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Adsorption Equilibria of Chloropentafluoroethane and Pentafluoroethane on Activated Carbon Pellet

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Equilibrium studies on the adsorption of chloropentafluoroethane (R-115, CF_3CF_2Cl) and pentafluoroethane (CF_3CF_2H, R-125) on an activated carbon pellet were made between 298.2 K and 373.6 K. Equilibrium parameters based on the Langmuir−Freundlich equation are derived. The Langmuir−Freundlich isotherms for R-115 and R-125 fit the experimental results within 2%. The isosteric enthalpies of adsorption of R-115 and R-125 were estimated.

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1. Introduction

Chlorofluorocarbons (CFCs) have been widely used as refrigerants, blowing agents, propellants, and cleaning agents. However, their roles in the ozone depletion are of great global concern (Lovelock, 1971; Molina and Rowland, 1974). In addition, CFCs also contribute to the "greenhouse effect" and hence to climate change (Molina and Rowland, 1974). Therefore, the Montreal Protocol was formulated to restrict the release of CFCs into the atmosphere (UNEP, 1987). This lead to research for ways to recover the halogenated hydrocarbons (Kodama et al., 1992; Kuo and Hines, 1992; Tsai and Chang, 1994) and the CFCs (Frere et al., 1994; Kobayashi et al., 1994; Cho and Lee, 1995).

Chloropentafluoroethane (CF_3CF_2Cl, R-115) has been used in refrigerants such as R-502, an azeotropic blend of R-115 and chlorodifluoromethane (CF_2HCl, R-22). Because of the high ozone-depleting potential (ODP) and the highest global warming potential (GWP), the recovery of R-115 is important. Moreover, recovered R-115 can be converted to pentafluoroethane (CF_3CF_2H, R-125), which is a promising substitute for R-115 (Moon, 1998).

An inexpensive way to reduce halogenated carbon emissions is adsorption on activated carbons. This technology is highly effective at low concentrations. Adsorption equilibria data is a prerequisite to the design of the adsorption facilities.

In this work, an equilibrium study for the adsorption of R-115 and R-125 on an activated carbon pellet was carried out between 298.2 K and 373.6 K and the equilibrium parameters based on the Langmuir−Freundlich equation were derived. The isosteric enthalpies of adsorption for the adsorption of R-115 and R-125 were also estimated.

2. Experimental Section

Material. An activated carbon pellet (Norit B4) was used as an adsorbent for the adsorption of R-115. The BET surface area for the adsorbent was measured by an ASAP-2000 (Micromeritics Inc Co.) using nitrogen adsorption. The measured properties and the manufacturers specification of the adsorbent are listed in Table 1. The chloropentafluoroethane, supplied from Elf Atochem, had a purity of 99.99%. The pentafluoroethane, obtained from Ashshi Glass. Co. Ltd., had a purity of 99.5%.

Table 1. Physical Properties of Activated Carbon Pellet

physical property	activated carbon pellet
BET surface area/($m^2 \cdot g^{-1}$)[a]	1198.23
pore volume and distribution[b]	
micropore (<1 nm)/($cm^3 \cdot g^{-1}$)	0.42
mesopore(1−100 nm)/($cm^3 \cdot g^{-1}$)	0.09
macropore (>100 nm)/($cm^3 \cdot g^{-1}$)	0.42
bulk density/($kg \cdot m^{-3}$ bed)	429
pellet diameter/cm	0.37
pellet length/cm	0.65

[a] Measured in this work from nitrogen adsorption. [b] Data that were supplied by manufacturer.

Apparatus and Procedures. A volumetric sorption analyzer (Micromeritrics, ASAP 2000) was used to measure the BET surface area. Before the adsorption, the adsorbent was evacuated to 1.33×10^{-3} Pa at 473 K for 15 h. A turbomolecular pump (Balzers Co., model TSH 065D) in combination with a rotary vacuum pump (model Duo 1.5A) was used to evacuate the system. An ion gauge (Granville-Phillips model 307) was used for the measurement of vacuum. During the adsorption run, pressure changes were measured by an MKS absolute pressure transducer (model 690A-13T) allowing measurements from 0 to 133 kPa with an accuracy of ±0.05% and power supply readout instrument (type 270). The dead volume of the system was determined by helium gas at 33.33 kPa and each adsorption temperature, and the mass of the adsorbent was measured within ±10 μg precision. A refrigerated−heated bath with circulator was used to control the adsorption temperature within ±0.05 K.

