Adsorption of Dichlorodifluoromethane, Chlorodifluoromethane, and Chloropentafluoroethane on Activated Carbon

Karl Berlier,* Marc Frère, and Jacques Bougard

Service de Thermodynamique, Faculté Polytechnique de Mons, Bd Dolez 31, B-7000 Mons, Belgium

Isotherms and enthalpies of adsorption curves of dichlorodifluoromethane (R12), chlorodifluoromethane (R22), and chloropentafluoroethane (R115) on three different activated carbons have been obtained at 303 K and at pressures to 602 kPa.

Introduction

The CFCs (chlorofluorocarbons) are used as working refrigerant fluids. The most commonly used are R12, R22, and R502 (azeotrope composed with 48.8 mass % R22 and 51.2 mass % R115). Recent concerns of the effects of CFCs on the ozone layer (Brian and Sauer, 1991; Frère et al., 1994; Kurylo, 1990) requires the development of efficient recovery methods. One technique is to adsorb the fluids onto a porous medium such as silica gel or activated carbon. A first study has been devoted to adsorption of five CFCs on silica gel over a wide range of pressure (Frère et al., 1994). Thermodynamic data (isotherm and integral enthalpy of adsorption) on the adsorption of dichlorodifluoromethane (R12), chlorodifluoromethane (R22), and chloropentafluoroethane (R115) on three different activated carbons are presented here.

Experimental Section

Materials. The CFCs were provided by Dehon Belgium (R12, R22) and Union Carbide (R115). The purity of these materials was 99.5 mol %. Table 1 lists the formulas, saturated pressures at 303 K, enthalpies of vaporization at 303 K, and critical constants of the three CFCs studied (Ekroth, 1990; McLinden, 1990; Mecarik and Masaryk, 1991; Riddick et al., 1986). Equations and parameters to calculate the vapor pressure of the compounds have been presented previously (Frère et al., 1994).

The activated carbon was provided by Chemviron Carbon (F30/470 and BPL) and Ceca Atochem (NC35). Table 2 lists the characteristics of different activated carbons as adsorbents.

Apparatus and Procedure. The apparatus allows measurement of integral enthalpies of adsorption and adsorbed masses (gravimetric method) of gases on microporous media in the ranges 0–1000 kPa and 303–373 K. The high volume of the adsorption cell and the accuracy of the enthalpies of adsorption are the two main advantages of this device.

A schematic diagram of the apparatus is shown in Figure 1. The main parts of this device are an adsorption cell (C), a Setaram calorimeter (CRMT), type CRMT, an RT400 electronic amplifier (A), a graphic recorder (G), a pressure transducer (P), a gas carboy (GC), a buffer reservoir (BT), valves (V1–V5), a voltmeter (mV), and a vacuum pump (VP).

Table 1. Formula, Saturated Pressure at 303 K (P_s), Enthalpy of Vaporization at 303 K ($\Delta_{vap}H$), and Critical Constants (T_c, P_c) of CFCs (Ekroth, 1990; McLinden, 1990; Mecarik, Masaryk, 1991; Riddick et al., 1986)

CFC	formula	P_s(303 K)/kPa	$-\Delta_{vap}H$(303 K)/(kJ·kg^{-1})	T_c/K	P_c/kPa
R12	CCl_2F_2	744	135.23	285.17	4125
R22	$CHClF_2$	1192	178.15	363.30	4990
R115	C_2ClF_5	1038	89.01	353.10	3157

Table 2. Characteristics of Activated Carbon (Internal Measurement)

name	supplier	specific surface area/(m^2·g^{-1}) (BET)	pore volume/(cm^3·g^{-1})
BPL	Chemviron Carbon	1180	0.55
F30/470	Chemviron Carbon	1150	0.62
NC 35	Ceca (Atochem)	870	0.35

