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A batch-type heat conduction microcalorimeter for immersion heat determinations: design, calibration and applications

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Abstract

A batch-type heat conduction microcalorimeter is designed and constructed for the determination of immersion heats of microporous solids in polar and non-polar solvents. The apparatus is of the twin type and uses high sensitivity thermopiles for the detection of thermal effects. The calibration constant of the equipment is determined for the constructed aluminum and Pyrex brand glass cells, at different levels of work and electric power (between 0.25 J and 2 J, and 1 mW and 16 mW, respectively). The values of the calibration constant vary between 18 WV^{-1} and 22 WV^{-1}.

Chemical calibrations are also carried out with the standard systems HCl-NaOH, and THAM-HCl (THAM = trishydroxymethylaminomethane). The results, -56.40 ± 0.08 kJ mol^{-1} for the neutralization heat of aqueous solutions of HCl and NaOH, and -47.40 ± 0.01 kJ mol^{-1} for the protonation heat of THAM with a dilute aqueous solution of HCl, are in good agreement with those reported in the literature and corroborate the correct functioning of the microcalorimeter.

The equipment was employed in the determination of surface areas of activated carbons, between 250 and 1500 $m^2\,g^{-1}$, with an imprecision of 0.45%; the results show better sensitivity with respect to previously reported determinations. Also, immersion heats of activated carbons in 0.1M NaOH and HCl were determined and related to the number of acid or basic groups of the carbon.

Keywords: Acidity and basicity of activated carbons; Heat conduction; Immersion heat; Microcalorimeter

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1. Introduction

Immersion calorimetry has been widely used to determine surface areas of porous solids such as carbon blacks and different types of catalysts, among others [1,2]. Also, combined with adsorption data, the technique has been employed in studies of pore distribution of these materials [3,4]. The combined use of calorimetric and adsorption titration data on the solid surface (CAL-AD method) has been proposed by Chronister and Drago [5] to differentiate hydrogen bonding sites in silica gel samples.

The determination of the immersion heat of a solid in acid and/or basic solvents allows to quantify basic and /or acid functional groups present on the solid surface [6]. The application of the technique in the characterization of activated carbon has been particularly interesting since this material

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is massively employed in food-, pharmaceutical-, petrochemical-, and nuclear industries [6], as well as in recovering and refining processes of noble metals such as silver and gold [3].

The total surface area of microporous solids can be evaluated by immersion calorimetry employing the model developed by Stoeckli and Kraehenbuelh [7], based on the Dubinin theory of the volume filling of micropores (TVFM) [8]. This method is faster and more precise than the classic ones based on adsorption isotherms.

Recently, we developed in our laboratory an isoperibol immersion macrocalorimeter to carry out determinations of the immersion heat of samples of activated carbon in carbon tetrachloride [9–11]. The samples were kindly donated by Dr. A. Polania (r.i.p.). Surface areas of about 1,000 $m^2 g^{-1}$ were obtained, with an imprecision of 0.5%.

The batch-type microcalorimeter described here was constructed to continue the above mentioned studies in activated carbons with surface areas of about 200 $m^2 g^{-1}$, in order to improve the sensitivity and to improve the imprecision of 0.5% obtained with the earlier macrocalorimeters; and also to quantify acid and/or basic functional groups by relating them to the immersion heat generated when the solids are placed in 0.1 M solutions of HCl and NaOH. The applications of the equipment to several types of activated carbons will be the subject of another publication.

2. Description and operation of the microcalorimeter

Figure 1 schematically shows the main parts of the microcalorimeter. The twin-type apparatus has two cells, one of which contains the samples (A) and the other is used as reference (A'). The cells are rectangular in shape and have an approximate capacity of 5 to 7 mL. Two sets of cells were built, in Pyrex brand glass and in aluminum, with dimensions of 45 mm long, 35 mm wide, and 11 mm thick. Each cell has two compartments in which the liquids or solutions (solution calorimetry), or the solvent and the porous solid (immersion calorimetry) are

