To test the removal potential and the adsorption reversibility of the selected trace contaminants, 2) to test the effect a preadsorbed trace contaminant has on the CO_2 adsorption capacity.

The experimental method for acquiring the adsorption equilibrium data used in this study is based on the volumetric (or displacement) concept of facuum adsorption.

From the experimental results, it has been found that the HSC adsorbent has good adsorption potential for contaminants of alcohol compounds, ester,s and benzene compounds; whereas, adsorption of ketone compounds, oxidizing and reducing agents are detrimental to the adsorbent. In addition, all 'liquid' contaminants reduce the CO_2 capacity of HSC adsorbent.

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CHAPTER 1

INTRODUCTION

1.1 Background

The buildup of contaminants from sources like metabolic processes, material degradation, off-gassing of materials, leaks, and scientific experiments in the enclosed atmospheres of manned spacecraft must be controlled by a suitable contaminant removal system, particularly for missions of extended duration.

For the early missions of Space Shuttle and Spacelab programs, the atmospheric control system (or Air Revitalization System) contains two or more lithium hydroxide (LiOH) canisters for carbon dioxide (CO_2) and odor removal, and a condensing heat exchanger (CHX) for removal of sensible heat and moisture. The material in the LiOH canisters and the CHX are also responsible for removing the trace contaminants (1,2,8).

However, the adsorption of CO_2 on LiOH is non-regenerable, since LiOH chemically reacts with CO_2 to form a solid carbonate (1). Therefore, the use of LiOH for removing CO_2 requires storage of sufficient LiOH canisters to last through an entire mission. When weight requirements in space flights become critical, such a system is only practical for short missions. In addition, the use of a CHX to control humidity is also a relatively inefficient process since cabin air must be cooled below its dew point (1,2). Consequently, the use of some kind of

regnerable enclosed atmospheric control system is logically indicated for extended manned space missions.

During the development of Space Shuttle and Spacelab program, a new vacuum regenerable type of atmospheric control system has been proposed and developed for missions of extended duration. This system uses an adsorbent called HS-C (a polyethylenimine coated acrylic ester) to adsorb both CO_2 and H_2O simultaneously (1,2,6). The adsorption of CO_2 and H_2O is reversed when the HS-C bed is exposed to vacuum at ambient temperature. One distinct characteristic of this adsorbent is that the presence of water in the adsorbent greatly enhances the adsorption capacity for CO_2 (6).

Due to the polyethylenimine's broad reaction capability, the HS-C adsorbent has also been proposed to serve as a trace contaminant remover (1, 6). Preliminary tests and studies have shown that the HS-C adsorbent indeed has adsorption potential for a variety of compounds. It is the intention of this thesis work to evaluate the overall trace contaminant removal potential of this HS-C adsorbent by acquiring the adsorption equilibrium data of selected trace contaminants. The experimental procedure for acquiring the adsorption equilibrium data used in this study was developed by Lawrence Kissinger (6). The experimental technique is based on the volumetric or displacement concept of vacuum adsorption.

1.2 Research Objectives

This research work was divided into two segments:

1. to test the removal potential and the adsorption reversibility of 15 selected contaminants,

2. to test the effect a preadsorbed trace contaminant has on the CO_2 adsorption capacity.

It is hoped that this experimental study will provide the basic equilibrium adsorption data to define the adsorption capacity of HS-C adsorbent for the 15 selected trace contaminants, and also to draw a preliminary classification of the contaminants as HS-C adsorbent a) poison or b) inert or c) potential active substance that could be removed from the atmosphere by the system.

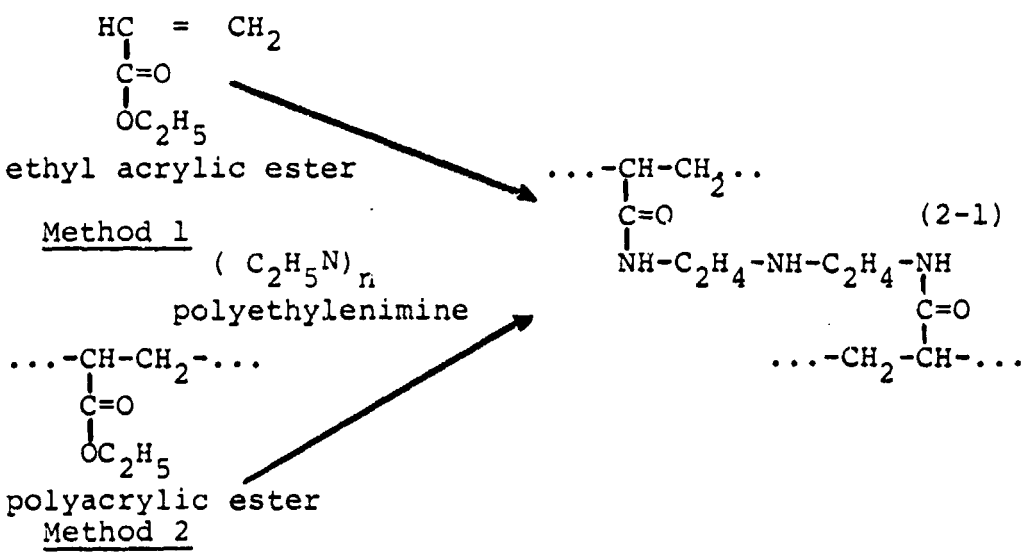
CHAPTER 2

PROPERTIES OF ADSORBENT AND ADSORBATES

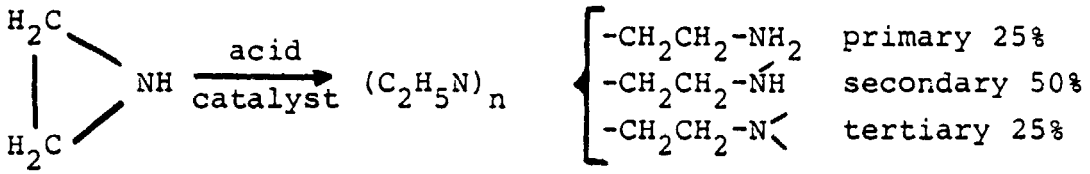
2.1 Properties of HS-C Adsorbent

HS-C is a designated name of a synthetic organic resin adsorbent, which is made from acrylic esters by adding with about 20% by weight of polyethylenimine (PEI) (6). The process of synthesizing this adsorbent was developed by Hamilton Standard Division of United Technologies Corporation. The polyethylenimine used is Dow PEI-18 (3).

Generally, there are two methods of synthesizing this kind of polyamine resin adsorbent. The first method consists of introducing polyethylenimine during the polymerization of acrylic esters, and the second method consists of first forming crosslinked polymeric esters and then subsequently introducing the polyethylenimine into the hard polymer structure (5,7). The reaction of these two methods may be represented as (5):



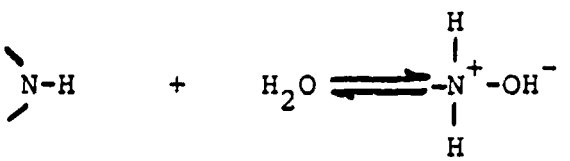
Polyethylenimine is a highly branched polyamine produced by the acid-catalyzed polymerization of the monomer, ethylenimine (3):



(2-2)

The polymer consists of units which have two carbon per nitrogen. These units are randomly distributed in the approximate ratios of one primary amino nitrogen/two secondary amino nitrogens/one tertiary amino nitrogen. These primary, secondary and tertiary amino nitrogens are responsible for the slight basicity of HS-C adsorbent, as well as its polyfunctional property.

The chemical properties of HS-C adsorbent are primarily governed by the presence of weak-base amino groups in the polymer. When HS-C adsorbent is contacted with water, the amino nitrogens react with the solvent to form positively charged nitrogens in the same manner as simple amines (3,6).



(2-3)

However, while simple amines dissolve into the water, the HS-C adsorbent does not dissolve. The adsorbent takes up the water and expands. The swelling goes to a limited

degree; when equilibrium is attained, the swelling does not proceed any further. This characteristic is particularly true for ion-exchange resins (5). Thus, HS-C adsorbent is actually a type of synthetic organic ion-exchange with weak-base amino groups: called weak-base anion exchanger.

Like any other synthetic organic resins, the frame work or matrix of the HS-C adsorbent is a flexible random network, which is made up of interconnecting hydrocarbon chains of the crosslink polymers (5). As a result, the mesh size or pore size of the adsorbent is not uniform; this is referred to as "heteroporosity". The average pore diameter of anhydrous HS-C adsorbent is 0.015 microns, and the net pore volume is 0.42 c c/gm. (6). The HS-C adsorbents are in the form of white spherical beads about 0.5mm in diameter.

The HS-C adsorbent has good chemical and thermal stability when compared to other organic anion exchange resins (3). However, HS-C adsorbent shows signs of thermal degradation when it is heated above 60°C for a prolonged period (6). It also experiences chemical degradation in the presence of strong oxidizing or reducing agents. Generally, oxidation is the main contributing factor in the degradation of the synthetic organic resins at high temperatures in air (3).

Although HS-C adsorbent is a type of synthetic organic ion-exchange resin, the adsorption process of

of anhydrous HS-C adsorbent with gaseous adsorbates is simply physical. However, in the presence of water, the HS-C adsorbent becomes ionized as described in reaction 2-3. The adsorption of ionized HS-C adsorbent with acidic adsorbates is a type of weak-base ion-exchange. For example, the adsorption of carbon dioxide on water loaded HS-C adsorbent is represented as the following reaction (6):

$$-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N^{+}}}-OH^{-} \quad + \quad CO_2(g) \rightleftharpoons -\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N^{+}}}-HCO_3^{-} \qquad (2\text{-}4)$$

Since the amino groups in the HS-C adsorbent are primarily responsible for the adsorbent active sites, it is possible to make a preliminary prediction of the adsorption preference of HS-C adsorbent from the solubility table of polyethylenimine(PEI-18) at room temperature, as shown in Table 2-1 (3). By reviewing the solubility table, it may be predicted that the HS-C adsorbent has adsorption potential for solvents like alcohols, glycols, benzene and toluene, whereas it may react with solvents like carbon tetrachloride, chloroform and acetone. The validity of these predictions will be discussed in Chapter 4 on Results and Interpretation of Adsorption Data.

2.2 Properties of Selected Trace Contaminants

Fifteen compounds were selected for the contaminant adsorption study. These compounds are divied into two

groups:

1) Liquid - compounds which are in liquid state at room conditions,

2) Gaseous - compounds which are in gaseous state at room conditions.

The physical properties of the two groups of compounds are listed in Table 2-2 and 2-3, respectively.

TABLE 2-1 Solubility of PEI at Room Temperature

Solvent Type	Solvent	Solubility in H_2O*	PEI6	PEI12	PEI18	in Water Solution PEI600
Highly Polar Solvents	Water	∞	∞	∞	∞	∞
	dimethylformamide	∞	S	S	S	S
	dimethylacetomide	∞	S	S	S	S
	methanol	∞			S	S
	isopropyl alcohol	∞	S	S	S	S
	n-propyl alcohol	∞			S	S
	ethyl alcohol	∞			S	S
	n-butyl alcohol	7.9^{20}			S	1
	propylene glycol	∞	S	S	S	S
	glycerine	∞	S	S	S	S
	ethylene glycol	∞			S	S
	triethylene glycol	∞	S	S	S	S
Hydrocarbon Solvents	benzene	$.082^{22}$	S	S	S	
	toluene	$.047^{16}$	S		<10g/100g	
	xylene	I	<22.7g/100g	<5.2g/100g	<4.4g/100g	
	turpentine	I	I	I	I	
	n-hexane	$.0138^{15.5}$				
	kerosene	I	I	I	I	
	naptha	I			I	
Hydrocarbon Oils	oleic acid	I			I	
Esters	ethyl acetate	8.6^{20}	S		<10.9g/100g	

Continued...

* Lange's Handbook of Chemistry S Soluble I Insoluble

∞ Soluble in all proportions

Chlorinated Solvents	methylene chloride	2^{20}	Reacts	Reacts	Reacts
	chloroform	I^{15}	Reacts	Reacts	Reacts
	carbon tetrachloride	$.08^{20}$	Reacts	Reacts	Reacts
	perchloroethylene	I	Reacts	Reacts	<2.3g/100g
	CHLOROTHENE**NU	I	Reacts	Reacts	Reacts
Ethers	diethyl ether	7.5^{20}	I	I	I
	tetrahydrafuran	V.S.	S	S	<75g/100g
Ketones	acetone				crosslinks on standing

I Insoluble S Soluble V.S. Very soluble

** Trademark of the Dow Chemical Company

Table 2-2 Selected Physical Properties of 'Liquid' Trace Contaminants

Contaminant	Molecular Weight	Melting Point °C., 1 atm.	Vapor Pressure at 25°C (torr)	Boiling Point °C., 1 atm.	Critical Pressure (atm.)	Critical Temperature (°C)
Methanol	32.04	- 93.9	114.9	64.96	79.2	239.4
Acetone	58.08	- 95.35	201.6	56.2	46.9	235.6
Methyl Acetate	74.08	- 98.1	187.2	57.0	46.3	233.7
Iso-butanol	74.12	-108	12.7	108.4	45.2	271.0
Benzene	78.12	5.5	73.1	80.1	49.0	289.4
Toluene	92.15	- 95	27.0	110.6	41.7	320.4
Freon 11 (Trichlorofluoro-methane)	137.37	-111.1	718.4	23.82	43.9	198

Table 2-3 Selected Physical Properties of Gaseous Trace Contaminants

Contaminant	Molecular Weight	Melting Point °C., 1 atm.	Vapor Pressure at 25°C (atm.)	Boiling Point °C., 1 atm.	Critical Pressure (atm.)	Critical Temperature (°C)
Methane	16.04	-182.5	--	-167	46.5	- 82.3
Ammonia	17.03	- 77.7	9.74	- 33.4	113.1	132.4
Carbon monoxide	28.01	-205.1	--	-191.5	35.68	-140.2
Ethylene	28.05	-169.2	--	-103.7	50.2	9.5
Hydrogen sulfide	34.08	- 85.5	21.20	- 60.7	90.4	100.38
Nitrogen dioxide	46.01	- 11.2	0.98	21.2	100.6	158.0
Methyl mercaptan (Methanethiol)	48.11	-123	1.68	6.2	72.6	196.8
Freon 23 (Trifluoromethane)	70.01	-155.2	--	- 82.0	48.1	25.9

CHAPTER 3

THE MEASUREMENT OF ADSORPTION ISOTHERMS

The experimental method used in acquiring the adsorption equilibrium data in this experimental work is based on the procedure developed by Kissinger (6) for his adsorption study of CO_2 and H_2O on HS-C adsorbent. A detailed description of this technique may be obtained from the reference cited previously. In this chapter, however, a brief description of the experimental measurements of adsorption isotherms for the selected trace contaminants are presented.

3.1 Basic Concepts

A volumetric (or displacement) method was used in the measurement of adsorption equilibria for this experimental study. The principle underlying this method is the determination of amount of adsorbate adsorbed by means of experimentally measured pressures using the ideal gas law for the gas phase (6,11). The evaluation of the amount adsorbed is determined from pressure measurements in an apparatus of the type shown schematically in Fig. 3-1. Initially, the pressure, volume and temperature of a quantity of adsorbate is measured and the number of moles present is calculated. This material is then brought into contact with the adsorbent and, when constant pressure reading shows the system to have attained equilibrium, the number of moles present is again calculated. The

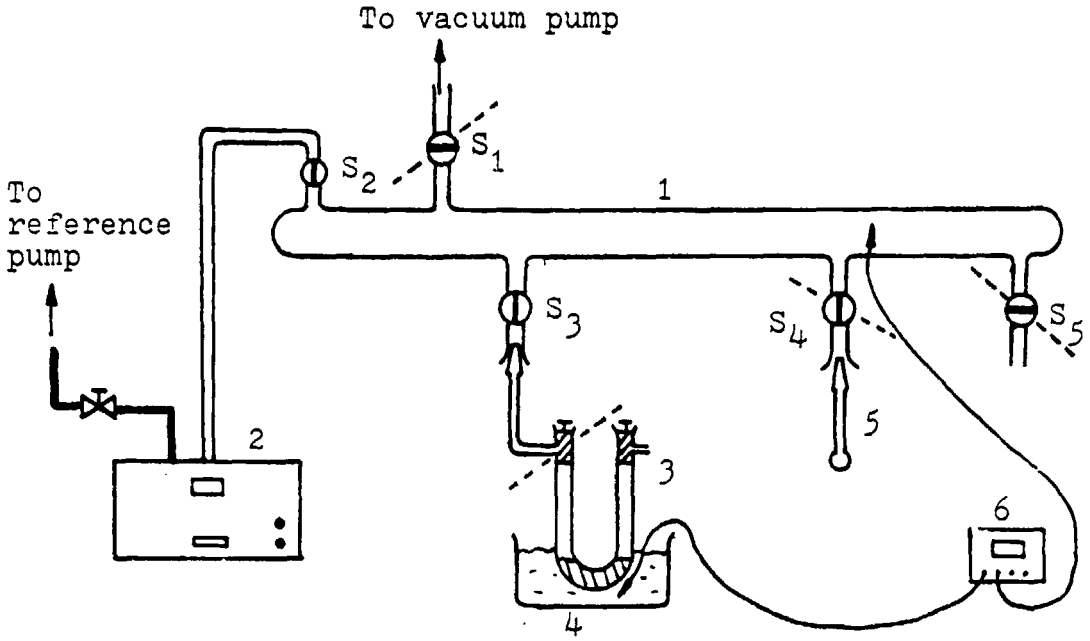


Fig. 3-1 Schematic Diagram of Volumetric Adsorption System: 1) Manifold Volume, V_1, 2) Pressure Gage, 3) Adsorbent Tube, 4) Constant Temperature Bath, 5) Liquid Contaminant Source Tube, 6) Temperature Recorder

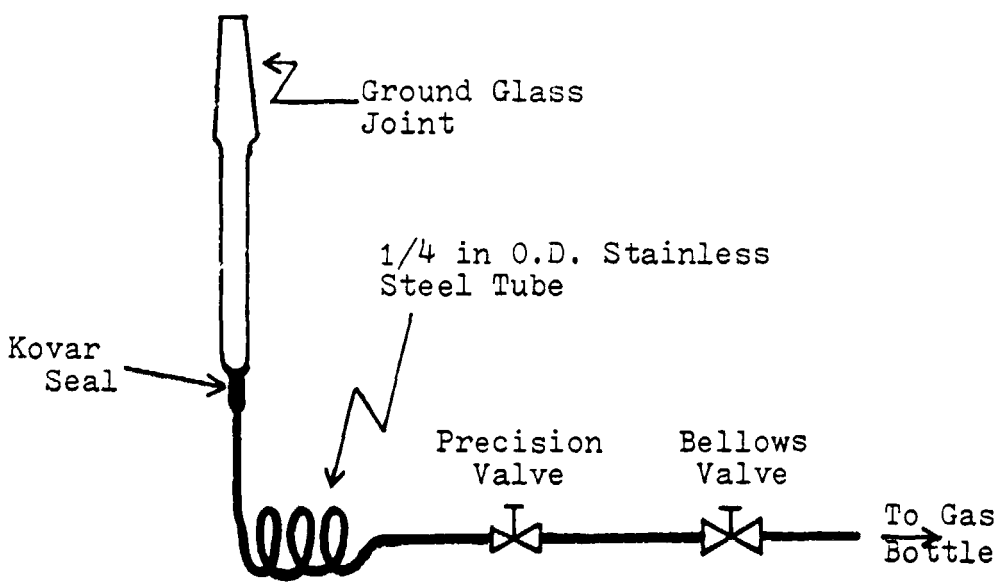


Fig. 3-2 Schematic Diagram of Gaseous Contaminant Source Connecting Tube

difference represents the amount adsorbed. The actual experimental procedures of this adsorption study and the algorithm of evaluating the amount adsorbed are described in section 3.3.2 and 4.1, respectively.

