CONTROLLED-RATE THERMAL ANALYSIS
Characterization of heterogeneity of active carbon surfaces and adsorbed water layers

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Abstract

Controlled-rate thermal analysis (CRTA) and differential scanning calorimetry (DSC) were used to investigate the adsorbed water layers and the surface properties of different commercial activated carbons. A simple method is proposed to obtain information on the properties of the adsorbed water film and the surface heterogeneity of the materials studied. This method utilizes TG mass loss and the first derivative of the DTG mass loss curves with respect to temperature and time, obtained during programmed liquid thermodesorption. The obtained TG mass loss curves, which reflect the energetic heterogeneity, consisted of steps and inflections which were associated with the mechanism of wetting of the solid surfaces. The heights of these steps and inflections depend on the adsorption capacity, the adsorption potential and the nature and number of the active centers of the carbon samples studied. The values of the total porosity and the surface phase capacity obtained by this method are in good agreement with those estimated on the basis of independent methods. The behaviour of water/carbon samples was studied by means of DSC at subambient and elevated temperatures. The experimental results provided novel data on the structural heterogeneity, the thermal stability of the water/carbon interface and its phase and structural transitions.

Keywords: active carbons, CRTA, heterogeneity of solid surfaces, programmed desorption, water layers

Introduction

The assessment of water/solid systems at a molecular level is a key problem in many areas of surface and materials science. The phenomenon of wetting of various solid surfaces, the formation, structure and stability of water films on solid surfaces, adsorbate–adsorbent interactions, chemical modification of solid materials and their stability in a wet environment, and chemical reactions at water/solid interfaces play very important roles in many branches of science and industry [1].

Microporous carbons are used in filter systems for industrial hygiene and air and food purification applications. Almost all solid surfaces, and especially active carbons, possess heterogeneous properties, and theoretical and experimental studies of adsorbate–adsorbent interactions are difficult. Active carbons are characterized by their strong sorption capacity because they have a unique high capacity, a large specific surface area, a high surface reactivity and a broad range of pore sizes. Estimation of these parameters is an important problem in the characterization of carbon sorption properties. This problem has been studied by means of adsorption, chromatography and spectroscopy. The equilibrium adsorption isotherms are usually used to obtain information about the surface and adsorption properties of active carbons and other adsorbents and solids (e.g. specific surface area, adsorption capacity, total number of surface hydroxyl, total volume of pores and pore size distribution) [2–6]. Conventional sorption measurements are time-consuming and require a specially constructed apparatus. The use of commercially available equipment is often limited to simple gases and vapors. Thus, there is great interest in elaborating simple and quick methods for the characterization of porous solids.

Thermal analysis is normally used to determine the changes in physicochemical properties of materials and liquids as a function of temperature [7]. The years 1960–1965 were especially important as concerns the development of modern controlled-rate thermal analysis (CRTA). During that time, J. and F. Paulik had the idea of automating the ultra-slow heating procedure in order to ensure quasi-equilibrium conditions and to increase the resolution of thermal analysis [8]. A similar problem was studied independently by Rouquerol [9] and discussed in connection with the investigation of water thermodesorption from zeolite surfaces [10]. As compared with studies carried out under classical dynamic conditions, the quasi-isothermal methods have certain advantages: among others, a wider range of application in studies, and much higher selectivity. CRTA under quasi-isothermal conditions has been widely applied in studies of the distribution of chemical compounds, and the kinetics and mechanisms of chemical reactions [11, 12].

Studies on the application of CRTA showed that, besides its classical applications, it is a simple, useful and effective method for the characterization of liquid/solid systems. One of the main ideas of such investigations as compared with the traditional methods (e.g. McBain balances, sorption balances, and adsorption gas chromatography to measure parameters accompanying the adsorption process) was to use and register the effects taking place in the processes opposite to adsorption, i.e. in the programmable thermodesorption of liquids from solid surfaces [13, 14]. The parameters obtained by the use of CRTA were correlated with the corresponding ones obtained with McBain balances, porosimetry, chromatography and other adsorption techniques, and good agreement was found [15, 16].

The present paper reports results of the application and evaluation of the possibilities of CRTA to study liquid–solid interactions, and the heterogeneous properties of active carbon surfaces and the water form adsorbed on them.

Experimental

Apparatus

Measurements of programmed water thermodesorption under dynamic and quasi-isothermal conditions from active carbon surfaces were made with a Q-1500 D derivatograph (MOM, Hungary) and a high-resolution model TGA 2950 thermogravimetric analyzer (TA Instruments, New Castle, USA) equipped with an open pan and capable of maintaining quasi-isothermal conditions. Before programmed thermodesorption measurements, the samples were wetted with water and transferred into a suitable platinum labyrinth crucible; measurements were made at 20–200°C. The T, TG, DTG, DTA and Q-TG curves were recorded.

The calorimetric effects corresponding to the changes in the water/solid samples in response to temperature changes were studied with a DSC 2910 differential scanning calorimeter (TA Instruments, New Castle, USA) equipped with a standard DSC cell and with subambient accessories. The heat-flow DSC curves were obtained over the temperature range form −70 to 650°C.

