Adsorption Equilibria Characteristics of Some Chlorinated Cleaning Solvent Vapors (CFC-113 and HCFC-141b)

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Abstract−Chlorinated cleaning solvents have been widely used industrially, but some chlorinated cleaning solvents are considered to be prime contributors to stratospheric ozone depletion. The use of activated carbons to adsorb specific solvent vapors has thus received great attention. The adsorption equilibrium characteristics of HCFC-141b (1,1-dichloro-1-fluoroethane) and CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane) vapors on an activated carbon pellet were studied at various temperatures. Adsorption isotherms were measured and fitted by Sips equations. Detail parameters and their values for the design of adsorption facilities are suggested. The heats of adsorption for two solvents were estimated from experimental data.

Key words: Adsorption, Chlorinated Cleaning Solvent, Activated Carbon

INTRODUCTION

Chlorofluorocarbons, first manufactured by Du Pont in the early 1930s, have been widely used for more than half a century. They are very popular because of their chemical stability, non-toxicity and high solubility. Currently, they are extensively used as refrigerant and as spraying, foaming and cleaning agents in a wide variety of industries. Table 1 lists typical examples of various industrial applications of CFCs [Wolf, 1989]. The CFCs shown in this table, i.e., CFC-11, CFC-12 and CFC-113, are among the most important and are produced in large quantity. CFC-12 is used as a refrigerant in air conditioning and commercial refrigeration systems and CFC-11 and CFC-113 are excellent cleaning solvents, spraying and foaming agents. These CFCs not only deplete the stratospheric ozone, but have a significant greenhouse effect on the atmospheric environment. Table 2 lists their effects on the atmospheric environment ["The 1995 International CFC and Halon alternatives conference proceedings," 1995].

According to the Montreal Protocol, all CFCs will be gradually phased out [Wolf, 1989; Barnett, 1992; Kerr, 1994] and a replacement will definitely be needed. While good replacement compounds of any kind may not be readily available within the next few year, CFC recovery is perhaps a more practical alternative for the time being. Furthermore, recovery provides a much more economic alternative to other methods of CFC disposal. Safe disposal of chlorofluorocarbons is not easy. They can be incinerated or destroyed chemically [Ogura et al., 1992]. Although destructive methods of CFC disposal have been receiving increasing attention in recent years [Ogura et al., 1992]. These methods have a major disadvantage in that the chlorinated and/or fluorinated compounds generated in the process can cause a subsequent air pollution problem. The purpose of this work was to investigate the gas-phase adsorption characteristics of 1,1-dichloro-1-fluoroethane (HCFC-141b) and 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) by activated carbon pellet. Currently, HCFC-141b is generally regarded as an excellent replacement for the foaming agent CFC-11 in the manufacture of rigid polyurethane foam although it can be also used as a substitute for CFC-113 and 1,1,1-trichloroethane (CCl_3CH_3) which have been employed in the electronic industries as cleaning agents. As these solvents are very volatile, losses due to work place emission in a typical plant can be as high as 90%.

For this reason, technologies for the removal and recovery of HCFC-141b and CFC-113 have been focused on as alternative techniques for protection of the environment. One of the several technologies is the use of adsorption beds [Cho and Lee, 1991; Kim et al., 2002]. This technology is a common one because it offers some advantages. The advantages include the possibility of high recovering efficiency at low concentration. Furthermore, this technology

Table 1. Uses of CFCs in various industries

Compound	Applications
CFC-11, CFC-12, HFC-22	Air conditioning
CFC-11, CFC-12	Pharmaceuticals, cosmetics
CFC-11, CFC-12, CFC-113	Plastics
CFC-113	Electronic industries

Table 2. Effects of CFCs on the atmospheric environment

Compound	Formula	Life (y)	ODP[a]	GWP[a]
CFC-11	CCl_3F	47-80	0.9-1.0	1.0
CFC-12	CCl_2F_2	95-150	0.8-0.9	2.8-3.4
CFC-113	$CClF_2CClF_2$	96-117	0.6-0.8	1.3-1.4
HCFC-141b	CH_3CCl_2F	9-11	0.07	0.083-0.097

[a]ODP, ozone depletion potential, based on 1 for CFC-11.
[a]GWP, global warming potential, based on 1 for CFC-11.