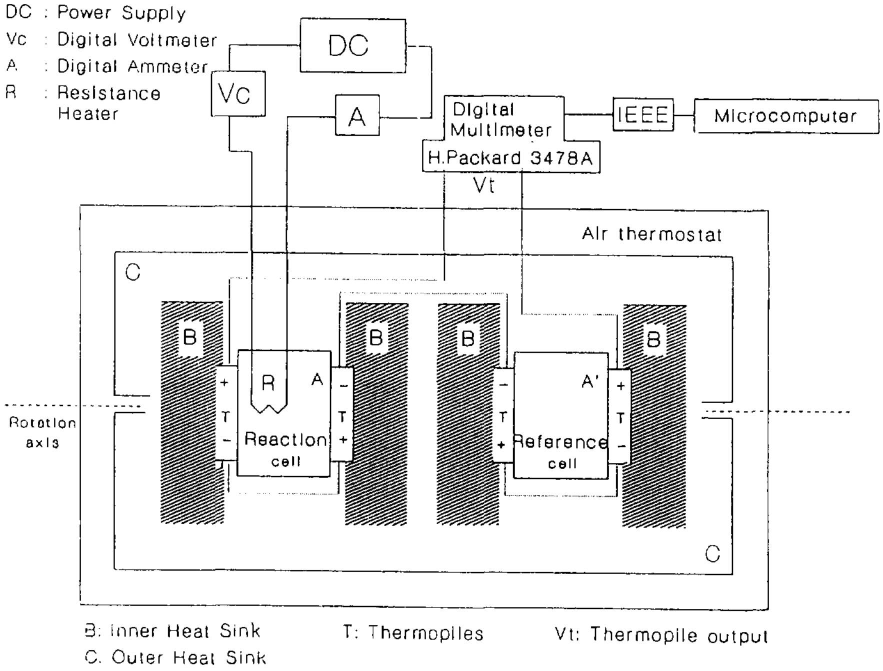


Fig. 1. Batch type microcalorimeter.

placed, and is hermetically sealed with either a Teflon or glass stopper. The mixing of liquids or the solid wetting processes take place by rotation of the apparatus around a central axis.

A high sensitivity thermopile (Tellurex Corp. C-1-2,8-127) is placed on each side of the cells; the two thermopiles are connected in series. This set is located between the inner heat sinks (B), which consist of two aluminum cylindrical pieces (75 mm diameter and 25 mm thick) that allow a fast heat transfer between the cells and the outer heat sink (C). The latter is a cylinder (175 mm long and 150 mm diameter) longitudinally divided in two sections; the lower accommodates the two calorimetric units (constituted by the calorimetric cells, the thermopiles, and the inner heat sinks), and the upper serves as a lid. The entire apparatus is supported by two stainless steel central axes (D) that act as the calorimeter rotation axis and are attached to metal bases (E). The apparatus is placed inside an air thermostat at 25.00 ± 0.02°C. Fig. 2 shows a detailed diagram of the assembled microcalorimeter. Since the thermopiles of the reference and measurement calorimetric cells are connected opposite to each other in order to subtract all external effects, the registered thermoelectric potential is a differential signal and the microcalorimeter operates as one of the twin type.

3. Electric calibration

The electric calibration is performed by passing a direct current through a low power 0.125 W or 0.250 W resistor having a nominal resistance of 100 Ω. The current source is a high precision DC power supply (Hewlett Packard 6114A). Two multimeters (Univolt DT-888) were used to mesure the voltage and the current. Data collection and processing is carried out by a digital precision multimeter (Hewlett Packard 3478A, sensitivity 0.1 μV) connected to an IBM PS1 microcomputer by means of an IEEE-488 interface. The software for data processing was developed in this laboratory [12].

The vessels are filled with 3 mL of water in each stoppered compartment. Then each vessel is placed in its calorimetric unit and the assembly is kept in the air thermostat for about 30 min before starting data collection. The first step in the electric calibration is to determine the stability of the baseline during long periods of time; the second step is to dissipate in the cell different amounts of electric

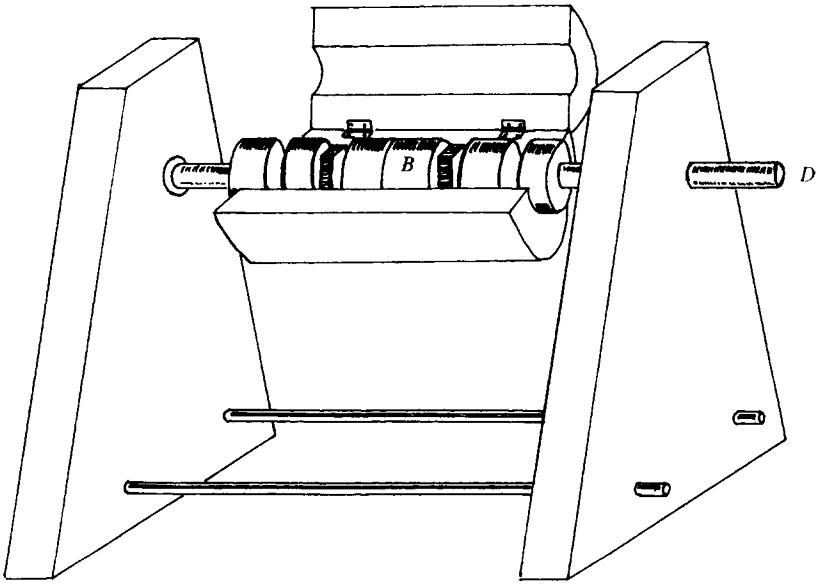


Fig. 2. Assembled microcalorimeter.

energy at several power levels. From these results, the calibration constant, ε, and the sensitivity $(1/\varepsilon)$ can be calculated by two methods [13]. In method I, the dissipated electric energy, W_{el}, is related to the area under the curve of thermoelectric potential *vs.* time. Then ε, expressed in WV^{-1}, is defined as:

$$\varepsilon = \frac{W_{el}}{\int V_t dt} = \frac{V_c i t}{\int V_t dt} \tag{1}$$

where V_c and V_t are the calibration and thermoelectric potentials in volts, i is the calibration current in amps, and t is the time of current flow in seconds.