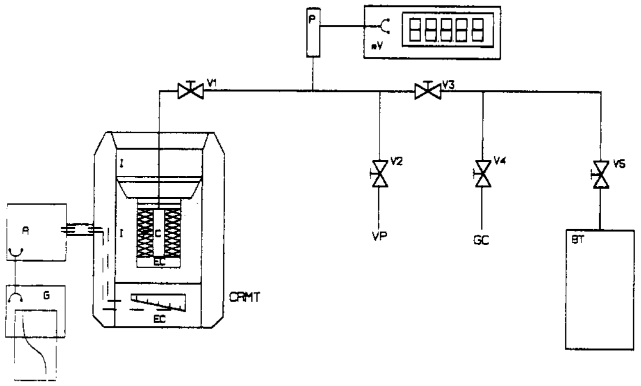

Figure 1. Experimental apparatus: (A) electronic amplifier; (BT) buffer tank; (C) adsorption cell; (CRMT) Setaram calorimeter; (EC) electric connection; (F) fluxmeter; (G) graphic recorder; (GC) gas carboy; (I) thermic isolation; (mV) millivolmeter; (P) pressure transducer; (V1–V5) valves; (VP) vacuum pump.

The adsorption cell (C) is a stainless steel reservoir. The maximum allowable pressure is 1500 kPa, and the volume is about 15 cm^3. Thanks to this volume, the mass of adsorbent can reach 5 g of activated carbon.

The main part of this calorimeter (CRMT) is a high-accuracy fluxmeter (F; 60 μV/mW) consisting of 200 thermocouples, in 20 layers of 10 thermocouples distributed around the adsorption cell (C). This system is connected via a regulator–amplifier RT400 (A) with a graphic recorder (G) to plot a signal proportional to the heat flux of adsorption. The regulator ensures that the chamber's temperature is kept rigorously stable (±0.05 K) during the experiment. A special cell (Joule effect) is used for the calibration. The accuracy of the fluxmeter has been measured thanks to this Joule effect cell. The Joule effect

---

* To whom correspondence should be addressed. e-mail: karl.berlier@fpms.fpms.ac.be.

0021-9568/95/1740-1137$09.00/0

Table 3. Adsorption of R12 on Different Activated Carbons at 303 K

F30/470			BPL			NC35		
N/(mol·kg^{-1})	Q/(kJ·kg^{-1})	P/kPa	N/(mol·kg^{-1})	Q/(kJ·kg^{-1})	P/kPa	N/(mol·kg^{-1})	Q/(kJ·kg^{-1})	P/kPa
0.148	8.30	<0.02	0.113	6.02	<0.02	0.160	9.32	<0.02
0.643	34.21	<0.02	0.315	16.34	<0.02	0.493	26.13	<0.02
0.841	44.77	1.82	0.528	26.92	0.08	1.093	54.49	<0.02
1.087	56.33	2.75	1.020	49.51	1.48	1.584	77.19	0.08
1.310	67.10	3.77	1.312	62.25	2.61	2.050	97.11	1.07
1.547	77.51	5.70	1.725	79.86	4.84	2.550	117.78	3.17
1.759	87.66	7.16	2.142	97.36	7.97	2.939	133.74	6.25
1.985	97.64	9.04	2.240	101.42	8.66	3.403	152.96	13.47
2.192	106.20	14.54	2.421	109.26	10.84	3.858	171.72	28.41
2.705	129.08	28.05	2.661	119.49	14.38	4.215	186.03	46.59
2.958	140.29	39.54	3.100	137.61	22.61	4.547	198.92	77.87
3.250	152.87	54.84	3.415	150.07	33.85	4.639	202.82	101.76
3.607	168.59	79.90	3.801	165.86	53.04			
3.711	172.80	89.91	4.091	177.18	78.83			
3.793	176.24	106.31	4.204	181.88	93.06			
4.452	197.57	213.91						
4.599	203.03	288.82						
4.741	208.01	368.15						
4.849	211.49	431.31						
5.079	218.16	456.87						
5.244	221.96	602.20						

Table 4. Adsorption of R22 on Different Activated Carbons at 303 K

F30/470			BPL			NC35		
N/(mol·kg^{-1})	Q/(kJ·kg^{-1})	P/kPa	N/(mol·kg^{-1})	Q/(kJ·kg^{-1})	P/kPa	N/(mol·kg^{-1})	Q/(kJ·kg^{-1})	P/kPa
0.089	5.36	<0.02	0.121	6.77	<0.02	0.201	10.81	<0.02
0.227	13.02	<0.02	0.449	22.40	<0.02	0.545	27.75	<0.02
0.619	32.20	<0.02	0.995	46.10	0.55	1.097	52.58	0.24
1.089	53.79	0.16	1.428	64.33	2.13	1.495	69.73	1.26
1.450	70.00	0.95	1.919	83.54	4.94	1.953	88.32	3.00
1.846	85.34	3.79	2.507	107.62	10.36	2.366	104.55	5.28
2.338	105.38	6.92	3.014	126.55	17.56	2.880	123.61	9.30
2.791	123.20	10.64	3.269	135.96	22.63	3.409	143.53	15.35
3.366	144.09	19.03	3.595	147.93	30.70	3.988	165.14	26.03
4.104	171.78	41.42	3.942	161.00	43.17	4.243	174.52	32.44
4.709	194.79	85.16	4.384	177.15	68.17	4.631	189.23	46.43
4.841	199.94	100.52	4.640	186.50	89.87	4.938	200.25	62.26
						5.158	207.99	77.43
						5.404	217.33	99.67