The accurate determination of the number of moles unadsorbed at equilibrium depends on a precise knowledge of the manifold system and 'dead-space' (space surrounding the adsorbent particles) (10,11). This volume is evaluated by expansion measurements using helium. The calibration procedures for evaluating manifold system and dead-space volumes are presented in Appendix A.

The amount adsorbed, A, is conveniently plotted vs the equilibrium pressure, P, at a specified temperature, T, to give an adsorption isotherm,

$$A = f(P)_T \qquad (3\text{-}1)$$

3.2 Experimental Apparatus

The volumetric system apparatus is shown schematically in Figure 3-1. This system consisted of four functional parts: a manifold system of known volume, V_1, an adsorbent bed of known dead-space volume in a constant-temperature bath, a precision pressure gage and an adsorbate dosing device.

The manifold system was made of pyrex glass tubing, fitted with high-vacuum stopcocks for the connections to other devices.

The adsorbent bed was a drying U-tube with ground glass joints added to its ends. On one end of the tube, a capillary tube 2 mm i.d. and 15.25 cm long was placed between the ground glass joint and the U-tube. This end of the tube was designed specifically for the co-adsorption study, because the capillary tube minimizes counter diffusion of adsorbate previously adsorbed on the adsorbent. The adsorbent bed was maintained at constant temperature by a constant-temperature water bath.

The adsorbate pressure was measured by a Texas Instrument Precision Pressure Gage of model 145-01, which had been calibrated. The result of pressure calibration is shown in Appendix D.

The dosing device for adsorbates from liquid state was simply a glass tube with a ground glass joint on one end and sealed on the other end. For gaseous adsorbates a special device was used to connect the high pressure gas source to the manifold system. This connecting device is shown schematically in Figure 3-2. The device consisted of a ground glass joint on one end of the tube and a stainless steel tube of 1/4 in. O.D. with several coils which connected to the ground glass joint. There were two control valves fitted on the stainless steel tube, one was a needle valve for precise control of the amount of adsorbate to the manifold system, and the other was a screw-type bellow valve for controlling gas flow from the gas bottle.

Two Welch Duo-Seal (Model 1402) vacuum pumps were used in this adsorption system. One pump provided a vacuum for the adsorption system, and the other pump provided a vacuum for the capsule of the pressure gage to serve as a reference pressure. The ultimate vacuum pressure of these two pumps were monitored by the pressure thermocouple gage. The ultimate vacuum achieved in this adsorption system was in the range of 10 to 20 microns of Mercury.

3.3 Experimental Procedures

3.3.1 Adsorbent Sample Preparation

Before any accurate measurement of an adsorption isotherm, the HS-C adsorbent sample must be thoroughly outgassed at an elevated temperature. For initial HS-C adsorbent outgassing, two grams of sample were carefully weighed out in air and placed in the adsorbent tube. The tube was then inserted into the manifold system and exposed to a vacuum. The bed temperature was then raised to 45°C in a constant-temperature water bath. (The 45°C temperature had been previously determined as the maximum allowable temperature for outgassing HS-C adsorbents without degradation, see reference 6.) The outgassing was continued until no further evolution of gas occurs. Outgassing was considered as complete when, heating of the sample with the adsorption system closed off from the vacuum pump, the vacuum pressure in the adsorption system remained constant after a long period of time. The result might be achieved in an

hour or it might take several hours depending on the kind of adsorbates previously adsorbed in the adsorbent. After the out-gassing process had been completed, the adsorbent bed temperature was set to the desired value.

3.3.2 Adsorption and Desorption of Pure Contaminants

The procedure for determining the amount of gas adsorbed in the apparatus (Figure 3-1) is based on the principles described in Section 3.1 if the equilibrium pressure is attained. For adsorbents which have significant internal diffusion resistances like HS-C adsorbent, a long adsorption time is required for equilibrium. The combined results of system leakage and counter diffusion may become detrimental to the accurate measurement of adsorption isotherms during these lengthy adsorptions. By taking pressure versus time data during adsorption, it is possible to extrapolate to the equilibrium pressure after a reasonable test time (6). Sample calculations for extrapolating equilibrium pressure are presented in Appendix B.

To determine an adsorption isotherm for pure contaminants, first, the adsorbent bed was prepared as described in Section 3.3.1. After the bed temperature was adjusted to the desired value at which the experiment was to be run, it was allowed to reach thermal equilibrium at that temperature for at least 20 minutes before any adsorption data were taken. Next, the manifold system was flushed two or three times with adsorbate vapor.

This procedure ensured that all trapped air was removed from the dosing device and provided the manifold system with a background of that adsorbate to be studied. After the manifold system was closed off from the vacuum pump, the adsorbate vapor was slowly admitted to the manifold by cracking stopcock no. 4 (Figure 3-1) until the desired adsorbate pressure was reached. Then, the ground glass cock of the adsorbent bed was opened and the stopclock was started simultaneously. The system pressure was recorded every two hundred seconds until the pressure change was less than 0.1 mm Hg or the total time reached six hundred seconds. The adsorbent bed was then closed off and the manifold pressure was increased to the next desired value. The last three steps were repeated until the desired isotherm was completed.

The experimental procedures for measuring desorption isotherms are roughly the reverse of adsorption procedures. In measuring the desorption isotherms, the preadsorbed adsorbents with known amount adsorbed and known adsorbate equilibrium pressure were exposed to the evacuated manifold system until the total system pressure became constant. The pressure was then recorded and the manifold was evacuated again for the next desorption point. These steps were repeated until a desired desorption isotherm was obtained. The sample calculations for desorption data are given in Appendix C.

3.3.3 Co-adsorption of Trace Contaminants and CO_2

The apparatus used for determining co-adsorption isotherms was the same as that described in Section 3.2, except that the capillary-end of the adsorbent tube was used instead of the end used for determining single component isotherms.

In determining the co-adsorption isotherm, the trace contaminant was adsorbed first by the HS-C adsorbents until the desired amount adsorbed of about 0.012 gm/gm was obtained, and the pressure was then noted. After the adsorbent bed was closed off from the manifold, the remaining adsorbate in the manifold was evacuated and the manifold was flushed with carbon dioxide two or three times. Next, the desired amount of carbon dioxide was admitted to the manifold and the adsorption sequences were then performed as described in Section 3.3.2 until a desired co-adsorption isotherm was completed. For an initial dose of carbon dioxide, the pressure in the manifold should be at least 2 or 3 mm Hg higher than the pressure of the first adsorbate in the adsorbent bed, otherwise counter diffusion by the first adsorbate would be significant. The calculations of co-adsorption data are presented in Section 5.1 and Appendix B.

3.4 Experimental Constraints

There are four experimental constraints to be observed in the application of displacement technique for

acquiring adsorption or co-adsorption data. The four constraints are (6):

a) negligible counter diffusion of preadsorbed adsorbate to manifold containing second adsorbate,

b) small internal pore diffusion resistances,

c) no inert or inert like compound in the adsorbent tube before acquiring co-adsorption data of the next adsorbate,

d) negligible adsorption of adsorbates on glassware or stop-cock grease.

A detailed analysis of each of these constraints may be obtained from the reference cited above.

CHAPTER 4

ADSORPTION RESULTS OF PURE CONTAMINANTS

In this chapter, first, the algorithms for computing adsorption and desorption equilibrium data are presented. Next, the adsorption and desorption equilibrium data are shown as isotherm plots, and finally these plots are discussed.

4.1 Computations of Adsorption and Desorption Equilibrium Data

4.1.1 Adsorption Algorithm

As described in Section 3.1, the amount adsorbed is calculated from the difference between the amounts of adsorbate present in the adsorption system initially and finally. The amount of adsorbate present in the adsorption system is determined from the measured adsorbate pressure.

Initially, the amount of adsorbate gas introduced into the manifold of volume V_1 cc from the adsorbate reservoir is calculated as cubic centimeters at STP by the relation

$$\Delta V_{dose} = \left(\frac{273}{760}\right)\left(\frac{V_1 \Delta P_{dose}}{T_r}\right) \qquad (4\text{-}1)$$

where ΔP_{dose} is the increase of adsorbate pressure in mm Hg at ambient temperature, T_r°K.

At time, t, the amount of adsorbate gas not adsorbed is calculated by the relation

$$V_{unads.,t} = \left(\frac{273}{760}\right)\left(\frac{V_1+V_d}{T_r}\right)P_t \qquad (4\text{-}2)$$

where P_t is the adsorbate pressure at time, t, and V_d is the 'dead-space' volume in cc at STP.

Therefore, the amount adsorbed at time, t, expressed as cm^3 at STP per gram of adsorbent is calculated by

$$V_t = [(\Sigma\Delta V_{dose}) - V_{unads,\ t}]/W \qquad (4\text{-}3)$$

where $\Sigma\Delta V_{dose}$ is the total amount of adsorbate in the system and W is the mass of the adsorbent in gm. The amount adsorbed can also be expressed in gram of adsorbate per gram of adsorbent by the relation

$$m_t = \left(\frac{760}{273}\right)\left(\frac{M}{R}\cdot\frac{V_t}{1000}\right) \qquad (4\text{-}4)$$

where M is the adsorbate molecular weight and R is the gas constant with value of 62.361 mmHg lit/gm°K.

In order to extrapolate the amount adsorbed at equilibrium, m_e, the equilibrium pressure, P_e, must first be obtained. The equation of the following form was suggested for extrapolating the pressure to equilibrium (6),

$$\ln P_t = A + B\frac{1}{t} + C(\frac{1}{t})^2 \qquad (4\text{-}5)$$

where t is the adsorption time and A, B, and C are constants to be evaluated. The third term of Eq. 4-5 was found to be negligible in this adsorption study. Therefore,

$$\ln P_t = A + B(\frac{1}{t}) \qquad (4\text{-}6)$$

As $t \to \infty$, Eq. 4-6 becomes

$$\ln P_e = A \qquad (4\text{-}7)$$

Eq. 4-6 can now be rewritten as

$$\ln P_t = \ln P_e + B(\frac{1}{t}) \qquad (4\text{-}8)$$

By substituting the last two time-versus-pressure points of (t_1, P_{t1}) and (t_2, P_{t2}) of each isotherm point, and solving the equations, B is evaluated as

$$B = \frac{\ln (P_1/P_2)}{(\frac{1}{t_1} - \frac{1}{t_2})} \qquad (4\text{-}9)$$

and P_e is given as

$$P_e = P_2/e^{B/t_2} \qquad (4\text{-}10)$$

The mass of adsorbate contained in the system remains constant during an exposure. As the adsorbent adsorbes the adsorbate, the pressure decreases and the loading increases along lines of constant mass (6). Therefore, the amount adsorbed at equilibrium, m_e, is then evaluated from the line of constant mass and is given as

$$m_e = \frac{(m_{t1} - m_{t2})}{(P_{t1} - P_{t2})} (P_e - P_{t2}) + m_{t2} \qquad (4\text{-}11)$$

Successive points on the isotherm are determined by repeating the calculation sequence from Eq. 4-1 to 4-11. A computer program based on this algorithm for calculating the isotherm data from raw adsorption data is given in Appendix B. The results are presented in Section 4.2 graphically by plotting P_e vs m_e.

4.1.2 Desorption Algorithm

The amount remaining adsorbed at a desorption point is obtained by subtracting the amount desorbed from the previous loading. The first approximation to the amount desorbed is calculated from the measured equilibrium pressure and known system volume by applying the ideal gas relation

$$m_d = \frac{P_e (V_1 + V_d) M}{1000\ T_r\ R} \qquad (4\text{-}12)$$

where m_d = the amount desorbed, gm

P_e = adsorbate equilibrium pressure, mm Hg

V_1 = manifold volume, cc at room conditions

V_d = dead-space volume, cc at room conditions

M = adsorbate molecular weight

T_r = ambient temperature, °K

and R = gas constant with value of 62.361 $\frac{\text{mm Hg lit}}{\text{gm °K}}$

However, this approximate amount desorbed must be corrected for the residual pressure (amount not absorbed) which is present in the adsorbent tube before desorption is performed. The correction factor is given as

$$m_R = \frac{P_R \, V_d \, M}{1000 \, T_b \, R} \qquad (4\text{-}13)$$

where m_R = the residual amount, gm

P_r = residual pressure in the adsorbent tube, mm Hg

and T_b = adsorbent bed temperature, °K

Suppose m_i is the previous amount adsorbed, then the amount remaining adsorbed, m_a, is given as

$$m_a = m_i - (m_d - m_R)/ W \qquad (4\text{-}14)$$

where W is the mass of adsorbent in gm.

4.2 'Liquid' Contaminants Equilibrium Data

The equilibrium data of the seven 'liquid' contami-

ınts (see Table 2-2) at 25°C were plotted on linear coordinates of pressure (torr) versus adsorbate loading (gm/gm adsorbent), as shown in Figs. 4-1 to 4-7. There are three isotherms plotted in each of these figures: an adsorption isotherm on fresh HS-C adsorbent, a desorption isotherm showing the path of desorption, and an adsorption isotherm on the same sample of HS-C adsorbent which has been regenerated to check reversability. The dotted line on the isotherm plots is the line extrapolating the experimental isotherm data to the origin of the axes.

The consistency of the adsorption results was checked by performing the adsorption experiment of a few representative contaminants several times. The results are shown in Fig. 4-2 for methanol adsorption, Fig. 4-3 for methyl acetate adsorption, Fig. 4-4 for acetone adsorption and Fig. 4-10 for carbon dioxide adsorption. It can be seen from these figures that the results were quite reproducible.

4.2.1 Adsorption Isotherms

It can be seen from Figs. 4-1 to 4-7 that the adsorption of these seven contaminants are only slightly nonlinear. In fact, the isotherm of methanol is almost an ideal Henry's law isotherm.

