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Adsorption of Dichlorodifluoromethane, Chlorodifluoromethane, Chloropentafluoroethane, 1,1-Difluoroethane, and 1,1,1,2-Tetrafluoroethane on Silica Gel

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Adsorption isotherms of dichlorodifluoromethane (R12), chlorodifluoromethane (R22), chloropentafluoroethane (R115), 1,1-difluoroethane (R152a), and 1,1,1,2-tetrafluoroethane (R134a) on silica gel have been measured at 303.15 K from 0 kPa to the vapor pressure.

Introduction

The CFC's (chlorofluorocarbons) are used as working refrigerant fluids. The most commonly used are R12, R22, and R502 (48.8% R22 and 51.2% R115). Recent concerns of the effects of CFC's on the ozone layer (*1–5*) require the development of efficient recovery methods. One technique is to adsorb the fluids onto a porous medium such as silica gel. Thermodynamic data on the adsorption of dichlorodifluoromethane (R12), chlorodifluoromethane (R22), chloropentafluoroethane (R115), 1,1-difluoroethane (R152a), and 1,1,1,2-tetrafluoroethane (R134a) on silica gel are required for the design of recovery units. The results are presented here.

Experimental Section

Materials. The CFC's have been provided by Dehon Belgium (R12, R22, R134a) and Union Carbide (R115 and R152a). The purity of these materials was 99.5%. The adsorbent used is silica gel KC-Trockenperlen Blau provided by Kali-Chemie AG. Table 1 lists the normal boiling point, critical constants, and acentric factor of the five CFC's studied (*6–9*).

Equation 1 has been used for the calculation of the vapor pressure of R12 (*6*). Equation 2 has been used for the calculation of the vapor pressures of R22, R115, R134a, and R152a (*7*). Table 2 lists the coefficients of eqs 1 and 2 (*6, 7*). For both eqs 1 and 2 P_s is in kilopascals and T is in kelvin.

$$\ln (1000P_s) = a_1 + a_2/T + a_3 \ln (T) + a_4T + a_5T^2 + a_6T^3 \quad (1)$$

$$\ln P_s = b_1/T + b_2 + b_3T + b_4(1 - T/T_c)^{1.5} \quad (2)$$

Table 3 lists the characteristics of silica gel as an adsorbent.

Apparatus and Procedure. The experiments have been carried out in an adsorption apparatus based on the volumetric method. A diagram of the apparatus is shown in Figure 1.

The main component is a two-part reactor (A) made of stainless steel (maximum outside diameter 100 mm, total height 200 mm, maximum allowable pressure 2000 kPa). The lower part (A′) is a gas reservoir which contains the gas before adsorption. The upper part (A″) contains the adsorbent. This part is closed by a screw cap (B) containing an O-ring seal (C) which allows the introduction of the adsorbent (D). These two parts are connected by a stainless steel tube; each part can be isolated from the other by two valves (V4 and V5). The temperatures in the two parts are measured by iron–constantan thermocouples (E) with an accuracy of ±0.03 K. The pressure in the reactor is measured by a 0 to 1000 kPa absolute pressure transducer (F) (Giravia P306 type) with an accuracy of ±2 kPa. The whole reactor is immersed in a constant-temperature bath (Lauda R400 type) with temperature control of ±0.1 K in a temperature range from 283 to 353 K. The lower part is connected via valves V2 and V3 to the gas carboy (G) and via valves V1 and V3 to a vacuum pump (H).

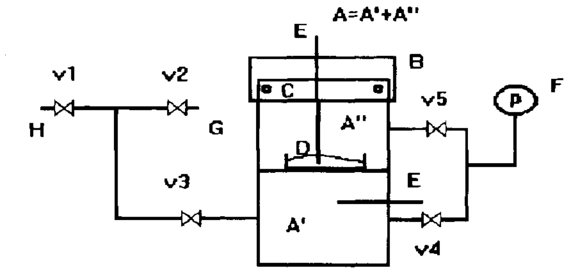

Figure 1. Experimental apparatus: (A) reactor; (A′) gas reservoir; (A″) adsorber; (B) screw cap; (C) O-ring seal; (D) adsorbent; (E) iron–constantan thermocouples; (F) pressure transducer; (G) gas addition; (H) vacuum.

Table 1. Normal Boiling Point T_b, Critical Temperature T_c, Critical Pressure P_c, and Acentric Factor ω of the CFC's

CFC	T_b/K	T_c/K	P_c/kPa	ω
R12	234.38	385.17	4125	0.177
R22	232.32	369.30	4990	0.221
R115	234.04	353.10	3157	0.286
R134a	247.10	374.21	4056	0.326
R152a	248.50	386.44	4520	0.275

Initially, the adsorbent is treated to eliminate any trace of pollutants by heating at 423 K in a drying oven for 24 h. A known mass (about 20 g with an accuracy of ±0.1 mg) is then put into the adsorber.

