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Water sorption measured by sorption calorimetry [☆]

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Abstract

A calorimetric method is described for the determination of adsorption and desorption of adsorptives that are liquid at room temperature, focussing on the sorption of water. Together with the isotherms, the sorption thermodynamics is determined in one experiment by determining the heat flow needed for generating the vapour and the heat flow generated by the adsorption process. An error analysis of the technique shows that reproducibility is good, and that absolute errors in relative vapour pressure and amount adsorbed are typically small. Only at very high loadings where the driving force for evaporation becomes small do larger errors occur in these parameters. The accuracy of the determination of the sorption thermodynamics is less good for the system water/activated carbon. This is partly due to the small net adsorption enthalpy for water in this system. Some proposals for improvement are given. An example of the adsorption of water vapour by activated carbons loaded with increasing amounts of residual surfactant shows the sensitivity of the technique.

Keywords: Activated carbon; Adsorption; Calorimetry; Carbon; Error analysis; Water

1. Introduction

Fairly recently, calorimetric methods have been developed for the determination of isothermal equilibrium sorption of gases and vapours by solids [1,2]. The single main advantage of calorimetry for these sorption measurements is that the sorption thermodynamics is fully determined in one experiment. In all other methods, a series of experiments at different temperatures is needed to obtain the same

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parameters, always on the assumption that these parameters are independent of temperature in the range studied.

Sorption calorimetry is suited in particular for adsorptives which are liquid at normal pressure and the temperature of interest. Water at room temperature is an example of technological importance. Adsorbed water interferes with the performance of gas masks and other filters in the open air and with the processing of, for example, food stuffs, polymers and pharmaceuticals. It causes deterioration of building materials, etc. We have focussed our work on this single adsorptive, although many others can also be studied.

Here, we describe new developments in the desorption part of the experiment, and focus on the methodical aspects of sorption calorimetry as we perform it (theory, experimental, error analysis). We include an example of the technique.

2. Theory

2.1. The specific molar amount adsorbed

The principle of adsorption calorimetry is fairly simple. In an evacuated system (Fig. 1), an amount of adsorptive is evaporated in a controlled manner by slightly

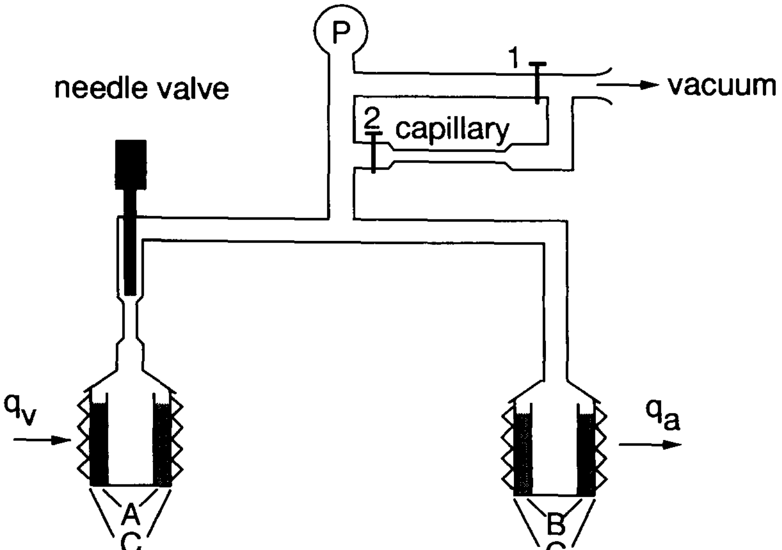

Fig. 1. Sketch of the principle of adsorption calorimetry. The needle valve is opened slightly to allow a small flow of adsorptive vapour from the evaporation to the sample cell: A, filtration paper saturated with water; B, adsorbent, positioned on the wall of the silver cell; C, thermopile; P, pressure transducer; q, direction of heat flow; 1, 2, valves, closed in adsorption.

opening the needle valve. In this way, adsorption is performed continuously. The rate of dosing is kept very small, so that the adsorption remains close to equilibrium, as will be proven later on. This is a precondition for the validity of the thermodynamic calculations. Also, continuous dosing is convenient from the experimental point of view.

The heat needed for evaporation is detected by a thermopile. The voltage from this thermopile and the pressure in the system (of known volume and temperature) are recorded continuously. The *specific* molar amount adsorbed $n(t)$ is calculated as the difference between the number of moles evaporated (N_{vap}) and the number of moles in the gas phase (N_{g}), divided by m, the dry sample weight. N_{g} is calculated from the experimental pressure $p(t)$ using the ideal gas law

$$n(t) = [N_{\mathrm{vap}}(t) - N_{\mathrm{g}}(t)]/m = [N_{\mathrm{vap}}(t) - p(t)V/(RT)]/m \tag{1}$$

where V is the internal or dead volume of the adsorption system (in m^3), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), and T the temperature of the experiment (in K).