Materials

The studies were carried out on active carbon samples with various heterogeneous surface properties. Charcoal (types M_1, M_2 and M_3, particle sizes 1.5–2 mm; Merck, Germany) and activated carbon (types N_1, N_3, A-5048, A-5066, A-4412 and B-4710, particle sizes 1–1.4 mm; Norit, The Netherlands; and types PA and PC, particle granulated; Barnebey-Cheney, USA) were used. These granular activated carbons are characterized by relatively low contents of mineral impurities. The ash contents of the activated carbons obtained from Merck and Norit are 2.8% and 4.8%, respectively. The silica contents in these carbons are 35 and 65 wt.% of the ash, respectively. Each carbon sample was characterized by the BET specific surface area obtained from the low-temperature nitrogen adsorption isotherms. The total BET specific surface area of the studied samples was 660–1430 m^2/g. More information concerning the methods and sample characterization were described earlier [16–18].

In order to obtain different thicknesses of the water layers adsorbed on the active carbon surface, samples were exposed to adsorption by various methods: (i) fully immersing the samples in pure water, (ii) exposing the samples to water vapor in a vacuum desiccator (where $p/p_o = 1$), and (iii) exposing the samples to water vapor in air.
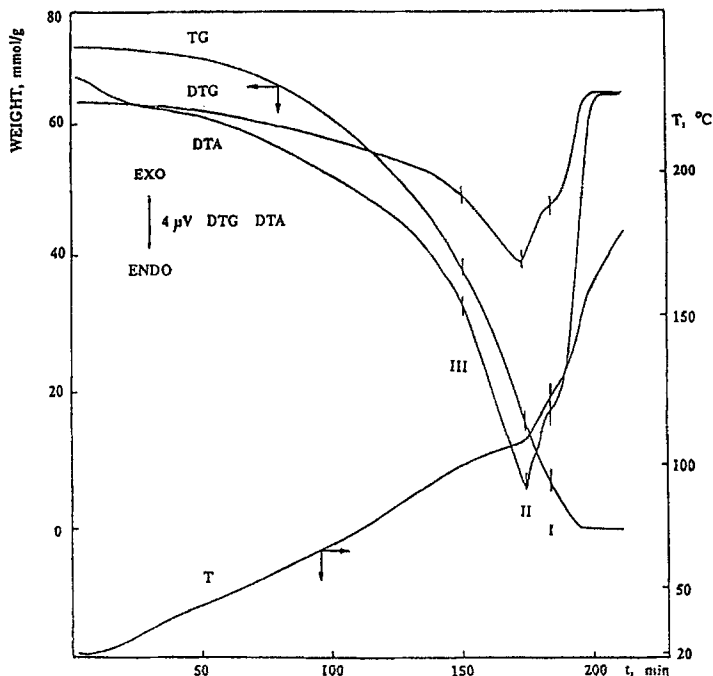
Fig. 1 Classical 'dynamic' TG, DTA, DTG and T curves of water thermodesorption from active carbon PA

Results and discussion

Figures 1 and 2 present the results of water thermodesorption measurements under classical 'dynamic' conditions from the active carbons PA and PC fully immersed in water, using a Q-1500D derivatograph with a furnace heating rate of $1.25°C$ min^{-1}. There are three inflections (I, II and III) in the DTG and DTA curves, which correspond to the differences in energy of the bonding of the water molecules with the carbon surfaces. Characteristic peaks II correspond to 16.0 mmol g^{-1} (Fig. 1) and 19.8 mmol g^{-1} (Fig. 2) of water desorption from the carbon surface.

For a more complete interpretation of the results presented in Figs 1 and 2, more precise quasi-isothermal measurements were carried out with a Q-1500D derivatograph. Figure 3 depicts curves relating to the data obtained during the evaporation of water from fully immersed carbon samples PA and PC under quasi-isothermal conditions. It appears that water thermodesorption is finished at 150°C, i.e. at a temperature about 50°C lower than under classical conditions. Three inflection points are again observed in these curves. Inflection II in Fig. 3 corresponds to 16.8 mmol g^{-1} (sample PA) and 19.1 mmol g^{-1} (sample PC) of water desorption i.e. results similar to those in the classical method and to those obtained with the high-resolution TGA 2950 analyzer: 16.8 mmol g^{-1}
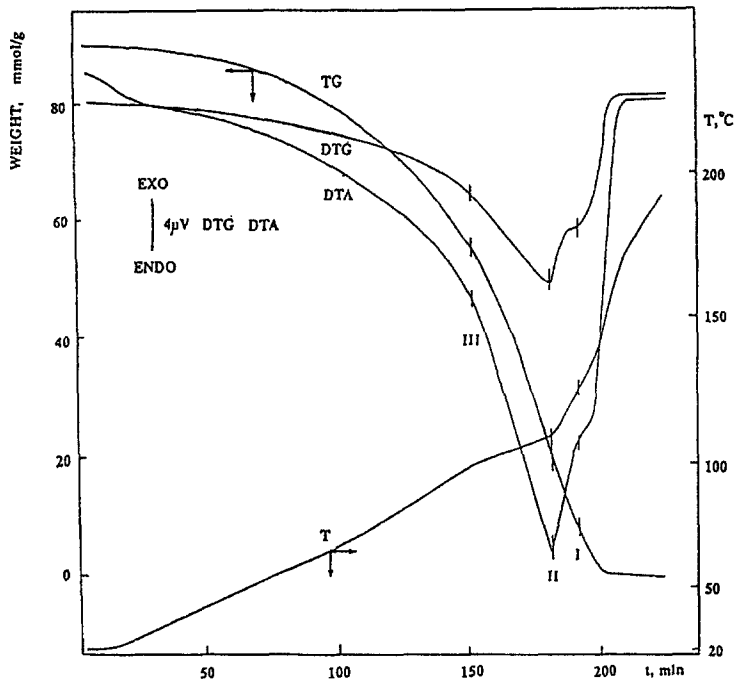
Fig. 2 Classical 'dynamic' TG, DTA, DTG and T curves of water thermodesorption from active carbon PC