The relative order of adsorption capacity of HS-C adsorbent for these seven contaminants is shown in Fig. 4-9, in which the isotherm data of the seven con-

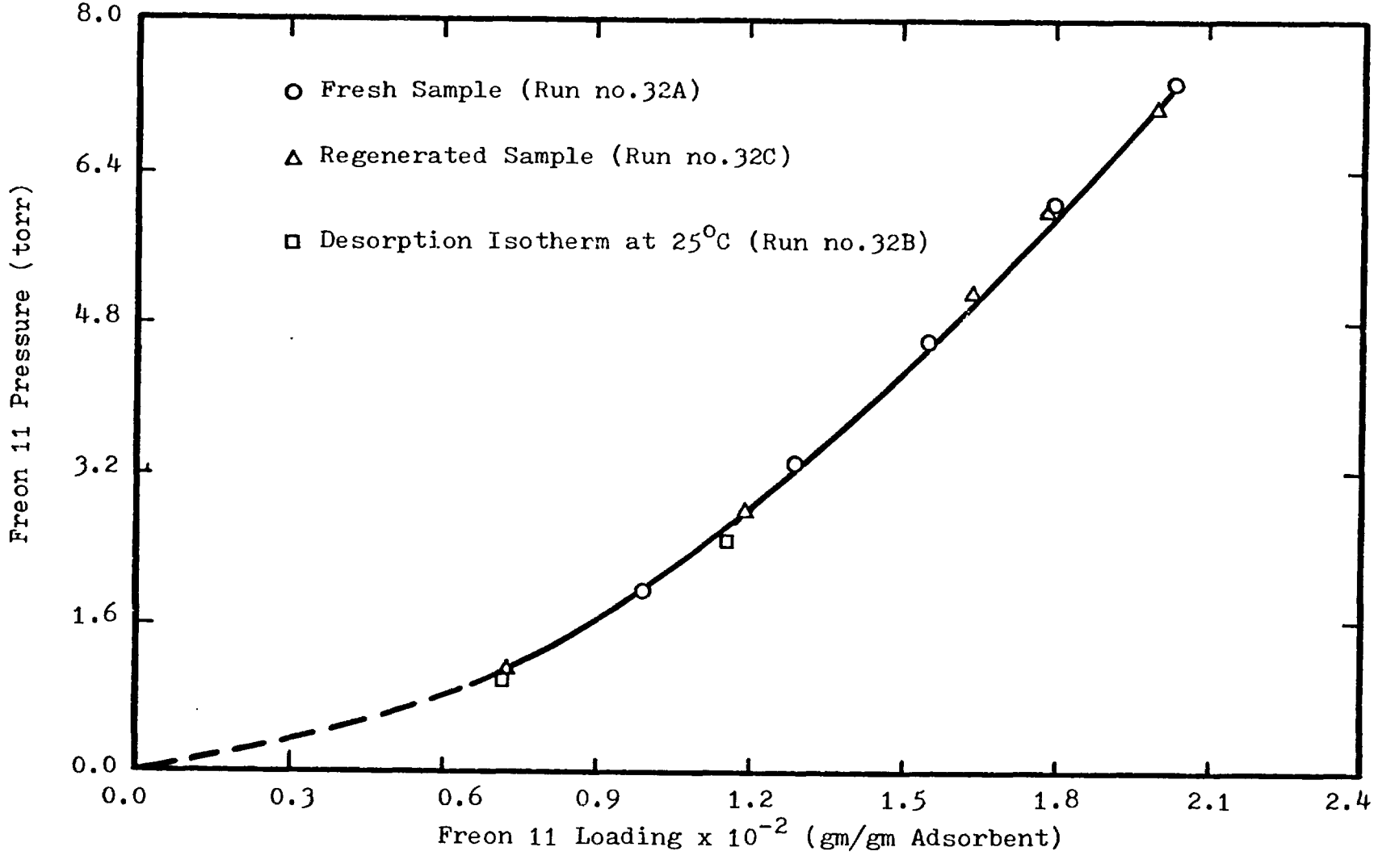


Fig.4-1 Isotherms of Freon 11 on HS-C Adsorbent at 25°C

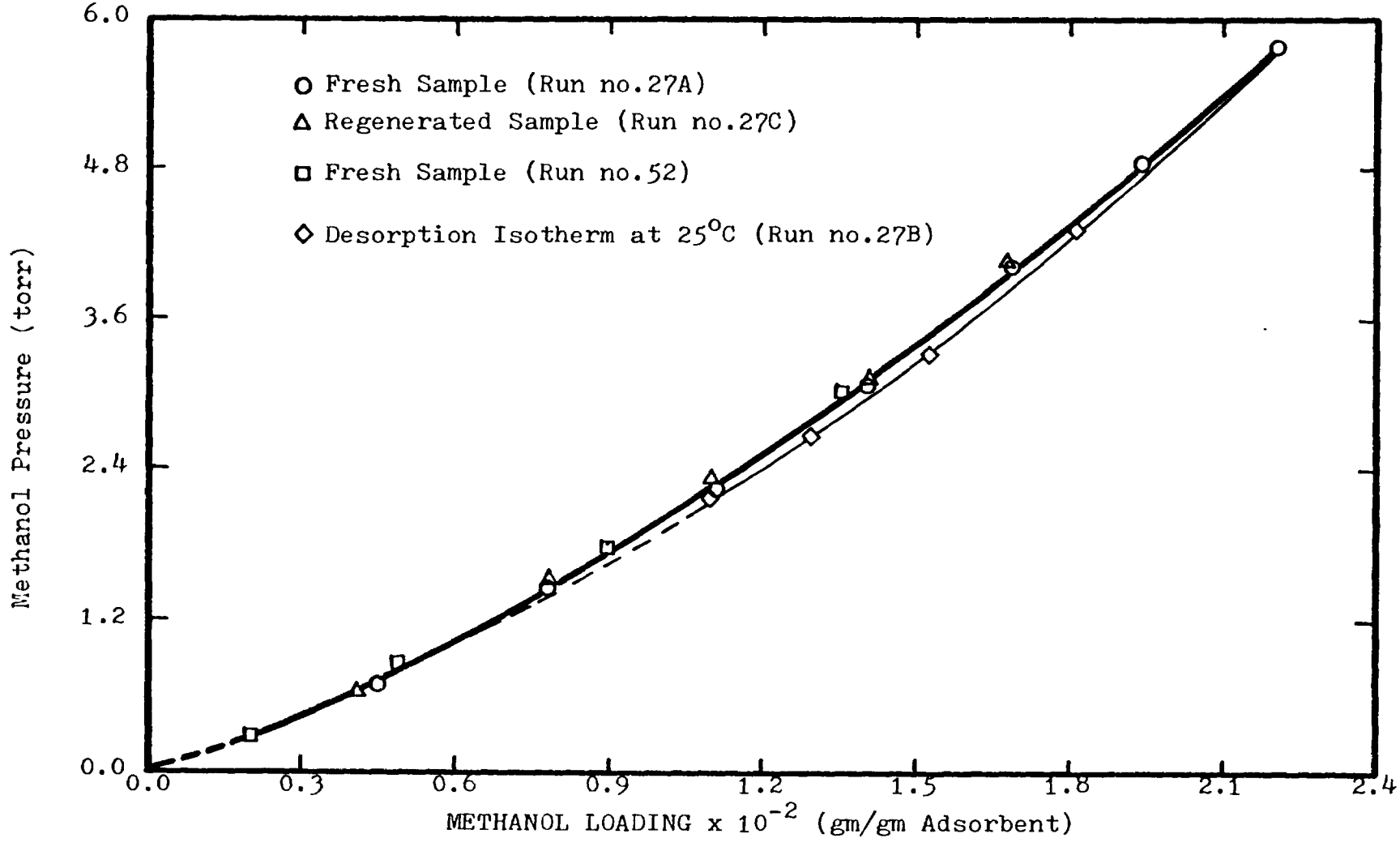


Fig.4-2 Isotherms of Methanol on HS-C Adsorbent at 25°C

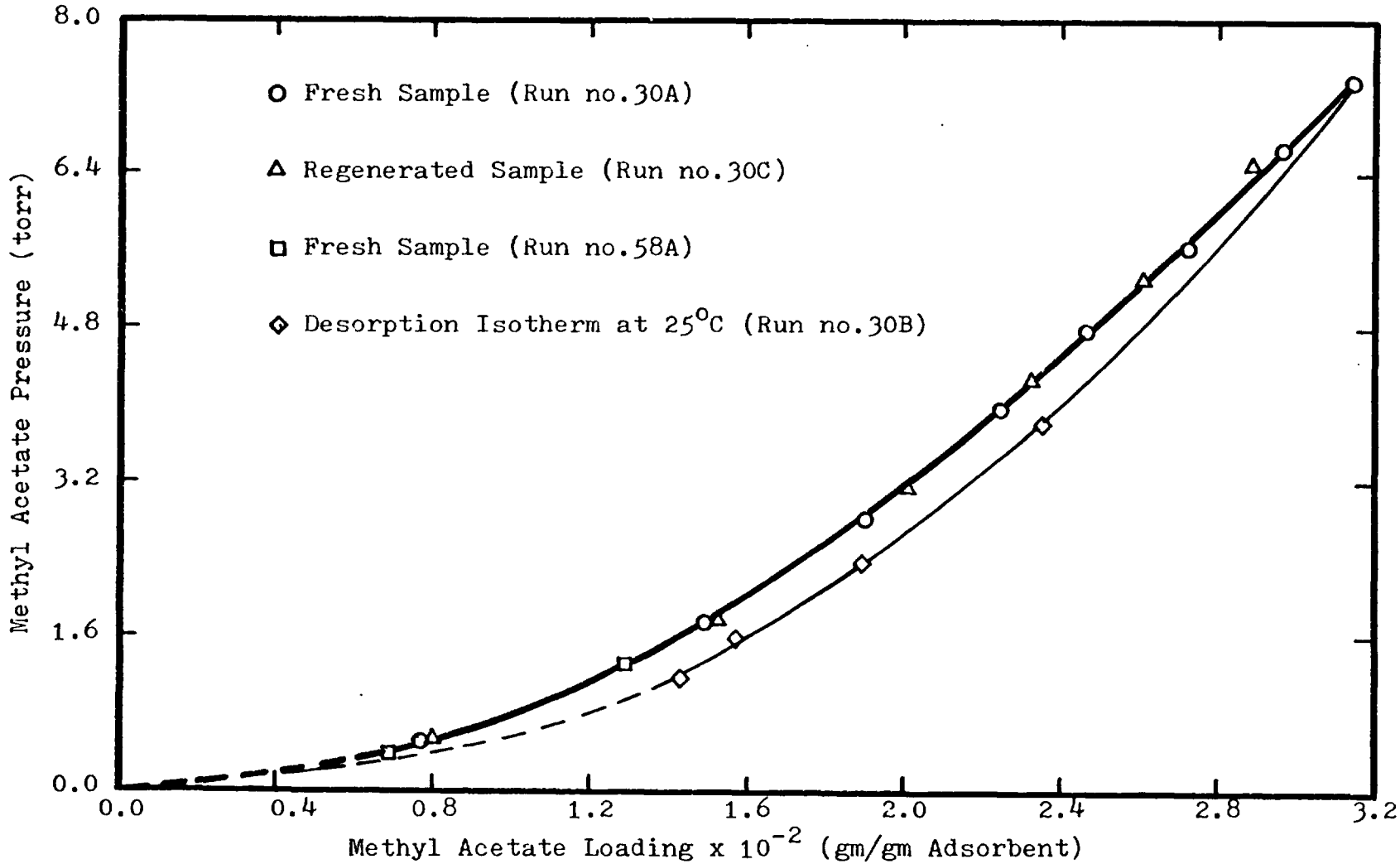


Fig.4-3 Isotherms of Methyl Acetate on HS-C Adsorbent at 25°C

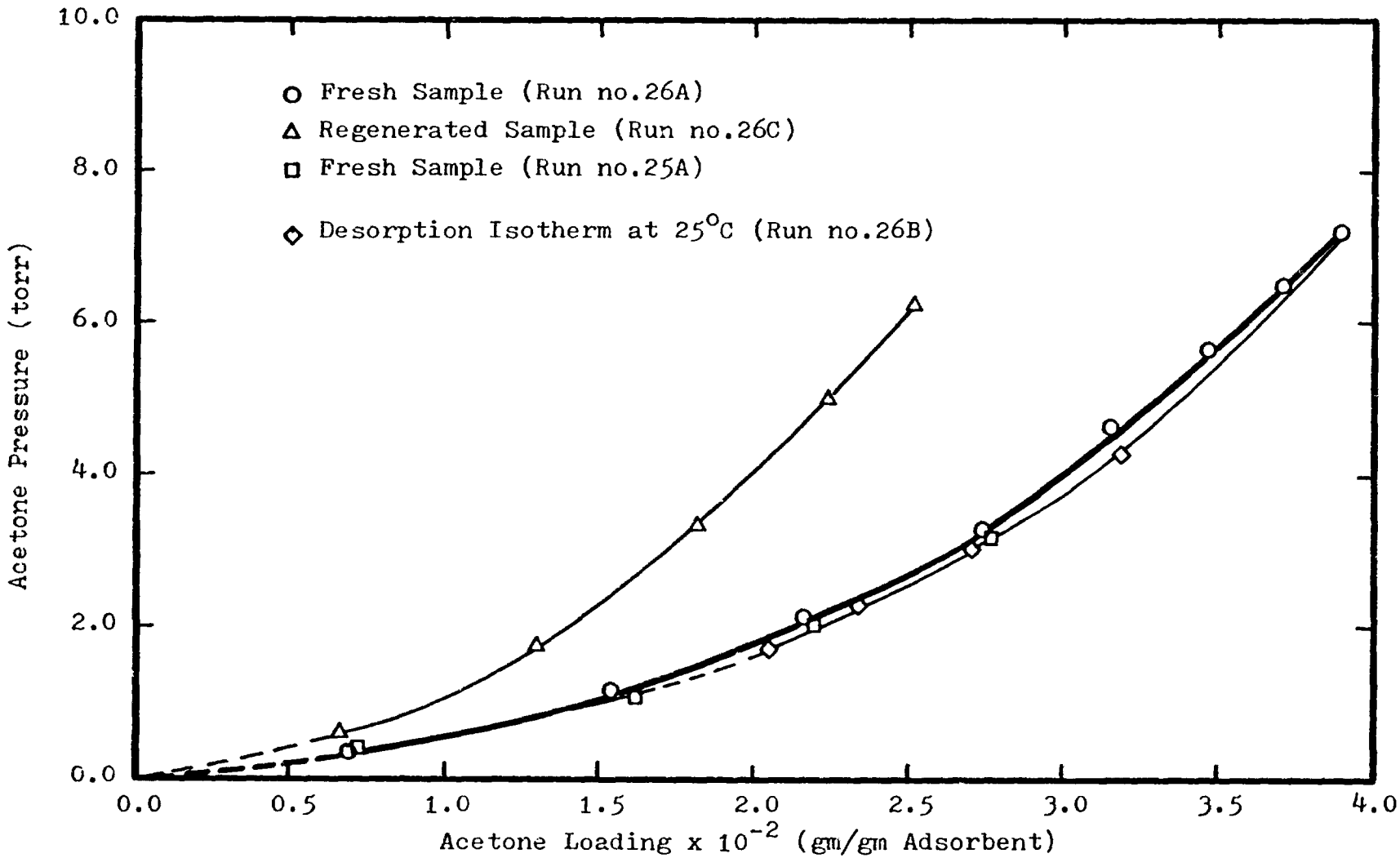


Fig.4-4 Isotherms of Acetone on HS-C Adsorbent at 25°C

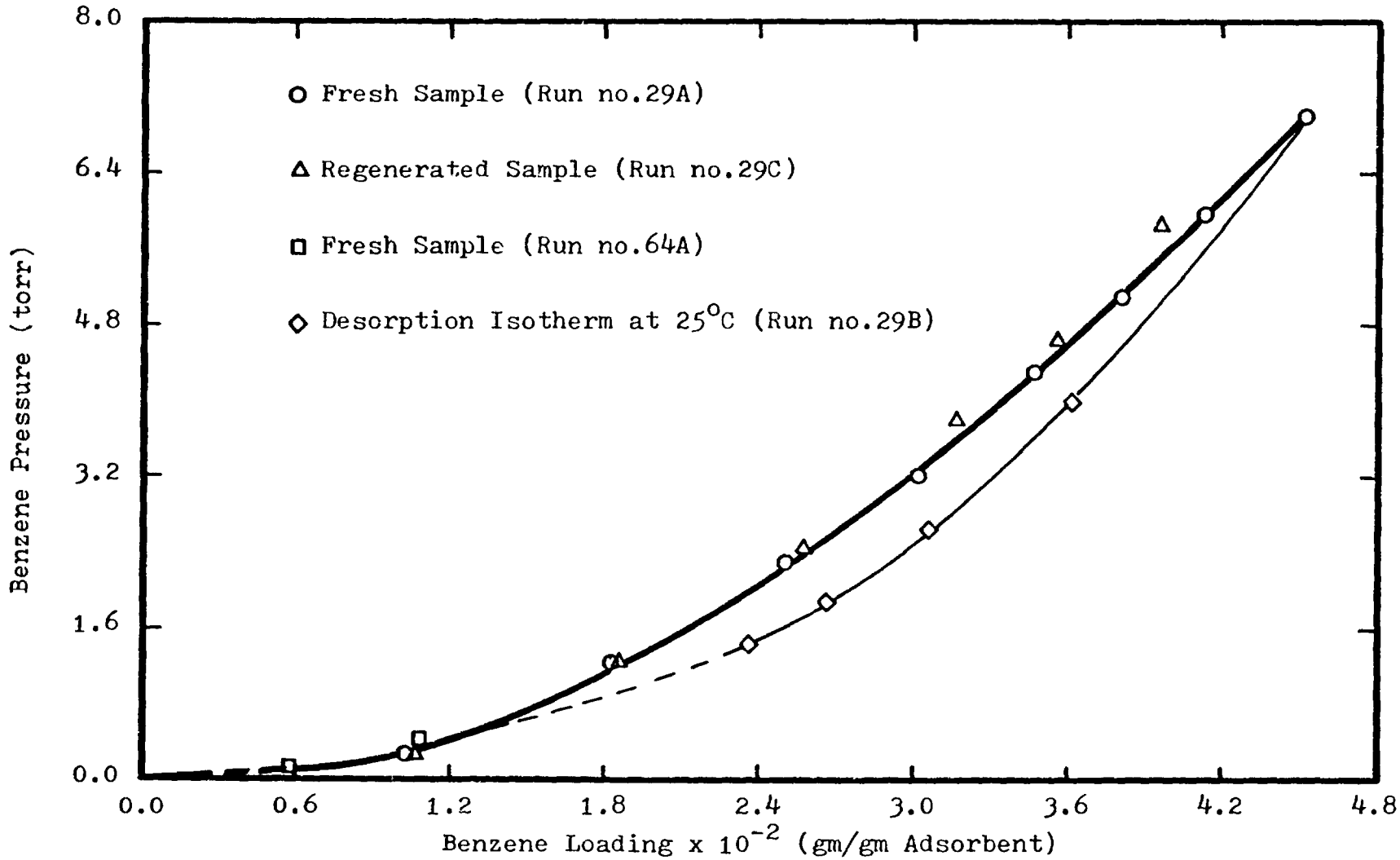


Fig.4-5 Isotherms of Benzene on HS-C Adsorbent at 25°C

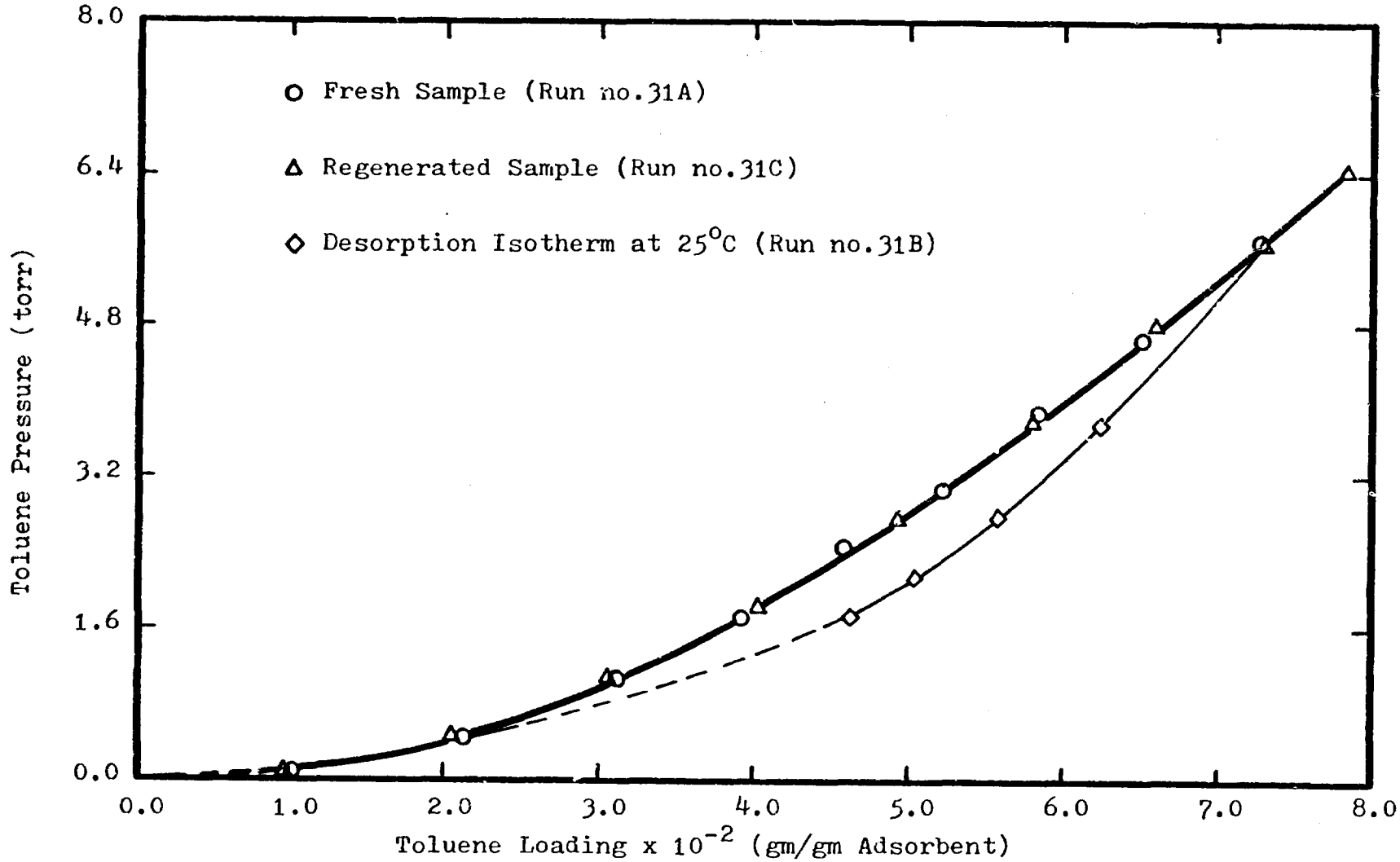


Fig.4-6 Isotherms of Toluene on HS-C Adsorbent at 25°C

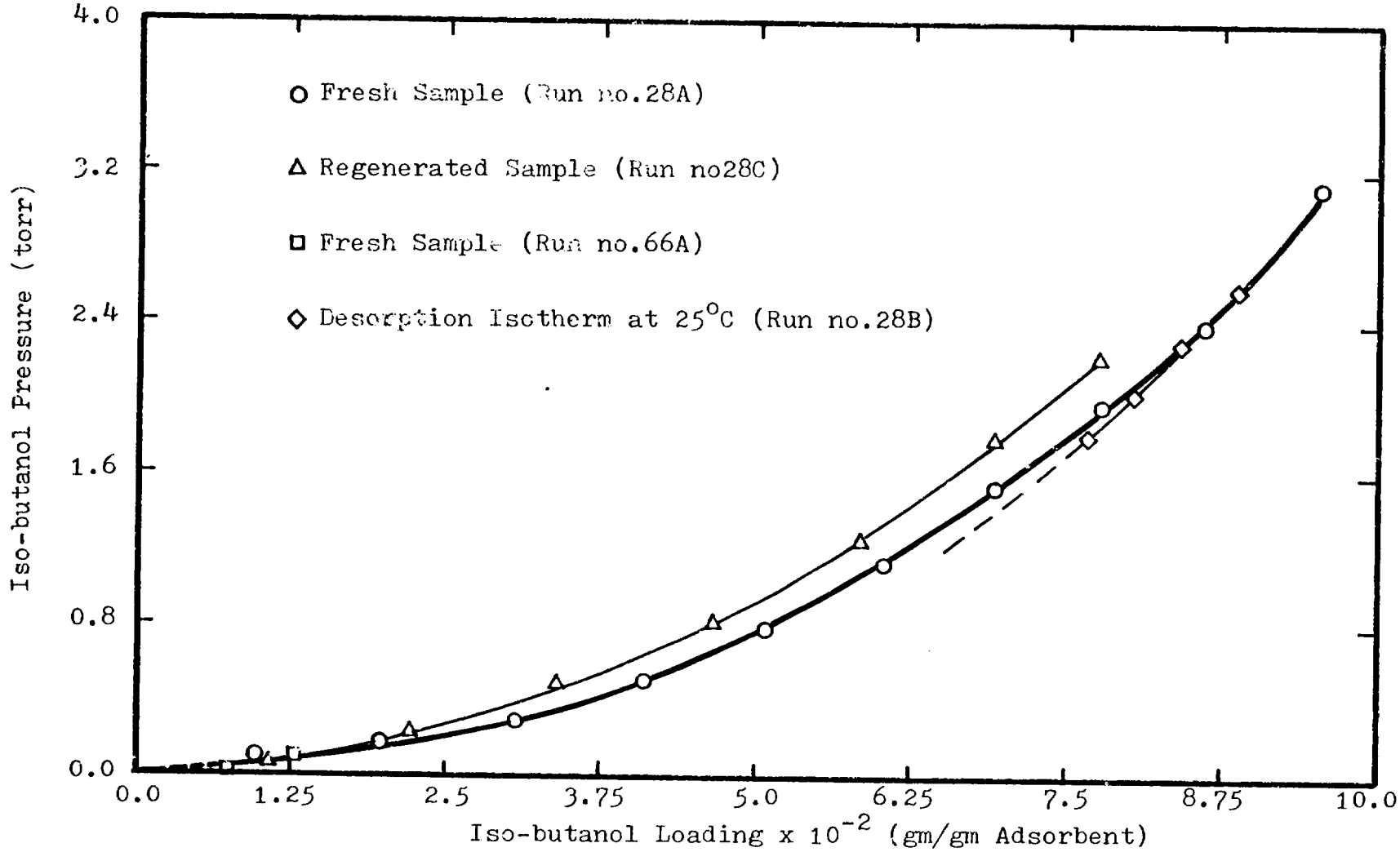


Fig.4-7 Isotherms of Iso-butanol on HS-C Adsorbent at 25°C

taminants are plotted on the same coordinates. The isotherm data of carbon dioxide is also plotted in this figure for comparison. It can be seen in this figure that the HS-C adsorbent has the highest adsorption capacity for iso-butanol, and the next in decreasing order of adsorption capacity is toluene, benzene, acetone, methyl acetate, methanol or Freon 11 depending on the pressure. For pressures above 2 torr, methanol is less adsorbed than Freon 11 while below 2 torr the reverse is true.