N_{vap} is calculated by numerical integration of the voltage from the evaporation thermopile ($\mathrm{EMF}_{\mathrm{vap}}$) over time t

$$N_{\mathrm{vap}}(t) = \int_0^t \mathrm{EMF}_{\mathrm{vap}} g_{\mathrm{vap}}/q_{\mathrm{vap}}\, \mathrm{d}t \tag{2}$$

where g_{vap} is the sensitivity of the evaporation cell/thermopile system (approx. 20 W V^{-1}), and q_{vap} is the actual heat needed to evaporate a mole of water in the system.

The evaporation part of the cell performs some work in the expansion to the sample vessel. Consequently, $\Delta_{\mathrm{vap}} U < q_{\mathrm{vap}} < \Delta_{\mathrm{vap}} H$ where the first and last terms denote the change in internal energy and enthalpy in kJ mol^{-1} during evaporation of the adsorptive at temperature T, respectively. We have assumed $q_{\mathrm{vap}} = \Delta_{\mathrm{vap}} U = \Delta_{\mathrm{vap}} H - RT$. The small error which is introduced in this assumption is reduced even further by using the same assumption in the calibration of g_{vap}. This calibration is performed by evaporating known amounts of water into vacuum.

2.2. The net differential adsorption energy and entropy

The EMF of a thermopile is a measure of the heat flux through the cell wall. Because no work is performed through the boundaries of the system, the heat flux reflects the differential change in internal energy ΔU for the process occurring in the cell multiplied by $\tilde{N}$, the rate of the process taking place: evaporation (vap), adsorption (ads) or desorption (des), where $\mathrm{EMF}_{\mathrm{dif}}$ denotes the differential EMF

$$\mathrm{EMF}_{\mathrm{dif}} = \mathrm{EMF}_{\mathrm{vap}} + \mathrm{EMF}_{\mathrm{ads}} = \Delta_{\mathrm{vap}} U \tilde{N}_{\mathrm{vap}}/g_{\mathrm{vap}} + \Delta_{\mathrm{ads}} U \tilde{N}_{\mathrm{ads}}/g_{\mathrm{ads}} \tag{3}$$

Now, the *net differential adsorption energy* $\Delta_{\mathrm{ads}} u$, i.e. the change of internal energy relative to the liquid state, equals ($\Delta_{\mathrm{vap}} U + \Delta_{\mathrm{ads}} U$), so that

$$\Delta_{\mathrm{ads}} u = \mathrm{EMF}_{\mathrm{dif}} g_{\mathrm{ads}}/\tilde{N}_{\mathrm{ads}} - \{\Delta_{\mathrm{vap}} H - RT\}\{(\tilde{N}_{\mathrm{vap}}/\tilde{N}_{\mathrm{ads}})(g_{\mathrm{ads}}/g_{\mathrm{vap}}) - 1\} \tag{4}$$

$\tilde{N}_{\mathrm{vap}}$ is evaluated using the differential form of Eq. (2). Furthermore

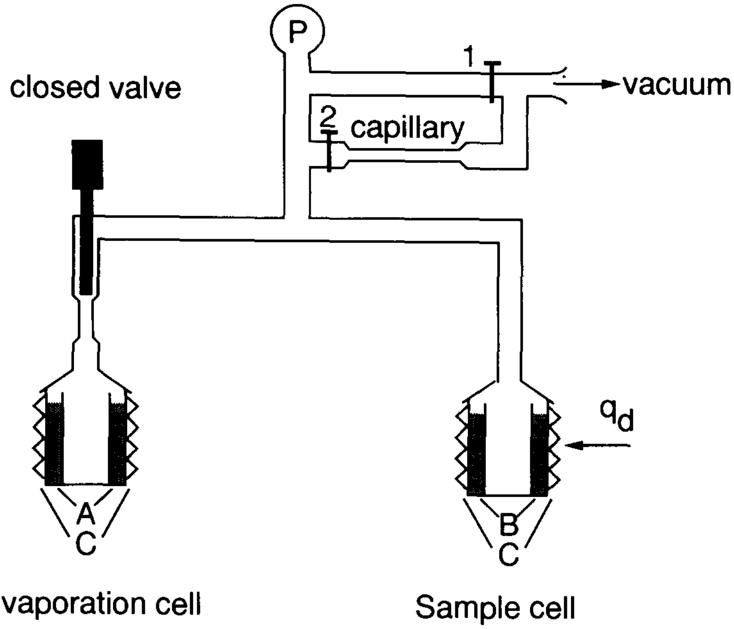

Fig. 2. Sketch of the principle of desorption calorimetry. The needle valve is closed but valve 2 is opened, allowing a small flow of adsorptive vapour from the sample cell to vacuum: A, filtration paper saturated with water; B, adsorbent, loaded with adsorbate, i.e. adsorbed adsorptive; C, thermopile; P, pressure transducer; q, direction of heat flow; valve 1 remains closed.

$$\tilde{N}_{\text{ads}} = \tilde{N}_{\text{vap}} - (V/RT)\, \mathrm{d}p(t)/\mathrm{d}t \tag{5}$$

Thus, the net differential adsorption energy is evaluated as a function of the amount adsorbed, as both are known as a function of experimentation time. For the sake of clarity, we note that $\Delta_{\text{ads}}u = q_d - q_L = q_{st} - q_L - RT$, where q_d is the differential heat of adsorption, q_L the heat of liquefaction (condensation) and q_{st} the isosteric heat of adsorption [3].