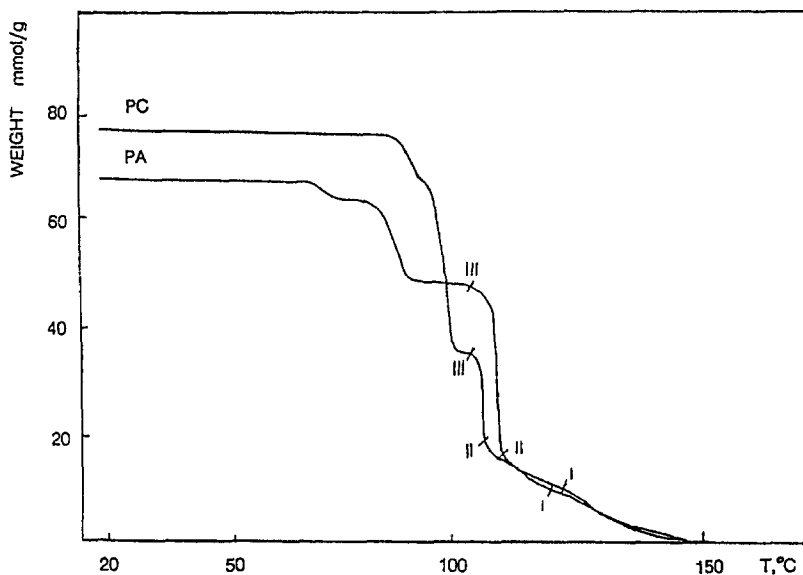**Fig. 3** Water thermodesorption under quasi-isothermal conditions from carbons PA and PC

for sample PA and 20.5 mmol g^{-1} for sample PC [19]. It seems very interesting that, despite the different measurement methods and apparatus, some steps of the water thermodesorption process may be correlated. Moreover, the water vapor adsorption isotherms measured gravimetrically show that the maximum amounts adsorbed at $p/p_o = 1$ are 14.5 mmol g^{-1} (sample PA) and 18.5 mmol g^{-1} (sample PC) [18, 19]. This result indicates that the TG heights connected with steps II are related to the total adsorption capacity of the sample studied. This value is equal to the total amount of water adsorbed in the micropores and condensed in the mesopores. This phenomenon was observed and discussed earlier in other systems [20].

The above data were used to investigate the adsorption properties of carbon samples, e.g. the film thickness and adsorption capacity. Figure 4 shows the TG mass loss curves of water thermodesorption for the different active carbon samples exposed to water vapor in a desiccator. From this Figure, it appears that carbons 2, 3, 4 and 5 are characterized by very similar water adsorption capacities. The highest adsorption water capacity was obtained for carbon 6, which contains 3% of phosphate [17, 21]. The differences in the runs of these curves are caused by the presence of different active centers (e.g. the oxide groups) on the studied samples. It may be noted that the above method permits a very simple and quick determination of the adsorption capacities of tested samples.

The current studies of active carbons and other adsorbents and solids immersed in liquids have demonstrated the usefulness of the first derivative of the
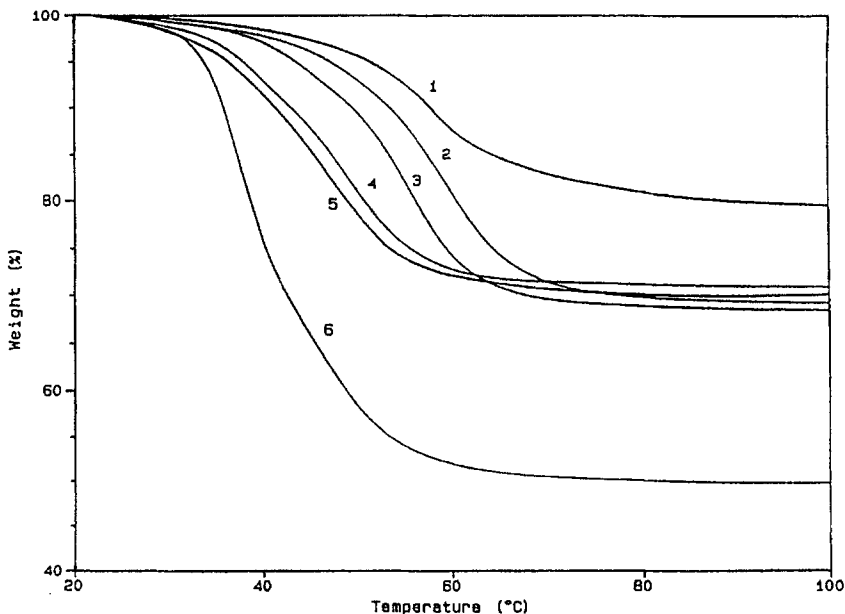

Fig. 4 TG curves of water thermodesorption under high-resolution conditions from carbons PA (1), A-5066 (2), B-4710 (3), A-5048 (4), PC (5) and A-4412 (6)

temperature and time-dependent DTG mass loss curves for the study of liquid/solid systems [15]. Figure 5 presents TG, T and DTG curves of water thermodesorption from active carbon A-5066 under high-resolution conditions [21]. The DTG curve reflects the distribution function of the activation energy of water desorption according to the Polanyi-Wigner equation [22]:

$$-d\Theta/dt = A(\Theta)\exp\{-E_a(\Theta)/RT\}\Theta^n \qquad (1)$$

where θ is the degree of coverage, E_a is the activation energy, A is the pre-exponential factor, n is the reaction order and t is the time of the desorption process.

