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Adsorption of CO_2 on Activated Carbon: Simultaneous Determination of Integral Heat and Isotherm of Adsorption

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Simultaneous measurements of isotherms and integral heats of adsorption of carbon dioxide (CO_2) at temperatures ranging from 278 K to 327 K (seven temperatures) and at pressures up to 110 kPa on activated carbon are presented.

Introduction

There remains a lack of thorough understanding of the phenomenon of adsorption on microporous sorbents. Numerous theoretical approaches have been developed since the first model by Langmuir (Langmuir, 1916; Hill, 1960; Dubinin and Radushkevich, 1947; Dubinin, 1985; Rudzinski and Everett, 1992; Berlier et al., 1994). All models require the knowledge of adsorption results in order to determine their parameters. Very often these data consist of experimental isotherms at various temperatures. Unfortunately, most models fail to represent adsorption data over wide ranges of temperatures and pressures. Using a given model for different adsorbate−adsorbent systems involves the determination of new parameters. Besides, the models usually fail to fit both gravimetric and calorimetric data. A systematic study of the performances of the existing models could be very helpful. Such a study will require adsorption data over a wide range of conditions. In previous papers we have presented high-pressure adsorption data (Berlier et al., 1995b). In the current one, we present an experimental procedure allowing the simultaneous measurement of integral adsorption heats and adsorption isotherms over a wide range of temperatures at low pressures (up to 110 kPa). Such results are particularly interesting in the field of simultaneous calculations of integral adsorption heats and isotherms. They have already been used for the determination of the pore volume distribution function of activated carbons (Frère et al., to be published).

There is interest (Cacciola and Restuccia, 1994) in thermal adsorption machines such as thermotransformers or heat pumps. The efficient design of such devices requires the knowledge of adsorption isotherms and integral adsorption heats for the studied adsorbate−adsorbent systems.

Thus, experimental results are particularly interesting for both fundamental and applied research.

Experimental Section

Materials. CO_2 was provided by Air Liquid Belgium with a minimum purity of 99.995 vol %. The impurities are O_2, H_2O, N_2, C_nH_m, and CO. Of these, the most important one is N_2 ($\leq$30 ppm). Saturated pressures and enthalpies of vaporization for experimental temperatures are presented in Table 1 (Stewart et al., 1986). The critical temperature and pressure are respectively 304.21 K and 7382.5 kPa (Stewart et al., 1986).

The activated carbon F30/470 was provided by Chemviron Carbon. The BET specific surface, determined in our laboratory on a Quantasorb Sorption System, was 1150 m^2/g, and the pore volume was 0.62 cm^3/g.

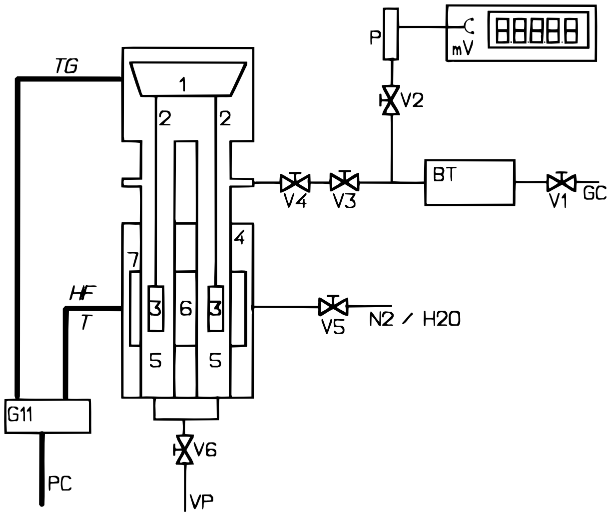

Figure 1. Experimental apparatus: (1) articulated beam; (2) suspension wires; (3) crucibles; (4) calorimeter block; (5) cylindrical tubes; (6) sensible part of the tube; (V1−V6) valves; (GC) gas cylinder; (BT) buffer tank; (P) pressure transducer; (mV) millivoltmeter; (N2) liquid nitrogen; (VP) vacuum pump; (G11) controller; (PC) computer.

Apparatus and Procedure. A thermobalance coupled to a calorimeter (model TG DSC 111 provided by SETARAM) was used for the simultaneous determination of the integral heat of adsorption and amount sorbed on the same sample. The maximum allowable pressure is 125 kPa. This apparatus can operate at temperatures ranging from 150 K to 1100 K.