The reversibility of the adsorption process of an adsorbate on the adsorbent is determined by observing whether the adsorption isotherm of regenerated adsorbent coincides with the adsorption isotherm of fresh adsorbent. By inspecting from Figs. 4-1 to 4-7, it is observed that the adsorption of Freon 11, methanol, methyl acetate, benzene and toluene on HS-C adsorbent are reversible. The adsorption of iso-butanol is only slightly irreversible. The poisoning effect of acetone is further illustrated in Fig. 4-8, in which the adsorption isotherms were obtained by repeating the adsorption experiment four times on the same sample of HS-C adsorbent. It can be seen from this figure that the adsorption capacity of HS-C adsorbent degraded further after each adsorption and desorption. This may be due to the fact that acetone chemically reacts with PEI.

4.2.2 Desorption Isotherms

Desorption isotherms of the seven 'liquid' contaminants

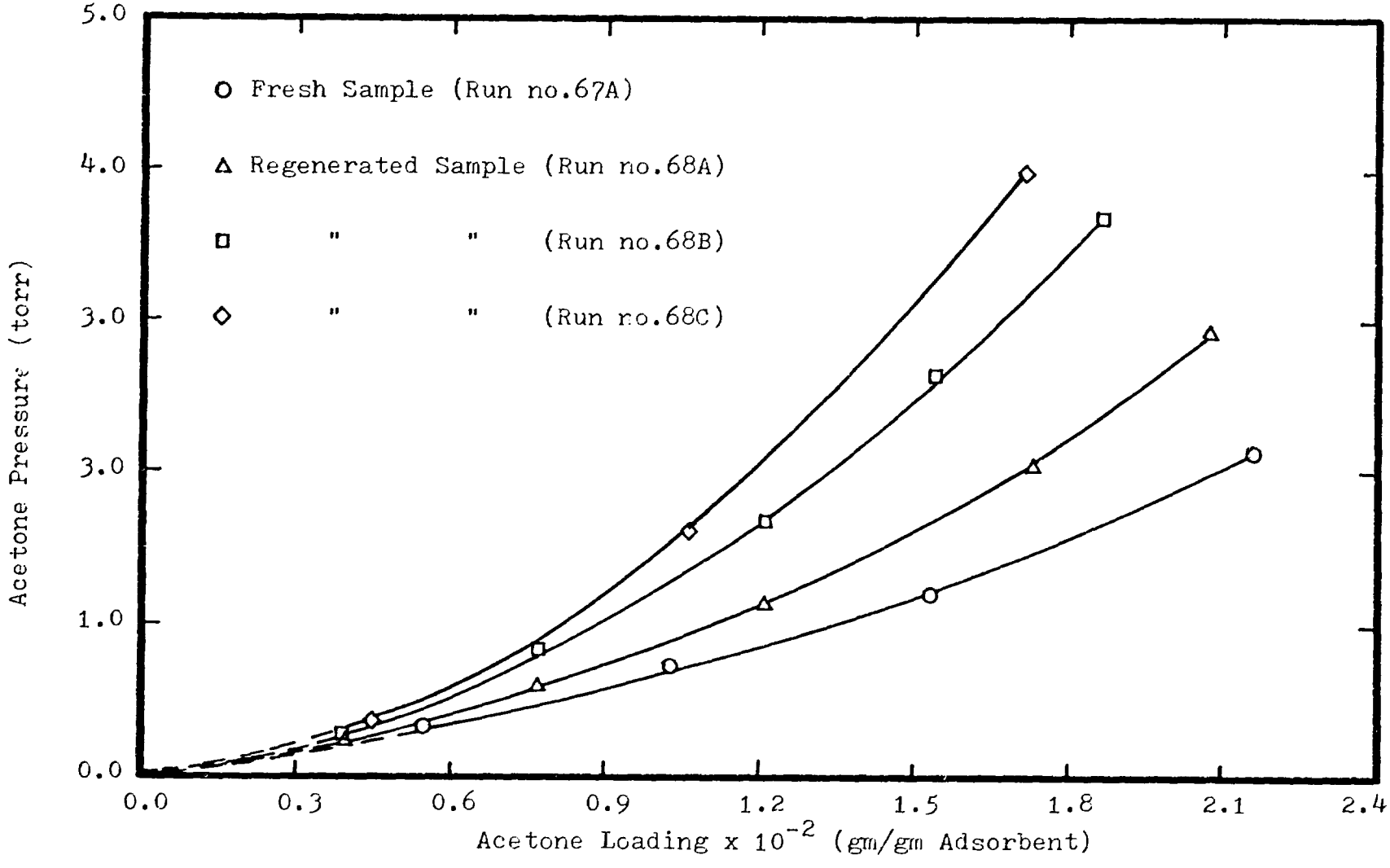


Fig.4-8 Isotherms of Acetone on HS-C Adsorbent at 25°C; showing the extent of poisoning after regeneration

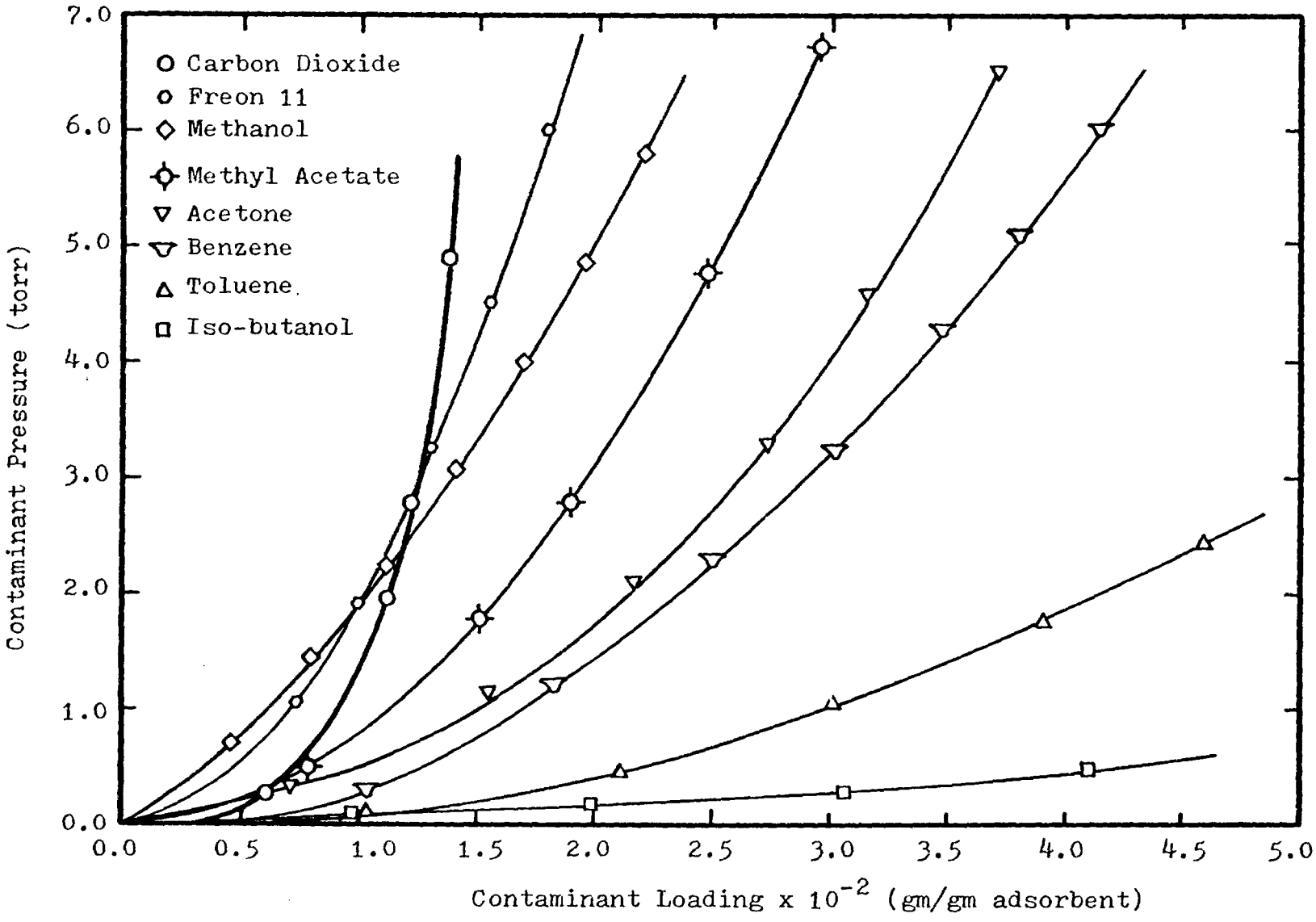


Fig.4-9 Isotherms of 'Liquid' Trace Contaminants on HS-C at 25°C; showing the relative order of adsorption capacity