The volumetric method requires a knowledge of the volume available to a gas. This volume is determined for each sample of adsorbent by expansion of an inert gas (helium). Once this volume is measured, the apparatus is evacuated for 24 h. This constitutes the second stage of the regeneration process of the adsorbent. During this operation, valves V1, V2, V3, V4, and V5 are open and the pressure is reduced to 10^{-1} Pa. V1 and V5 are then closed, and the adsorbing gas is added via valves V2 and V3. Once the gas has been introduced, V3 is closed. After equilib-

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Table 2. Coefficients of the Vapor Pressure Equations (1 and 2)

	a_1	a_2	a_3	a_4	a_5	a_6
R12	93.343804516	−4396.1875629	−12.47152	$1.9606033129 \times 10^{-2}$	0	0

	b_1	b_2	b_3	b_4
R22	−2907.443	17.05244	−0.001796055	2.204052
R115	−3809.750	21.78658	−0.00832400	4.744543
R134a	−3353.464	17.36056	−0.002908044	2.783663
R152a	−3110.511	17.02405	−0.001445740	2.105154

Table 3. Main Characteristics of Silica Gel as an Adsorbent

specific surface	750 m^2/g
apparent density	800 kg/m^3
particle size	2−5 mm
mean diameter of pores	20 Å
volume of pores	0.35 cm^3/g

Table 4. Adsorption Isotherm Data for R12 on Silica Gel at 303.15 K

P/kPa	exp ads mass/(kg/kg)	*P*/kPa	exp ads mass/(kg/kg)
50	0.134	351	0.421
80	0.180	355	0.428
134	0.244	398	0.456
194	0.307	456	0.487
218	0.320	498	0.504
247	0.349	549	0.514
316	0.389	624	0.529

Table 5. Adsorption Isotherm Data for R22 on Silica Gel at 303.15 K

P/kPa	exp ads mass/(kg/kg)	*P*/kPa	exp ads mass/(kg/kg)
103	0.173	442	0.334
170	0.220	465	0.343
246	0.257	484	0.349
274	0.270	512	0.359
305	0.282	558	0.376
354	0.300	591	0.387
390	0.314	620	0.397
420	0.326		

Table 6. Adsorption Isotherm Data for R115 on Silica Gel at 303.15 K

P/kPa	exp ads mass/(kg/kg)	*P*/kPa	exp ads mass/(kg/kg)
70	0.149	421	0.396
90	0.173	454	0.411
112	0.197	485	0.422
160	0.238	550	0.445
181	0.254	579	0.454
227	0.284	613	0.465
270	0.309	645	0.474
283	0.317	678	0.483
312	0.331	711	0.492
340	0.349	779	0.505
369	0.363		

Table 7. Adsorption Isotherm Data for R134a on Silica Gel at 303.15 K

P/kPa	exp ads mass/(kg/kg)	*P*/kPa	exp ads mass/(kg/kg)
58	0.183	323	0.336
93	0.207	338	0.345
113	0.224	360	0.355
141	0.247	375	0.366
164	0.257	398	0.378
187	0.270	429	0.394
210	0.282	471	0.411
236	0.290	505	0.429
257	0.301	546	0.446
281	0.313	577	0.457
306	0.328		

rium, the pressure is measured by the absolute pressure transducer. Valve V5 is then opened. The pressure in the reactor drops because of the expansion of the gas and because of the adsorption. When equilibrium is reached, the temperature and the pressure in the reactor are measured. Valve V5 is closed, and a second amount of gas is introduced into the lower cell. The operation is repeated until a pressure of about 0.9 of the vapor pressure of the gas at the measurement temperature is obtained. The knowledge of the temperature, pressure, and gas volume before and after each step of adsorption gives the moles of gas before and after adsorption and by difference the moles adsorbed. The calculation of the moles of gas has been made using the simplified Redlich−Kwong equation of state (*10*, *11*). The maximum deviation observed for the molar volume of saturated R12 is ±2.2% at $T = 0.95T_c$. These extreme conditions are not met in this study so that the accuracy of the Redlich−Kwong equation of state is estimated to be better than ±1% in molar volume.

$$\frac{Pv}{RT} = \frac{v}{v-b} - \frac{a}{RT^{3/2}(v+b)} \qquad (3)$$

where

$$a = \Omega_a(R^2T_c^{2.5}/P_c) \qquad b = \Omega_b(RT_c/P_c)$$

and

$$\Omega_a = 0.42137 \exp(0.27868\omega)$$

$$\Omega_b = 0.0855 \exp(0.29161\omega)$$

The critical constants and the acentric factors are given in Table 1.

Results

Each isotherm was measured at 303.15 over a wide range of pressures. The results are given in Tables 4−8. Graphical representations for R12 and R134a are given in Figures 2 and 3.