The complete apparatus is shown in Figure 1. It is composed of a microbalance (1−3), a calorimeter (4−7), a controller (G11), a computer (PC), and an external circuit (V1−V6, BT, P, mV, GC, VP).

The microbalance is composed of an articulated beam (1) loading two suspension wires (2) with their crucibles (3). One of these crucibles remains empty (it is the reference). The other one is filled with the adsorbent sample. The volume of these crucibles is 150 μL, that is to say a more or less 50 mg sample of activated carbon. During the adsorption process the sample mass increases. This change in mass is found by measuring the change in the current needed to adjust an electromagnetic force provided by solenoids to keep the beam in a constant position. In order to not overload the diagram, this electromagnetic circuit around the beam is not drawn in

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Table 1. Saturated Pressure (P_s) and Enthalpy of Vaporization ($\Delta_{vap}H$) of CO_2 at Experimental Temperatures (Stewart et al., 1986)

	T/K						
	327.2	317.4	307.4	302.3	297.3	298.7	277.4
$P_s(T)$/kPa	$T > T_c$	$T > T_c$	$T > T_c$	7078.2	6314.0	5283.9	3898.2
$-\Delta_{vap}H(T)/(J \cdot g^{-1})$	$T > T_c$	$T > T_c$	$T > T_c$	76.30	125.99	169.98	218.06

Table 2. Mass of CO_2 Adsorbed per Unit Mass of Activated Carbon F30/470 (M_r) and Heat of Adsorption (Q) at 327.2 K and 317.4 K

T = 327.2 K			T = 317.4 K		
P/kPa	M_r	$Q/J \cdot g^{-1}$	P/kPa	M_r	$Q/J \cdot g^{-1}$
5.09	0.0039	2.40	4.71	0.0047	3.03
8.00	0.0066	4.07	7.04	0.0076	4.78
11.24	0.0094	5.73	9.81	0.0107	6.62
14.27	0.0119	7.16	13.06	0.0141	8.60
17.08	0.0140	8.41	16.13	0.0170	10.27
21.37	0.0171	10.18	18.88	0.0194	11.66
25.11	0.0196	11.61	21.59	0.0218	12.95
29.24	0.0222	13.11	25.81	0.0252	14.86
33.60	0.0249	14.58	28.74	0.0274	16.08
37.03	0.0269	15.70	31.23	0.0293	17.09
41.40	0.0293	17.06	33.86	0.0312	18.10
45.40	0.0315	18.24	36.45	0.0330	19.09
49.29	0.0336	19.36	39.60	0.0351	20.23
53.47	0.0357	20.52	41.86	0.0366	21.01
57.38	0.0376	21.55	44.80	0.0385	22.00
61.31	0.0395	22.57	47.24	0.0401	22.80
65.07	0.0413	23.50	50.15	0.0418	23.74
69.24	0.0431	24.52	53.53	0.0439	24.78
73.32	0.0450	25.49	55.99	0.0453	25.51
77.53	0.0468	26.47	59.13	0.0471	26.45
81.75	0.0486	27.43	62.10	0.0488	27.30
85.52	0.0502	28.26	65.47	0.0506	28.25
89.55	0.0518	29.12	68.18	0.0520	29.00
93.67	0.0535	29.98	71.41	0.0537	29.88
97.56	0.0550	30.79	74.20	0.0552	30.60
102.34	0.0568	31.75	77.21	0.0566	31.38
107.54	0.0587	32.77	80.14	0.0581	32.13
111.55	0.0602	33.53	83.15	0.0595	32.87
			85.56	0.0607	33.46
			88.31	0.0620	34.12
			91.46	0.0634	34.86
			94.67	0.0649	35.59
			96.96	0.0659	36.10
			99.41	0.0670	36.64
			102.38	0.0683	37.28
			104.97	0.0694	37.83

Figure 1. This electrical signal (TG signal) is sent to the computer via the controller.

The calorimeter block is a rectangular parallelpiped (4) pierced by two parallel cylindrical tubes (5). This block is linked to the balance so that the crucibles are located in the sensitive part of the tubes (6). In these sensitive areas, the thermocouple-carrying heat-flux transducers wrap around the tubes. They transduce the heat-flux due to adsorption and the temperature of the sample into electrical signals: heat-flux (HF signal) and temperature (T signal). They are sent to the computer via the controller.