In method II, a stationary electric power is dissipated in the cell and this parameter is related to the stationary thermoelectric potential generated by the thermopiles $(V_t)_{stat}$; under these conditions, ε, expressed in WV^{-1}, is defined as:

$$\varepsilon = \frac{(V_c i)_{stat}}{(V_t)_{stat}} \tag{2}$$

In method I, values of electric energy between 0.5 J and 2.0 J were used at power levels between 16 mW and 1 mW, for the glass cells. Electric energies of 0.5 J and 16 J at power levels of 4 mW and 16 mW, respectively, were used for the aluminum cells. In method II, powers of 0.990 mW, 1.980 mW, 3.970 mW, 7.920 mW, and 15.90 mW were dissipated.

4. Chemical calibration

The accuracy and precision of the calorimeter were evaluated by determining the heat of neutralization of HCl with NaOH, and the heat of protonation of THAM by HCl. These are traditional calorimetric standards [14–20]. These experiments were carried out in the glass cells. Analytical grade Merck reagents and demineralized water were employed; the reagents were weighed to ± 0.0001 g.

For the determination of the heat of neutralization, 1g of 0.1081 M HCl and 2 g of 0.0940 M NaOH were placed in the reaction cell; 1 g of water and 2 g of the same solution of NaOH were placed in the reference cell, in order to correct for the dilution heat of NaOH. Additional experiments were performed to correct for the dilution heat of HCl.

For the determination of the protonation heat of THAM in solution, 2 g of 0.083 M THAM and 2 g of 0.1046 M HCl were placed in the reaction cell; the reference cell was filled with 2 g of the same solution of HCl and 2 g of water in order to take into account the dilution heat of HCl. The dilution heat of THAM was determined in additional experiments.

5. Application to the determination of the total surface area of activated carbon

The amount of heat generated when a liquid wets a solid is directly proportional to the solid surface, provided that there are no chemical reactions between them. Under these conditions, the immersion heat can be used to rapidly determine the surface area of the solid.

Stoeckli and Kraehenbuehl [21] studied the immersion heats of activated carbons with different polarities and gave an Equation for the calculation of the immersion enthalpy of the microporous solid in organic liquids. For activated carbons, the immersion enthalpy of the micropores, $-\Delta H_{imi}$, can be calculated by the equation:

$$-\Delta H_{imi} = \frac{\beta E_0 W_0 \sqrt{\pi}(1 + \alpha T)}{2 V_m} \tag{3}$$

where β is the affinity coefficient of the organic liquid and V_m ($cm^3\ mol^{-1}$) is its molar volume; α is the thermal expansion coefficient of the liquid (K^{-1}); E_0 is the characteristic energy of the solid ($J\ mol^{-1}$), T is the absolute temperature and W_0 is the micropore total volume ($cm^3\ g^{-1}$).

Since the generated immersion heat, ΔH_{iexp}, is the sum of the contributions from the external surface and from the micropore surfaces, the enthalpy for the immersion of the external surface, ΔH_{iext}, is:

$$\Delta H_{iext} = \Delta H_{iexp} - \Delta H_{imi} \tag{4}$$

It is possible to calculate the external surface, S_{ext} ($m^2\ g^{-1}$), from this equation, because the immersion enthalpies of non-porous open surfaces are related by the equation:

$$\Delta H_{iexp} = \Delta H_{imi} + \Delta H_{ist} * S_{ext} \tag{5}$$

where ΔH_{ist} is the standard immersion enthalpy per square meter of the reference solid.

Thus, the external surface of the activated carbon is:

$$S_{\text{ext}} = \frac{\Delta H_{i\,\text{exp}} - \Delta H_{\text{imi}}}{\Delta H_{\text{ist}}} \tag{6}$$

and also:

$$S_{\text{ext}} = A_{\text{t}} - A_{\text{mi}} \tag{7}$$

where A_{t} is the total area of the porous solid, and A_{mi} is the area of the micropores of the same solid.

Samples previously prepared and characterized by the B.E.T. method by Polanía [3] were used for the determinations. Activated carbons of high area, prepared from wood (Ex-bois), and of low area, obtained from African palm tree (Cuesco) were employed for the determinations.

The samples were purified by a combination of the methods of Bloom [22] and Morgan et al. [23], then dried in the oven at 110°C for 72 hours, and kept in a dessicator until the time of use. Samples (mass = 80 mg to 300 mg) were placed in the basket of a vessel especially designed by us (Fig. 5). Then, 2 mL of CCl_4 (Merck, analytical grade) were added to the reaction and reference cells, to take into account thermal effects different to those related to the immersion process. Once the temperature has stabilized in the microcalorimeter, readings of potential, V_{t}, as a function of time are taken for about 15 min, then the carbon is immersed in the solvent, and the readings are taken for 20 more min. Finally, the electric calibration is performed.

6. Application to the determination of the amount of acid and basic functional groups on the surface of activated carbon

The porous structure of an activated carbon is developed during the activation process. The adsorption properties of activated carbon are not only determined by its porous structure but also by the presence of acid and basic functional groups, located in the sides of polyaromatic rings [24].