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requires the low energy costs. In the design of such adsorption facilities, the characteristics of adsorption equilibria are very important [Chihara et al., 2000]. In this study, an activated carbon pellet was used as efficient adsorbents for the adsorption of HCFC-141b and CFC-113. Experimental equilibria were measured and correlations for these data are suggested.

Many literature reports are replete with theories and equations describing the equilibrium between adsorbates and adsorbents [Kuo and Hines, 1992; Lewis et al., 1950; Wood, 1992; Kim et al., 2001]. Numerous empirical and theoretical approaches have been proposed to characterize adsorption equilibria. However, no one theory has yet been devised which satisfactorily explains a majority of the observations on a theoretically rigorous basis. For a given gas, the amount of gas adsorbed per unit mass of a given adsorbent at equilibrium can be expressed as a function of vapor concentration and temperature. One of the important factors for designing an adsorption facility is the adsorption equilibria of adsorbates on adsorbents [Linders et al., 2001]. The most common method of presenting data is in the form of plotted isotherms. Many isotherms are commonly developed for an adsorbate-adsorbent system for utilization in design. It is convenient that adsorption equilibria are represented by explicit equations. Therefore, two correlations were derived to describe the effects of vapor concentration and temperature on the equilibrium adsorption capacity for the two different adsorbates.

EXPERIMENT

A pellet-type (Norit B4) activated carbon was employed as an adsorbent for the adsorption of HCFC-141b and CFC-113. The BET surface area for each adsorbent was measured by an automatic volumetric sorption analyzer (QUANTACHROME) using nitrogen adsorption at 77 K. The measured and supplied properties of this adsorbent are listed in Table 3. HCFC-141b and CFC-113 were employed as adsorbates. These adsorbates were obtained from the Daikin Company and had a purity of 99.8%. A flow diagram of the apparatus employed in this study is given in Fig. 1. This equipment employs a manometric method for the measurement of adsorption equilibria [Cho and Lee, 1991]. A weighed sample of the adsorbent was placed in a U-tube, as shown in Fig. 1. An oil diffusion pump (Veeco Instrument Inc., Model 4530-009-02) and a mechanical vacuum pump (Sargent Welch, Model 1402B-01) in combination provided vacuum down to 10^{-5} mmHg. Two thermistor gauges

Table 3. Physical properties of activated carbon pellet

Physical properties	Activated carbon pellet
Supplier	Norit (B4)
Pellet diameter (cm)	0.37
Pellet length (cm)	0.65
BET surface area $(m^2/g)^a$	826
Pore distribution^b (%)	
Micropore distribution (<1 nm)	45.16
Transition pores (1-100 nm)	9.68
Macropores (>100 nm)	45.16

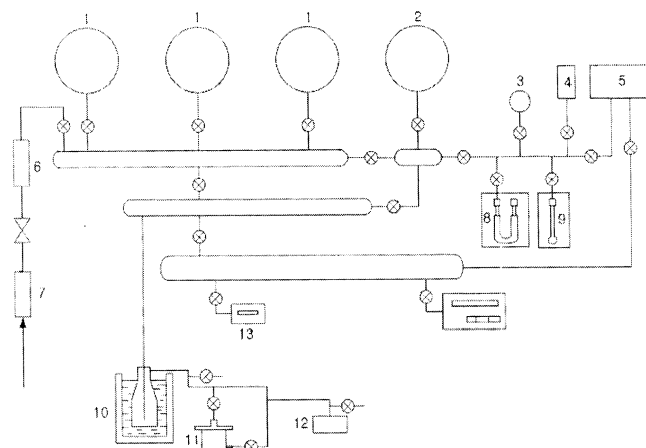^{a}From nitrogen adsorption at 77 K (0.162 nm^2/molecule); ^{b}From manufacturer.