The electrical furnace (7) and the cooling system (water or liquid nitrogen (V5, N_2/H_2O)) located by these tubes allow temperature programming of the sensitive part (from 150 K to 1100 K).

The computer and controller perform the amplification, acquisition, digitalization, and visualization of the TG, T, and HF signals. They also control and program the temperature of the calorimetric block.

The external circuit consists of tubes and valves (V1−V6), a pressure transducer (P) which allows the measurement of 0 kPa to 150 kPa pressure, a gas cylinder (GC), a buffer tank (BT), and a vacuum pump (VP). This system evacuates the apparatus, feeds it with the reactive gas, and measures the equilibrium pressure.

Table 3. Mass of CO_2 Adsorbed per Unit Mass of Activated Carbon F30/470 (M_r) and Heat of Adsorption (Q) at 307.4 K

P/kPa	M_r	$Q/J \cdot g^{-1}$	P/kPa	M_r	$Q/J \cdot g^{-1}$
3.33	0.0039	2.62	48.41	0.0505	29.29
3.51	0.0038	2.49	49.13	0.0514	29.44
4.61	0.0065	4.20	51.46	0.0515	29.61
5.03	0.0070	4.55	52.78	0.0540	30.80
5.56	0.0073	4.64	54.11	0.0545	31.42
6.50	0.0094	5.99	55.45	0.0558	31.76
7.80	0.0116	7.26	55.53	0.0543	31.07
9.09	0.0125	7.83	57.62	0.0569	32.64
10.69	0.0155	9.55	59.43	0.0568	32.45
11.34	0.0164	10.11	59.55	0.0586	33.25
12.64	0.0171	10.56	63.38	0.0594	33.80
13.48	0.0191	11.64	64.36	0.0610	34.92
15.53	0.0205	12.47	67.27	0.0618	35.10
15.91	0.0220	13.29	67.60	0.0630	35.97
18.82	0.0251	15.25	70.65	0.0648	36.95
19.18	0.0256	15.37	73.32	0.0664	37.80
19.26	0.0246	14.82	73.52	0.0655	37.04
23.44	0.0288	17.22	76.25	0.0681	38.69
23.58	0.0301	17.92	79.26	0.0698	39.58
25.29	0.0316	18.95	79.96	0.0692	38.96
26.87	0.0333	19.68	82.53	0.0717	40.53
27.01	0.0322	19.09	85.50	0.0733	41.38
29.46	0.0357	20.98	85.78	0.0724	40.60
30.16	0.0361	21.43	88.51	0.0749	42.23
31.13	0.0359	21.14	91.50	0.0765	43.04
32.73	0.0385	22.54	91.72	0.0756	42.25
35.50	0.0409	23.81	94.75	0.0782	43.91
35.52	0.0395	23.15	97.08	0.0784	43.69
35.76	0.0409	24.05	97.62	0.0798	44.68
38.29	0.0432	25.03	100.89	0.0814	45.53
39.11	0.0424	24.70	101.76	0.0807	44.88
41.58	0.0458	26.43	103.96	0.0829	46.31
41.70	0.0456	26.61	106.59	0.0842	46.97
43.21	0.0456	26.38	107.18	0.0834	46.23
45.50	0.0487	28.03	109.44	0.0856	47.67
47.12	0.0484	27.94	111.61	0.0867	48.19

The activated carbon sample is introduced into one of the crucibles. The installation is then evacuated at 513 K during a 10-h period (with all valves open, except V1). During this outgassing operation, the pressure (controlled by a Pyrani vacuum gauge) is 10^{-2} mmHg. The TG signal shows a sharp decrease in the beginning of the operation. The complete outgassing of the inner parts of the installation takes about 10 h. The sample is then cooled to the adsorption temperature. Valves V3 and V6 are then closed and gas is admitted into the buffer tank by opening V1. At this step of the procedure, the TG, HF, and T signals remain constant. The gas is put into contact with the sample by opening the valve V3; V4 is a micrometric valve regulating the gas flow. The mass of the sample increases, the heat-flux signal deviates and the pressure drops in the constant volume device. The temperature remains constant at its set value. Once the other signals are constant, equilibrium is reached. Knowing the mass signals before and after adsorption and the mass of sample, it is possible to calculate the adsorbed mass (kg of adsorbate/kg of adsorbent or relative mass M_r) at the equilibrium pressure which is measured by the pressure transducer. Integration of the heat-flux signal gives the corresponding integral heat of adsorption. Afterward, valve V3 is closed and a new quantity of gas is introduced in the buffer tank by opening V1. A second set of temperature, pressure, adsorbed mass,