As follows from the data presented above, it may be stated that the method of programmed liquid thermodesorption from solid surfaces under quasi-isothermal and high-resolution conditions is useful for characterization of the energetic heterogeneity of solids, but not for that of the structural heterogeneity (i.e. pore size distribution functions), as was suggested in the literature
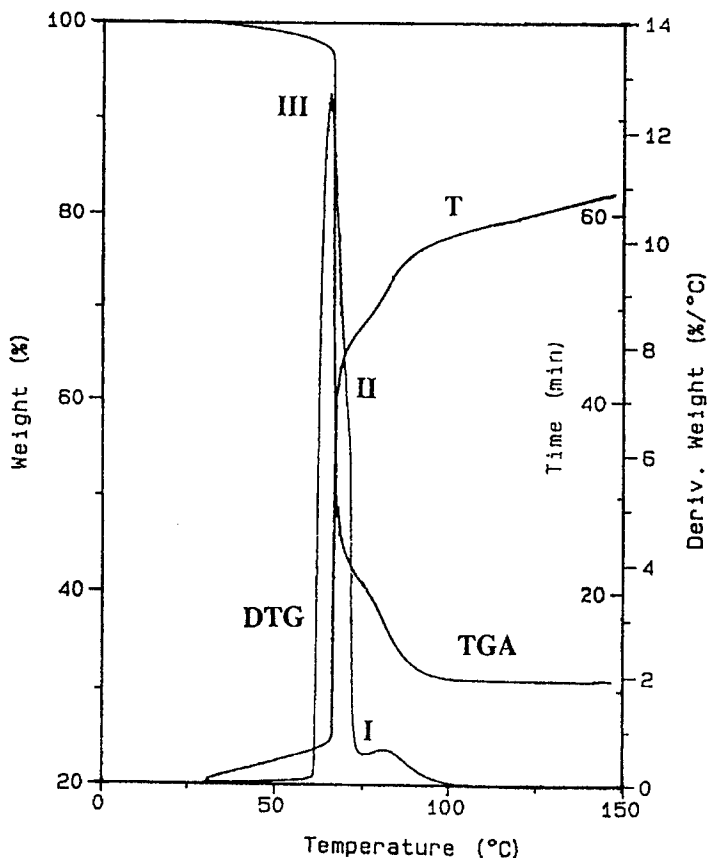

Fig. 5 Changes in TG, DTG and T curves of water thermodesorption from carbon A-5066 under high-resolution conditions in relation to temperature
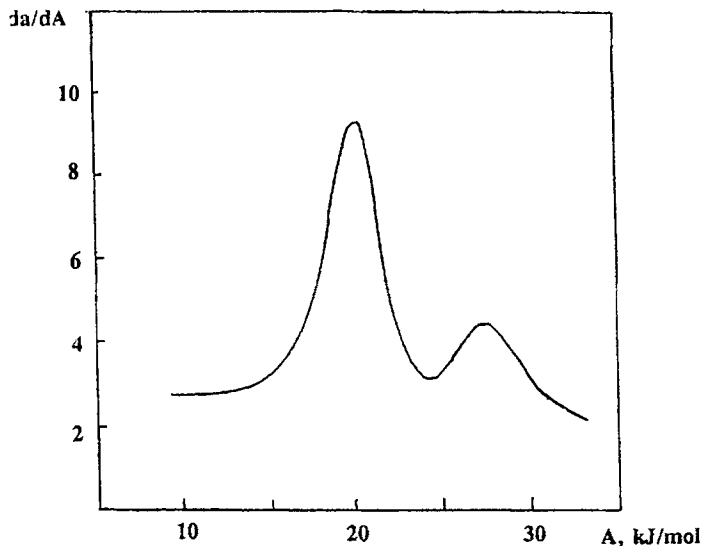
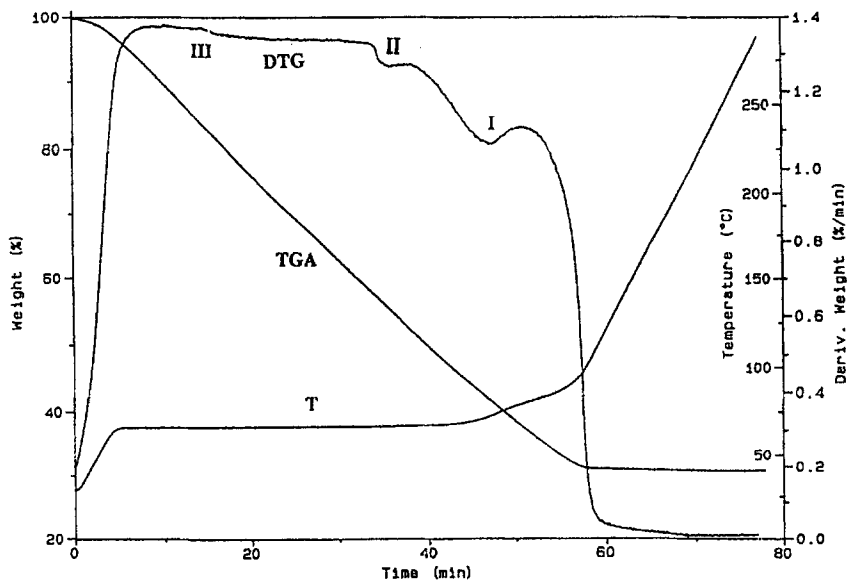Fig. 6 Adsorption potential distribution of water on active carbon A-5066

