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On application of an isothermal sorption microcalorimeter

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Abstract

A wide scope of application of a novel isothermal sorption microcalorimeter is presented. With the technique, it is possible to simultaneously and independently in one experiment obtain the sorption isotherm of a sample along with the corresponding differential enthalpies of sorption. The method is suited for measurements with water vapor as well as organic vapors and has been tested at temperatures between 25 and 40°C. The technique is suitable for the thermodynamic characterization of the sorption process. It is demonstrated that the method can be applied to the study of a wide range of physico-chemical phenomena associated with the uptake of vapor by a substance/material including capillary condensation, crystallization, lyotropic phase transitions and hydrate/solvate formation. The calorimetric data are reproducible and agree well with the results of well-established techniques such as solution calorimetry, differential scanning calorimetry, sorption microbalance and osmotic stress measurements. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Vapor sorption; Solid–vapor interactions; Microcalorimetry; Sorption isotherm; Sorption enthalpy

1. Introduction

Sorption of water and organic vapors by solid substances and materials may influence their physical and chemical properties such as phase state, crystal structure, density, solid state reactivity, permeability and rate of dissolution. As an example, stability and performance of pharmaceuticals may be strongly affected by hydration [1]. Water content and water activity in foods is an important factor for chemical, textural and microbial stability [2].

Sorption can be looked upon as a phase transition of a vapor to a condensed (sorbed) state of some sort. In general, a sorption process can be presented as the uptake of Δn mol of vapor by a material accompanied by an integral enthalpy of sorption, ΔH (kJ/mol). If the admission of the vapor to the sorbent is slow enough, the vapor sorption is taking place at virtually constant value of vapor content and vapor activity and the corresponding enthalpy represents the differential enthalpy of sorption, $\Delta_{\mathrm{sorp}}\overline{H}$ (kJ/mol (H_2O)).

A number of methods have been developed for studying water vapor sorption and for characterizing energetics of hydration:sorption isotherms as well as differential or integral enthalpies of sorption can be obtained separately or simultaneously. The major groups of methods are as follows:

1. Gravimetric methods like desiccator storage [3], climatic test chambers [4] and automated sorption balances of different types where a sorbent is exposed to controlled vapor conditions. Vapor transfer to the sample can be by diffusion in a

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stationary gas, but measurements can be made in shorter time if a gas stream is flowed past the sample or if the measurement is made in the absence of a carrier gas [5]. The vapor activity can be controlled in steps or ramps. Although gravimetric techniques are mainly used for determinations of sorption isotherms, it is possible to calculate differential isosteric enthalpy of sorption from sorption isotherms measured at different temperatures [6]. However, such calculations can be uncertain due to a number of assumptions used in application of the Clausius–Clapeyron equation.

2. Calorimetric techniques can be used to obtain sorption isotherms or/and enthalpies of sorption. Differential enthalpies of sorption can be derived from the data of immersion calorimetry where samples equilibrated at a number of vapor pressures are immersed into a vapor-forming liquid [7]. It is also possible to subject a sample in an isothermal microcalorimeter to a stream of inert gas with controlled vapor activity [8] or combine a vacuum sorption instrument with a calorimeter [9–11]. In these cases, one usually changes the vapor activity step-wise and thus measures integral sorption enthalpies in small intervals.

A double twin isothermal microcalorimeter [12,13] developed at University of Lund, Sweden, makes it possible to obtain simultaneously both the vapor sorption isotherm and differential enthalpies of sorption under atmospheric pressure in an optimum time. Here we present the application scope of the new method.

2. Method

In the present work two versions of double twin isothermal microcalorimeters [12–16] were used to study vapor sorption by a number of different samples. The new technique allows to measure vapor sorption under quasi-equilibrium conditions and to scan the whole range of vapor pressures from very low up to near-saturation conditions.

The calorimetric cell consists of two chambers positioned one above the other. The chambers are connected by a stainless steal tube. For the measurement, the sorption chamber of the cell is charged with 30–200 mg of a dry sample. The experiment is initiated by injecting the vapor-forming liquid into the vaporization chamber. Experiments are run under atmospheric pressure and the rate of admission of the vapor to the sample is controlled by diffusion through the gas phase in the tube and the sorption properties of the sample.