$\Delta_{\text{ads}}u$ can be used to calculate the *net differential adsorption entropy* $\Delta_{\text{ads}}s$, using

$$\Delta_{\text{ads}}g = \Delta_{\text{ads}}h - T\Delta_{\text{ads}}s = \Delta_{\text{ads}}u - T\Delta_{\text{ads}}s = RT \ln(p/p_s) \tag{6}$$

where $\Delta_{\text{ads}}g$, $\Delta_{\text{ads}}h$ are the net differential free energy and the enthalpy of adsorption (kJ mol^{-1}), and p_s is the saturated vapour pressure (Pa) of the adsorptive at temperature T.

In the above, $\Delta u \approx \Delta h$ is taken for the 'phase transition' from liquid to adsorbate. This is allowed because pV in $U = H - pV$ is small and $\Delta(pV)$ is almost zero [4]. No attention is given to the adsorption entropy in this paper, because this parameter contains little information additional to the adsorption energy due to this equality.

2.3. The specific amount adsorbed during the desorption

We have developed a technique for performing desorption in the sorption calorimeter. Adsorptive is removed by evacuating through a capillary (Fig. 2). The system pressure and the EMF of the adsorption cell are recorded continuously. The total amount of adsorbate desorbed $N_{\text{des}}(t)$ at a given time t is calculated from the integral

$$N_{\text{des}}(t) = \int_0^t \{\tilde{N}_{\text{cap}} - (V/RT)(-\mathrm{d}p/\mathrm{d}t)\}\,\mathrm{d}t \tag{7}$$

where $\tilde{N}_{\text{cap}}$ is the molar flow through the capillary as a function of the pressure in the system. N_{cap} is known from calibration. The specific amount still adsorbed is obtained from the maximum specific amount adsorbed at the end of the adsorption process, $n_{\max}$

$$n(t) = n_{\max} - N_{\text{des}}(t)/m \tag{8}$$

2.4. The net differential energy and entropy of desorption

Analogous to the derivation of $\Delta_{\text{ads}}u$, we have obtained for $\Delta_{\text{des}}u$, the net differential desorption energy (reference state, liquid)

$$\Delta_{\text{des}}u = (g_{\text{ads}}/\tilde{N}_{\text{des}})\text{EMF}_{\text{dif}} - \Delta E_{\text{vap}} \tag{9}$$

The net differential entropy of desorption is calculated from the analogue of Eq. (6).

3. Experimental

3.1. Apparatus

The main part of the apparatus has been described previously [1]. A sketch is given in Fig. 1, showing the cylindrical evaporation and sample cells, made of silver. An inert metal support is used to position the sample against the walls of the cell. In the same way, filter paper saturated with 'milli-Q' water is placed against the wall of the evaporation cell to ensure good thermal contact. The cells fit closely in cylindrical thermopiles, described extensively in Ref. [5]. The heat flows through the thermopiles cause voltage differences (EMFs), which are determined by accurate voltmeters (Keithley 174 and 177, accuracy of 4 and 10 μV, respectively) and recorded automatically on a PC.

The pressure is determined with a Barocel pressure sensor type 570D-100T-3A1-H5X (0.01% accuracy) and read with a Data metrics electronic manometer type 1018 (1.3 Pa accuracy). Pressure data are also recorded automatically. Thus, the evolution of the sorption isotherms can be followed on line. The temperature of the well-isolated adsorption system is controlled by a TEV 70 thermostat to 0.1°C. The

