Adsorption Equilibria of Hexafluoropropene and 1,1,1,2,3,3,3-Heptafluoropropane on Activated Carbon at 283, 303, 333, and 363 K

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The adsorption equilibrium relationships for hexafluoropropene and 1,1,1,2,3,3,3-heptafluoropropane on commercially available activated carbon were measured by a static volumetric technique. The equilibrium isotherms were obtained at (283.15, 303.15, 333.15, and 363.15) K and pressures up to 100 kPa. In this study, the experimental equilibrium data were correlated satisfactorily by employing a thermodynamic method applied by Yun et al. (1998a).

Introduction

Bromotrifluoromethane (Halon-1301) and bromochlorodifluoromethane (Halon-1211) have been used as clean, nontoxic, and effective fire-extinguishing agents for a long time. However, these compounds are being phased out because of their ozone-depleting potential. HFC-227ea (1,1,1,2,3,3,3-heptafluoropropane, CF_3CFHCF_3) is known to be one of the promising replacements for Halon-1301 and Halon-1211. It has been proposed to synthesize HFC-227ea by a procedure involving either vapor-phase or liquid-phase reaction between hexafluoropropene and hydrogen fluoride (Allied Chem., 1962; Anderson, 1992; Aoyama and Shibata, 1996; Gann et al., 1990). It is therefore necessary to separate the products from the unreacted raw materials after they leave a reactor. To ensure meeting the specification for HFC-227ea, an adsorption stage is employed for separating out hexafluoropropene.

To design an adsorption process, thermodynamic data on adsorption equilibria must be known over a wide range of temperature. Until quite recently, however, there was no reliable information concerning adsorption of hexafluoropropene and 1,1,1,2,3,3,3-heptafluoropropane on activated carbon at various temperatures. In this regard, the present study has been devoted to the measurement of adsorption isotherms of hexafluoropropene and 1,1,1,2,3,3,3-heptafluoropropane on activated carbon at 283, 303, 333, and 363 K.

Experimental Section

Materials. The activated carbon pellet Xtrusorb-600, produced by Calgon Co., was chosen as the adsorbent. Samples were crushed to 20−30-mesh in order to attain rapid equilibrium. Prior to measurement, the sample was kept in a drying vacuum oven at 423 K for >24 h to remove impurities. The physical properties of the activated carbon can be found elsewhere (Yun et al., 1998b).

Table 1. Physical Properties of Hexafluoropropene (HFP) and 1,1,1,2,3,3,3-Heptafluoropropane (HFC-227ea)

	HFP	HFC-227ea
molecular formula	C_3F_6	C_3HF_7
molecular weight	150.02	170.03
purity/%	99.5	99.5
boiling point/K	243.6	256.8
T_c/K	367.1	374.8
P_c/bar	28.98	29.10

The hexafluoropropene (HFP) and 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea) were supplied from Daikin Industry and Great Lakes Chemical Co. The physical properties of these materials were supplied by each manufacturer and are presented in Table 1.

Apparatus and Procedure. The experimental apparatus used was a static volumetric type. The total quantity of gas admitted to the system and the amount of gas in the vapor remaining after adsorption equilibrium were established by appropriate $P-V-T$ measurements. The system pressure measurements were made using a Baratron absolute pressure transducer (MKS type 690A13TRA) with a high-accuracy signal conditioner (MKS type 270D). During the adsorption, the adsorption cell was placed in a water bath and the temperature was maintained constant within ±0.02 K by the refrigerating circulator (Haake type F3). The experimental temperature was measured with a T-type thermocouple.

The mass of the carbon sample was determined with an accuracy of $\pm 10\ \mu$g, and it was introduced into the adsorption cell. Prior to each isotherm measurement, the charged activated carbon was regenerated at 523 K under high vacuum for 12 h. An oil diffusion pump and a mechanical vacuum pump in series (Edward type Diffstak 63/150M) provided a vacuum down to 10^{-3} Pa, and the evacuation was monitored by both ion and convectron gauges with a vacuum gauge controller (Granville-Phillips type 307). The volume of the adsorption cell was determined by expansion of helium gas at the experimental temperature. Details of the equipment and the operating procedures used are described in the previous publication of Yun et al. (1998b).