Table 4. Mass of CO_2 Adsorbed per Unit Mass of Activated Carbon F30/470 (M_r) and Heat of Adsorption (Q) at 302.3 K and 297.3 K

$T = 302.3$ K			$T = 297.3$ K		
P/kPa	M_r	Q/J·g^{-1}	P/kPa	M_r	Q/J·g^{-1}
3.25	0.0045	3.05	4.03	0.0071	4.66
3.99	0.0061	4.11	6.98	0.0133	8.52
5.35	0.0089	5.78	10.13	0.0191	11.93
7.50	0.0127	8.18	13.24	0.0240	14.82
7.84	0.0133	7.88	16.47	0.0286	17.47
10.07	0.0169	9.99	19.30	0.0324	19.59
11.88	0.0195	12.21	22.07	0.0359	21.51
12.60	0.0206	12.13	25.37	0.0398	23.65
15.63	0.0247	14.45	28.32	0.0430	25.43
18.20	0.0277	17.05	31.39	0.0463	27.19
19.16	0.0290	16.94	34.34	0.0493	28.80
23.86	0.0343	19.92	37.09	0.0519	30.25
27.09	0.0377	21.82	40.32	0.0550	31.89
31.53	0.0421	24.22	43.59	0.0579	33.48
35.44	0.0457	26.22	46.14	0.0601	34.68
35.72	0.0459	27.30	49.57	0.0630	36.21
40.12	0.0498	28.45	52.60	0.0655	37.51
44.03	0.0531	30.18	56.10	0.0683	38.96
46.04	0.0547	32.09	59.55	0.0709	40.35
48.87	0.0569	32.26	62.92	0.0734	41.69
52.90	0.0601	33.91	66.37	0.0760	42.98
54.79	0.0615	34.72	69.94	0.0785	44.29
58.04	0.0638	35.92	73.36	0.0812	46.18
63.94	0.0680	38.11	76.63	0.0831	47.17
65.87	0.0693	38.89	80.50	0.0857	48.50
68.16	0.0708	39.60	84.62	0.0883	49.86
74.62	0.0750	41.80	88.99	0.0910	51.27
76.63	0.0764	42.58	92.85	0.0934	52.47
80.50	0.0787	43.70	97.20	0.0960	53.79
86.08	0.0820	45.43	101.38	0.0984	55.04
89.25	0.0840	46.54	105.15	0.1006	56.11
94.25	0.0867	47.88	108.52	0.1025	57.06
101.48	0.0906	49.89	111.65	0.1043	57.92
101.62	0.0908	50.09			
108.00	0.0940	51.65			
111.03	0.0958	52.65			

Table 5. Mass of CO_2 Adsorbed per Unit Mass of Activated Carbon F30/470 (M_r) and Heat of Adsorption (Q) at 289.7 K and 277.4 K

$T = 289.7$ K			$T = 277.4$ K		
P/kPa	M_r	Q/J·g^{-1}	P/kPa	M_r	Q/J·g^{-1}
4.97	0.0112	7.47	5.03	0.0165	11.13
7.08	0.0163	10.57	7.18	0.0238	15.37
9.09	0.0205	13.10	9.17	0.0295	18.76
11.34	0.0250	15.66	11.16	0.0347	21.69
14.33	0.0303	18.73	13.08	0.0392	24.26
16.90	0.0344	21.08	15.23	0.0439	26.88
19.26	0.0381	23.10	18.14	0.0498	30.13
21.93	0.0420	25.23	21.45	0.0559	33.56
25.27	0.0464	27.69	24.16	0.0605	36.09
27.83	0.0498	29.49	29.42	0.0689	40.65
30.89	0.0535	31.51	33.49	0.0748	43.81
33.78	0.0570	33.30	37.67	0.0805	46.85
37.67	0.0613	35.61	43.39	0.0878	50.73
40.66	0.0645	37.27	48.79	0.0941	54.16
43.89	0.0679	39.03	53.63	0.0996	57.05
46.78	0.0708	40.52	61.41	0.1077	61.33
51.32	0.0753	42.82	66.03	0.1123	63.70
55.11	0.0788	44.62	70.77	0.1167	66.01
59.25	0.0825	46.51	75.50	0.1211	68.24
64.08	0.0865	48.63	81.28	0.1261	70.83
69.08	0.0905	50.71	87.43	0.1312	73.45
73.44	0.0939	52.45	93.67	0.1361	76.00
76.93	0.0965	53.76	101.11	0.1418	78.86
81.61	0.0999	55.50	106.01	0.1455	80.67
85.64	0.1028	56.96	111.43	0.1493	82.59
90.26	0.1060	58.58			
95.50	0.1095	60.32			
100.53	0.1128	61.94			
104.51	0.1153	63.19			
107.54	0.1171	64.11			
111.43	0.1195	65.30			