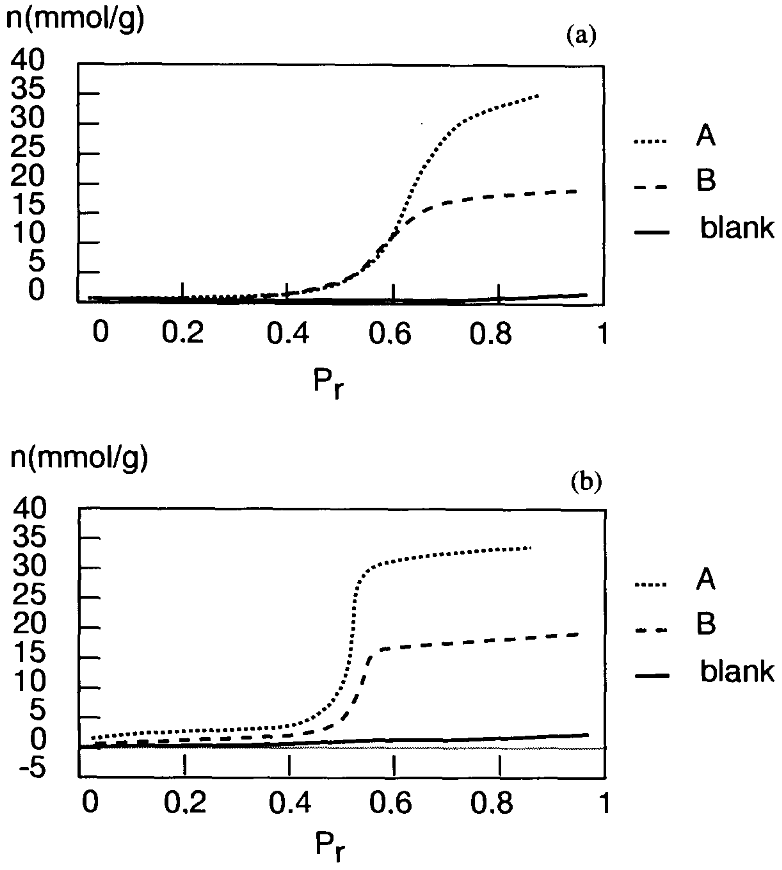

Fig. 3. Blank sorption of water vapour by the internals of the sample cell in adsorption (a) and desorption (b) compared with that of two activated carbons. Carbon A is a cylindrical activated carbon used for evaporative loss control; carbon B is a spherical general-use activated carbon.

thermometer of this bath is thermostatted using an FJ junior thermostat. The adsorption system is made of glass and has a dead volume of about 65 cm^3.

3.2. Procedure

A sample of approx. 1 g is dried carefully at 120°C under vacuum (approx. 0.13 Pa) overnight in the sample unit, which can be closed and disconnected from the rest of the system. After the drying, the sample unit is weighed accurately, connected to the system, opened and evacuated overnight to approx. 10^{-3} Pa. During this time, thermal equilibrium is also established. The valve to the vacuum pump is closed and the pressure increase into the dead volume is determined for about ten minutes. When this pressure increase is smaller than 25 Pa day^{-1}, the

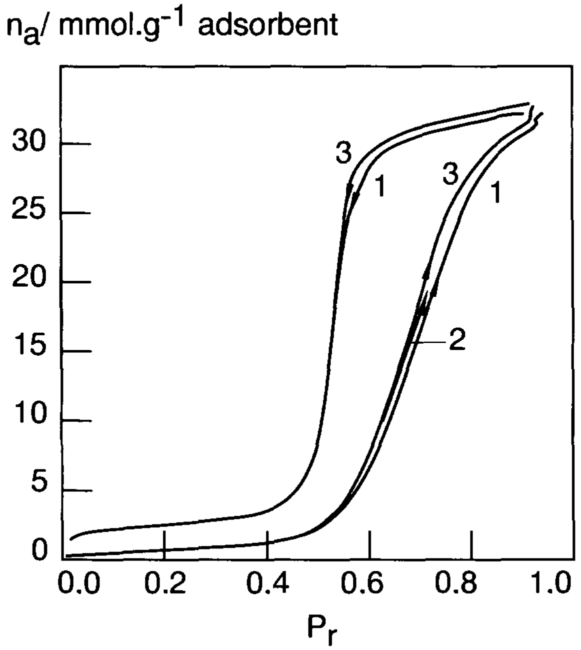

Fig. 4. Reproducibility test of the amount adsorbed and desorbed on samples of an activated carbon from Norit, The Netherlands. Experiment 2 was stopped at a pressure of 2400 Pa to check for equilibrium.

experiment is initiated. The sample unit is closed and the needle valve is opened such that a flow rate of approx. 0.01 mmol min^{-1} is established as determined from the evaporation heat signal. During this period, the system is evacuated continuously. When the flow is established, the valve to the vacuum pump is closed and the sample unit is opened, starting the actual experiment.

When a relative pressure of about 0.9 is reached, which may take more than a week, the needle valve and the sample unit are closed. Final equilibrium is attained within 30 min. The sample unit is again weighed, providing a check for the total amount adsorbed at the final pressure.

After reconnecting the sample unit to the system and renewed thermal equilibration, desorption is started by opening the sample unit and the valve to the capillary. After desorption, the sample unit is weighed again.

3.3. Experimental error reduction

A number of measures are taken to help in reducing experimental errors. First, reference cells are used: the actual apparatus contains two pairs of an evaporation and a sample cell. These are electrically coupled such that spurious heat flows through the thermopiles due to uncontrolled temperature fluctuations are largely compensated. This reduces zero-line fluctuations by a factor 50 [1].

Also, the thermal inertia of the heat flow system (sample, cell and thermopile) is corrected for using a simple linear approach. A more complex approach using Fourier analysis could also be used [1].