Fig. 1. Flow diagram of the apparatus.

1. Gas reservoir	8. Sample packing part
2. He gas reservoir	9. Solvent reservoir
3. Standard volume bulb	10. Liquid nitrogen trap
4. Absolute pressure gauge	11. Oil diffusion pump
5. Diffrential pressure gauge	12. Mechanical pump
6. Moisture trap	13. Thermocouple gauge
7. Oxygen trap	14. Ionization gauge

(Veeco Instrument Inc., Model TG-70 and Model RG1000) were used to monitor the pressure when the system was evacuated. During the adsorption run, the pressure changes were measured by a MKS Baraton gauge (absolute pressure transducer, Model 122A-00100BB, with readout unit PDR-C-2C) and a pressure measuring system made by Datametrics (type 590 differential pressure transducer, 1400 electronic manometer).

Before every run, the adsorbent was prepared by a standard degreasing procedure consisting of evacuating the system at 423 K and regenerating for a time which was typically about 15 h. The weight of the sample was measured within 10 μg precision. The dead volume was determined by introducing measured amounts of
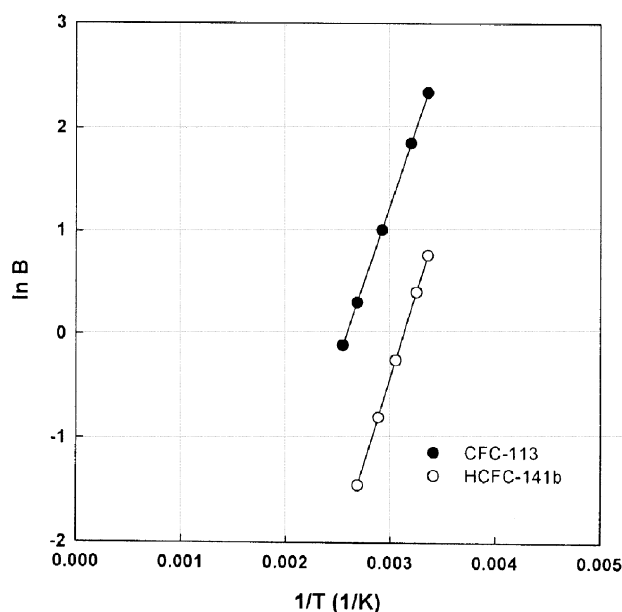

Fig. 2. Temperature effects on the equilibrium constants B.

helium gas into the evacuated adsorption chamber and noting the corresponding pressure. The adsorption of helium gas was assumed to be negligible under these conditions. Adsorption isotherms were obtained by admitting successive increments of measured volumes of sample gas to the adsorbent sample. After each increment of gas was admitted, some time was allowed for attainment of equilibrium and the system pressure was then noted. Correction of the known volume of gas admitted for the amount unadsorbed in the dead space yielded a point on the adsorption isotherm. The equilibrium data for each run were obtained by the same procedure but with variation of the temperature.

RESULTS

1. Equilibria of CFC-113 and HCFC-141b on Activated Car-

bon Pellet

The Sips equation, which is a combination of the Langmuir and Freundlich equation, is [Sips, 1948]