Adsorption isotherms were obtained by admitting successive increments of known volumes of sample gas to the adsorbent sample. After each increment of gas, the equi-

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Table 2. Adsorption Isotherms for the R-115 on an Activated Carbon Pellet

P/kPa	Q/ μmol·g^{-1}	Q(cal)/ μmol·g^{-1}	abs. diff./ %	P/kPa	Q/ μmol·g^{-1}	Q(cal)/ μmol·g^{-1}	abs. diff./ %
	$T = 298.2$ K				$T = 308.2$ K		
0.137	612	624	1.90	0.228	607	597	1.68
0.155	650	658	1.16	0.977	1113	1115	0.20
0.361	920	944	2.50	2.548	1575	1584	0.58
1.184	1424	1477	3.60	5.827	2043	2044	0.03
3.264	2019	2028	0.45	12.020	3467	2454	0.51
7.859	2502	2526	0.95	19.931	2737	2730	0.26
21.398	3006	3051	1.47	28.251	2912	2909	0.11
37.876	3255	3309	1.65	35.650	3024	3022	0.08
53.355	3394	3448	1.56	42.716	3107	3106	0.04
66.647	3485	3530	1.28	54.235	3213	3211	0.06
80.352	3552	3595	1.20	66.913	3303	3298	0.14
93.644	3616	3645	0.81	80.832	3382	3382	0.28
111.935	3682	3701	0.51	93.911	3433	3428	0.13
				112.002	3504	3490	0.38
absolute average difference			1.46	absolute average difference			0.32
	$T = 318.2$ K				$T = 348.2$ K		
0.273	522	503	3.68	0.405	309	308	0.44
1.093	968	946	2.36	1.159	550	533	3.15
2.680	1367	1351	1.18	2.384	781	759	2.89
4.870	1687	1665	1.30	4.517	1034	1014	1.94
7.294	1920	1891	1.54	7.041	1240	1222	1.51
9.927	2102	2067	1.71	9.960	1411	1399	0.89
14.999	2343	2302	1.78	15.052	1642	1623	1.18
21.691	2551	2508	1.71	21.691	1852	1829	1.23
29.024	2710	2665	1.69	32.210	2017	2056	1.92
35.783	2818	2774	1.59	35.663	2144	2115	
47.155	2950	2911	1.33	47.102	2304	2272	1.39
60.541	3069	3029	1.33	60.167	2437	2408	1.21
73.933	3152	3118	1.10	73.673	2541	2517	0.96
91.618	3236	3208	0.87	91.964	2654	2632	0.84
111.695	3307	3287	0.62	112.028	2732	2731	0.05
absolute average difference			1.59	absolute average difference			1.40
	$T = 373.2$ K						
0.532	196	217	9.68				
1.213	333	347	3.92				
2.298	482	491	1.86				
3.952	642	651	1.41				
5.994	790	800	1.30				
8.226	916	929	1.45				
10.808	1036	1052	1.48				
15.825	1216	1237	1.73				
22.131	1391	1414	1.61				
33.237	1615	1640	1.50				
46.315	1803	1830	1.46				
60.061	1951	1979	1.44				
73.766	2067	2097	1.44				
92.004	2203	2222	0.84				
111.989	2309	2330	0.90				
absolute average difference			2.14				

librium pressure of the system was measured. A correction was made for the dead space in calculating each point on the adsorption isotherm.

3. Results and Discussion

The adsorption data of R-115 and R-125 on the activated carbon pellet were obtained at four temperatures between 298.2 K and 373.6 K after overnight regeneration of the adsorbent. The results were reproducible within ±1%.

The absolute differences (abs. diff.) between the experimental data and the calculated values are estimated by eq 1

$$\text{abs. diff.} = \left(\frac{1}{N}\right)\sum_{i=1}^{N}\frac{|V_i^{\text{cal}} - V_i^{\text{exp}}|}{V_i^{\text{cal}}} \tag{1}$$

where V^{cal} and V^{exp} are calculated values and experimental values and N is the number of data points at a given temperature. V^{cal} was calculated from the Langmuir−Freundlich equation.

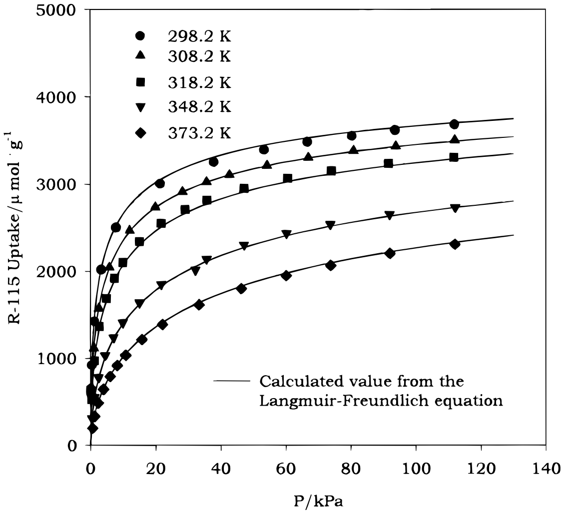

Figure 1. Calculated Langmuir−Freundlich isotherms for R-115 on activated carbon pellet with the experimental data.