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Table 2. Experimental Isotherm Data for HFP on Activated Carbon (Xtrusorb-600)

P/kPa	N/mmol g^{-1}	P/kPa	N/mmol g^{-1}	P/kPa	N/mmol g^{-1}	P/kPa	N/mmol g^{-1}
T = 283.15 K							
0.0123	0.2759	5.9639	2.2611	37.706	3.0326	71.572	3.3050
0.1031	0.6867	12.896	2.5834	40.039	3.0607	76.211	3.3236
0.1309	0.7568	16.360	2.6853	49.825	3.1536	81.985	3.3937
1.0305	1.5057	21.346	2.7914	50.732	3.1693	92.491	3.4190
3.6346	2.0296	24.839	2.8593	63.185	3.2442		
5.4399	2.2263	30.666	2.9444				
T = 303.15 K							
0.0301	0.2474	8.0798	1.9589	24.733	2.4687	45.906	2.7472
0.3091	0.6967	11.984	2.1431	31.373	2.5770	51.945	2.8188
1.6320	1.2611	18.226	2.3322	38.359	2.6729	73.811	3.0050
4.6132	1.7062	21.733	2.3861	44.879	2.7287	89.784	3.0949
T = 333.15 K							
0.0883	0.1293	5.5492	1.1250	26.213	1.8949	64.265	2.3542
0.3300	0.3187	8.0398	1.3211	36.066	2.0336	73.571	2.4586
0.5001	0.4219	8.6491	1.3390	36.266	2.0476	76.598	2.4697
0.7728	0.4821	11.896	1.4744	44.412	2.1576	82.945	2.4959
1.7640	0.7574	12.034	1.5139	49.865	2.2107	90.104	2.5657
2.6453	0.8219	17.933	1.7119	54.185	2.2631	93.291	2.5726
4.6146	1.1091	22.973	1.7928	63.238	2.3499		
T = 363.15 K							
0.2287	0.0857	5.3492	0.6787	21.613	1.1918	55.932	1.6674
0.2323	0.0956	5.8812	0.6807	27.119	1.2949	64.678	1.7407
0.2467	0.1074	7.4438	0.7849	27.506	1.3169	65.158	1.7941
0.8256	0.2424	8.2091	0.8162	31.399	1.3577	73.745	1.8212
0.9285	0.2627	8.8918	0.8266	37.292	1.4525	74.225	1.8898
1.1706	0.3118	12.245	0.9317	37.612	1.4591	83.331	1.8938
1.9840	0.4020	12.868	0.9841	45.946	1.5468	83.598	1.9453
2.6079	0.4781	13.212	0.9879	46.226	1.5706	93.678	1.9744
3.0293	0.5175	19.400	1.1242	55.132	1.6486		
3.7172	0.5489	19.466	1.1613				

Results and Discussion

The design of adsorptive separation and purification processes requires primarily a knowledge of thermodynamic data on adsorption equilibria for the system of interest. For practical applications, the adsorption equilibria must be known over a broad range of operating temperatures. This information is used to calculate the cycle time for a specific bulk concentration, to derive optimum sizes of adsorbers, and to determine optimum operating conditions. In addition, the equilibrium isotherms of pure species are fundamental to the dynamic simulation of adsorbers.

In this study, the adsorption isotherm data for hexafluoropropene and 1,1,1,2,3,3,3-heptafluoropropane on activated carbon at 283, 303, 333, and 363 K were obtained at pressures up to 100 kPa using the static volumetric method. The experimental data are presented in Tables 2 and 3.

For practical utility, the experimental data should be correlated by an analytical expression that includes the adjustable parameters as functions of temperature. The choice of isotherm equation for a specific adsorption system has been a topic of great interest for many decades, to researchers working in the area. As a result, a number of theories and empirical methods have been presented, ranging from the traditional kinetic approach to molecular simulations. In many cases, however, it still may not be easy to determine a set of isotherm parameters that can represent all the experimental data at various temperatures with good accuracy.

For the prediction/correlation of adsorption equilibria of pure substances, a simple, yet very powerful, method was applied by Yun et al. (1998a). This method is based on the assumption that the value of the isosteric enthalpy of adsorption does not depend on temperature, for a given surface loading. According to Yun et al., such an approach can be successfully used even for very complex adsorption systems. To calculate the isosteric enthalpy of adsorption, the Clausius−Clapeyron equation was applied as follows:

$$-\frac{\Delta H}{RT^2} = \left[\frac{\partial \ln P}{\partial T}\right]_N \tag{1}$$

In this equation, $-\Delta H$ is the isosteric enthalpy of adsorption and is sometimes denoted as q_{st}. When integrated, eq 1 allows one to calculate $-\Delta H$ from adsorption isotherms obtained at two or more temperatures. If experimental isotherms are available at two temperatures only, the value of $-\Delta H$ is given by (Ross and Olivier (1964):

$$-\Delta H = R\left[\frac{\ln P_1 - \ln P_2}{1/T_2 - 1/T_1}\right]_N \tag{2}$$

where P_1 and P_2 are the equilibrium pressures at temperatures T_1 and T_2, respectively, when the amount adsorbed is a constant N. As mentioned earlier, the estimation of $-\Delta H$ is based on the assumption that it is independent of temperature, and therefore, one can obtain the following useful relation:

$$\Delta H^{\mathrm{I}}(T_1,T_2)_N = \Delta H^{\mathrm{II}}(T,T_2)_N \tag{3}$$

$$\frac{\ln P_1 - \ln P_2}{1/T_2 - 1/T_1}\Big|_N = \frac{\ln P - \ln P_2}{1/T_2 - 1/T}\Big|_N \tag{4}$$

where P is the equilibrium pressure at the specific temperature T of interest, and finally one gets the following equation for a given N.