Fig. 7 Changes in TG, DTG and T curves of water thermodesorption from carbon A-5066 under high-resolution conditions in relation to time

[23, 24]. Additionally, it is worth noticing that Goworek *et al*. did not develop the quasi-isothermal apparatus program, the platinum labyrinth conical crucible and thermodesorption method of liquids from solid surfaces under quasi-iso-

thermal conditions, as was mentioned in the papers [24, 25]. Many parameters influence the above CRTA shape of Q-TG curves. The main ones are the nature of the liquid and surface sample studied, the heating rate and decomposition, the type of apparatus, the crucible, the program for recording the experimental data, some kinetic parameters of the desorption processes, etc. One very difficult and important problem involves the accurate determination of the inflection points in the Q-TG curves, relating to certain parts of the adsorbed liquid. The first derivatives of the DTG mass loss curves with respect to temperature and time are very interesting and useful. Moreover, the Kelvin equation [23, 24, 25] is not sufficient and convenient for determination of pore size distribution functions on the basis of CRTA liquid desorption data because of its large limits connected with the kinetic parameters, and, for example, the properties of liquid films change with the distance to the surface. For this reason, each CRTA liquid desorption process must be examined separately, carefully interpreted and correlated with other independent methods.

On the other hand, on the basis of data relating to programmed liquid thermodesorption from the surfaces and adsorption potential calculations, the energetic heterogeneity of the surface studied can be determined. The adsorption potential A, which is the molar free energy related to the change in liquid vapor pressure, was calculated from the well-known equation [15]:

$$A = RT_n \ln(p_n/p_o) \tag{2}$$

where p_n is the equilibrium pressure of the adsorbate, p_o is the saturated vapor pressure of the adsorbate at temperature T_n, and R is the gas constant.

The dependence $da/dA = f(A)$ (where a is the amount of liquid desorbed) was then calculated and plotted by using a method described earlier [15]. Figure 6 demonstrates the two characteristic peaks relating among others to the surface heterogeneity properties of carbon A-5066. The distribution function calculated from the Q-TG data obtained under quasi-isothermal conditions exhibits two peaks, which reflect the bi-potential character of the adsorption field with respect to this adsorbate.

Figure 7 shows TG, T and derivative time-dependent DTG curves of the processes of water film thermodesorption from active carbon A-5066 under high-resolution conditions [21]. It appears that the characteristic inflection in the DTG curve is larger and more selective than that in Fig. 5. The nature and type of the differential DTG curve with respect to time in Fig. 7 reflect the kinetics of the thermodesorption process and are more useful in accurate determination of the inflection points in the TG curves relating to certain parts of the adsorbed water and calculations of the adsorption capacity of the sample studied. Figure 8 presents the first derivative of the DTG mass loss curve with respect to time for carbon samples exposed to a water vapor in air atmosphere.
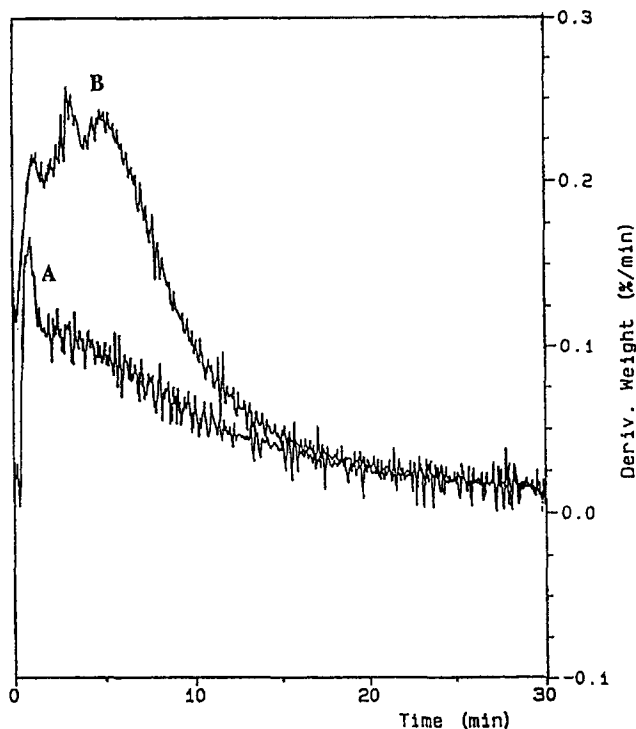
Fig. 8 Time-dependent TG mass loss curves as a function of time for water thermodesorption from different active centers of active carbons A-5048 (curve A) and B-4710 (curve B)

These data provided clear information as to the nature and number (in connection with the TG curve) of the active sites of the carbon studied [17] and other adsorbents, e.g. silica gel [15]. From this Figure, it appears that active carbon B is more heterogeneous (three types of active centers) than sample A (one type of active centers on the surface).