Calorimetric signals from the vaporization and sorption chambers are registered simultaneously and separately in the microcalorimeter. From these two measurements, as a function of time, one may calculate vapor activity (vapor pressure) in the sorption chamber, vapor uptake and the differential enthalpy of sorption at any moment of the measurements [15].

The results of the calorimetric measurement can be presented as a sorption isotherm and differential enthalpies of sorption. In this paper, we describe a number of applications of this new sorption microcalorimetric technique.

3. Application of the method

3.1. Bulk sorption

Microcrystalline cellulose (MCC), Avicel PH 101 (FMC Corp., Philadelphia, PA, USA) was used to test the present method of vapor sorption measurement. MCC contains an amorphous fraction (>25 wt.%) [17] which can take up a substantial amount of water [18]. Fig. 1 shows a comparison between our measurements with a 60 mg sample and the result of a study on sorption reference materials [19]. The agreement is good. Fig. 1 also shows good agreement between our own measurements with the sorption calorimetric technique and with desiccators with saturated salt solutions carried out for the sodium form of carboxymethylated cellulose (CMC-Na) with degree of substitution of 0.3 (Akzo Nobel, The Netherlands). The semisynthetic polymer has low solubility in water and high degree of amorphicity introduced during the manufacturing process.

Comparison of the sorption isotherms for CMC-Na and MCC shows an increase in water sorption as a result of increased amorphicity and the addition of ionizable groups into the cellulose structure. However, at water activities below 0.15, CMC-Na samples show

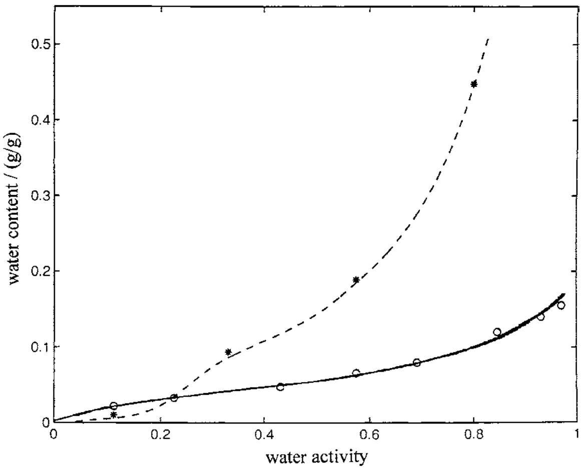

Fig. 1. Calorimetrically obtained sorption isotherms of microcrystalline cellulose (—) and the sodium form of carboxymethylated cellulose with a degree of substitution 0.3 (dashed line). Data obtained with desiccator technique: (○), microcrystalline cellulose; (∗), sodium form of carboxymethylated cellulose. All data refer to 25°C.

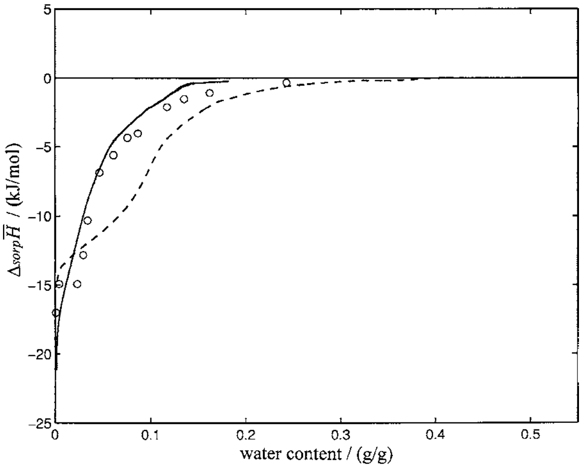

Fig. 2. Calorimetrically obtained differential enthalpies of sorption of microcrystalline cellulose (—) and the sodium form of carboxymethylated cellulose with a degree of substitution 0.3 (dashed line) at 25°C; (○), data recalculated from the heats of immersion of microcrystalline cellulose [7] at 20°C.

very low sorption. This can be due to the interactions between the chains of the polymer enhanced by the polar groups at low water content or can be an artifact introduced by a slow vapor transport in the dry CMC-Na leading to non-equilibrium sorption conditions. The latter case is partly confirmed by a higher value of water uptake at 11% RH obtained for CMC-Na with the desiccator method in the present study (Fig. 1).