Various methods have been employed to study the chemical structures on solid surfaces: adsorption of dyes [25], base titrations in non-aqueous solvents [26], thermometric titrations, potentiometric titrations, polarography, IR spectroscopy, and X-ray spectroscopy [27]. One of the most frequently employed is that recommended by Boehm [28], that consists of neutralization with bases of different strength.

Previous to the determinations, the equipment was tested at the experimental conditions by determining the immersion enthalpy of a standard carbon sample in pyridine (Illinois coal #6, from Argonne National Laboratories; see Ref. [29]).

The same above mentioned types of activated carbon were employed for these determinations, whose amount of acid and basic functional groups have been previously determined by Polanía [3], using the Boehm method.

Samples between 30 mg and 50 mg were weighed to ± 0.0001 g and placed in the basket of the reaction cell (Fig. 5); then 2 mL of 0.1 M NaOH (Mol-Labs) were added; the same amount of carbon and 2 mL of water were placed in the reference cell, to take into account the effects between the water and the solid surface. The immersion heat was determined as previously described. The same experiments were repeated using 0.1 M HCl (Mol-Labs) to determine the amount of basic functional groups.

7. Results and discussion

Table 1 shows the performance characteristics of the equipment. The stability of the baseline during 12 hour periods is ± 2.5μV for the aluminum cells and ± 3.5 μV for the glass cells. This stability is not as good as that of 100 nV reported by Steckler et al. [13] for a similar calorimeter developed at the NBS, where temperature was controlled to ± 0.2 mK during a 24 hour period. We recently built a heat-conduction flow microcalorimeter, for which we obtained a baseline stability of ± 1 μV employing a water thermostat stabilized to ± 0.005°C [30]. These observations show that better baseline stability would be obtained if the temperature control was better. However, these baseline stabilities do not significantly affect the precise evaluation of the immersion heat of activated carbon in different solvents, since the registered signals are greater than 2 mV.

The calibration constants (22 WV^{-1} for the glass cells and 18 WV^{-1} for the aluminum cells) and the

Table 1
Characteristics of the microcalorimeter

	Aluminum cells	Glass cells
1. Stability of the baseline (μV)	± 2.5	± 3.5
2. Calibration constant ($W V^{-1}$)	18	22
3. Sensitivity ($V W^{-1}$)	0.056	0.045
4. Time constant (s)	100	150

Table 2
Calibration constants for the glass cells by method I at 25.00 ± 0.02°C

Electric energy (J)	Electric power ($W \times 10^3$)	$\varepsilon(WV^{-1})^{a,b}$
1.000	2.000	22.38 ± 0.14
	1.000	23.78 ± 0.27
2.000	16.0	22.77 ± 0.30
	8.0	22.20 ± 0.47
	4.0	22.34 ± 0.77
	2.0	21.62 ± 1.23
	1.0	21.62 ± 0.57

[a] Each value corresponds to the average of ten determinations.
[b] The uncertainty on each determination is calculated as the variance at 95% confidence.
ε = calibration constant.

Table 3
Calibration constants for the glass cells by method II at 25.00 ± 0.02°C

Voltage (V)	Electric power ($W \times 10^3$)	$\varepsilon(WV^{-1})^{a,b}$
0.3150	0.9900	21.19 ± 0.55
0.4450	1.980	21.43 ± 0.91
0.6300	3.970	22.38 ± 0.42
0.8900	7.920	22.38 ± 0.38
1.260	15.90	22.67 ± 0.10

[a] Each value corresponds to the average of five determinations.
[b] The uncertainty on each determination is calculated as the variance at 95% confidence.
ε = calibration constant.

Table 4
Calibration constants for the aluminum cells by method I at 25.00 ± 0.02°C

Electric energy (J)	Electric power ($W \times 10^3$)	$\varepsilon(WV^{-1})^{a,b}$
0.5000	4.000	18.40 ± 0.01
2.000	16.00	18.41 ± 0.08

[a] Each value corresponds to the average of three determinations.
[b] The uncertainty on each determination is calculated as the variance at 95% confidence.
ε = calibration constant.