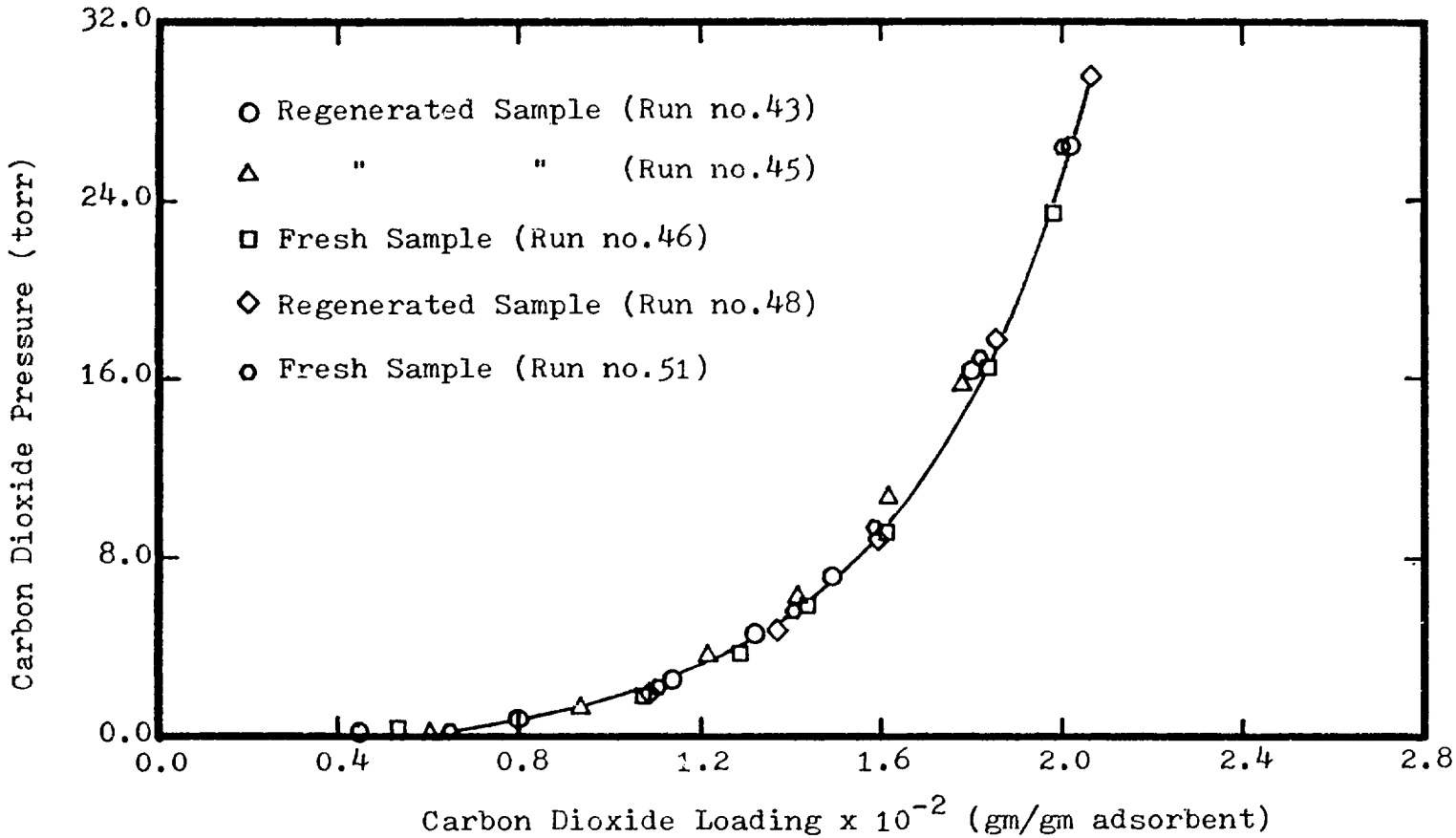


Fig.4-10 Isotherms of Carbon Dioxide on HS-C at 25°C; showing reproducibility

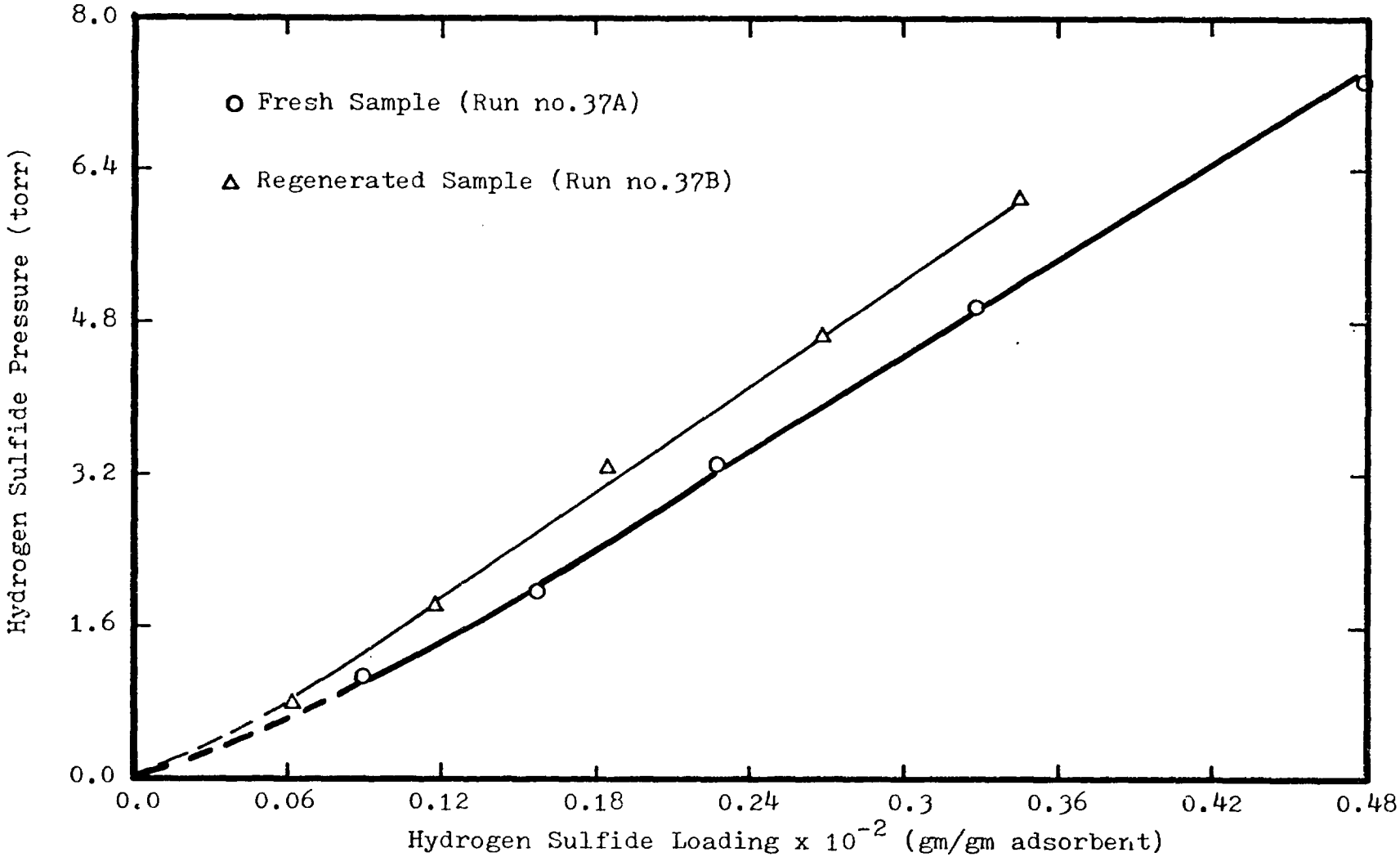


Fig.4-11 Isotherms of Hydrogen Sulfide on HS-C Adsorbent at 25°C

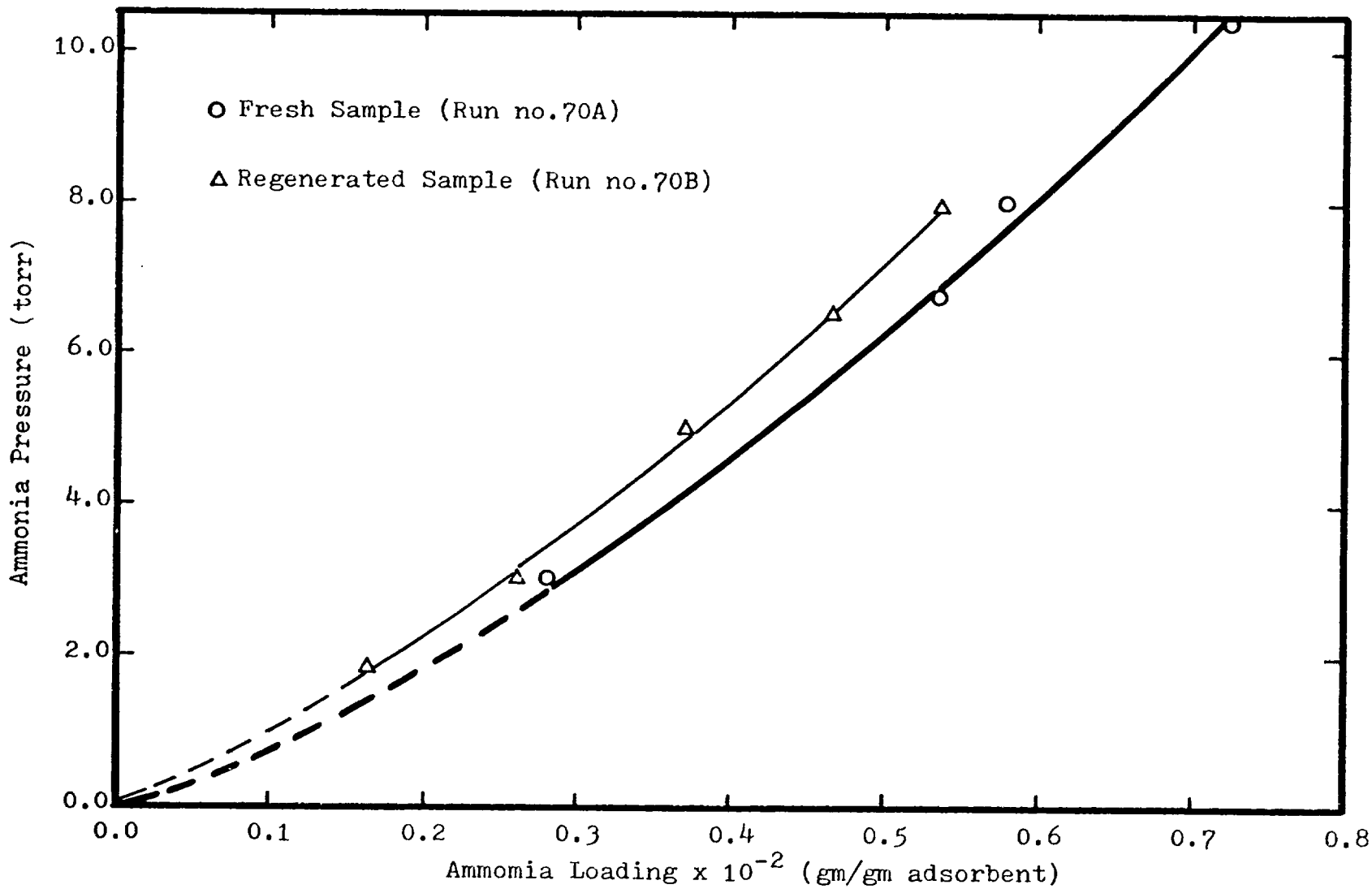


Fig.4-12 Isotherms of Ammonia on HS-C Adsorbent at 25°C

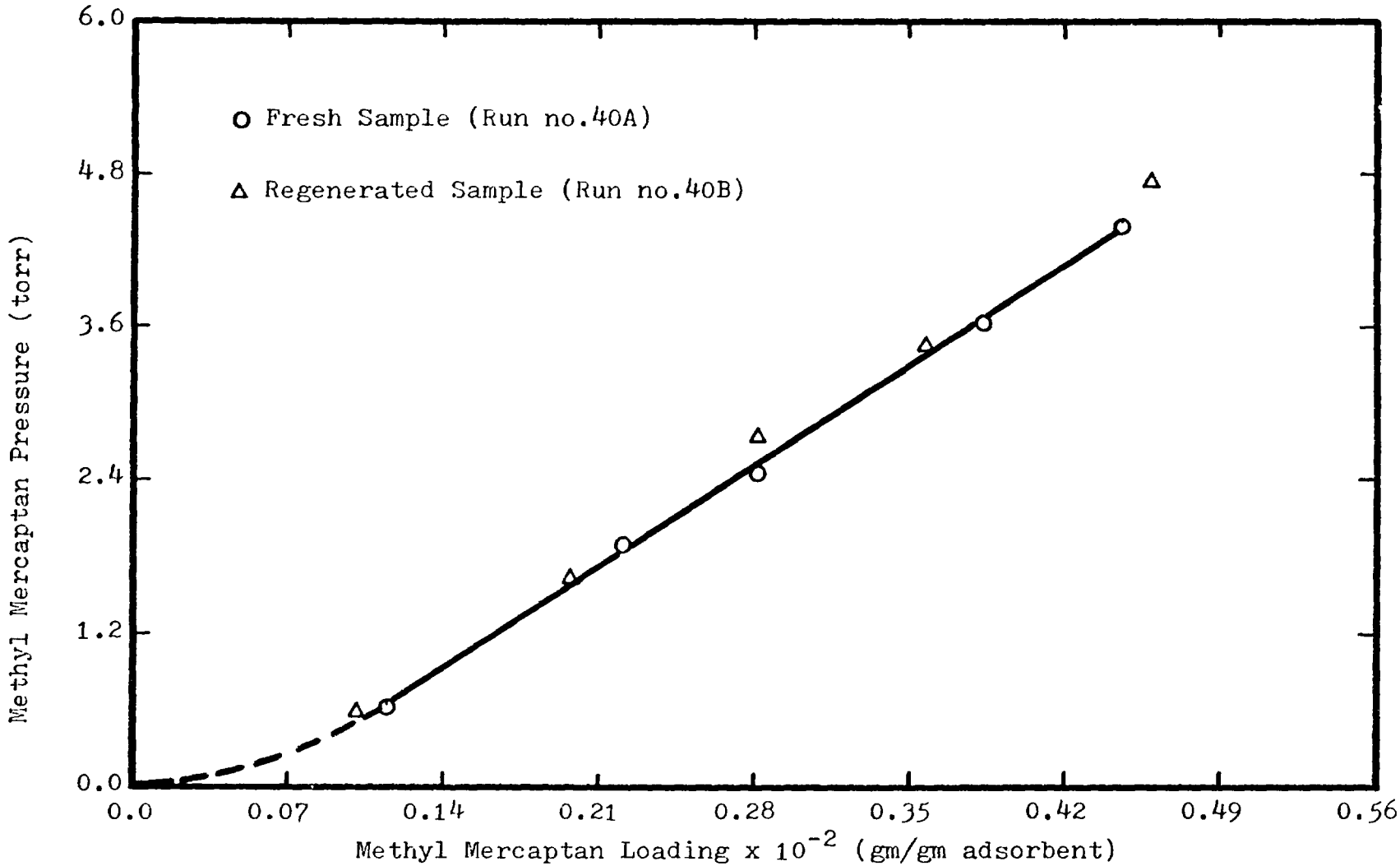


Fig.4-13 Isotherms of Methyl Mercaptan on HS-C Adsorbent at 25°C

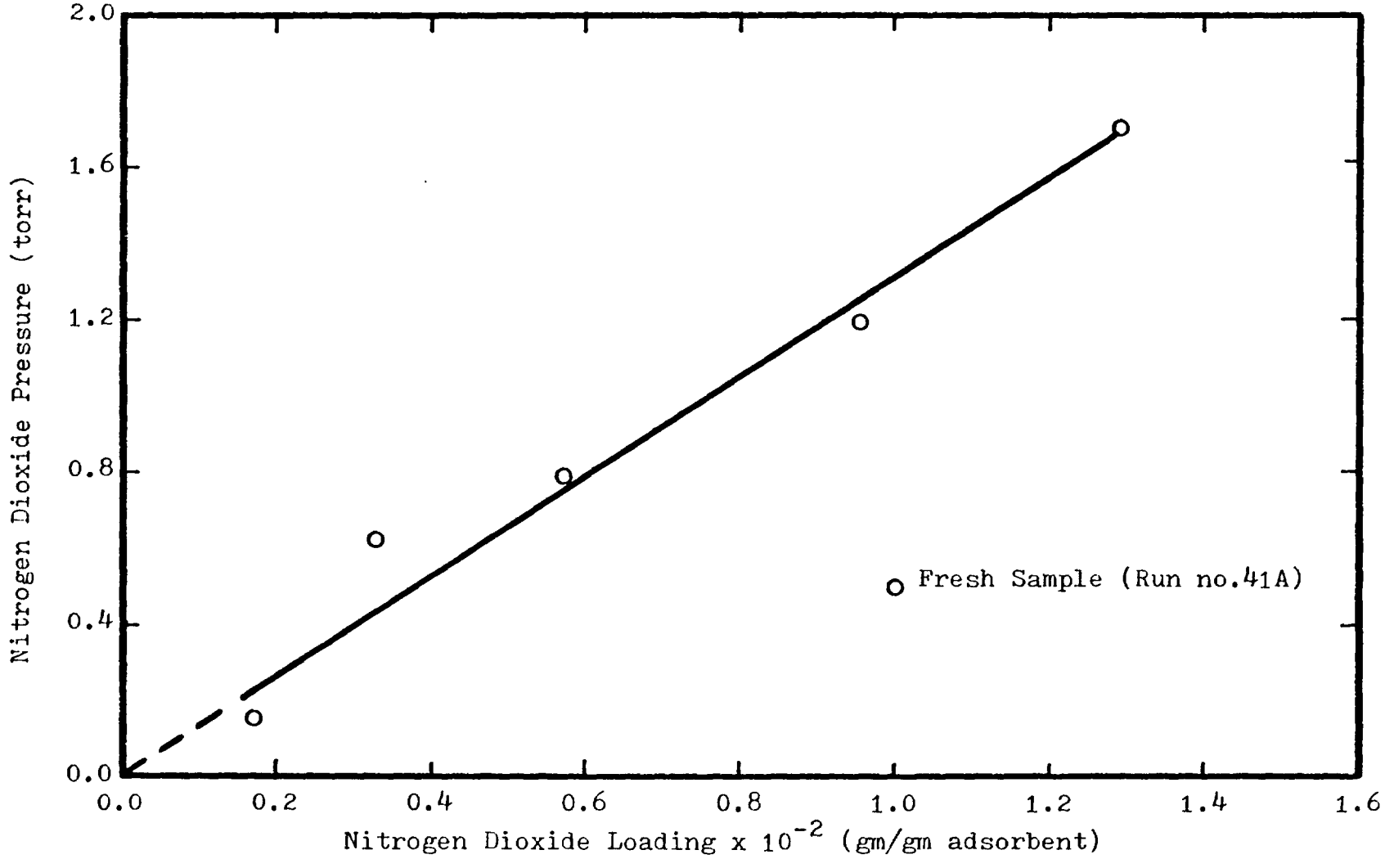


Fig.4-14 Isotherm of Nitrogen Dioxide on HS-C adsorbent at 25°C

at 25°C are also shown in Figs. 4-1 to 4-7. The desorption experiments was performed immediately after the completion of adsorption experiment on the fresh sample of HS-C adsorbents. Therefore, the initial l ding for desorption is actually the final loading in the a sorption experiment. All the desorption data were obtained according to the procedures described in Section 3.3.2.

Hysteresis loops can be seen in these isotherm plots. Several explanations have been proposed to account for such hysteresis. One acceptable explanation is that the presence of hysteresis phenomena is the effect of internal diffusional resistances. The amount of resistance may depend on the adsorbate. Thus Freon 11 and methanol may have negligible resistance while others appreciable

4.3 Gaseous Contaminants Equilibrium Data

Eight gaseous trace contaminants (see Table 2-3) had been tested for adsorption capacity on HS-C adsorbents at 25°C. The results of the tests are preliminary classified into three groups, as shown in Table 4-1. The equilibrium data of the gaseous contaminants that have adsorption capacity on HS-C adsorbents were plotted on linear coordinates of pressure (torr) versus adsorbate loading (gram per gram adsorbent), as shown in Figs. 4-11 to 4-14.