Reasonably good agreement was found between differential enthalpies of sorption of MCC measured directly in the sorption microcalorimeter and the ones recalculated from the results of the immersion experiments [7] (Fig. 2). The presence of the ionizable groups in the cellulose increases the exothermic character of the differential enthalpy of sorption for CMC-Na compared with the data for MCC (Fig. 2) except for the very low water content values. The differential enthalpies of sorption increase from about −15 kJ/mol at low water content up to near 0 at the high water content values when the partial molar enthalpy of sorbed water is close to that of the bulk water.

3.2. Capillary condensation

Microporous VYCOR brand glass no. 7930, (Corning Glass Works, Corning, NY, USA) with pore size 40–70 Å was reduced to a fine powder, chemically cleaned from organic contamination and dried in vacuum at 100°C. Its sorption properties were then measured in the sorption microcalorimeter.

The steep slope observed on the sorption isotherm (Fig. 3) corresponds to capillary condensation in the pores with a narrow range of sizes. This part of the sorption isotherm between water activities 0.75 and

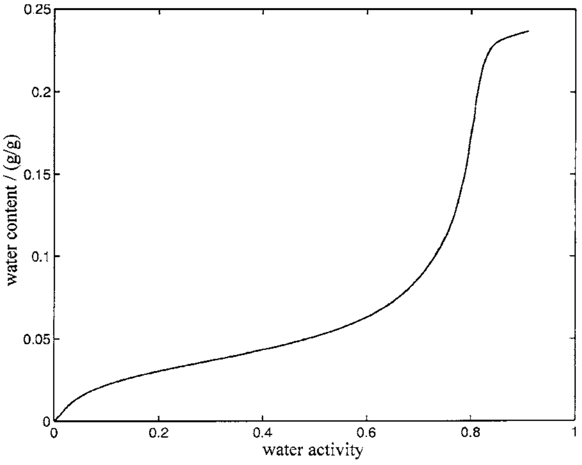

Fig. 3. Calorimetrically obtained sorption isotherm of Vycor porous glass at 25°C.

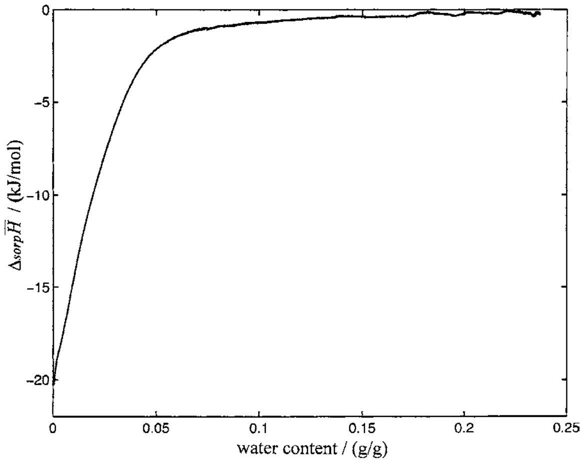

Fig. 4. Differential enthalpies of sorption of the Vycor porous glass vs. water content at 25°C.

0.82 according to the Kelvin equation corresponds to the filling of the pores with the radius between 40 and 55 Å. The calorimetric experiment confirms the narrow pore distribution in the sample. In calculations, we assumed that the pores are cylindrical, the properties of water in the pores are the same as for the bulk water and the contribution of the thickness of the adsorbed water film to the dimensions of the pores is negligible. At water activity higher than 0.82, the isotherm levels off indicating the saturation of the volume of the pores in the sample.

Fig. 4 presents differential enthalpy of sorption for the glass. The exothermic differential enthalpy of sorption at low values of water content decreases as the active polar sites on the surface of the glass are hydrated. The change in partial molar enthalpy of water becomes close to zero during capillary condensation indicating that water absorbed into the pores is approaching the properties of nonperturbed bulk water.