and integral adsorption heat is obtained by opening V3. This experiment is repeated until the pressure reaches 100 kPa to 110 kPa. At this step, we dispose of a first isotherm (adsorbed mass versus pressure) and the corresponding integral adsorption heats (integral adsorption heat versus pressure). The sample must be outgassed as explained previously in order to start a new experiment at another temperature.

Measurement Accuracy. The main advantage of this TG-DSC apparatus is that it allows simultaneous measurement of adsorption heat and adsorbed amount. Besides, the mass is directly determined so that the accuracy of the mass measurement does not depend on the adequacy of the gas equation of state, as is the case for adsorption devices based on the volumetric method (Berlier et al., 1995b). On the other hand, the mass sample is small, which may affect the quality of the measurement for heterogeneous sorbents. Besides, the mass measurement at different pressures leads to systematic errors due to the Archimede effect. In fact the intrinsic sensitivity of the thermobalance (0.25 to 10 μg given the maximum mass) leads to very weak relative errors on the mass measurements (0.04% on the mass sample, an average of 0.1% on the mass change with a maximum value of 1% for the smallest adsorbed mass observed at 327.2 K, and a minimum value of 0.01% for the largest adsorbed mass at 277.4 K). On the other hand, the Archimede effect can lead to important absolute errors within high-pressure and low-temperature conditions (for which the gas phase is dense). Fortunately, such conditions correspond to high adsorbed mass so that the evolution of the relative error due to Archimede's effect as a function of temperature and pressure is not a priori known. However, the maximum relative error is often observed at high pressures (high density of the gas phase) and high temperatures (low adsorbed mass). The highest observed relative error was 2.8% at 327 K and 111.55 kPa. The average value in most cases was below 1%. This error due to the Archimede effect is of the same order of magnitude as the observed discrepancies when the same experiments are run with two different samples of the same sorbent.

The accuracy of the pressure measurement is about 0.1 kPa, that is to say a maximum relative error of 4% at lower pressures with average values of 0.2%.

The temperature is measured with an absolute error equal to 0.1 K.

As to the heat flow, the sensitivity of the calorimeter leads to typical values of the absolute error on the integral heat equal to about 4 mJ, giving relative average errors of about 0.4%. This is less than the deviations observed between the results of two different runs of the same experiment.

Results and Discussion

Adsorption isotherms for CO_2 on activated carbon F30/470 at seven experimental temperatures (327.2, 317.4, 307.4, 302.3, 297.3, 298.7, and 277.4) K were obtained at pressures up to 100 kPa to 110 kPa. The results are presented in Tables 2–5 and in Figures 2 and 3. Several sets of measurements were reproduced with differences of less than 2% and 1%, respectively for TG and HF signals. An example can be observed in Figures 2 and 3 at 307.4 K where experiments have been conducted three times (○, +, and *).

The experimental isotherms and integral heats of adsorption are presented in Figures 2 and 3. The isotherms are similar in shape and have a classic isotherm form.