Furthermore, blank experiments have been performed (Fig. 3). Water is adsorbed by the walls and the interior of the sample cell. Typically, the amount adsorbed is expected to be small compared to the amount adsorbed on the sample because the available surface area is much smaller (less than 1.2×10^{-2} m^2 for the internal walls, compared to at least 1 m^2 and up to 1500 m^2 for the sample). The blank experiment shows that the amount adsorbed is indeed negligible for the activated carbons used. As the determination of the blank is not very reproducible, experiments on activated carbons and other materials which adsorb fair or large amounts of water are not corrected for the blank adsorption. Blank sorption is significant in the desorption, especially at low relative pressure.

4. Error analysis

4.1. Repeatability

Three experiments were performed on samples of R1 activated carbon (Norit, The Netherlands) (Fig. 4). R1 is a peat-based cylindrical extrudate. Up to a relative vapour pressure $p_r = p/p_s$ of 0.5, the experiments agree perfectly. The differences at higher relative pressures (and consequently larger amounts adsorbed) may be due to sampling errors. For a highly comparable activated carbon, the standard deviation in the pore volume due to differences in the sample has been estimated to be as large as 3% for samples of 1 g [6]. At high relative pressure, the isotherm flattens. The amount adsorbed at high pressure reflects the total pore volume of the sample. The difference between the two experiments is less than 2%. This difference can therefore be explained fully as a sampling error. Of course, the differences noted may also be partially due to experimental errors. The largest difference in amount adsorbed is about 10% at one pressure, but a small shift in the relative pressure in one of the experiments would suffice to explain this error.

4.2. Weight checks

An easy and reliable check for the amount adsorbed is obtained by comparing the final amount adsorbed (or desorbed) to the overall weight changes. For the three experiments mentioned above, differences of −0.3, −0.5 and +1.5% were found for the adsorption step. In general, we find that the adsorption results of weighing and calorimetry usually agree within 1%, and very seldom are larger than 3%.

Because the amount adsorbed typically is much larger than the amount of adsorptive in the gas phase, the predominant contribution to the error in $n(t)$ is due to the error in $N_{vap}(t)$, which is determined by integrating the EMF signal in time. It follows that the relative error in $n(t)$ becomes large when the recorded EMF signals are small, i.e. at the final stage of the adsorption experiments. Indeed, of the three examples given above, the experiments which were continued to very high relative pressure showed the largest deviation in the weight check (1.5%). The irregularities at $p_r > 0.9$ are probably due to noise in the EMF signal. This error would be decreased by opening wider the valve controlling the evaporation rate. In the current set-up, this has several disadvantages, however.

For gypsum ($CaSO_4 \cdot 2H_2O$), we have found that the amount weighed was consistently much smaller than the amount found in calorimetry. During the overnight evacuation in the calorimeter at approx. 10^{-4} Pa, crystal water had been removed from the sample. Because weighing was performed before this step, the weighing results only showed the amount adsorbed, and not the amount of crystal water absorbed by the evacuated sample. Of course, both are recorded in the calorimetric determination. Far better agreement was observed when the sample unit was closed during equilibration, so that no evacuation occurred and no crystal water was removed.

The difference in amount desorbed as determined by weighing and by calorimetry appears to be larger, typically about 3%. More research is needed to find the cause for these differences and to improve the measurements. Possibly the fact that the evacuation pressure is not controlled plays a role. Also, the calibration of the capillary transport rate was not extrapolated to very low water vapour pressures.

4.3. *The possible error in the relative water vapour pressure*

There is no independent check for determination of the relative vapour pressure. Therefore, a possible error must be found from an analysis of the experiment. Four possible sources for errors in the relative water vapour pressure are discerned: (i) errors in the determination of the saturated vapour pressure; (ii) errors in the measurement of the pressure; (iii) errors in the pressure increase correction; and (iv) non-attainment of adsorption equilibrium.

Source (i). The saturated water vapour pressure is calculated from literature data using the experimentally determined temperature, which is determined with an accuracy of ±0.1°C. Using the well-known Clausius–Clapeyron equation, $\Delta p_s/p_s$, the possible relative error in p_s, is estimated to be ± 0.006, assuming the literature values to be without inaccuracy.

Source (ii). The pressure measurement is calibrated to the saturated vapour pressure. A first estimate of the possible relative error in the experimental value of p is therefore ± 0.006, assuming the relative error to be constant over the full pressure range.

Source (iii). Although leakage is minimized by specially designed valves [1], a pressure increase is always found at the start of the experiment, approx. 25 Pa $day^{-1} \approx 0.7$ µmol day^{-1}. The pressure increase is smaller at the end of the experiment, i.e. after about 10 days. The pressure readings have been corrected for the ‘leakage rate’ using the starting value. The total leakage correction for an experiment of 10 days amounts to 4.5% of the total pressure. There are some reasons to expect that this is an overestimate [7]. As a first approximation, we assume that the pressure is underestimated by 2.5% by using too large a correction term, i.e. roughly half of the total correction ($-0.025 \le \Delta p/p \le 0$).