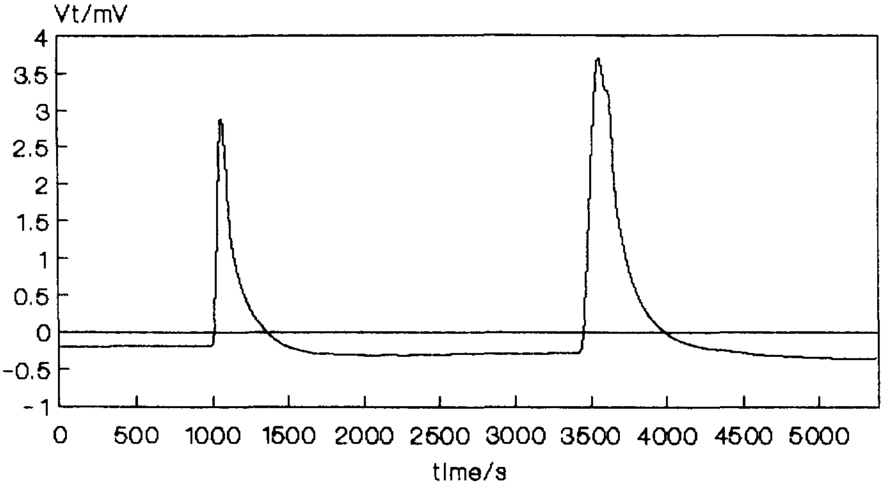
respective sensitivity values are very similar to those found by Steckler et al. [13]. The aluminum cells show a higher sensitivity (0.056 VW^{-1}) than the glass ones (0.045 VW^{-1}). This observation may be explained by the better contact between the metal cells and the thermopiles with respect to the glass ones because they can be better adjusted inside the inner heat sinks; also, the higher thermal conductivity of aluminum with respect to glass contributes to the greater sensitivity of the metal cells. This fact is also responsible for the smaller time constant of the aluminum cells (100 s) as compared to those of glass (150 s). Our values for the time constant are higher than those reported by Steckler et al. [13], but lower than those reported by Wadsö [31].

Table 2 summarizes the results for the calibration constant, ε, at different values of electric energy and power when the determinations are carried out in the glass cells by method I; it is observed that the constant does not appreciably vary with these parameters. Table 3 gives the values of the calibration constant when the determination is carried out by method II, also using the glass cells. The results are in agreement with those shown in Table 2. These values, when determined by method I in the aluminum cells, are given in Table 4.

No significant differences in the values of the calibration constant are observed when the microcalorimeter is rotated during the application of electric energy, nor when the cells are full or empty.

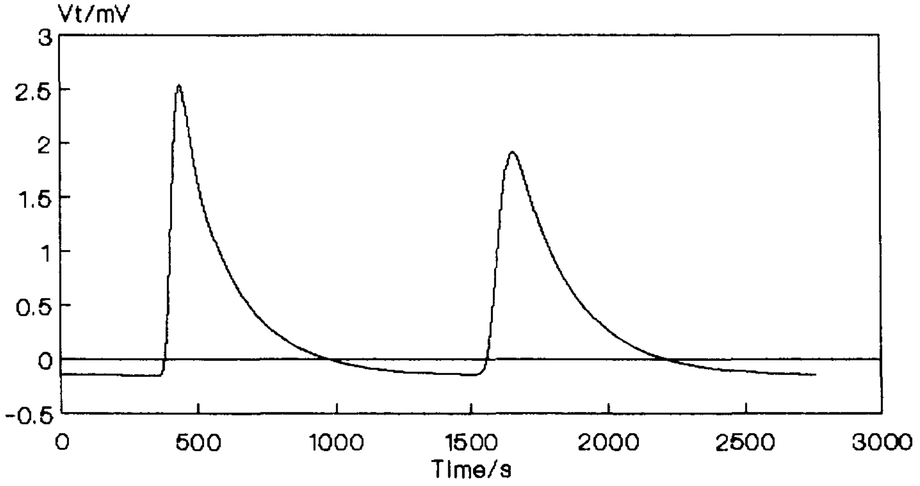
Figures 3 and 4 show typical thermal curves for the HCl-NaOH and THAM-HCl systems, respectively. In both cases, the first maximum corresponds to the heat generated by the reaction, and the second, to the electric energy dissipated to measure the calibration constant after the experiments were performed.

The results of the neutralization heat for the system HCl-NaOH are given in Table 5, as well as



HCl : 1 g ; 0.1081 M
NaOH: 2 g : 0.0940 M
Calibration constant:15.05 W/V

Fig. 3. Neutralization heat of HCl–NOH.



THAM : 2 g ; 0.083 M
HCl : 2 g ; 0.1046 M
Calibration constant: 16.50 W/V

Fig. 4. Protonation heat of THAM-HCl.

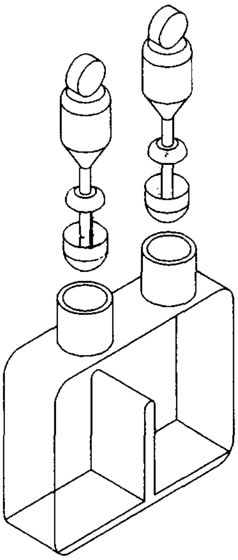


Fig. 5. Immersion cell.

Table 6
Protonation heat of them – HCl in the glass cells at 25.00 ± 0.02°C

mmoles of THAM	Q (J)	ΔH (This work) (kJ mol^{-1})	ΔH (Other authors) (kJ mol^{-1})
0.1695	−8.371	−49.37	−47.53 [17]
0.1699	−8.393	−49.41	−47.36 [19]
0.1719	−8.489	−49.37	−47.49 [33]
0.1978	−9.791	−49.33	−47.45 [34]
0.2090	−10.32	−49.37	
0.2133	−10.53	−49.37	
0.2327	−11.48	−49.33	
0.2374	−11.72	−49.37	
0.2444	−12.07	−49.37	
0.2607	−12.87	−49.37	
0.2647	−13.06	−49.33	
0.2670	−13.18	−49.37	
0.2767	−13.66	−49.37	

Q = experimental protonation heat; ΔH = molar enthalpy of THAM protonation.