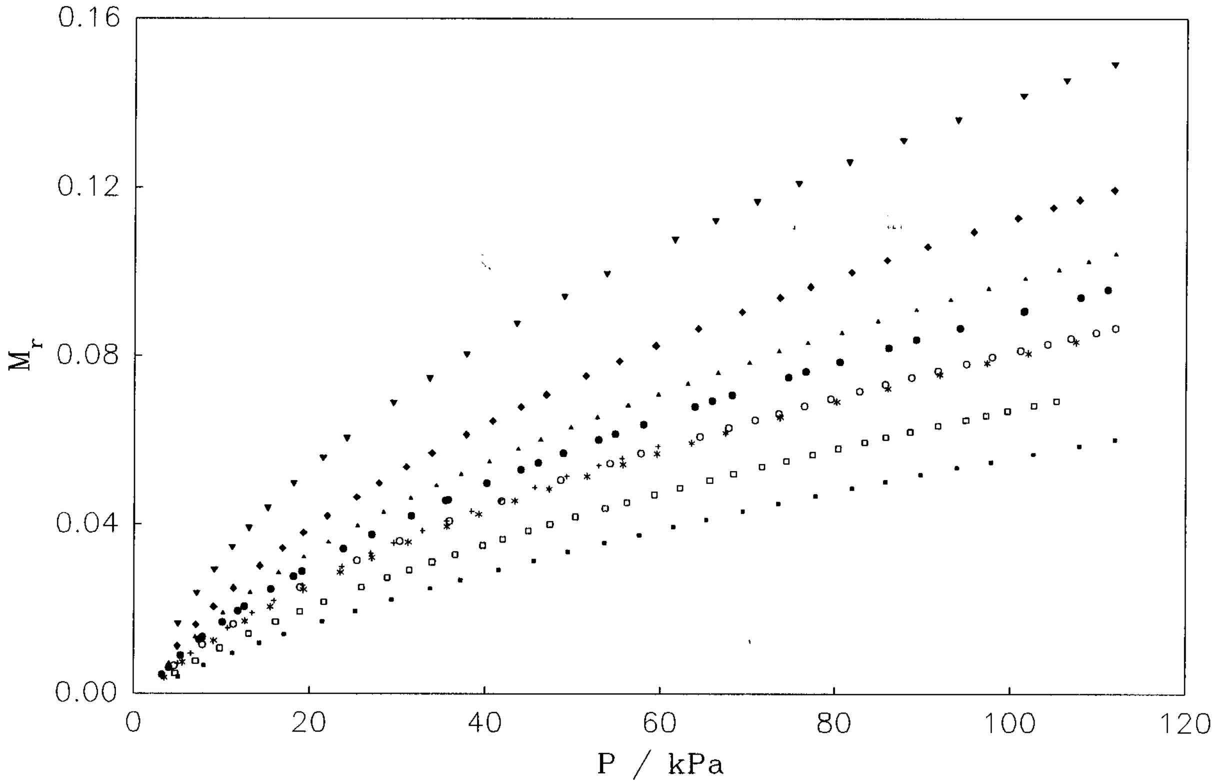

Figure 2. Isotherm for adsorption of CO_2 on activated carbon F30/470 at 327.2 (■), 317.4 (□), 307.4 (○, +, *), 302.3 (●), 297.3 (▲), 289.7 (◆), and 277.4 K (▼).