3.3. Lactose recrystallization

Lactose is a common pharmaceutical excipient that may have different degrees of amorphicity depending on how it has been processed. Amorphous regions in materials introduced during processing are metastable and can under certain conditions (temperature, plasticizers, presence of impurities) transfer into a stable crystalline state. A number of methods employing isothermal microcalorimetry (controlled RH perfusion cell, miniature hygrostat techniques) is used for accurate determination of the degree of amorphicity of the lactose. However, often there are variations in the parameters of crystallization (enthalpy of crystallization per gram of amorphous lactose, critical water content, etc.) obtained by different methods. One of the reasons for the discrepancy lies in the fact that lactose can be present in a variety of states at the start of the measurements as well as it may crystallize into different forms depending on temperature, water content and relative humidity upon the measurements. Artifacts can also be introduced by the experimental set-up (uncontrolled evaporation/condensation effects, crystallization/dissolution of salts in a saturated salt solution in the miniature hygrostat) which contribute to the overall response and are difficult to correct for.

In this study, we have used lactose samples with different degrees of amorphicity kindly provided by Dr. L.-E. Briggner (Astra-Zeneca, Lund, Sweden). The samples are of the same origin as the ones described in [20]: two samples of micronized lactose of low amorphous content and one of 100% amorphous spray dried lactose. We have also run measurements on the lactose samples after recrystallization to obtain the sorption isotherm and the thermal power of sorption of the 100% crystalline lactose. All samples were stored in a desiccator over P_2O_5 prior to the measurements. Zero calorimetric response of the 100% crystalline lactose confirms that no additional amorphicity was introduced during handling of the samples.

The thermal power produced by the lactose samples in the sorption chamber corrected for the contribution from the condensation of vapor resembles the calorimetric results reported by Briggner et al. [20] and Sebhatu et al. [21]. Three well-resolved regions were observed. According to Sebhatu et al. [21], they can be identified with the sorption of water followed by highly cooperative crystallization and then possible mutarotation of β-lactose into α-lactose with subsequent formation of the α-lactose monohydrate.

The thermal power of sorption was integrated and normalized with the mass of the respective sample. The values of the integral enthalpies for the micronized lactose samples were 2.99 and 9.60 J/g. The enthalpy of crystallization of 100% amorphous lactose was found to be 80 J/g. The sample of 100% crystalline lactose gave zero response in this region which is consistent with the finding reported by Angberg et al. [22]. The degree of amorphicity of the samples of micronized lactose was then calculated assuming a linear relationship between the amorphous content and the heat output (J/g). A good agreement was observed between our results and the values obtained independently for the lactose samples of the same batches with the technique described by Briggner et al. [20], cf. 3.7 and 12.0% as determined by the sorption microcalorimeter and 3.3 and 11.5% obtained by a miniature hygrostat method.

Fig. 5 presents the sorption isotherms of the four lactose samples. It can be seen that the amount of water needed to trigger crystallization decreases as the degree of amorphicity goes down. The crystalline sample shows very little water uptake up to the water activity values close to saturation where it increases significantly. The experimental values of the water uptake by 100% amorphous lactose of 0.12 and 0.10 g/g at 75 and 50% RH, respectively, agree well with the data reported by Darcy and Buckton [23], cf. 0.13 g/g at 75% RH and around 0.10 g/g at 50% RH.

The sorption isotherms for the 100% crystalline and 100% amorphous samples indicate lower and upper limits of hydration of lactose at a given water activity. The curves are made up from a large number of data points taken at 50 s intervals. The parts of the top three curves in which one can see the individual data points correspond to a jump in the isotherms following the crystallization. As the amorphous regions of the lactose samples crystallize, they become oversaturated with water relative to the RH value at the onset of crystallization as the same amount of water in the crystalline sample corresponds to much higher values of RH (cf. Fig. 5). Therefore, the equilibrium water activity in the lactose sample after crystallization increases.

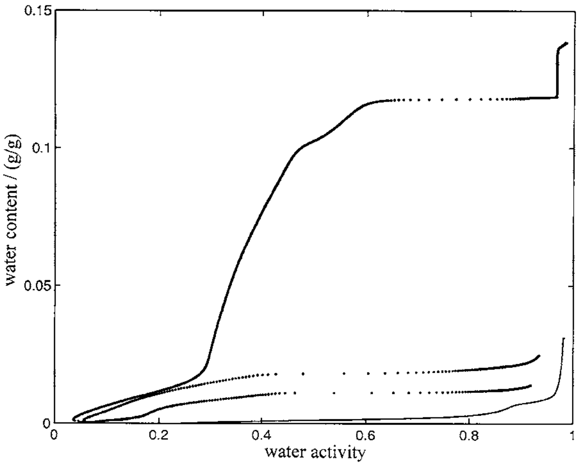

Fig. 5. Calorimetrically obtained sorption isotherms of lactose samples with different amorphous content. Curves from top to bottom: 100, 11.5, 3.3 and 0 wt.% amorphous (i.e. 100 wt.% crystalline) lactose.