Table 5
Neutralization heat of HCl-NaOH in the glass cells at 25.00 ± 0.02°C

mmoles of HCl	Q (J)	ΔH (This work) (kJ mol^{-1})	ΔH (Other authors) (kJ mol^{-1})
0.1046	−6.115	−58.45	−56.36 [14]
0.1052	−6.130	−58.28	−57.03 [15]
0.1052	−6.150	−58.45	−55.94 [32]
0.1053	−6.158	−58.49	
0.1055	−6.137	−58.16	
0.1056	−6.136	−58.12	
0.1057	−6.178	−58.45	
0.1058	−6.154	−58.16	
0.1059	−6.189	−54.45*	
0.1059	−6.173	−58.28	
0.1065	−6.224	−54.45*	
0.1069	−6.213	−58.12	
0.1076	−5.427	−50.46*	
0.1077	−6.300	−58.49	
0.1080	−6.287	−58.20	
0.1082	−6.322	−57.61	
0.1083	−6.329	−58.45	
0.1089	−6.365	−58.45	
0.1097	−6.382	−58.16	
0.1105	−7.005	−63.69*	

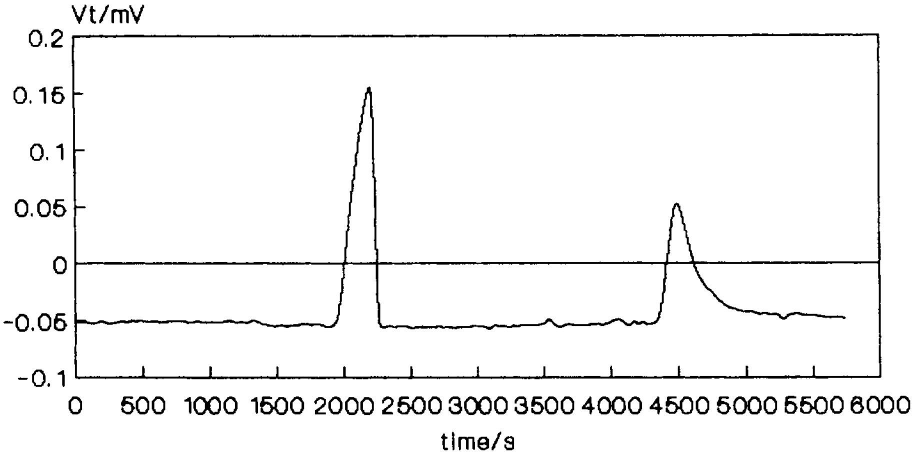
* Rejected data in the statistical analysis.
Q = experimental neutralization heat; ΔH = molar enthalpy of neutralization.

those obtained by other authors. Our average value, -56.40 ± 0.08 kJ mol^{-1} is in good agreement with those reported in the literature [14,15,20,32].

Table 6 lists the results of the protonation heat for the system THAM-HCl. This system is suggested by Nelander [17] and Wadsö [19] as a standard for microcalorimeter calibration; the average value, -47.40 ± 0.01 kJ mol^{-1} is in good agreement with those reported in the literature [17,19,33,34].

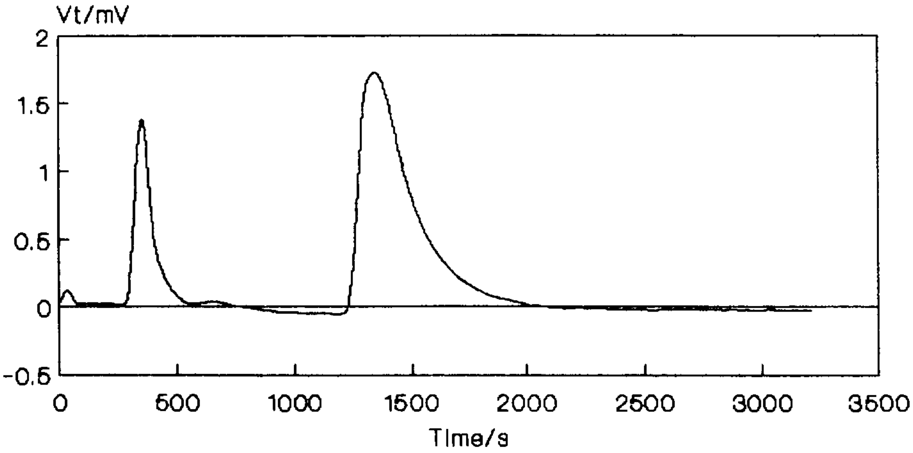
Figures 6 and 7 show typical thermal curves obtained for the immersion of Cuesco and Ex-bois carbons, and Tables 7 and 8 give the results for the determination of the total surface area, A_t, in these activated carbons. In the calculations, a value of ΔH_{ist} of -115 mJ m^{-2} was used, for the immersion heat of graphite in CCl_4 [23]. Cuesco carbon gave a total surface area of 280.2 ± 1.3 m^2 g^{-1}, and Ex-bois carbon gave a value of 1559 ± 7 m^2 g^{-1}; these average values are in good agreement with those determined by Polanía [3] by the method of adsorption isotherms. Thus, the results show that the microcalorimetric technique can be used to determine the total surface area in this type of solids.