$$P = \exp\left[\frac{\ln P_1 - \ln P_2}{1/T_2 - 1/T_1}\left(\frac{1}{T_2} - \frac{1}{T}\right) + \ln P_2\right]\Big|_N \tag{5}$$

Table 3. Experimental Isotherm Data for HFC-227ea on Activated Carbon (Xtrusorb-600)

P/kPa	N/mmol g^{-1}	P/kPa	N/mmol g^{-1}	P/kPa	N/mmol g^{-1}	P/kPa	N/mmol g^{-1}
			T = 283.15 K				
0.0109	0.4214	10.892	2.6958	41.146	3.1381	71.652	3.3357
0.0140	0.4545	11.301	2.7024	46.106	3.1847	80.438	3.3684
0.1403	1.0469	18.080	2.8697	51.652	3.2135	80.545	3.3818
0.3456	1.3768	20.653	2.9081	56.985	3.2587	93.944	3.4219
1.5866	1.9554	27.079	3.0058	61.358	3.2704	93.958	3.4588
4.2679	2.3687	31.066	3.0401	67.745	3.3132		
6.0785	2.4844	36.052	3.1021				
			T = 303.15 K				
0.0187	0.3079	5.9665	2.0886	33.946	2.7394	63.852	3.0148
0.0213	0.3091	10.869	2.3196	38.732	2.7843	70.732	3.0234
0.2649	0.8771	11.277	2.3241	42.879	2.8262	71.265	3.0865
0.2740	0.9064	18.266	2.5175	48.105	2.8665	78.171	3.0560
1.8986	1.6027	19.800	2.5344	52.265	2.8971	86.918	3.1160
2.0279	1.6410	26.773	2.6512	55.425	2.9387	96.798	3.1767
5.9465	2.0747	29.093	2.6846	61.625	2.9568		
			T = 333.15 K				
0.0613	0.2442	2.9159	1.1882	15.426	1.8918	41.906	2.3198
0.0636	0.2473	5.8639	1.4805	18.013	1.9696	51.039	2.3928
0.5531	0.6577	7.2785	1.5661	23.039	2.0654	63.625	2.4779
0.6504	0.6980	10.024	1.7099	26.906	2.1830	76.691	2.5392
2.4239	1.1258	11.701	1.7708	32.106	2.2062	95.424	2.6517
			T = 363.15 K				
0.2416	0.1803	4.2226	0.8035	27.973	1.5344	57.692	1.8478
0.2495	0.1856	8.7811	1.0613	37.572	1.6108	68.212	1.9244
1.2810	0.4699	9.7611	1.0986	37.586	1.6692	81.265	2.0548
1.2964	0.4790	17.546	1.3327	47.119	1.7174	95.411	2.1092
3.6426	0.7634	17.600	1.3392	48.239	1.7664		

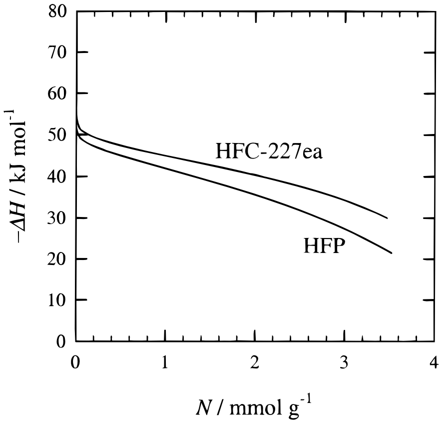

Figure 1. Isosteric enthalpy curves for HFP and HFC-227ea on activated carbon.

Table 4. Toth Isotherm Parameters of HFP and HFC-227ea on Activated Carbon (Xtrusorb-600) at 283 and 363 K

adsorbate	T/K	m/mmol g^{-1}	b/[kPa]^t	t	100D
HFP	283.15	5.8279	0.3722	0.2306	0.645
	363.15	9.3805	1.2908	0.2357	3.002
HFC-227ea	283.15	5.0663	0.2770	0.2328	0.523
	363.15	5.6947	0.9644	0.2591	1.775

Equation 5 enables one to estimate the adsorption equilibrium relation of P and N at T using two sets of equilibrium isotherms of $P_1 = f(N)_{T_1}$ and $P_2 = f(N)_{T_2}$, obtained by fitting the experimental data at two different temperatures. In this study, the Toth equation was employed to fit the experimental isotherm data at 283 and 363 K.

$$N = \frac{mP}{(b + P^t)^{1/t}} \tag{6}$$

To find the Toth parameters (m, b, and t), we used the Nelder−Mead simplex pattern search algorithm. For HFP and HCFC-227ea at 283 and 363 K, the parameters are summarized in Table 4, along with the average absolute deviation parameter D.