$$\frac{q^*}{q_m} = \frac{BC^n}{1+BC^n} \tag{1}$$

If n is equal to unity, then this equation becomes the Langmuir equation. On the other hand BC^n is much greater than unity, it becomes the Freundlich equation. If BC^n is much less than unity, which occurs at low concentrations, then it becomes a linear isotherm equation. Hence, this correlation, having three parameters, has many desirable properties and should be capable of describing the isotherm behavior over a wide concentration range. The parameters q_m, B_o and n were determined by the best statistical representation of the experimental data. Detailed parameter searches for the iso-
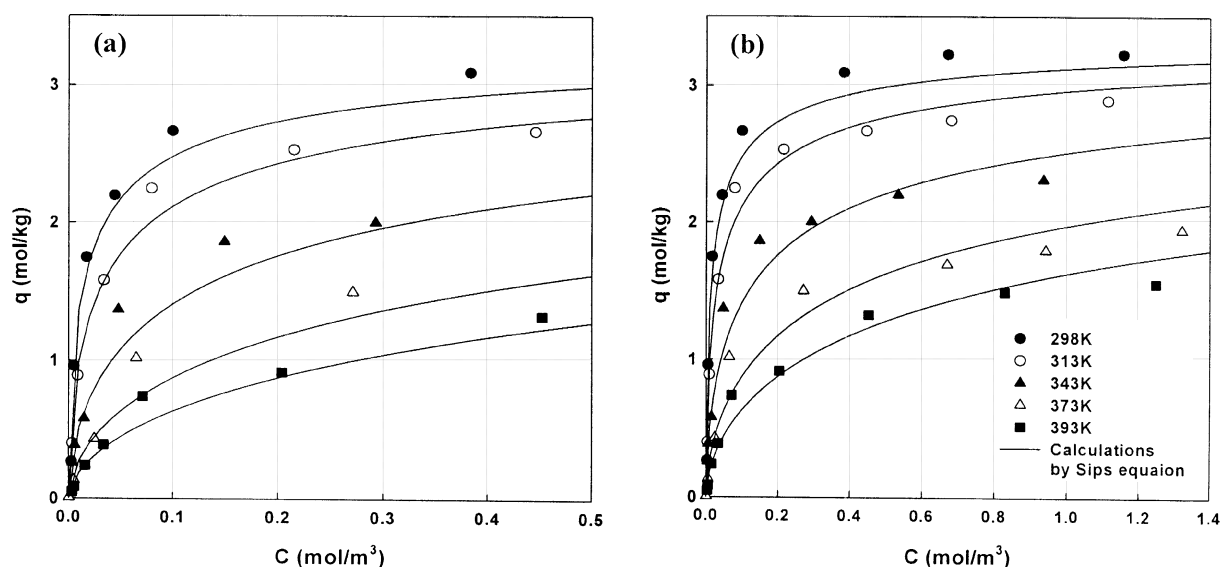

Fig. 3. Comparative plots of experimental isotherms with calculated values for CFC-113 on activated carbon pellet by Sips model. (a) in low concentration ranges, (b) in wide concentration ranges.
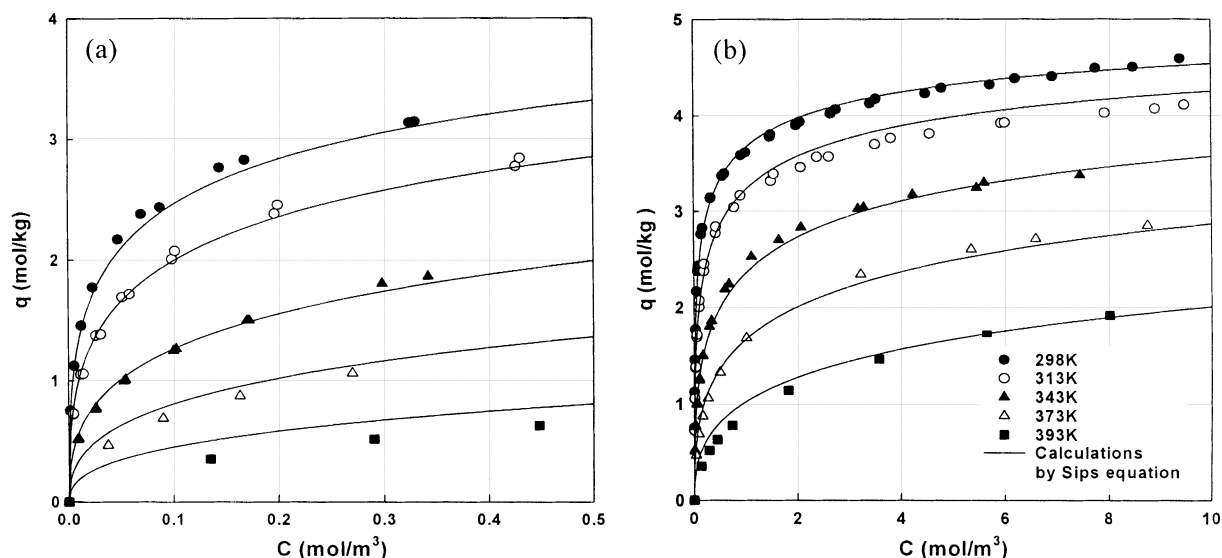