Figure 8 shows a typical thermal curve for the immersion of Illinois carbon #6 in pyridine, and



Mass of sample(g): 0.0375
Δ HI exp. : - 32.35 Jg
Solvent: CCl4

Fig. 6. Immersion heat of cuesco activated carbon (low surface area).



Mass of sample (g):0.01521
Δ HI exp.: - 170.0 Jg
Solvent : CCl4

Fig. 7. Immersion heat of ex-bois activated carbon (high surface area).

Table 7
Immersion heat of cuesco activated carbon in CCl_4 at 25 ± 0.02°C

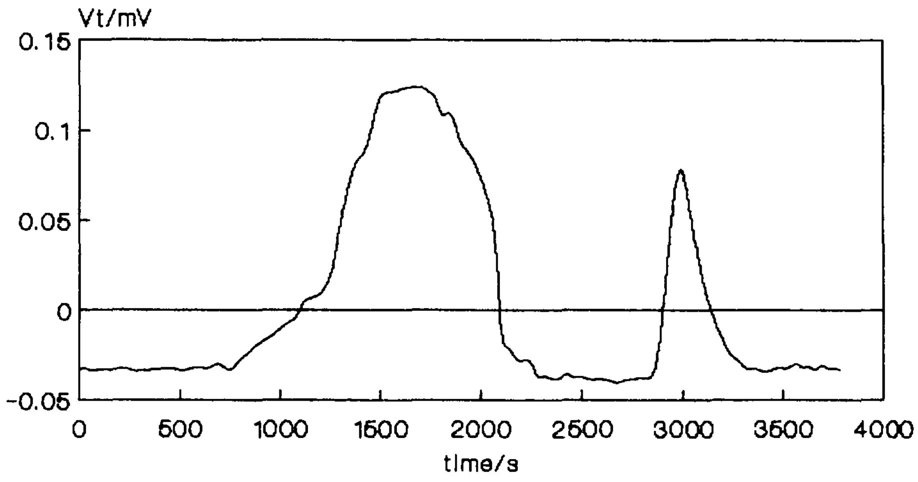
Experiment number	Weight (g)	ε (WV^{-1})	Q_{iexp} (J)	ΔH_{iexp} ($J\,g^{-1}$)	A_t ($m^2\,g^{-1}$)
1	0.0145	26.60	−0.4720	−32.55	283.1
2	0.0097	24.70	−0.3120	−32.17	279.5
3	0.0096	26.60	−0.3140	−32.71	284.5
4	0.0127	26.63	−0.4160	−32.76	285.0
5	0.0104	25.85	−0.3350	−32.21	279.8
6	0.0245	21.92	−0.7970	−32.53	282.4
7	0.0323	26.92	−1.045	−32.35	281.3
8	0.0238	18.95	−0.7710	−32.40	281.5
9	0.0219	22.64	−0.7140	−32.60	283.4
10	0.0375	29.67	−1.213	−32.35	281.4

ε = calibration constant; Q_{iexp} = experimental immersion heat of the sample in CCl_4; ΔH_{iexp} = experimental immersion enthalpy per gram of carbon in CCl_4; A_t = total area.

Table 8
Immersion heat of ex-bois activated carbon in CCl_4 at 25.00 ± 0.02°C

Experiment number	Weight (g)	ε (WV^{-1})	Q_{iexp} (J)	ΔH_{iexp} ($J\,g^{-1}$)	A_t ($m^2\,g^{-1}$)
1	0.01401	22.14	−2.508	−179.1	1558
2	0.01521	23.41	−2.721	−170.0	1557
3	0.01182	21.42	−2.120	−179.7	1562

ε = calibration constant; Q_{iexp} = experimental immersion heat of the sample in CCl_4; ΔH_{iexp} = experimental enthalpy per gram of carbon in CCl_4; A_t = total area.



Mass of sample(g): 0.0263
Δ Hlexp: - 127.4 J/g

Fig. 8. Immersion heat of Illinois carbon #6 in pyridine.

Table 9
Immersion heat of Illinois carbon in pyridine at 25.00 ± 0.02°C

Experiment number	Weight (g)	ε (WV^{-1})	Q_{iexp} (J)	ΔH_{iexp} ($J\ g^{-1}$)
1	0.0370	24.83	-4.694	-126.9
2	0.0211	32.15	-2.690	-127.5
3	0.0263	27.14	-3.351	-127.4

ε = calibration constant; Q_{iexp} = experimental immersion heat in pyridine; ΔH_{iexp} % experimental immersion enthalpy per gram of carbon in pyridine.