cell is switched on with a minimum current in order to record the minimum detectable signal on the graphic recorder. The accuracy of the energy measurement so obtained is ±0.5%.

For experiments at low pressure, the pressure transducer allows measurements from 0 up to 100 kPa with an accuracy of ±0.02 kPa. To measure enthalpies of adsorption when the pressure approaches the saturated pressure of the CFC, we use a pressure transducer with a range of 1000 kPa with an accuracy of ±0.2 kPa.

Firstly, the adsorbent is treated in order to eliminate any trace of pollutants by heating it at 423 K for 24 h in a drying oven. It is then weighed (about 5 g with an accuracy of ±0.1 mg) and introduced into the adsorption cell. The installation is then evacuated at 303 K over a 10-h period (all the valves are open). Valves V1, V2, and V3 are then closed, and gas is admitted into the buffer tank (BT). The gas is introduced into the first volume via valve V3. The pressure is measured, and this gas quantity is expanded in the calorimetric cell (C) by opening valve V1. The mass of the sample increases, the heat-flux signal deviates, and the pressure drops. Once the two last signals are constant, equilibrium is reached. The mass can be measured using an analytic balance (±0.1 mg). Knowing the mass before and after adsorption, it is possible to calculate the adsorbed mass at the equilibrium pressure. In order to compare different isotherms, the adsorbed mass is divided by the mass of adsorbent to plot N (kg/kg or mol/kg adsorbent) versus pressure. Integration of the heat-flux signal gives the corresponding integral enthalpy of adsorption. This experiment is repeated until the pressure reaches 100 kPa.

Results

Each experiment has been conducted at 303 K over a range of pressure from 0 to 100 kPa except for adsorption of R12 on activated carbon F30/470 where pressures were to 600 kPa.

Experimental results are given in Tables 3–5, and examples of isotherms are presented in Figure 2. Examples of integral enthalpies of adsorption are presented in Figure 3.

Experimental errors are independent; i.e., each measurement (adsorbed mass, enthalpies of adsorption, and pressure) is connected with only one apparatus with its own error presented in the Experimental Section.

Isotherms of adsorption are classical for adsorption on activated carbon (Figure 2). At a given pressure, the maximum of adsorption is observed for R22 (the smallest molecule with a dipole moment) and the minimum is for R115 (size effect) except at the begining of the isotherm where the polarity of the molecule is dominant compared to the size effect (pores of the adsorbent are empty). R12 shows intermediate behavior.

Integral enthalpies of adsorption are similar for the different gases on activated carbon studied (Figure 3); i.e., for the adsorption of a given gas quantity, the calorimetric effect is nearly the same. To study specific effects with the gas's size or polarity, it could be necessary to study

Table 5. Adsorption of R115 on Different Activated Carbons at 303 K

F30/470			BPL			NC35		
N/(mol·kg^{-1})	Q/(kJ·kg^{-1})	P/kPa	N/(mol·kg^{-1})	Q/(kJ·kg^{-1})	P/kPa	N/(mol·kg^{-1})	Q/(kJ·kg^{-1})	P/kPa
0.133	6.08	<0.02	0.120	6.69	<0.02	0.151	7.96	<0.02
0.661	30.32	<0.02	0.536	26.78	<0.02	0.823	41.83	1.13
0.948	45.10	<0.02	0.897	43.55	0.35	1.078	52.94	1.72
1.297	59.92	0.275	1.219	57.68	1.44	1.307	62.83	2.43
1.580	73.41	1.284	1.560	72.25	3.06	2.033	93.46	6.98
1.889	86.98	3.124	1.920	86.91	5.93	2.248	102.75	9.30
2.154	98.70	4.310	2.193	98.46	9.53	2.622	118.28	16.40
2.528	115.02	15.211	0.384	105.94	14.38	2.914	130.32	26.65
2.704	123.79	24.371	2.607	115.21	21.98	3.282	144.95	52.86
3.025	138.20	59.388	2.849	125.53	38.16	3.485	152.82	80.48
3.155	143.80	87.579	3.090	136.05	72.11	3.597	157.42	102.75
3.191	145.26	97.431	3.173	140.07	92.72			