The classification of carbon monoxide, ethylene, methane and Freon 23 under the inert group is based on

TABLE 4-1

Classification of Gaseous Contaminants Adsorption Results

Inert	Adsorbed	
	Reversible	Irreversible
Carbon Dioxide	Methyl Mercaptan	Hydrogen Sulfide
Ethylene		Ammonia
Methane		Nitrogen Dioxide
Freon 23		

the experimental results that there was no significant amount of these four contaminants adsorbed on HS-C. The adsorption of methyl mercaptan appears to be reversible as shown in Fig. 4-13. However, the adsorptions of hydrogen sulfide, ammonia and nitrogen dioxide are shown to be irreversible. It can be seen in Figs. 4-11, 4-12, and 4-14 that the adsorption capacity of regenerated HS-C adsorbents degraded quite significantly.

The gaseous contaminants are so lightly adsorbed by the HS-C adsorbents that their isotherms are almost linear. However, the isotherm data for nitrogen dioxide are quite scattered; this may be due to chemical reactions. The poisoning effect of nitrogen dioxide on the adsorbents is so severe that the regenerated adsorbents have practically no adsorption capacity.

4.4 Discussion

By combining the adsorption results of 'liquid' and gaseous trace contaminants, the fifteen trace contaminants can now be classified into three groups according to their respective adsorption affinity with HS-C adsorbents. The resulting classification is listed in Table 4-2. From studying the classification table, it may draw a general conclusion that the HS-C adsorbent has good adsorption potential for removing trace contaminants of lower alcohol compounds like methanol, ester compounds like methyl acetate, and benzene compounds like toluene, with no degradation effect.

TABLE 4-2

Classification of Trace Contaminants Adsorption Results

Inert	Adsorbed	
	Reversible	Irreversible
Carbon Monoxide	Methyl Mercaptan	Ammonia
Ethylene	Freon 11	Hydrogen Sulfide
Methane	Methanol	Nitrogen Dioxide
Freon 23	Methyl Acetate	Acetone
	Benzene	Iso-butanol
	Toluene	

However, contaminants with strong oxidizing and reducing

properties such as nitrogen dioxide have potential detrimental or poisoning effects on HS-C adsorbents. In addition, other contaminants with potential reactivity with PEI (polyethylenimine), such as ketone compounds, also should be detrimental to the HS-C adsorbents.

CHAPTER 5

CO-ADSORPTION RESULTS OF TRACE CONTAMINANTS AND CARBON DIOXIDE

While adsorption isotherms such as those presented in Chapter 4 given one an excellent feeling for the performance of adsorbents beds under conditions in which only one contaminant is present, they do not indicate how the presence of another adsorbate such as carbon dioxide will affect adsorptivity. Therefore, the next step of this experimental study was to perform experiments in which there were two adsorbates present.

Since the primary purpose of HS-C adsorbent is to remove carbon dioxide and water in the cabin of spacecraft, it is important to know whether the adsorbed trace contaminants on HS-C adsorbent will affect or poison its adsorption capacity for carbon dioxide if this adsorbent is also used for removing trace contaminants. Thus, in order to answer this question, the trace contaminant is adsorbed first until to a desired loading, then the adsorption of carbon dioxide is performed. In this chapter, the results of this co-adsorption study are presented.

5.1 Determination of Co-adsorption Isotherms

Before any co-adsorption experiments are carried out, it is important to note that the trace contaminant

being adsorbed first must be more strongly adsorbed than the carbon dioxide; otherwise the trace contaminant will be displaced by the carbon dioxide and it will affect the accuracy of the co-adsorption isotherm (9). By comparing the isotherm data of pure contaminants presented in Chapter 4 with the isotherm data of carbon dioxide, it can be seen that only the 'liquid' contaminants meet the above constraint. Therefore, only the 'liquid' contaminants were included in this co-adsorption study.

The detailed procedure for determining these co-adsorption isotherms was given in Section 3.3.3. The calculation procedures for determining the initial loading is the same as described in Section 3.1.1. However, in order to determine the amount of the second adsorbate, the partial pressure of the second adsorbate is first obtained by subtracting the initial pressure of the first adsorbate from the total system pressure at each point in the isotherm determination, and then the partial pressure is used to compute the amount adsorbed. This calculation is based on the assumption of no displacement taking place during co-adsorption (6,9). The co-adsorption isotherm data are computed from the raw adsorption data by the computer program shown in Appendix B.

5.2 Co-adsorption Isotherms

Isotherm plots showing adsorption of carbon dioxide at 25°C with seven different preadsorbed contaminants

are presented in Figs. 5-1 to 5-7. These isotherms were also plotted on the same graph to show the relative displacement of CO_2 adsorption with same amount of pre-adsorbed contaminants as shown in Fig. 5-8. It can be seen in these figures that none of the trace contaminants in this co-adsorption study enhances the adsorption of CO_2 as in the case of CO_2-H_2O co-adsorption. On the contrary, almost all the contaminants studied have more or less displaced CO_2. The amount depends on the type of contaminants preadsorbed as is shown in Fig. 5-8. However, care has to be taken in interpreting these co-adsorption data due to the fact that the contaminant loadings are many times the MAC (maximum allowable concentration) in a typical spacecraft.

In Table 5-1 blockage of carbon dioxide by trace contaminants when carbon dioxide is at MAC pressure of 4 torr is shown as a function of amounts of preadsorbed contaminants. Also shown is the partial pressures of contaminants needed to obtain this amount adsorbed. As can be seen, the blockage of CO_2 of over 30% is due to acetone loading of 0.0107 gm/gm and toluene loading of 0.0122 gm/gm. However, when toluene loading is 0.0102 gm/gm, the blockage of CO_2 is only about 8%. This blockage is significantly less than the blockage of CO_2 with about the same loading of acetone. If, for example, the MAC of contaminants in a spacecraft cabin of one atmospheric pressure is 30 ppm, then the loadings listed in Table 5-1

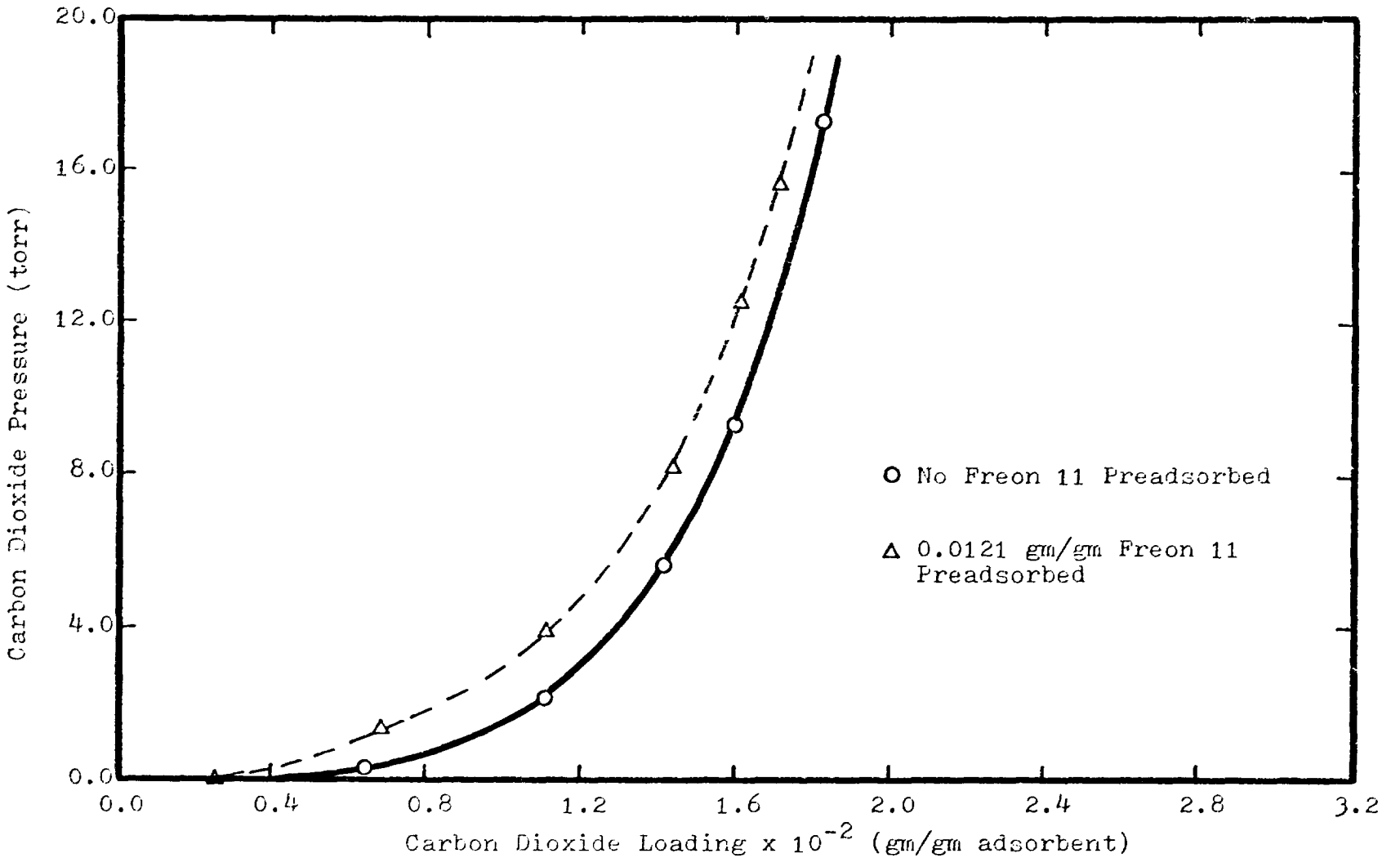


Fig.5-1 Isotherms of Carbon Dioxide on HS-C at 25°C: Blockage by Freon 11

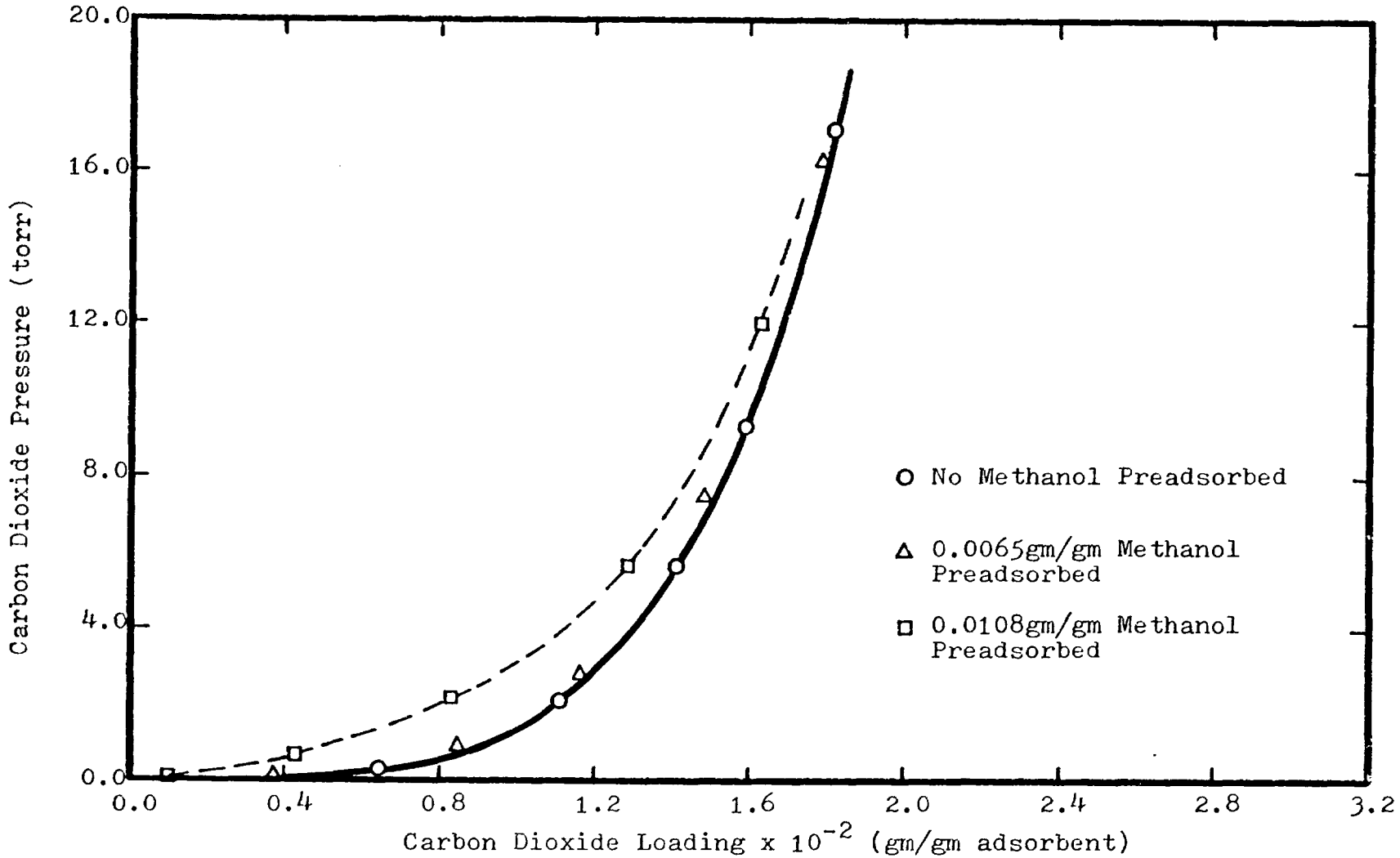


Fig. 5-2 Isotherms of Carbon Dioxide on HS-C at 25°C: Blockage by Methanol.