Table 9 gives the results of the immersion heat, Q_{iexp}, for this sample. The average value of ΔH_{iexp}, -127.28 ± 0.79 J g^{-1}, is in very good agreement with the one reported in the literature (-127.57 ± 3.35 J g^{-1}) [29]; the relative error is 0.2%.

The amount of acid groups, AG, in mmol g^{-1}, determined by Polanía [3], can be related to the immersion enthalpies determined in this work, ΔH_{iexp}, by the equation:

$$AG = 1.787 + \frac{22.570}{\Delta H_{iexp}} \qquad (8)$$

Eq. (8) was tested for some other activated carbons previously characterized by Polanía [3] by the method of Boehm, and it also showed an excellent agreement.

The number of basic groups, BG, determined by the method of Boehm, in relation to the immersion enthalpies, ΔH_{iexp}, determined by us, fit the equation:

$$BG = -0.00335\,\Delta H_{iexp} - 0.0141 \qquad (9)$$

Eq. (9) was also valid for the immersin heats of some other activated carbons characterized by the same method.

Acknowledgments

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References

[1] H.F. Stoeckli, D. Huguenin and A. Laederach, Carbon, 7 (1994) 1359.

[2] J.A. Spivey and S.K. Agarwal, Royal Society of Chemistry (1994) 480.

[3] A. Polanía, Thèse de Doctorat en Chimie Physique, Université de Haute-Alsace, France, 1986, p. 44.

[4] R.C. Bansal, J.B. Donnet and H.F. Stoeckli, Active Carbon, Marcel Dekker Inc., New York, 1988, p. 147.

[5] C.W. Chronister and R.S. Drago, J. Am. Chem. Soc., 115 (1994) 4793.

[6] C. P. Huang, Carbon Adsorption Handbook, F. Ellerbush, E. Ellerbush, Ann. Arbor Sci., Michigan, 1980.

[7] H.F. Stoeckli and F. Kraehenbuehl, Carbon, 19 (1981) 353.

[8] M.M. Dubinin and V.V. Serpinsky, Carbon, 19 (1981) 402.

[9] L. Giraldo and J.C. Moreno, Tesis de Grado, Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia, Bogotá, 1989.

[10] L. Giraldo, J.C. Moreno and A. Gómez, Rev. Col. Quim., 23 (1994) 1.

[11] L. Giraldo, J.C. Moreno and A. Gómez, Rev. Col. Quim., 23 (1994) 27.

[12] D.A. Barragán, Tesis de Grado, Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia, 1995.

[13] D.K. Steckler, R.N. Goldberg, Y.B. Tewari and T.J. Buckley, J. Res. Natl. Bur. Stand., 91 (1986) 113.

[14] G. Kegeles, J. Phys. Chem., 62 (1941) 3230.

[15] H. Pardo, Tesis de Grado, Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia, Bogotá, 1987.

[16] S.R. Gunn, J. Phys. Chem., 69 (1965) 2902.

[17] L. Nelander, Acta Chem. Scand., 18 (1964) 973.

[18] J.M. Sturtevant, J. Am. Chem. Soc., 77 (1955) 1495.

[19] I. Wadsö, Acta Chem. Scand., 22 (1968) 927.

[20] E.C. Vanderzee and J.A. Swanson, J. Phys. Chem., 67 (1963) 285.

[21] H.F. Stoeckli and F. Kraehenbuehl, Carbon, 22 (1984) 297.

[22] C. Karr, Analytical Methods for Coal and Coal Products, Vol. II, Academic Press, New York, 1978, pp. 220–230.

[23] M.E. Morgan, R.G. Jenkins and P.L. Walker, Fuel, 60 (1981) 189.

[24] J.J. Matson and H.B. Mark, Activated Carbon, Marcel Dekker Inc., New York, 1971, pp. 9–38.

[25] J.W. Hassler, Activated Carbon, Chemical Publishing Company Inc., New York, 1963, pp. 204–215.

[26] H.A. Benesi, J. Phys. Chem., 78 (1956) 5490.

[27] L. Forni, Catalysis Reviews, 8(1) (1973) 65.

[28] H.P. Boehm, in D.D. Eley, H. Pines and P.B. Weisz (ed.), Advances in Catalysis, Academic Press, New York, 1966, pp. 179–274.

[29] K.S. Vorres, User's Handbook for the Argonne Premium Coal Samples, Argonne National Laboratory, Argonne, 1993, p. 46.

[30] L. Giraldo, J.C. Moreno and A. Gómez, sent for publication.

[31] I. Wadsö, in K.N. Marsh and P.A.G. O'Hare (Ed.), Solution Calorimetry. Experimental Thermodynamics, Vol. 4, Blackwell Scientific Publications, Oxford, 1994, chapter 12.

[32] P. Bender and W.J. Biermann, J. Am. Chem. Soc., 74 (1952) 322.

[33] I. Wadsö and G. Öjelund, Acta Chem. Scand., 22 (1968) 2691.

[34] I. Grenthe, H. Ots and O. Ginstrup, Acta Chem. Scand., 24 (1970) 1067.