The accuracy of the pressure transducer was ±2 kPa, giving the maximum relative error in the pressure of 4.25% for the first point of the R152a isotherm (Table 8). The error on the adsorbed mass is due to the accuracy of the equation of state used for the calculation of the vapor molar volumes (<±1%), the experimental error on the mass of adsorbent due to the accuracy of the balance ($\pm 5.10^{-4}\%$), the experimental error on temperature (±0.01%), the experimental error in the gas volumes (estimated to less than ±1%), and the experimental error in pressure (variable). The prime source of error is in the pressure measurement, and this results in a maximum relative error on the adsorbed mass of ±5% with typical values of ±4%. Such experimental errors are common for the volumetric method in which the adsorbed mass is not directly measured. High-pressure gravimetric methods could provide

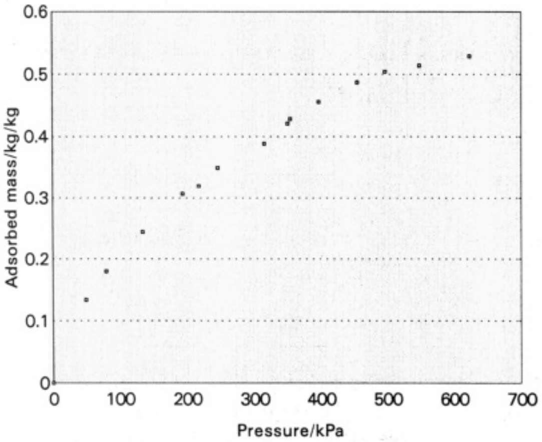

Figure 2. Adsorption isotherm for R12 + silica gel at 303.15 K.

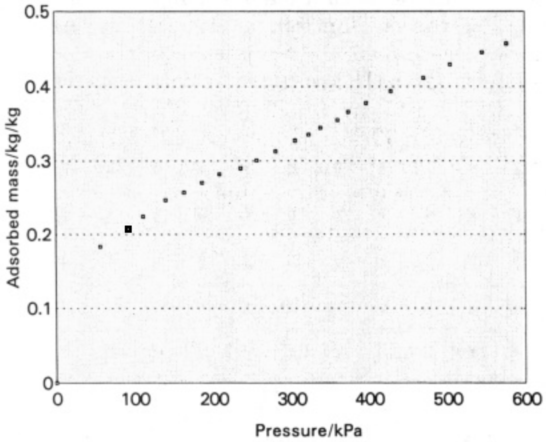

Figure 3. Adsorption isotherm for R134a + silica gel at 303.15 K.

Table 8. Adsorption Isotherm Data for R152a on Silica Gel at 303.15 K

P/kPa	exp ads mass/(kg/kg)	P/kPa	exp ads mass/(kg/kg)
47	0.103	300	0.251
80	0.141	320	0.261
99	0.159	350	0.272
117	0.170	375	0.283
137	0.183	399	0.295
152	0.194	425	0.303
175	0.205	450	0.313
202	0.211	479	0.322
229	0.222	508	0.333
257	0.233	530	0.345
281	0.243	557	0.356

more precise results, but this technique requires further development.

Conclusions

The apparatus allows the determination of adsorption isotherms at pressures up to 1000 kPa.

The experimental results shown in Figures 2 and 3 are characteristic of the adsorption of CFC's on silica gel. The maximum adsorbed mass can reach 0.5 kg/kg. The high slope of the isotherms at medium and high pressures allows a high cycled mass Δm where Δm is defined by

$$\Delta m = m(T, P_1) - m(T, P_2) \qquad (4)$$

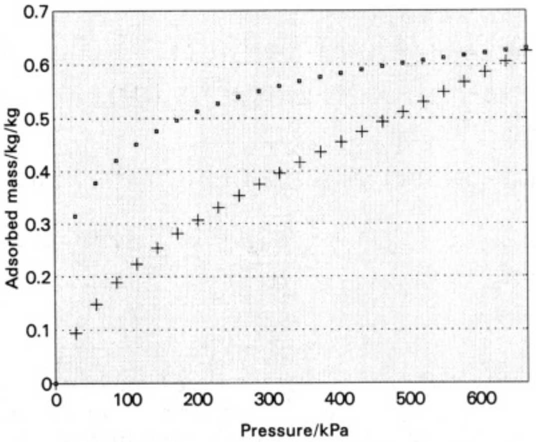

Figure 4. Adsorption of R12 at 303.15 K. Comparison between silica gel and activated carbon: (+) silica gel; (□) activated carbon.

with $P_1 > P_2$ and where $m(T,P_i)$ is the adsorbed mass at temperature T and pressure P_i. The higher Δm is, the lower the required mass of the adsorbent for a defined amount of recovery is. Figure 4 shows the difference in the adsorption isotherms of R12 on silica gel and activated carbon. In each case the maximum adsorbed mass is 0.6 kg/kg, but the particular shape of the adsorption isotherm on silica gel results in a higher value of Δm.

The experimental error in the pressure and adsorbed mass is better than ±5%. The wide range of pressure studied allows the results to be used for the design of recovery units (*12*).

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