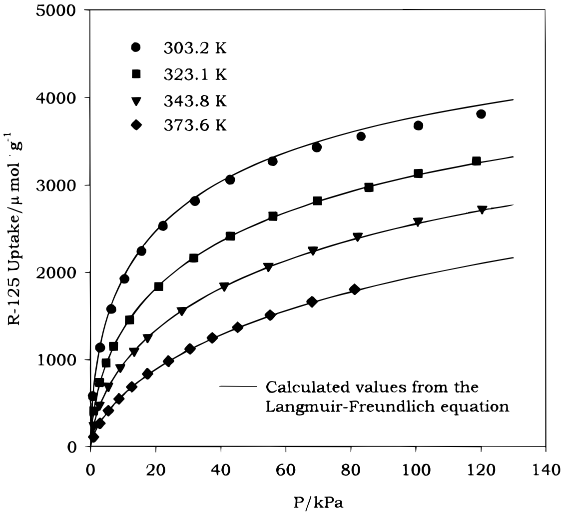

Figure 2. Calculated Langmuir−Freundlich isotherms for R-125 on activated carbon pellet with the experimental data.

The Langmuir−Freundlich equation is a hybrid isotherm of the Langmuir and the Freundlich isotherms (Sips, 1948; Ruthven, 1984).

$$Q = \frac{Q_{\text{m}}\cdot B\cdot P^{(1/n)}}{1 + B\cdot P^{(1/n)}} \tag{2}$$

where Q_{m} is a monolayer uptake per unit weight of adsorbent, B is the Langmuir−Freundlich adsorption parameter, and n is larger than a unit. The temperature dependences of the Langmuir−Freundlich parameters, Q_{m}, B and n, were calculated by the nonlinear regression analysis using a modified Levenberg−Marquardt algorithm (Marquardt, 1963).

Equilibria of R-115 on Activated Carbon Pellet. The adsorption data for R-115 on activated carbon pellet were obtained at five temperatures, (298.2, 308.2, 318.2, 348.2, and 373.2) K. The temperature dependences of the Q_{m}, B, and n were obtained by eqs 3, 4, and 5, respectively.

$$Q_m/(\mu\text{mol}\cdot\text{g}^{-1}) = 2043.96\cdot\exp\left(\frac{227.729}{T/K}\right) \qquad (3)$$

$$B/\text{kPa} = 1.322 \times 10^{-4}\cdot\exp\left(\frac{2435.006}{T/K}\right) \qquad (4)$$

$$n(-) = 8.4415 \times 10^{-1}\cdot\exp\left(\frac{245.786}{T/K}\right) \qquad (5)$$

Figure 1 shows the Langmuir−Freundlich isotherms for R-115 on activated carbon pellet with experimental data. The absolute differences between the experimental data and the calculated values from the Langmuir−Freundlich equation were considerably small, about 2%. This isotherm equation gave a good representation for the R-115-activated carbon pellet system. Table 2 lists the calculated value by the Langmuir−Feundlich isotherms for R-115 on activated carbon pellet with the equilibrium data and the absolute differences.

Equilibria of R-125 on Activated Carbon Pellet. The adsorption data for R-125 on the activated carbon pellet were obtained at four temperatures, (303.2, 323.1, 343.8, and 373.6) K. The temperature dependences of the Q_m, B, and n were obtained by eqs 6, 7 and 8, respectively.

$$Q_m/(\mu\text{mol}\cdot\text{g}^{-1}) = 2292.520\cdot\exp\left(\frac{285.959}{T/K}\right) \qquad (6)$$

$$B/\text{kPa} = 3.7 \times 10^{-5}\cdot\exp\left(\frac{2482.951}{T/K}\right) \qquad (7)$$

$$n(-) = 6.4958 \times 10^{-1}\cdot\exp\left(\frac{304.748}{T/K}\right) \qquad (8)$$

Figure 2 shows the Langmuir−Freundlich isotherms for R-125 on activated carbon pellet with experimental data. The absolute differences between the experimental results and the calculated values from the Langmuir−Freundlich equation were 2%. This equation gave a good representation for the R-125-activated carbon pellet system. Table 3 lists the calculated values by Langmuir−Feundlich isotherms for R-125 on the activated carbon pellet with the data and the absolute differences.