Source (iv). Because water is dosed continuously, the adsorption process is never quite in equilibrium. For activated carbons, the relative pressure at which the typical upswing in amount adsorbed occurs is of great importance. Therefore, equilibrium was checked in this upswing by stopping the dosing and recording the pressure changes in one of the above-mentioned triplicate experiments. The pressure dropped from 2448 to 2413 Pa in 2 h and to 2407 Pa after 6 h, remaining equal thereafter. Typically, the experimentally determined isotherm is shifted less than 1.8% to higher values than the true isotherm ($0 \le \Delta p/p \le 0.018$).

In conclusion, the possible error in the relative water vapour pressure obtained by adding these four contributions is found to be $-0.037 \le \Delta p_r/p_r \le 0.030$. Because the errors in (iii) and (iv) partially counterbalance, an optimistic estimate would be $-0.02 \le \Delta p_r/p_r \le 0.01$. The largest improvement would be gained by a better description of the leakage.

4.4. The possible error in the adsorption enthalpy

The calculation of $\Delta_{\mathrm{ads}}u$ involves two terms (Eq. (4)): $\mathrm{EMF}_{\mathrm{dif}}g_{\mathrm{ads}}/\tilde{N}_{\mathrm{ads}}$ describes the main effect, while $\{\Delta_{\mathrm{vap}}H - RT\}\{(\tilde{N}_{\mathrm{vap}}/\tilde{N}_{\mathrm{ads}})(g_{\mathrm{ads}}/g_{\mathrm{vap}}) - 1\}$ describes a correction due to the small differences in evaporation and adsorption rates and in cell sensitivities. Because $(\tilde{N}_{\mathrm{vap}}/\tilde{N}_{\mathrm{ads}})(g_{\mathrm{ads}}/g_{\mathrm{vap}}) \approx 1$, the relative error in this term is quite large. Thus, as long as the first term is significant, i.e. larger than a few kJ mol^{-1}, the error is predominantly determined by the first term, while at small values of $\Delta_{\mathrm{ads}}u$, the correction term determines the error. Neglecting this correction term for the moment, the *possible* error in $\Delta_{\mathrm{ads}}u$ is given by

$$|\Delta(\Delta_{\mathrm{ads}}u)/\Delta_{\mathrm{ads}}u| = |\Delta g_{\mathrm{ads}}/g_{\mathrm{ads}}| + |\Delta\tilde{N}_{\mathrm{ads}}/\tilde{N}_{\mathrm{ads}}| + |\Delta(\mathrm{EMF}_{\mathrm{dif}})/\mathrm{EMF}_{\mathrm{dif}}| \tag{10}$$

where to a first approximation

$$|\Delta\tilde{N}_{\mathrm{ads}}/\tilde{N}_{\mathrm{ads}}| \approx |\Delta\tilde{N}_{\mathrm{vap}}/\tilde{N}_{\mathrm{vap}}| \approx \Delta g_{\mathrm{vap}}/g_{\mathrm{vap}}| + |\Delta\mathrm{EMF}_{\mathrm{vap}}/\mathrm{EMF}_{\mathrm{vap}}| \tag{11}$$

$\Delta g_{\mathrm{vap}}/g_{\mathrm{vap}}$ is found from repeated calibration to be approx. 0.01 (see the Experimental section). The sensitivity of the adsorption cell is not determined as accurately because it is influenced slightly by the heat transfer properties of the sample. The heat transfer properties of the sample will even change during the adsorption process, but this is of limited significance.

The step in the water vapour adsorption isotherm of activated carbon at $p_r \approx 0.5$ is usually attributed to capillary condensation in the micropores of the activated carbon [8,9]. We have assumed the accompanying heat effect to be zero and have obtained $g_{\mathrm{ads}} = 18.25$ W V^{-1} with this assumption. This value agrees surprisingly well with the value of g_{vap} (19.25 ± 0.2 W V^{-1}). The effects of the heat transfer properties of the sample on the sensitivity of the cell are indeed quite small. When $|g_{\mathrm{ads}}|$ is changed by 0.5 W V^{-1}, the calculated curve of $|\Delta_{\mathrm{ads}}u(n)|$ shifts about 1 kJ mol^{-1} over the entire range of amount absorbed. Thus, an error in g_{ads} causes a systematic error in $\Delta_{\mathrm{ads}}u$, rather than local fluctuations. As pointed out by Mahle