Figure 9 depicts the change in the number of statistical monolayers of water desorbed from carbon samples, corresponding to inflection II in the TG curves, in relation to the micropore volume V_m of the sample surfaces. V_m was evaluated by application of the method described by Dubinin [27] for the analysis of water vapor adsorption data determined by a static method, using the following equations [16]:

$$V_m = S_w x_w \qquad (3)$$

$$S_w = A_w a^{0.6} \qquad (4)$$

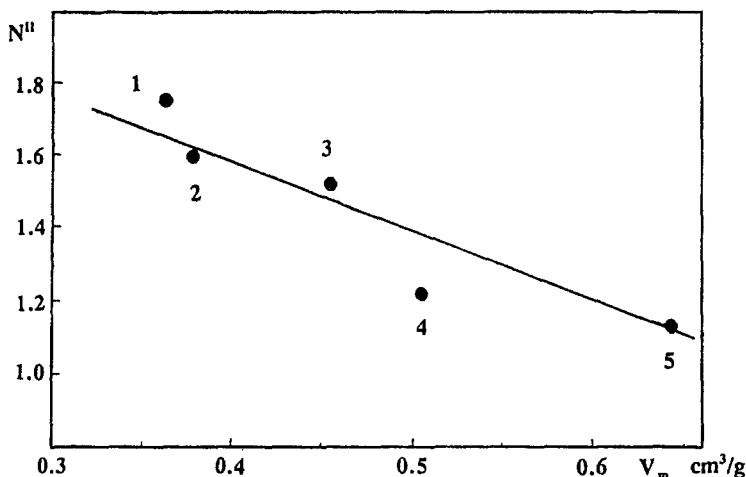$$x_w = na/a^{0.6} \qquad (5)$$

Fig. 9 Number of statistical monolayers of desorbed water corresponding to inflection II in Q-TG curves as a function of water micropore volume V_m on active carbons M_1 (1), M_2 (2), M_3 (3), N_1 (4) and N_3 (5)

where A_w is the surface area occupied by 1 mmol of water (63.27 m^2 mmol^{-1}), $a^{0.6}$ is the adsorption value at $p/p_o = 0.6$, n is the monolayer thickness and a is the boundary adsorption at $p/p_o = 1$.

From the above result, it follows that the Norit carbons (samples 4 and 5) possess lower micropore volume values than those of the Merck carbons (samples 1, 2 and 3). The overlap of the adsorption potential (originating from the opposite walls of the active carbon micropores) increases the vicinal water on the surface and the degree of water structuralization. This leads to an increase in the packing of molecules in the bonded water film, due to the formation of ice-like structures, and to an increase in N^{II}, with a decrease in the micropore volume V_m [16].