In conclusion, the equilibria of R-115 and R-125 on an activated carbon pellet were represented by the Langmuir−Freundlich equation within 2% absolute differences, respectively.

Isosteric Enthalpies of Adsorption of R-115 and R-125. The enthalpy of adsorption is a significant property for characterization of the type of adsorption and of the degree of heterogeneity of a surface. The isosteric enthalpies of adsorption were not obtained experimentally but are estimated from equilibrium data by using the Clausius−Clapeyron equation

$$q_{\text{iso}}/(\text{kJ}\cdot\text{mol}^{-1}) = -R\left[\frac{\partial \ln P/\text{kPa}}{\partial(1/(T/K))}\right]_v$$

where R is a gas constant and the subscript v refers to a constant adsorption amount (μmol/g).

Table 4 shows the comparison of the isosteric enthalpies of adsorption for R-115 and R-125 with the enthalpies of condensation (Ishikawa, 1990). It shows that the isosteric enthalpy of adsorption of R-125 slightly decreased with the increase of the amount adsorbed but that of R-115 remained almost constant. It means that more energetic sites at the beginning of adsorption will be filled preferentially so that more heat will be released, and the remaining less active sites filled as the adsorption proceeds will release less heat. The isosteric enthalpies of adsorption of R-115 and R-125 are approximately of the same order of magnitude as the enthalpies of condensation. It may be concluded that the adsorption of R-115 and R-125 on activated carbons are primarily due to physical forces.

Table 3. Adsorption Isotherms for the R-125 on an Activated Carbon Pellet

P/kPa	Q/ μmol·g^{-1}	Q/(cal)/ μmol·g^{-1}	abs. diff./ %	P/kPa	Q/ μmol·g^{-1}	Q/(cal)/ μmol·g^{-1}	abs. diff./ %
	T = 303.2 K				T = 323.1 K		
0.680	577	572	0.91	0.895	406	389	4.51
2.965	1135	1164	2.56	2.712	734	709	3.49
6.457	1578	1628	3.09	4.796	963	949	1.46
10.526	1923	1971	2.43	7.089	1151	1147	0.34
15.758	2242	2280	1.63	12.000	1456	1461	0.38
22.358	2530	2560	1.19	20.998	1839	1850	0.59
32.157	2819	2859	1.42	31.730	2164	2166	0.13
42.982	3059	3100	1.31	42.982	2415	2411	0.16
56.034	3272	3318	1.39	56.021	2643	2630	0.53
69.646	3431	3494	1.79	69.713	2820	2811	0.29
83.298	3554	3636	2.24	85.658	2974	2982	0.29
100.910	3678	3784	2.80	100.817	3134	3116	0.57
120.228	3808	3915	2.74	118.708	3275	3250	0.77
absolute average difference			1.96	absolute average difference			1.04
	T = 343.8 K				T = 373.6 K		
0.944	243	245	1.04	0.856	109	123	11.63
2.800	476	467	1.89	2.845	265	270	1.93
5.430	695	680	2.15	5.459	410	409	0.24
9.163	912	902	1.15	8.692	550	544	1.09
13.359	1098	1095	0.26	12.593	686	679	0.95
17.572	1255	1253	0.12	17.558	835	823	1.49
28.064	1565	1558	0.45	23.944	981	978	0.31
41.036	1847	1835	0.66	30.557	1123	1115	0.73
54.675	2073	2058	0.71	37.370	1247	1237	0.80
68.340	2259	2238	0.91	45.155	1370	1361	0.73
82.125	2416	2390	1.11	55.221	1512	1500	0.80
100.710	2589	2559	1.18	68.047	1666	1652	0.85
120.521	2729	2709	0.74	81.205	1804	1787	0.97
absolute average difference			0.95	absolute average difference			1.73

Table 4. Isosteric Enthalpies of Adsorption for R-115 and R-125 on Activated Carbon Pellet

adsorbate	V^a/ (μmol·g^{-1})	isosteric enthalpy of adsorption q_{iso}/(kJ·mol^{-1})	enthalpy of condensation^b q_{con}/kJ·mol^{-1})
R-115	500	38.70	14.62
	1000	38.35	
	2000	38.03	
R-125	400	36.70	13.19
	1200	32.46	
	2000	30.94	

[a] A constant adsorption amount. [b] Enthalpy of condensation (Ishikawa, 1990).

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