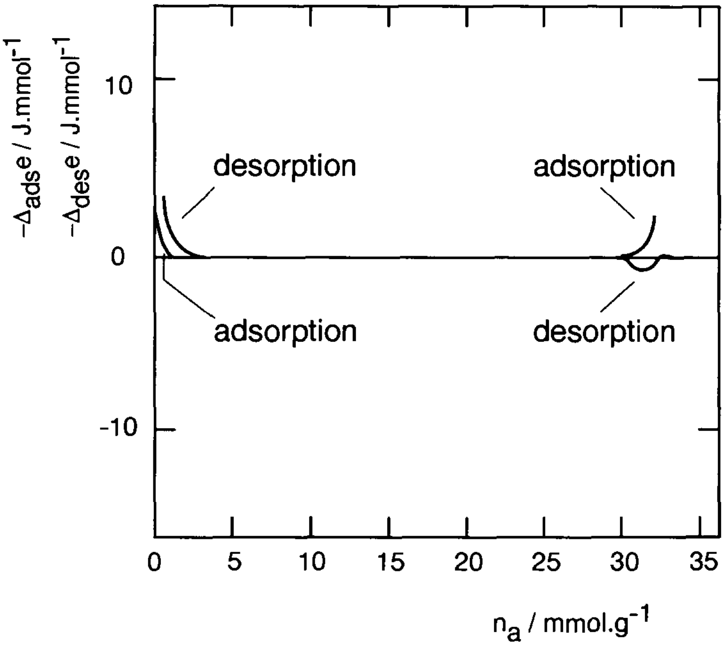

Fig. 5. The net differential energy of adsorption and desorption as a function of amount adsorbed for one of the samples in Fig. 4.

and Friday [8], the adsorption energy due to capillary condensation can be calculated, by introducing the Kelvin equation into the Clausius–Clapeyron equation, to be approximately 2.5 kJ mol^{-1} (pore radius 1 nm), which agrees well with experimental data of Friedrich et al. [9] determined by immersion calorimetry. Consequently, the absolute value of $\Delta_{ads}u$ is probably not determined exactly, but the changes in this parameter with amount adsorbed are reliable.

The relative errors in the EMFs depend strongly on the absolute values, i.e. on the progress of the adsorption process. It has been proven that changes of ±0.001 mV in the EMFs (10 times the resolution for $\mathrm{EMF_{dif}}$) cause differences in the calculated $\Delta_{ads}u$ values of ±0.4 and ±0.1 kJ mol^{-1} for $\mathrm{EMF_{dif}}$ and $\mathrm{EMF_{vap}}$, respectively. This includes errors due to the zero signal not being exactly zero. In short

$$\Delta(\Delta_{ads}u)/\Delta_{ads}u| \approx 0.01 + |\Delta g_{ads}/g_{ads}| + 0.5/\Delta_{ads}u \qquad (12)$$

where $\Delta_{ads}u$ is given in kJ mol^{-1}. Consequently, when $\Delta_{ads}u$ falls below 10 kJ mol^{-1}, which is very usual for water adsorption isotherms, the error in this parameter is more than 10%.

This, together with the larger influence of the error in the correction term, is probably the explanation for the phenomena at high loadings in Fig. 5, which gives the plots of $\Delta_{ads}u$ versus n of the triplicate measurement on the activated carbon. We believe that the small increase in $\Delta_{ads}u$ is an artefact.

The uncertainty in g_{ads} and the inaccuracy in the determinations of the EFMs, in particular EMF_{dif}, give the largest contributions to the probable error in $\Delta_{ads}u$.

4.5. Errors in the desorption isotherm and energy

In the experimental section, we have already observed that the error in the total amount desorbed is usually about 3%. Desorption measurements are never continued to very low values of the relative water vapour pressure because the error in the amount desorbed becomes quite large due to the integration of $\tilde{N}_{cap}$ with time and the subtraction of two almost equal values. Also, the blank adsorption becomes important in this pressure range (Fig. 3).

Analogous to the adsorption case, the possible error in the relative pressure has been estimated to be $-0.037 \leq \Delta(p/p_s)/(p/p_s) \leq 0.030$. Experiments have shown the system not to be more out of equilibrium than in the adsorption case.

For the possible error in $\Delta_{des}u$, $\Delta(\Delta_{des}u)/\Delta_{des}u$, we find

$$\Delta(\Delta_{des}u)/\Delta_{des}u = \Delta g_{ads}/g_{ads} + \Delta\tilde{N}_{cap}/\tilde{N}_{cap} + \Delta(EMF_{dif})/EMF_{dif} \qquad (13)$$

Using $\Delta\tilde{N}_{cap}/\tilde{N}_{cap} \approx \Delta n_{des}/n_{des} \approx 0.03$ and the fact that a change in EMF_{dif} of 0.001 mV gives a change in $\Delta_{des}u$ of about 0.2 kJ mol^{-1}, we find

$$|\Delta(\Delta_{des}u)/\Delta_{des}u| = 0.03 + \Delta g_{ads}/g_{ads} + 0.2/\Delta_{des}u \qquad (14)$$