A differential scanning calorimeter equipped with a standard cell and with cooling accessories was used to carry out supplementary calorimetric investigations [28, 29]. Prior to the DSC experiments, the carbon samples were exposed to water vapor in a desiccator. Subsequently, the DSC measurements were carried out as follows; the immersed sample of carbon was first cooled to about −70°C under controlled conditions, and it was next gradually heated up to 650°C. Figure 10 reveals the complete DSC curve as a complex shape with peaks relating to (1) freezing and (2) melting of surface adsorbed water at the subambient temperatures, and thermodesorption of physically adsorbed water molecules (3) form the active carbon pores, and (4) from the surface at temperatures between 120 and 160°C. The DSC data at the elevated temperatures (160–650°C) suggest oxidation of the carbon sample (peak 5). The shapes of DSC peaks 1 depend on the type of the carbon surface, and can be used to obtain information about the structural heterogeneity of samples studied.
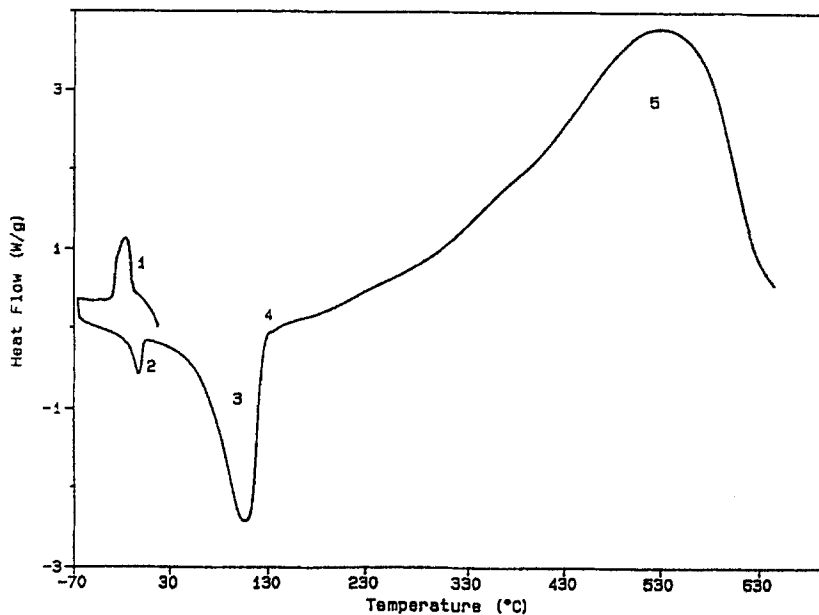
Fig. 10 DSC curve for active carbon A-4412 saturated with water vapor in a desiccator. Peaks 1–5 are described in the text
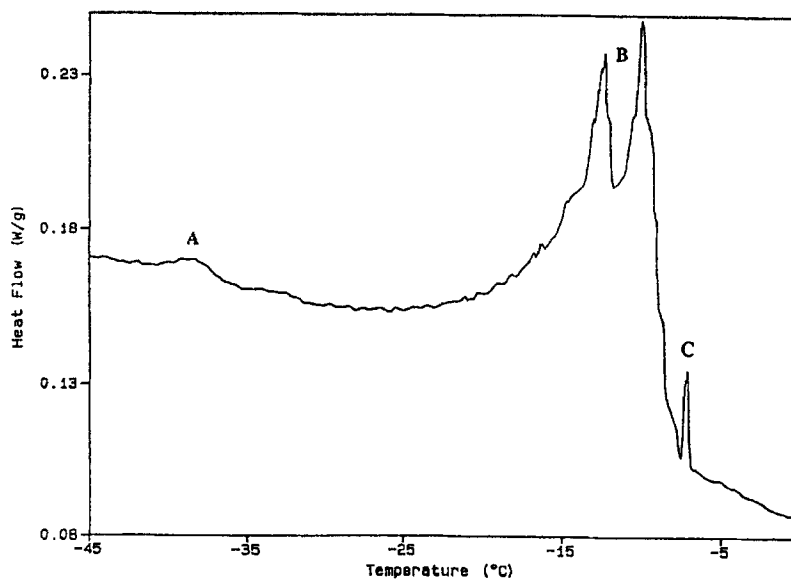
Fig. 11 Part of the DSC curve relating to the freezing of water in the micropores (A), mesopores (B) and macropores (C) of carbon A-4412
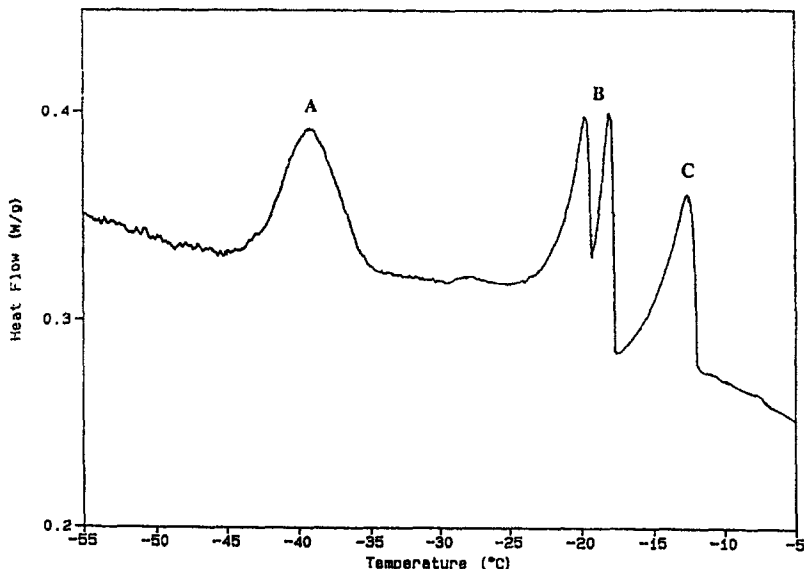
Fig. 12 Part 1 of the DSC curve relating to the freezing of water in the micropores (A), mesopores (B) and macropores (C) of carbon A-5048

Figures 11 and 12 present enlarged peaks 1 of the DSC curves. The freezing temperature of water adsorbed on a carbon surface is proportional to the pore radius [30]. Thus, the peaks at the lowest temperatures (e.g. at $-40°C$) in the above Figures are associated with the freezing of water in the fine pores, and their shapes reflect the structural heterogeneity of a given porous carbon. DSC peaks 1 can be used to evaluate the pore size distribution functions by utilizing the relationship between the equilibrium temperature T and the radius R via the Gibbs-Duhem and Laplace equation [31, 32]:

$$T-T_o = 2\gamma T_o/(\rho_w \chi R) \tag{6}$$

where T_o is the normal melting temperature of ice, ρ_w is the density of water at T_o, χ is the normal heat of fusion of ice per unit mass, and γ is the interfacial tension.

Figures 11 and 12 reveal that there are different numbers and magnitudes of the micro- (peaks A), meso- (peaks B) and macropores (peaks C) in the investigated samples: mainly mesopores and small numbers of micro- and macropores in the A-4412 surface (Fig. 11), and all types of pores in the A-5048 surface, which is more heterogeneous (Fig. 12).