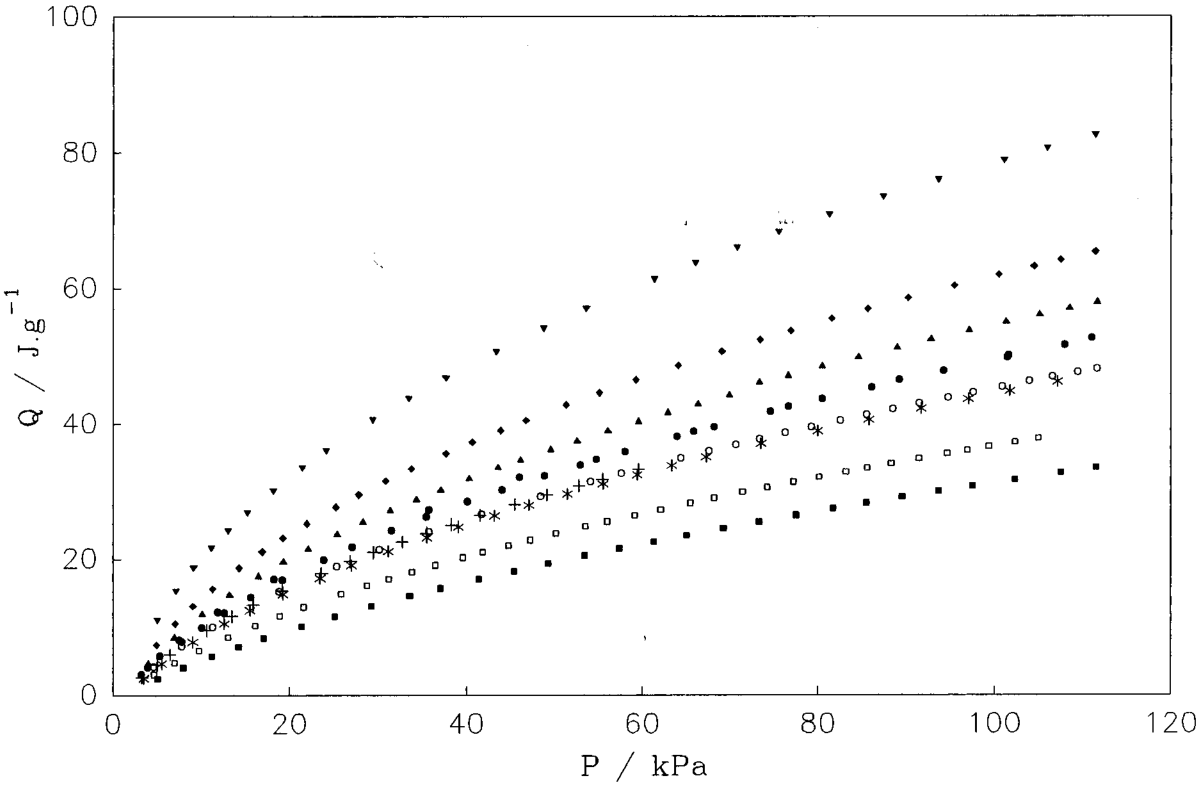

Figure 3. Heat of adsorption of CO_2 on activated carbon F30/470 at 327.2 (■), 317.4 (□), 307.4 (○, +, *), 302.3 (●), 297.3 (▲), 289.7 (◆), and 277.4 K (▼).

Integral heats of adsorption are presented as heat (*Q*) versus pressure (*P*). It is also possible to present heat (*Q*) versus adsorbed mass (*M*).

Theoretically, it is possible to obtain integral heats of adsorption from adsorption isotherms so the direct measurement of calorimetric data seems useless. The well-known procedure consists of plotting ln *P* versus 1/*T* at constant adsorbed mass. The slope of such curves gives the ratio q_{isost}/R (q_{isost} being the isosteric adsorption heat and *R* the ideal gas constant). By determining such a ratio for each adsorbed mass at a given temperature, we obtain the isosteric adsorption heat as a function of the adsorbed mass. The corresponding differential adsorption heats are obtained by translating the isosteric heat curve by *RT*. The integration from 0 to a given adsorbed mass gives the corresponding integral adsorption heat. Such a procedure requires that the numerous isotherms have a sufficient number of points in the ln P vs $1/T$ curves. Very often such curves are considered to be straight lines. However, considering other mathematical expressions for these curves may lead to great discrepancies (compared to the linear behavior) when derivating to obtain the isosteric heats. Besides, the q_{diff} (q_{diff} being the differential adsorption heat) curves are often characterized (for activated carbons) by high values at zero coverage with a sharp decrease at low adsorbed mass. This part of the curve is particularly difficult to obtain, as it requires very accurate measurements at very low adsorbed mass, that is to say at very low pressure. Unfortunately, this starting part of the q_{diff} curves is of great importance in the integration results. As we see, this procedure requiring derivation and integration of experimental data is rather delicate. It leads to typical deviations between experimental and calculated integral heats of 10%. This is why we will not present in this paper the extensive results of this procedure, mentioning only that we have obtained an average deviation of 7%. Such considerations reveal the necessity of the direct measurement of integral adsorption heats.

Conclusion

The TG-DSC 111 Setaram has been equipped in order to perform simultaneous measurement of isotherms and heats of adsorption using a simple experimental procedure. Adsorption data for CO_2 on activated carbons at temperatures ranging from 277 K to 337 K and for pressures up to 110 kPa are presented. The wide range of temperature allowable (from 150 to 1100 K) and the availability of integral adsorption heats make this device an interesting tool for the adsorption data acquisition. The experimental errors remain within acceptable values and can be evaluated. The direct measurement of calorimetric data is useful for the design of thermal adsorption machines. On a more fundamental side, they could play an important role in gas adsorption modeling and porous solids characterization.

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