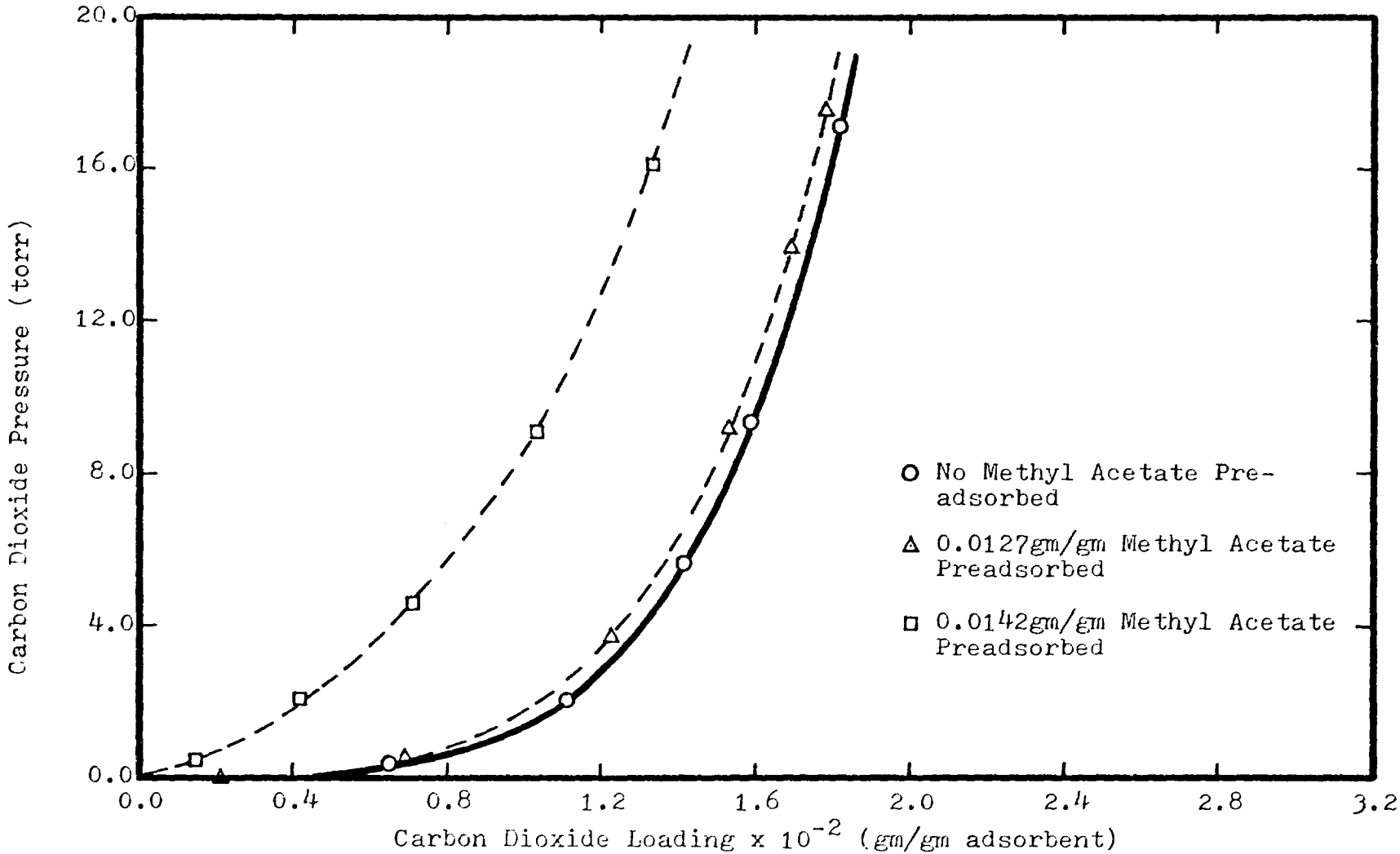


Fig. 5-3 Isotherms of Carbon Dioxide on HS-C at 25°C: Blockage by Methyl Acetate

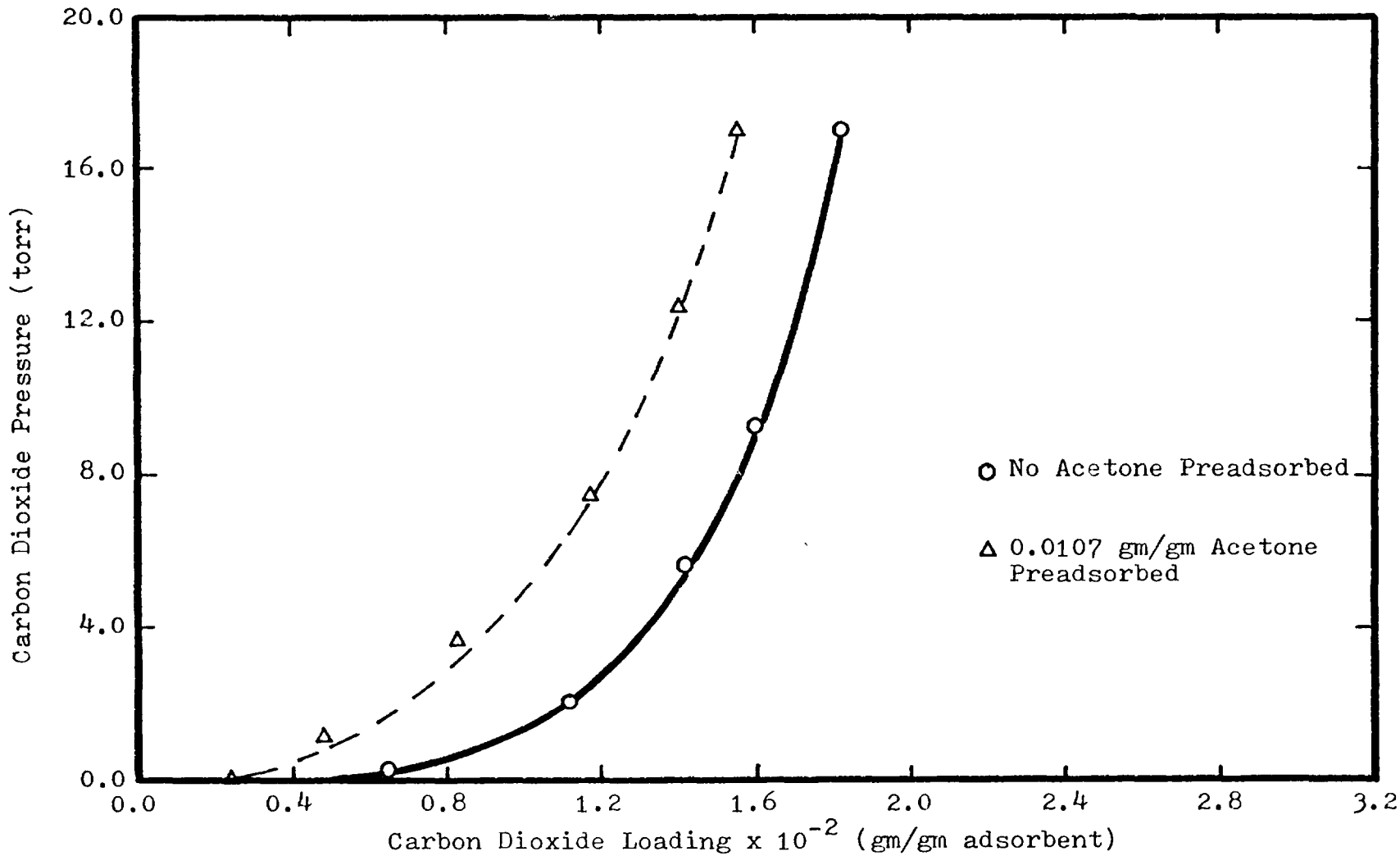


Fig. 5-4 Isotherms of Carbon Dioxide on HS-C at 25°C: Blockage by Acetone

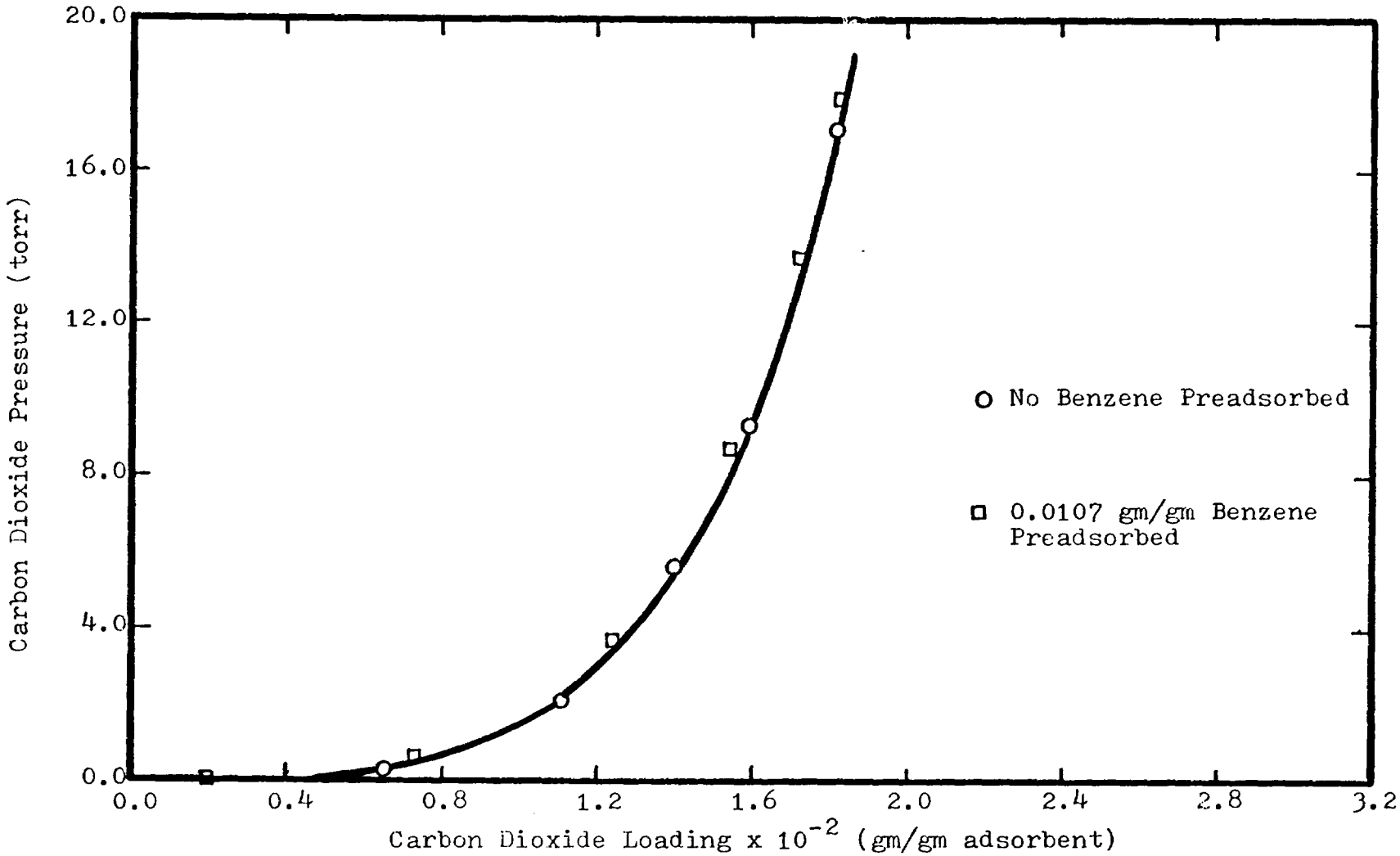


Fig. 5-5 Isotherms of Carbon Dioxide on HS-C at 25°C: Blockage by Benzene

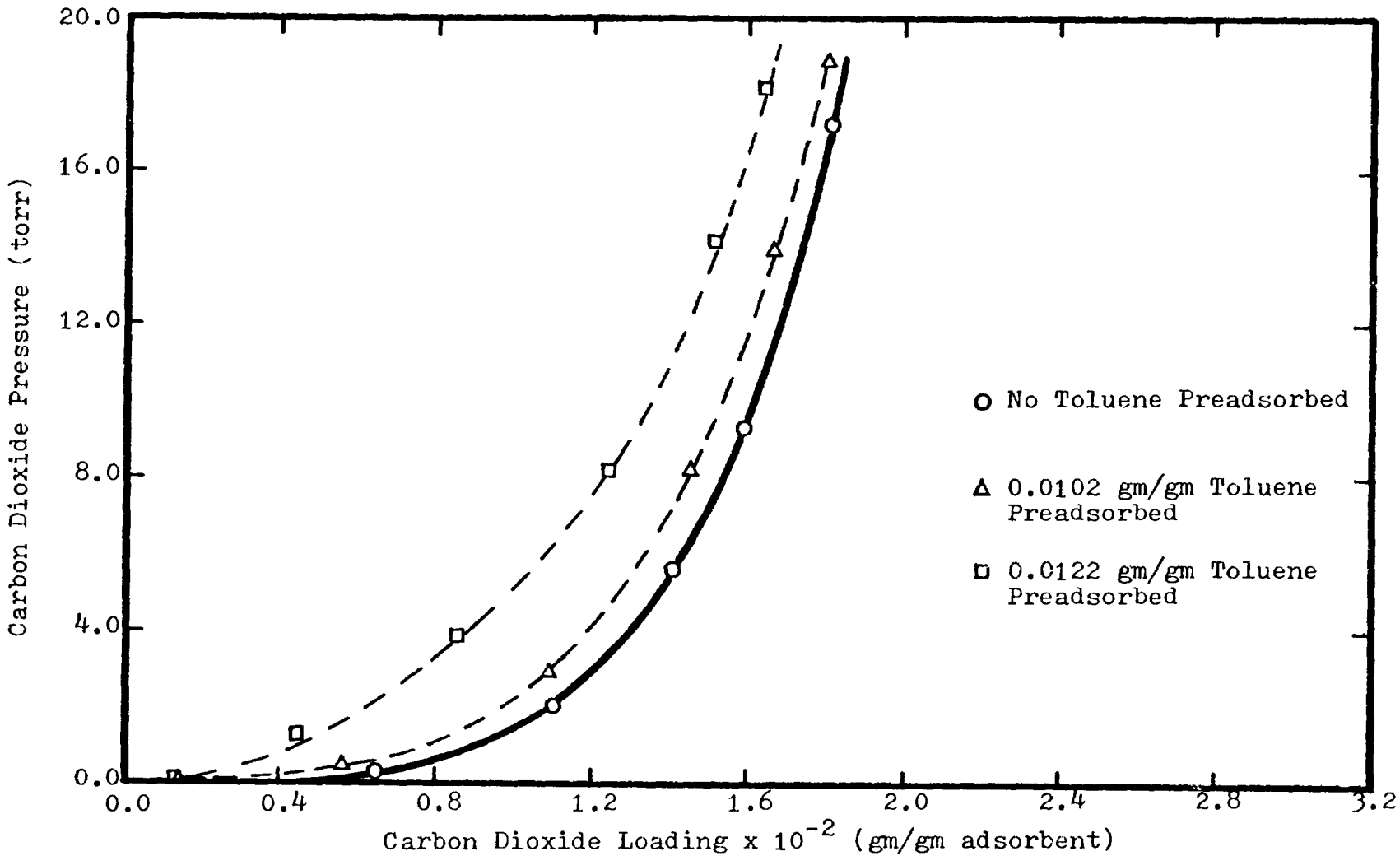


Fig. 5-6 Isotherms of Carbon Dioxide on HS-C at 25°C: Blockage by Toluene

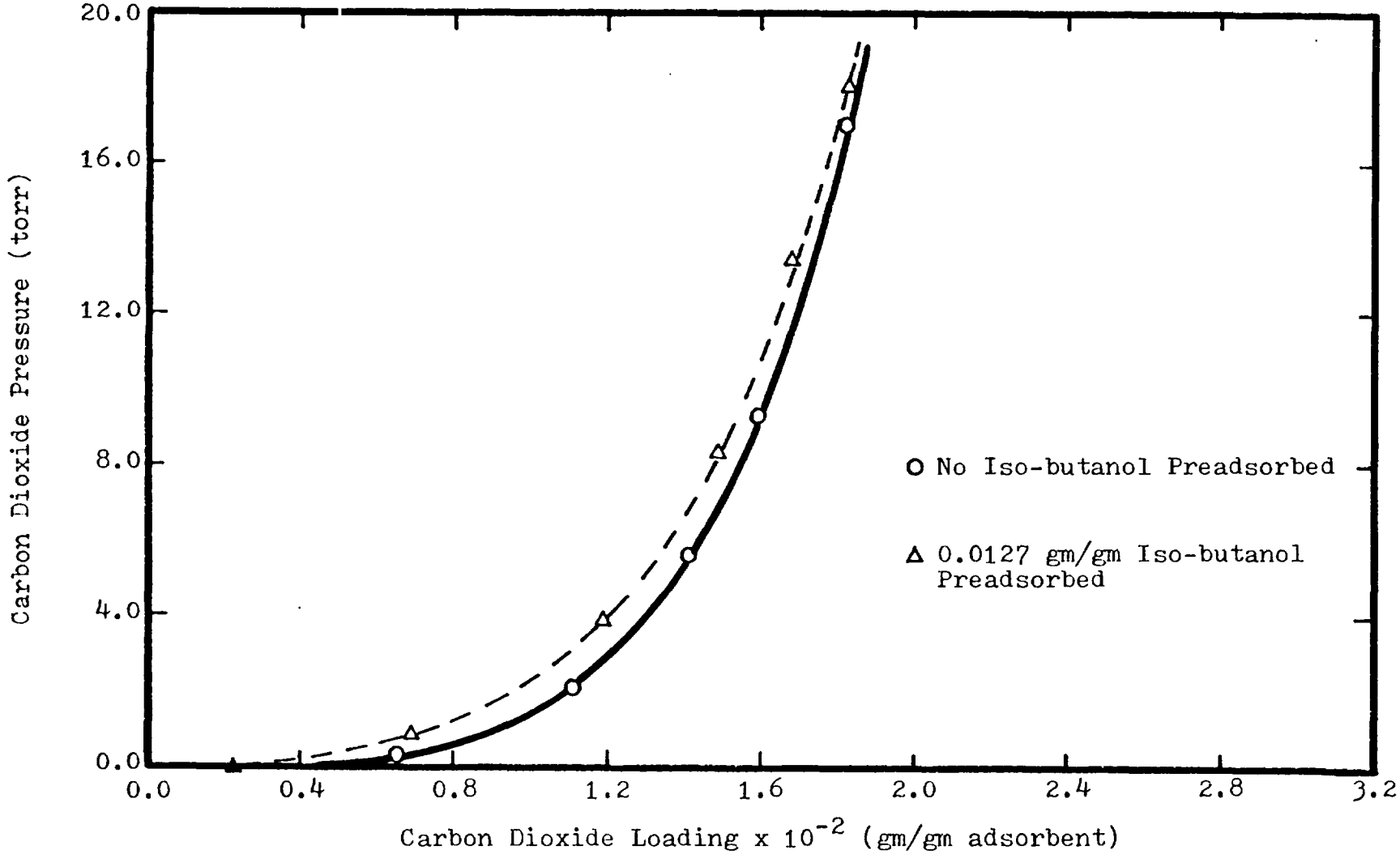


Fig. 5-7 Isotherms of Carbon Dioxide on HS-C at 25°C: Blockage by Iso-butanol

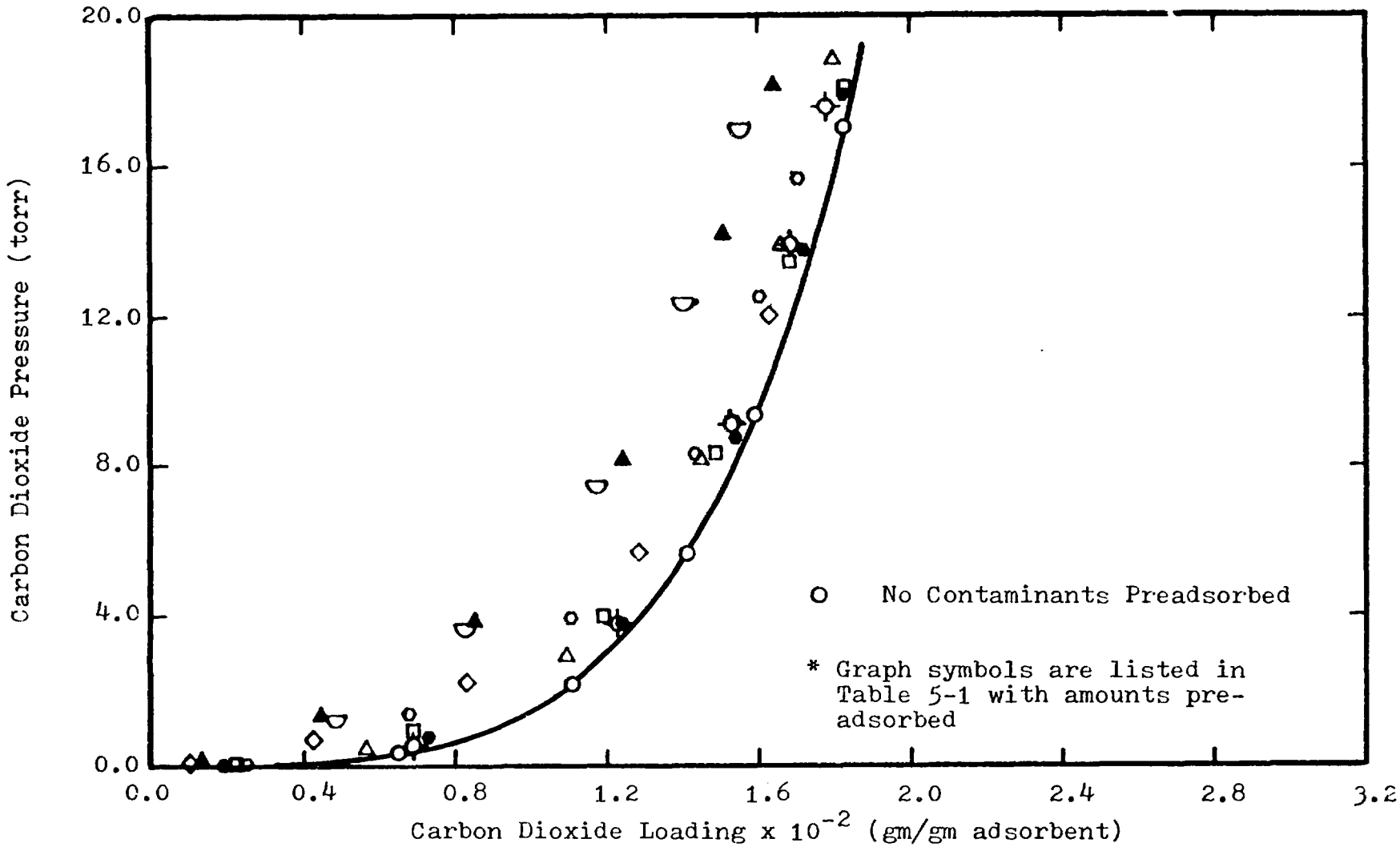


Fig. 5-8 Isotherms of Carbon Dioxide on HS-C at 25°C: Blockage by 'Liquid' Trace Contaminants at Approximately Same Amount Preadsorbed

are many times the MAC value ranging from 4 times for iso-butanol to 120 times for Freon 11. Therefore, only contaminants which give blockage of CO_2 of well over 30% seem to have significant detrimental effect on HS-C adsorbents. As a result, it seems to be in this co-adsorption study only acetone shows significant detrimental effect on HS-C adsorbents; this is to be expected of acetone.