Moreover, from the DSC data it is possible to calculate the calorimetric parameters of the liquid phase and structural transitions and thermodesorption from the surfaces. Figure 13 presents an enlarged DSC curve relating to the evaporation of water from a carbon surface (peak 4). The evaporation heat
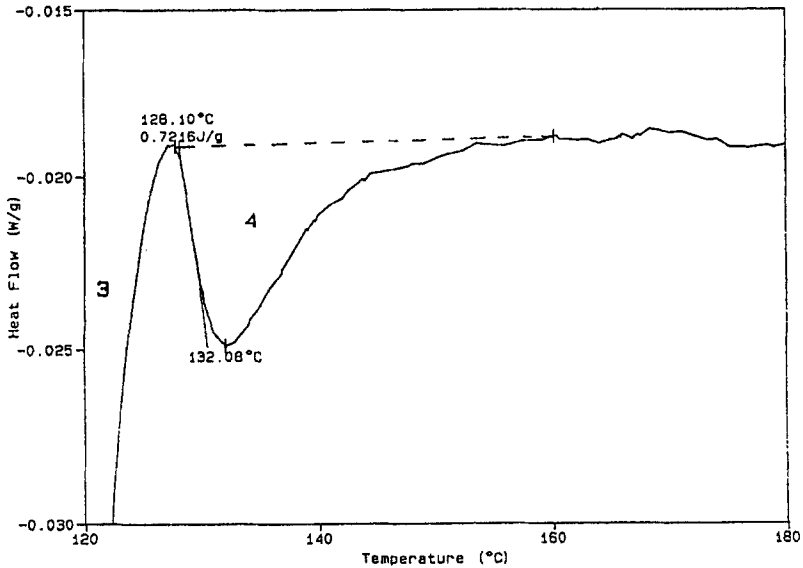
Fig. 13 Part of the DSC curve relating to water thermodesorption from the carbon A-4412 surface (peak 4)
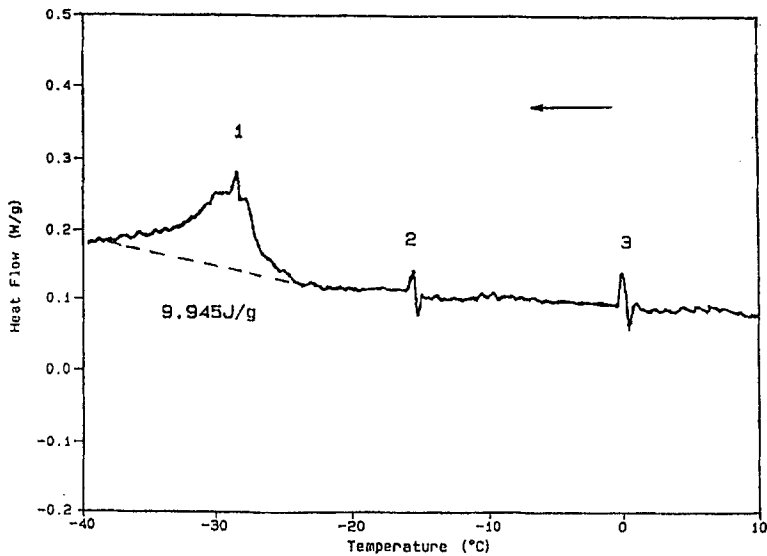
Fig. 14 Part of the DSC curve relating to water freezing in active carbon B-4710 pores (peak 1) and structural transitions of adsorbed water films (peaks 2 and 3)

$(0.7216 \text{ J g}^{-1})$ was calculated from the peak area. In the same way, the phase and structural transition heats of water films adsorbed on material surfaces can

be calculated. Figure 14 presents, for instance, the DSC curve of freezing water layers adsorbed on carbon (peak 1), with a calculated transition heat of 9.945 J/g. Inflections 2 and 3 are observed in the DSC curve relating to the structural transitions of adsorbed water layers during the cooling process. These are due to cyclic changes in some properties of the adsorbed water layers, and particularly of a tetrahedral ice-like structure found in the vicinal water [33]. Depending on the process course (cooling or heating of the sample), an ice-like water structure undergoes reproduction (during the cooling process) or decay (during heating) in a studied system including water. The above thermoanalytical measurements provided novel data on the structure and phase transitions of water films adsorbed on solid surfaces [33].

Such methods of modern CRTA are extremely useful for study of the thermal stability of water films, the phase and structural transitions of water/solid interfaces as and the surface capacity, surface, energetic and structural heterogeneity of materials. Additionally, these measurements yield quantitative information on the types of interfacial adsorbed water present on the surface and demonstrate the dependence between the degree of surface hydration and the sorption properties.

Conclusions

The results obtained demonstrate the great applicability of CRTA for the determination of physicochemical properties of solid surfaces and adsorbed liquid films. From the analysis of CRTA curves, the properties of water present on the surface of macro-, meso- and micropores of active carbons can be determined. The time-dependent DTG curves are very useful for exact detection of the inflection points in TG curves and for calculation of the water amounts relating to the various active centers present on the carbon surfaces, the different types of interfacial water and the adsorption capacities of the samples studied. The TG mass loss curves reflect the energetic heterogeneity of the solid surface, and the derivative of mass loss with respect to time and temperature DTG curves are connected with a function of the activation energy of desorption.

The heat effects corresponding to the phase and structural changes in the liquid adsorbed on the surface with temperature can be studied by means of DSC. The DSC peaks recorded at subambient temperatures provide information about the pore sizes and their distribution functions. At elevated temperatures, DSC curves yield data about the mechanism of desorption of liquid films from pores and surfaces, which supplements the results obtained from TG measurements.

By means of the above methods, the derivatograph may be effectively applied in adsorption studies other than classical ones, and for the determination of the energetic heterogeneity of adsorbents and other materials. The presented methods are very quick, simple, useful and convenient in studies of heterogeneity with respect to different solids. It was established that the above methods can be applied successfully for a more convenient characterization of liquid/solid systems in comparison with traditional adsorption methods.

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