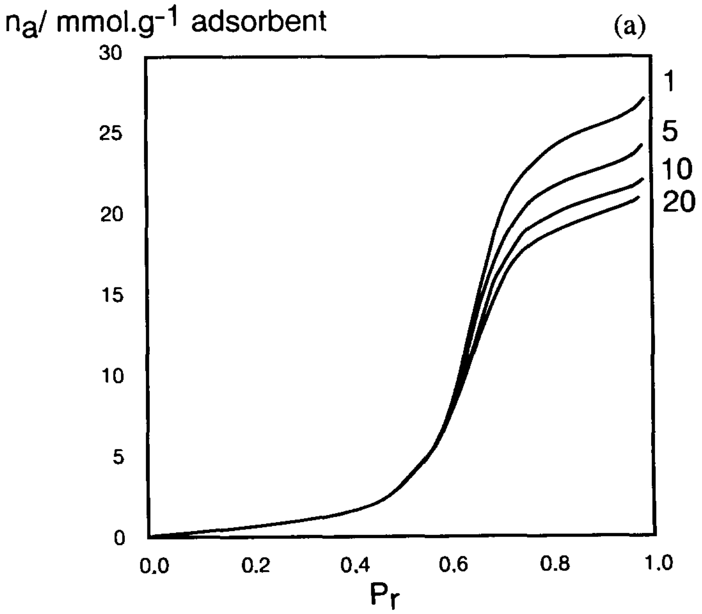

Fig. 6(a).

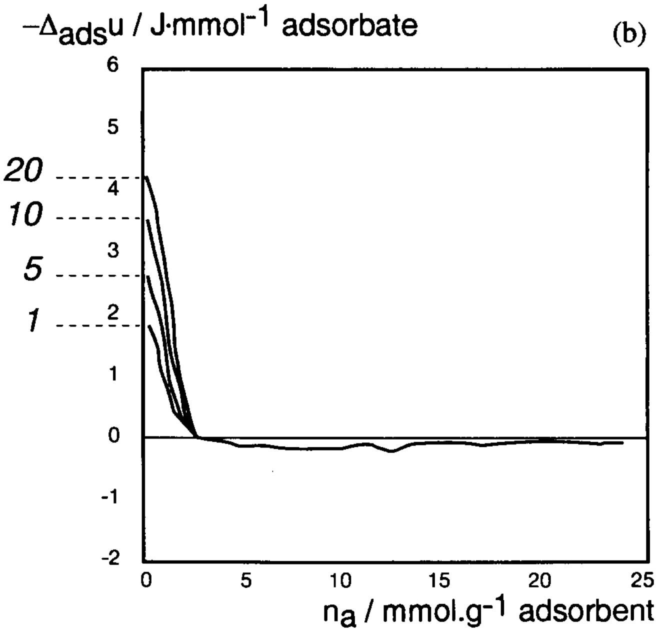

Fig. 6. (a) and (b) Adsorption isotherms and net differential energy of adsorption as a function of amount adsorbed for an activated carbon used in protective garments. The figures next to the plots indicate the number of times the samples have been washed with a solution of a soap in water.

where $\Delta_{des}u$ is to be given in kJ mol^{-1}. The possible error in the net differential desorption energy is quite large, several factors being of importance. For the desorption of water from activated carbons, $\Delta_{des}u$ is very small for the part of the desorption isotherm which is experimentally accessible. Therefore, no reliable desorption energy data are retrieved as yet.

5. An example: surfactant residues on activated carbon

Activated carbons used in protective garments undergo several washings during their service life. Surfactants used in washing are adsorbed well in the micropores of the activated carbon and are probably not fully removed during the rinsing of the garments. Fig. 6 shows that the residual surfactants affect the adsorption of water in two ways: the total available volume for adsorption decreases, whereas the net differential adsorption energy at low loadings becomes larger. The former effect must be due by the occupancy of the pores, which apparently equals about 5 mmol or 0.09 cm^3 of water per gram of carbon going from one to 20 washings. The increase in $\Delta_{ads}u$ is expected to be due to adsorption by the ionic or polar parts of the surfactant molecules. Assuming a liquid density of 0.8 g cm^{-3}, a molar weight of 300 g mol^{-1}, and an interaction energy of 22 kJ mol^{-1} (one hydrogen bridge per surfactant molecule), the adsorption energy should increase about 5 J per gram of active carbon. This agrees well with the difference in the integral adsorption energy obtained by calculating the area below the $\Delta_{\mathrm{ads}}u$ versus n curves for 20 and 1 washings (3 J g^{-1}). This confirms the above explanation of the adsorption behaviour.

6. Conclusion

Sorption calorimetry is a method which enables the direct and accurate determination of adsorbed amount and adsorption energy as a function of amount adsorbed in one experiment. The accuracy in the amount adsorbed is comparable to that of standard nitrogen adsorption methods (approx. 1.5% [6]). An error analysis shows that measurements of sorption isotherms should not be continued to very high values of p_r (adsorption) or very low values of p_r (desorption). Improved accuracy in the determination of the relative water vapour pressure may be obtained by a better understanding of the 'leakage' into the system. The accuracy of the measurement of the adsorption energy may be improved by more accurate determination of the EMFs and, significantly, by a better determination of the value of adsorption cell sensitivity. Other calibration procedures for this parameter are being studied at present.

The amount desorbed can also be obtained quite easily, but not as accurately as the amount adsorbed. Net differential desorption energies can only be determined with sufficient accuracy when the absolute value is quite large. More research is needed into this aspect of the technique.

Finally, an example has been shown of small but significant effects in water adsorption isotherms which can be determined with sorption calorimetry.

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