In measurements with a miniature hygrostat technique, the recrystallized sample looses water when the RH of the saturated salt solution is below the equilibrium water activity in the sample. This effect may be responsible, for the irregular shape of the net microcalorimetric response observed for example, by Gustafsson et al. [24], when two different saturated salt solutions with RH of 57 and 81% were used. The endothermic peak observed in their study directly after the crystallization peak which was substantially larger in the experiments where 57% RH was employed.

A peculiar region of water uptake at virtually constant RH of 96% was observed on the sorption isotherm of the spray dried lactose (Fig. 5). It may be caused by the phase transition of β-lactose into α-lactose monohydrate suggested in a number of papers [21,22,25]. The presence of a transition involving two coexisting phases in this region is further supported by the constant value of the change in the partial molar enthalpy of water of around −22 kJ/mol (H_2O) shown in Fig. 6. The amount of water taken up during the transition would correspond to about 35 wt.% β-lactose present in the crystallized sample of the spray dried lactose. This value agrees well with β-lactose content of 36–42 wt.% reported by Buckton on the results of NIR studies [26,27].

The sorption microcalorimetric technique may provide an alternative procedure for analysis of amorphous content of lactose since, in some cases, the shape of the crystallization peak is simplified (no desorption as the result of the reversed water activity gradient). It may also prove to be useful in detecting details of the process (e.g. mutarotation). The technique provides a better control over the water content and water activity in the sample.

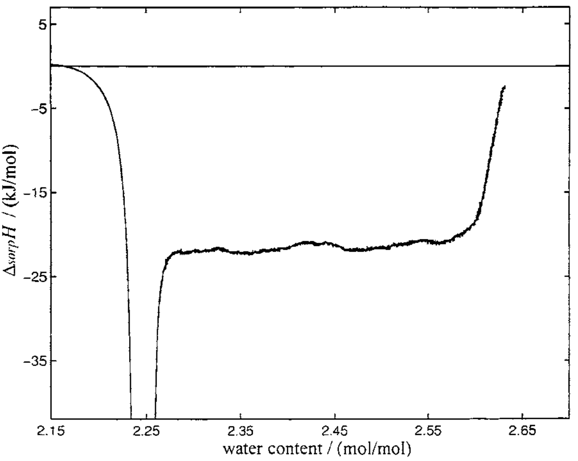

Fig. 6. A detail of a plot of the differential enthalpy of sorption of spray dried lactose vs. water content.

3.4. Lyotropic phase transitions

For some substances water uptake can lead to lyotropic phase transitions resulting in a number of mesophases [28–30]. We have used the isothermal sorption microcalorimeter to study lyotropic phase transitions of phospholipids and dimethyldecylphosphine oxide surfactant. The thorough analysis of the results obtained for the phospholipid–water systems is given in [14]. Below we give just an outline of that study. The results of the calorimetric measurements on dimethyldecylphosphine oxide hydration are discussed in more detail.

Fig. 7(a) presents a theoretically calculated phase diagram of dimyristoyl phosphatidyl choline (DMPC), reported in [14] where L_α is a liquid crystalline phase, $L_{\beta'}$ denotes a gel phase and P_β is a rippled gel phase. The characteristic DSC traces of DMPC–water system scanned at constant composition in a range of temperatures are shown in Fig. 7(b) and (c). The appearance of the peaks (shape, width and size) on the DSC curves obtained at a low scanning rate is known to serve as an indication of the type of the corresponding phase transition. A sharp peak in Fig. 7(c) corresponds to an eutectic phase transition ($P_\beta + H_2O \rightarrow L_\alpha$) in the system at high water content while the peak on the thermogram on Fig. 7(b) points to the existence of a two-phase region ($L_{\beta'} + L_\alpha$) at low water content [30].