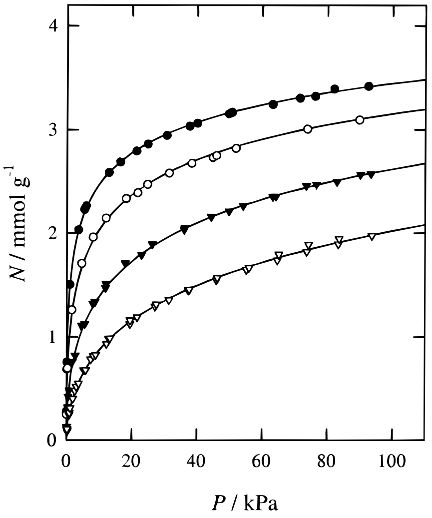

Figure 2. Adsorption isotherms for HFP on activated carbon (Xtrusorb-600) at 283, 303, 333, and 363 K: (●) 283 K; (○) 303 K; (▼) 333 K; (▽) 363 K; (—) calculated by eq 5.

$$D = \frac{1}{k}\sum_i^k \left|\frac{N_i^{\mathrm{obs}} - N_i^{\mathrm{cal}}}{N_i^{\mathrm{obs}}}\right|,\ k = \text{number of data points} \tag{7}$$

By using the Toth parameters obtained at the two temperatures 283 and 363 K, the isosteric enthalpy of adsorption for each temperature was calculated by eq 2. The resulting isosteric enthalpy curves are plotted in Figure 1. The isosteric enthalpy of adsorption, which is a measure of the interactions between adsorbate molecules and adsorbent lattice atoms, may be used as an indicator of the degree of energy heterogeneity of a surface. As shown in

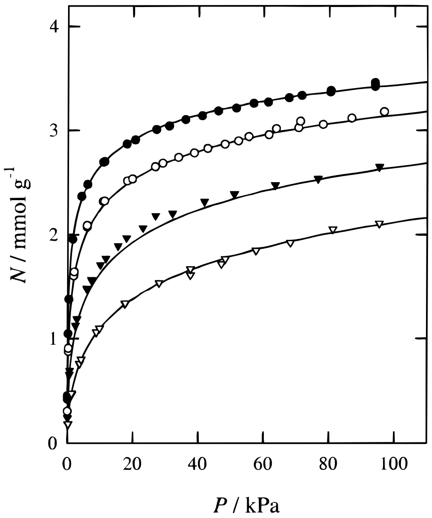

Figure 3. Adsorption isotherms for HFC-227ea on activated carbon (Xtrusorb-600) at 283, 303, 333, and 363 K: (●) 283 K; (○) 303 K; (▼) 333 K; (▽) 363 K; (—) calculated by eq 5.

Figure 1, the isosteric enthalpy varied with surface loading for both adsorbates, suggesting that adsorption occurred on an energetically heterogeneous surface. At the limit of zero coverage, the values of the isosteric enthalpy of adsorption are 55 kJ mol^{-1} for HFP and 52 kJ mol^{-1} for HFC-227ea, respectively.

In this study, the adsorption equilibrium of HFP and HFC-227ea on activated carbon has been correlated by applying eq 5 rather than by using an equation that includes the parameters as functions of temperature. With two sets of data, at 283 K (T_1) and 363 K (T_2), the adsorption equilibria of HFP and HFC-227ea on activated carbon were predicted at other temperatures and the results are presented in Figures 2 and 3. The correlations obtained by the isosteric enthalpy of adsorption method were in excellent agreement with the experimental data. Although there is some departure in the case of HFC-227ea at 333 K, the overall accuracy of the correlation is favorable.

The proceeding results show that the proposed method of Yun et al. (1998a) can give reliable results of good accuracy for predicting the adsorption equilibria of HFP and HFC-227ea on activated carbon. Moreover, this method is simple enough for use in dynamic simulations of adsorption.

Conclusion

This article presents new experimental data for the equilibrium adsorption of hexafluoropropene and 1,1,1,-2,3,3,3-heptafluoropropane on a commercial activated carbon. The isotherms were measured at 283, 303, 333, and 363 K and pressures up to 100 kPa. To represent the experimental data at several temperatures simultaneously, we applied a simple thermodynamic method based on the assumption that the isosteric enthalpy of adsorption is independent of temperature. The results showed that such an approach satisfactorily represented the temperature-dependent adsorption of hexafluoropropene and 1,1,1,2,3,3,3-heptafluoropropane on activated carbon. This semipredictive method will aid the analysis of adsorption systems.

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