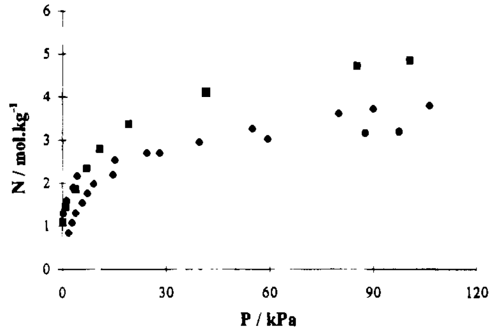

Figure 2. Isotherm of adsorption of R12 (◆), R22 (■), and R115 (●) on activated carbon F30/470 at 303 K.

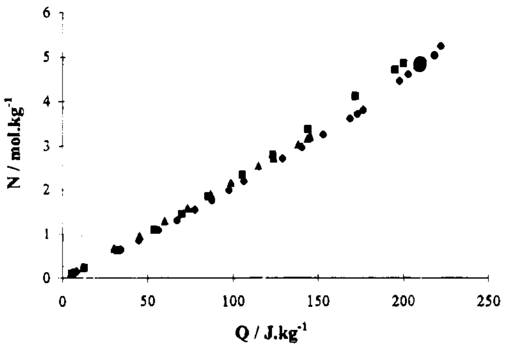

Figure 3. Integral enthalpy of adsorption of R12 (◆), R22 (■), and R115 (●) on activated carbon F30/470 at 303 K.

isosteric enthalpies and/or differential enthalpies of adsorption using a geometric or theoretical method (Ross and Olivier, 1954). Indeed, the adsorbed mass derivative of the integral enthalpy (i.e., differential enthalpy) is connected with adsorption of the adsorbate without explicit dependence on the adsorbent. A first approximation of the differential enthalpy could be obtained by geometric derivation of curves such as those in Figure 3. For the applications discussed above, the exothermic effects connected with the adsorption phenomena would not be a determinant quantity in any recovery method.

Conclusion

An apparatus is described for the measurement of isotherms and integral enthalpies of adsorption at pressures up to 1000 kPa. The adsorption isotherms are related to quantities such as the size and the polarity of the molecules. As shown in Figure 3, the integral enthalpies of adsorption are undeterminant in the study of specific gas−adsorbent interactions connected with physical quantities such as size and polarity. A new approach to determine differential enthalpies of adsorption is now being studied (geometric and/or theoretical method).

Acknowledgment

This paper presents results of the Belgian Programme on Interuniversity Poles of Attraction initiated by the Belgian State, Prime Minister's Office, Science Policy Programming. The scientific responsibility is assumed by its authors.

Literature Cited

Brian, C.; Sauer, F. Communication written for the 18th International Congress of Refrigeration, Montreal, 1991, No. 164.

Ekroth, I. A. Thermodynamic properties of refrigerants. Private communication, The Royal Institute of Technology, Stockholm, 1990.

Frère, M.; Berlier, K.; Bougard, J.; Jadot, R. *J. Chem Eng. Data* **1994**, *39*, 697.

Kurylo, M. J. *Int. J. Refrig.* **1990**, *13*, 62−72.

McLinden, M. O. Physical Properties of Alternatives to Fully Halogenated Chlorofluoro-carbons. Private communication, National Institute of Standards and Technology, Boulder, 1990.

Mecarik, K.; Masaryk, M. *Heat Recovery Syst. CHP* **1991**, *11*, 1993−1997.

Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents*, 4th ed.; Interscience: New York, 1986; pp 452, 557, 559, 564.

Ross, S.; Olivier, J. P. *On physical adsorption*; Interscience Publishers: New York, 1954.

Received for review April 1, 1995. Accepted May 30, 1995.[⊗]

JE9500800

[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1995.