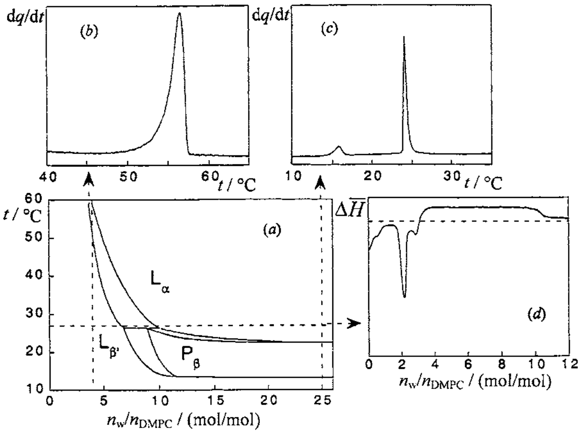

Fig. 7. A scheme presenting: (a) a theoretically calculated phase diagram of DMPC [14]; (b) DSC trace of the hydrated DMPC at low water content; (c) DSC trace of the hydrated DMPC at high water content; (d) differential enthalpy of sorption vs. water content of DMPC measured isothermally in the sorption microcalorimeter at 25°C.

The sorption microcalorimetric technique makes it possible to follow an isothermal line on a phase diagram scanning the system in a broad range of water content from very low up to near-saturation values of water activity (Fig. 7(a) and (d)). Characteristic features are expected to be observed both on the sorption isotherm and on the differential enthalpy of sorption versus water content plots in case of a lyotropic phase transition. According to the phase rule coexistence of two phases in a two-component system at constant temperature should result in a region of constant water activity on a sorption isotherm. A constant differential enthalpy of sorption would accompany the water uptake in the corresponding range of compositions. A constant differential enthalpy of sorption observed on Fig. 7(d) corresponds to the region of coexistence of $L_{\beta'}$ and L_α phases indicated in the phase diagram. The water uptake takes place at constant water activity [14]. Complemented with the data characterizing the structure of the phases and their relative composition the calorimetric data can be used to map the phase diagram of the binary system [14].

Below, we give an example of the application of the sorption microcalorimeter to the study of the phase behavior of a surfactant, dimethyldecylphosphine oxide ($C_{10}PO$) upon the uptake of water. The sample of $C_{10}PO$ ($M_w = 218.3$ g/mol), >99% purity was

Table 1
Parameters of the phase transitions of $C_{10}PO$ obtained by the sorption microcalorimeter and DSC [30]

T(°C)	Phase transition	Phase boundaries (wt.%)		$\Delta_{sorp}\overline{H}$ (kJ/mol (H_2O))	ΔH (kJ/mol ($C_{10}PO$))
		This work	Reference		
25	$C + H_2O \rightarrow L$	0–17.5	[0–18]	11.7	25.5
25	$I + H_2O \rightarrow H$	36.5–38	[38–39]	–	–
27	$C + H_2O \rightarrow L$	0–16.5	[0–17]	12.6	25
39	$C + H_2O \rightarrow I$	0–13.5	[0–13]	13.5	20
39	$L + H_2O \rightarrow I$	34.5–35	[35–36]	–	–

obtained from ICN Biochemicals Inc., OH, USA. The phase behavior of $C_{10}PO$–water system is well characterized by DSC, X-ray diffraction (XRD) and polarizing microscope techniques [31,32]. The substance is known to exist in crystalline state (C) and go through liquid crystalline hexagonal (H) and lamellar (L) mesophases acquiring a state of isotropic solution (I) at higher water contents and temperatures (Table 1).

The sorption microcalorimetric technique makes it possible to isothermally scan the $C_{10}PO$–water system in a broad range of water content (from 0 up to 45 wt.%) from very low up to near-saturation values of water vapor pressure. Both sorption isotherms and differential enthalpies of sorption (Figs. 8 and 9) indicate a complex phase behavior of the $C_{10}PO$, suggesting lyotropic phase transitions. The regions of constant water activity on the sorption isotherms of $C_{10}PO$ measured at 25, 27 and 39°C correspond to a coexistence of two phases in the two-component system at constant temperature. The phase boundaries obtained in the present study agree well with the phase diagram (cf. Table 1). However, not all of the reported phase transitions of $C_{10}PO$ spanning over a narrow range of water content were detected. This is, probably, due to a rate-limiting vapor transport or kinetically slow nucleation of a new phase upon the hydration leading to non-equilibrium results. The sensitivity of the technique to such type of the transitions is higher at the higher water activities when the rate of vapor flow to the sample is significantly lower.