Fig. 4. Comparative plots of experimental isotherms with calculated values for HCFC-141b on activated carbon pellet by Sips model. (a) in low concentration ranges, (b) in wide concentration ranges.

Table 4. Sips parameters for CFC-113 and HCFC-141b on activated carbon pellet

Parameter	CFC-113	HCFC-141b
q_m (mol/kg)	3.42	5.37
B_o	2.6724	0.7210
n	0.4058	0.5971
Q (KJ/mol)	25.11	27.45
Error (%)	36.86	3.37

$$\text{Error } (\%) = \frac{100}{N_d} \sum_{j=0}^{N_d} \frac{|q_{j,}(\text{expt}) - q_{j,}(\text{pred})|}{q_{j,}(\text{expt})}$$

therm constants were conducted for the activated carbon pellet by using nonlinear regression analysis. The parameters B in Eq. (1) are, of course, functions of temperatures.

The temperature effects on the two parameters B of CFC-113 and HCFC-141b for the activated carbon pellet are depicted in Fig. 2. The values B of CFC-113 and HCFC-141b decrease with increasing temperatures for both adsorbate. Therefore, the best fit was obtained with the following equation:

$$\frac{q^*}{q_m} = \frac{B_o \exp\left[\frac{Q}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)\right]C^n}{1 + B_o \exp\left[\frac{Q}{R}\left(\frac{1}{T} - \frac{1}{T_o}\right)\right]C^n} \tag{2}$$

Figs. 3, 4 shows the comparison of experimental data for the activated carbon pellet with the isotherm curves fitted by Eq. (2). It was found that the experimental data of CFC-113 and HCFC-141b on the activated carbon pellet could be described by the Sips relationship. Table 4 lists Sips parameters for CFC-113 and HCFC-141b on activated carbon pellet.

2. Heats of Adsorption

The parameter Q was determined by the best statistical representation of the experimental data. Heats of adsorption determined by the best statistical representation of the experimental data are listed in Table 4. Heats of adsorption for HCFC-141b (Q=27.45 KJ/mol) are slightly larger than that for CFC-113 (Q=25.11 KJ/mol) on the activated carbon pellet. Heats of adsorption are lower than the heats of condensation ($q_{condensation/T=300k}$=28.66 KJ/mol) for CFC-113 [Benning and McHarness, 1934]; the former are of the same order of magnitude as the latter. This means that the adsorption of two solvents on the activated carbon pellet is due primarily to physical forces.

CONCLUSIONS

The adsorption characteristics of two kinds of chlorinated solvents on activated carbon pellet were investigated. The adsorption equilibria were obtained at various temperatures. The equilibrium data of CFC-113 and HCFC-141b vapor on activated carbon pellet were well correlated by Sips equation. The heats of adsorption for two solvents were estimated from experimental data. Although the heats of adsorption are lower than the heats of condensation, the former are of the same order of magnitude as the latter.

ACKNOWLEDGMENT

NOMENCLATURE

q_m : maximum adsorption capacity of adsorbent [mol/kg]
q^* : moles of adsorbate adsorbed per unit mass of adsorbent [mol/kg]
q : equilibrium amount adsorbed on the adsorbent [mol/kg]
B : constant
B_0 : constant
C : concentration in vapor phase [mol/m³] and constant in Eq. (3)
n : constant in Eq. (1)
Q : heat of adsorption [KJ/mol]
$q_{condensation}$: heat of condensation [KJ/mol]
R : gas constant [8.314 J/(mol·K)]
T : absolute temperature [K]

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