5.3 Summary and Conclusions

The general summary of the results of this reseach work may be found in Tables 4-2 and 5-1. From these experimental results, the following conclusions may be drawn:

1) HS-C adsorbent has good adsorption potential for alcohol compounds, esters, and benzene compounds,

2) contaminants of ketone compounds, oxidizing and reducing agents are very detrimental to the HS-C adsorbents,

and 3) 'liquid' contaminants more or less displace the adsorption of CO_2 on HS-C adsorbents.

TABLE 5-1 - Data for Blockage of Carbon Dioxide by Trace Contaminants on HS-C

Run No.	Contaminants	Graph Symbols	Sample Weight (gm)	Contaminants Loading (gm/gm)	Contaminant Equilibrium Pressure (torr)	Blockage of CO_2 at 4 torr (%)
65	Freon 11	⬡	2.0006	0.0121	2.74	14
54	Methanol		2.0010	0.0065	1.34	1.5
55	Methanol	◇	2.0014	0.0108	2.51	14
58	Methyl Acetate	✧	2.0014	0.0127	1.4	3
69	Acetone	⬭	2.0048	0.0107	0.87	30
64	Benzene	●	2.0006	0.0107	0.46	2.3
59	Toluene	△	2.0014	0.0102	0.14	8
60	Toluene	▲	2.0014	0.0122	0.21	32
66	Iso-butanol	□	2.0006	0.0127	0.098	8

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APPENDIX A

CALIBRATION OF MANIFOLD AND ADSORBENT TUBE VOLUMES

The manifold and adsorbent tube volumes, V_1 and Vd respectively, of the volumetric adsorption system, shown in Fig. 3-1, were calibrated according to the procedure described below. These volumes of the system, V_1 and Vd, were measured with about 2 grams of HSC adsorbent present inside the adsorbent tube.

The calibration procedure was as follows:

1) Volumes V_1, Vd and Vc (accurately measured volume of a calibrated bulb which is attached to stopcock, S_4) were thoroughly evacuated.
2) Stopcocks S_1, S_4 and adsorbent tube stopcock were closed.
3) Stopcock S_5 was opened until a desired pressure of helium gas was reached in volume V_1 and then the pressure P_1 in V_1 was recorded.
4) Stopcock S_4 was then opened and the new system pressure P_2 was recorded.
5) Finally, adsorbent tube stopcock was opened and another new system pressure P_3 was recorded.

The manifold and adsorbent tube volumes were calculated from the following two equations, respectively;

$$V_1 = \frac{P_2 \ Vc}{(P_1 - P_2)} \qquad \text{(A-1)}$$

$$V_d = \frac{(P_2 - P_3)(V_1 + Vc)}{P_3} \qquad \text{(A-2)}$$

These two equations were derived from ideal gas relationship by assuming constant temperature in the adsorption system.

APPENDIX B

COMPUTER PROGRAM FOR COMPUTING PURE ADSORPTION AND CO-ADSORPTION ISOTHERM DATA

The computer program listed in Fig. B-1 is based on the algorithms that are desribed in Secs. 4.1.1 and 5.1. Samples of the computer calculation of pure adsorption and co-adsorption isotherm data are listed in Table B-1 and B-2, respectively.

The list of input parameters and its definitions are presented as follows:

Program Input Symbol	Definition
V1	Manifold volume, c.c. at STP
V2	Adsorbent tube volume, c.c. at STP
AVP	Ultimate pressure reading on pressure gage
VCF	Factor for correcting pressure gage reading to true pressure in mm Hg
BW	Weight of adsorbant sample
ACC	Adsorbate characteristic constant, k, which is defined as $k = \frac{RT(1000)}{M}$ where R = gas constant $(62.361 \frac{\text{mm Hg lit}}{\text{gm-moles °K}})$ T = 273°K M = molecular weight
PVP	Initial amount preadsorbed pressure, mm Hg

BLI	Initial loading or amount preadsorbed

Figure B-1

Program Listing

```
C$JOB
      DIMENSION TM(10), PP(10), T1(10), T2(10), PPC(10), TT(10)
     1, PPS(10), AA(10), A(15)
      READ(5,100) MN
100   FORMAT(I5)
      DO 1000 K=1,MN
      READ(5,120) (A(I),I=1,15)
      READ(5,150) V1,V2,M,N
      READ(5,200) AVP,VCF,BW,ACC
      READ(5,340) PVP,BLI
      WRITE(6,250) (A(I),I=1,15)
      WRITE(6,300) V1,V2,AVP,VCF,BW,ACC,PVP,BLI
      WRITE(6,325)
      SVP=0.0
      P2=0.0
      SM=0.0
      W2=0.0
      DO 1000 I=1,M
      READ(5,350) PA,RT,BT
      PC=(PA-AVP)*VCF
      IF(PVP.GT.0.0) PC=PC-PVP
      PS=PC*273.18/(RT+273.18)
      SM=SM-V1*(SVP-PS)/ACC
      NN=N-1
      WRITE(6,400) PC,RT,P2,BT,SM,W2
      READ(5,350) (TM(J),PP(J),T1(J),T2(J),J=1,N)
      DO 2000 J=1,N
      PPC(J)=(PP(J)-AVP)*VCF
      TT(J)=T1(J)-(T1(J)-T2(J))*7.2/960.2
      IF(PVP.GT.0.0) PPC(J)=PPC(J)-PVP
      PPS(J)=PPC(J)*273.18/(TT(J)+273.18)
      SMT=(V1+V2)*PPS(J)/ACC
      AA(J)=SM/BW-SMT/BW
      IF (J.NE.NN) GO TO 10
      P1=PPC(J)
      W1=AA(J)
      S1=TM(J)
      WRITE(6,500) S1,P1,T1(J),P1,T2(J),SMT,W1
10    IF(J.NE.N) GO TO 2000
      SVP=PPS(J)
      P2=PPC(J)
      W2=AA(J)
      S2=TM(J)
      WRITE(6,500) S2,P2,T1(J),P2,T2(J),SMT,W2
2000  CONTINUE
      IF(P1.EQ.P2) GO TO 20
      V=ALOG(P1/P2)
      B=V/(1/S1-1/S2)
      X=EXP(B/S2)
      PE=P2/X
      C=(W1-W2)/(P1-P2)
      W3=C*(PE-P2)+W2
      WRITE(6,550) PE,W3
      GO TO 1000
20    WRITE(6,600)
1000   CONTINUE
      WRITE(6,650)
120   FORMAT(15A4)
150   FORMAT(2F10.3,2I5)
200   FORMAT(3F10.7,E15.6)

250   FORMAT('1',35X,15A4,///)
300   FORMAT(     10X,'INPUT PARAMETERS :=',//,10X,'V1 = ',F10.3,10X,
     1'V2 = ',F10.3,//,10X,'AVP = ',F10.5,10X,'VCF = ',F10.5,//,10X,
     2'BW = ',F10.5,10X,'ACC = ',E15.6,//,10X,'PVP = ',F10.4,10X,
     3'BLI = ',E15.6,///)
325   FORMAT(     4X,'TIME(SEC.)',5X,'MAN. PRESS.',6X,'MAN.TEMP.',6X,
     1'BED PRESS.',6X,'BED TEMP.',6X,'SYS. MASS',8X,'AMT. ADS.(WT/WT)',
     2//)
340   FORMAT( F10.4,E15.6)
350   FORMAT(4F10.4)
400   FORMAT(3X,'ADDED MASS',2(5X,E14.6,5X,F7.2),2(5X,E14.6),/)
500   FORMAT(5X,F8.2,2(5X,E14.6,5X,F7.2),2(5X,E14.6),/)
550   FORMAT(4X,'AT EQUIL.',2(36X,E14.6),///)
600   FORMAT(//)
650   FORMAT('1')
      STOP
      END
```

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Table B-1

EXP.60A: PURE ACETONE ADSORPTION ON HS-C AT 25 DEG.C

INPUT PARAMETERS :-

V1 =	943.930	V2 =	28.600
AVP =	-0.03000	VCF =	0.98370
BW =	2.00060	ACC =	0.293320E 06
PVP =	0.0000	BLI =	0.000000E 00

TIME(SEC.)	MAN. PRESS.	MAN.TEMP.	BED PRESS.	BED TEMP.	SYS. MASS	AMT. ADS.(WT/WT)
ADDED MASS	0.295110E 01	28.00	0.000000E 00	25.00	0.861399E-02	0.000000E 00
500.00	0.275436E 00	28.10	0.275436E 00	25.00	0.828121E-03	0.389177E-02
600.00	0.265599E 00	28.10	0.265599E 00	25.00	0.798545E-03	0.390655E-02
AT EQUIL.			0.221440E 00			0.397291E-02
ADDED MASS	0.322653E 01	28.20	0.265599E 00	25.00	0.172506E-01	0.390655E-02
500.00	0.708264E 00	28.20	0.708264E 00	25.00	0.212875E-02	0.755868E-02
600.00	0.688590E 00	28.20	0.688590E 00	25.00	0.206962E-02	0.758823E-02
AT EQUIL.			0.598121E 00			0.772414E-02
ADDED MASS	0.426926E 01	28.20	0.688590E 00	25.00	0.276952E-01	0.758823E-02
500.00	0.140669E 01	28.20	0.140669E 01	25.00	0.422794E-02	0.117301E-01
600.00	0.135751E 01	28.20	0.135751E 01	25.00	0.408011E-02	0.118040E-01
AT EQUIL.			0.113622E 01			0.121365E-01
ADDED MASS	0.587269E 01	28.30	0.135751E 01	25.00	0.408599E-01	0.118040E-01
500.00	0.253795E 01	28.40	0.253795E 01	25.00	0.762301E-02	0.166134E-01
600.00	0.244941E 01	28.40	0.244941E 01	25.00	0.735709E-02	0.167464E-01
AT EQUIL.			0.205098E 01			0.173445E-01
ADDED MASS	0.570546E 01	28.40	0.244941E 01	25.00	0.503500E-01	0.167464E-01
500.00	0.337409E 01	28.00	0.337409E 01	25.00	0.101278E-01	0.201055E-01
600.00	0.329539E 01	28.00	0.329539E 01	25.00	0.989158E-02	0.202235E-01
AT EQUIL.			0.292862E 01			0.207739E-01

Table B-2

EXP.698: ACETONE - CO2 - HSC COADSORPTION AT 25 DEG.C

INPUT PARAMETERS :-

V1 = 944.130 V2 = 28.600

AVP = 0.01008 VCF = 0.90370

BW = 2.00480 ACC = 0.387180E 06

PVP = 0.8657 BLI = 0.106654E-01

TIME(SEC.)	MAN. PRESS.	MAN.TEMP.	BED PRESS.	BED TEMP.	SYS. MASS	AMT. ADS.(MT/MT)
ADDED MASS	0.218381E 01	22.00	0.000000E 00	25.00	0.492828E-02	0.000000E 00
500.00	0.137717E 00	22.00	0.137717E 00	25.00	0.320181E-03	0.229653E-02
600.00	0.983699E-01	22.00	0.983699E-01	25.00	0.228702E-03	0.234416E-02
AT EQUIL.			0.182909E-01			0.243703E-02
ADDED MASS	0.340368E 01	22.00	0.983699E-01	25.00	0.123873E-01	0.234416E-02
500.00	0.145587E 01	22.00	0.145587E 01	25.00	0.338479E-02	0.449049E-02
600.00	0.140669E 01	22.00	0.140669E 01	25.00	0.327044E-02	0.454753E-02
AT EQUIL.			0.118459E 01			0.480510E-02
ADDED MASS	0.783345E 01	22.00	0.140669E 01	25.00	0.250857E-01	0.454753E-02
500.00	0.396431E 01	22.00	0.396431E 01	25.00	0.921678E-02	0.791549E-02
600.00	0.390529E 01	22.00	0.390529E 01	25.00	0.907948E-02	0.798394E-02
AT EQUIL.			0.362311E 01			0.831148E-02
ADDED MASS	0.108994E 02	22.00	0.390529E 01	25.00	0.408782E-01	0.798394E-02
500.00	0.793846E 01	22.10	0.793846E 01	25.00	0.184501E-01	0.111832E-01
600.00	0.785976E 01	22.10	0.785976E 01	25.00	0.182672E-01	0.112744E-01
AT EQUIL.			0.747786E 01			0.117172E-01
ADDED MASS	0.149522E 02	22.10	0.785976E 01	25.00	0.568719E-01	0.112744E-01

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APPENDIX C

SAMPLE CALCULATION OF VACUUM DESORPTION DATA

The desorption algorithm for computing the desorption isotherm data from raw data is described in Sec. 4.1.2. For example, the following experimental raw data were collected for benzene desorption at 25°C:

V_1 = 1033.42 c.c. at Tr

Vd = 31.22 c.c. at To

Tr = 25.9°C

Tb = 25.0°C

Pe = 3.9 mm Hg

Pr = 7.32 mm Hg

Mi = 4.46×10^{-2} gm/gm adsorbent

W = 2.0135 gm

M = 78.12

The approximate amount desorbed, Md, and the correction facotr, Mr, are then calculated from Eqs. 4-12 and 4-13, respectively. Therefore,

$$Md = \frac{(3.99)(1033.42+31.22)(78.12)}{(1000)(299.08)(62.361)} = 1.7793\text{x}10^{-2} \text{ gm}$$

$$Mr = \frac{(7.32)(31.22)(78.12)}{(1000)(298.18)(62.361)} = 9.6 \times 10^{-4} \text{ gm}$$

Now, by substituting the values of Md and Mr into Eq. 4-14, the amount remaining adsorbed, Ma, is calculated.

Therefore,

$$Ma = 4.46 \times 10^{-2} - (1.7793 \times 10^{-2} - 9.6 \times 10^{-4})/2.0135$$

$$= 3.6240 \times 10^{-2} \text{ gm/gm adsorbent}$$

APPENDIX D

CALIBRATION TABLE OF TI PRECISION PRESSURE GAGE

TEXAS INSTRUMENTS INCORPORATED, DIGITAL SYSTEMS DIVISION
P.O. BOX 1444, HOUSTON, TEXAS 77001
TELEPHONE: 713-494-5115

********** PRECISION PRESSURE CALIBRATION TABLE **********

CAPSULE S/N: 4324 INSTR. S/N: 1919 CAL'N DATE: 06/03/78
CAPSULE RATED PRESSURE: 1000 TORR MAX PRESS: 1280 TORR
CAPSULE TYPE: 1 INSTRUMENT MODEL: 145-01
CAPSULE TEMPERATURE AT CALIBRATION: 44.2 DEG. C.
CALIBRATION STANDARD: P1605-1270 CTR GEARING: 1.00:1
CALIBRATED BY: DAN SINENI

TRUE PRESSURE (TORR)	COUNTER READING (COUNTS)
0.0	0.
50.00	5085.
100.00	10168.
150.00	15240.
200.00	20310.
250.00	25374.
300.00	30432.
350.00	35488.
400.00	40542.
450.00	45588.
500.00	50620.
550.00	55640.
600.00	60659.
650.00	65672.
700.00	70688.
750.00	75689.
800.00	80677.
850.00	85668.
900.00	90651.
950.00	95630.
1000.00	100586.

NOTES:

1. THIS CALIBRATION TRACEABLE TO THE NBS THRU THE ABOVE STANDARD.

2. THIS SECONDARY STANDARD SHOULD BE RECALIBRATED PERIODICALLY: AT 6 - 12 MO. INTERVALS OR, AS USE, HISTORY, OR POLICY DICTATE.

3. PRESSURE CALIBRATION STANDARDS CORRECTED TO STANDARD GRAVITY, 980.665 CM/SEC/SEC. UNITS OF MERCURY CORRECTED TO ZERO DEG.C.

4. COUNTER READING VS TRUE PRESSURE APPLIES ONLY AT ABOVE SPECIFIED CAPSULE TEMPERATURE. FOR OTHER TEMPERATURE, COUNTER READING VS PRESSURE FOR FUSED QUARTZ BOURDON CAPSULE MAY BE CORRECTED BY +0.013% OF COUNTER READING PER + DEG.C. DEVIATION FROM CALIBRATION TEMP.(REFER TO MANUAL IF TEMPERATURE SETTING NEEDS READJUSTMENT.)

5. DIRECT READING CAPSULES (S/N'S 10000 - 19999): W A R N I N G ABOVE CALIBRATION DATA APPLIES ONLY IF DPR MODULE INSTALLED BEARING ABOVE CAPSULE AND INSTRUMENT S/N'S.

S/O:0762-0150--RC1 CUSTOMER: RICE UNIV.