The phase transitions taking place over a broad range of water content are accompanied by the constant values of differential enthalpies of sorption (Fig. 9 and Table 1). The transitions over the narrow

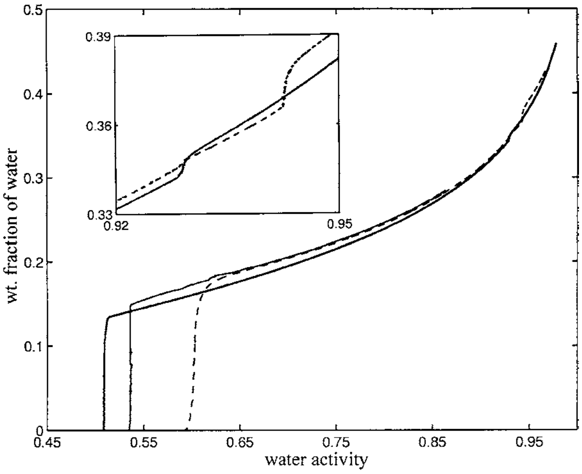

Fig. 8. Calorimetrically obtained sorption isotherms of dimethyldecylphosphine oxide: solid thick line, at 39°C; solid thin line, at 27°C; dashed line, at 25°C.

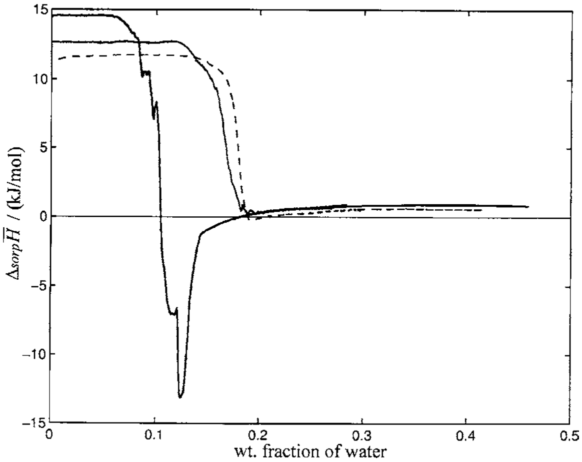

Fig. 9. Differential enthalpies of sorption of dimethyldecylphosphine oxide vs. weight fraction of water: solid thick line, at 39°C; solid thin line, at 27°C; dashed line, at 25°C.

range of water content are not seen on the plot of differential enthalpy of sorption versus water content. However, small endothermic values of the enthalpies of these phase transitions measured by DSC (e.g. 0.505 vapor kJ/mol ($C_{10}PO$) for H → I phase transition at 47 wt.% H_2O at 32°C [30]) indicate that it might be below the resolution of the present technique.

In general, the experimentally determined differential enthalpies of sorption demonstrate that the lyomesophases and liquid phase of $C_{10}PO$ at water weight fraction higher than 20% do not differ significantly in the energetics of water uptake. This is consistent with the small values of the enthalpies of phase transitions between these phases measured by DSC [30].

From these measurements, it follows that the detection of broad two-phase regions is more probable on the sorption isotherms and differential enthalpy of sorption versus water content plots. This could be due to the fact that the ideal appearance of a lyotropic phase transition on the sorption isotherms and plots of differential enthalpy of sorption can be corrupted by rate-limiting diffusion of water into a sample and kinetically slow nucleation of a new phase. These lead to smearing effect in analogy to the thermal lag phenomena observed in DSC experiments.

In addition, for the phase transition to be detected by the present technique, the values of differential enthalpy of sorption should be sufficiently high, i.e. production of heat measured during sorption should differ substantially from the heat production associated with condensation of pure water. The values of $\Delta_{\mathrm{sorp}}\overline{H}$ should also vary significantly between different lyotropic phases.

In analogy with the DSC technique, the scanning rate, i.e. rate of vapor admission (vapor flow), should be low to minimize possible water activity gradients leading to inhomogeneity in the sample.

3.5. Solvate formation

Vapor uptake by a sample can lead to the formation of solid solutions and solvates. When water vapor molecules are incorporated into the crystal structure of the solid in stoichiometric proportion, a hydrate formation occurs. The sorption microcalorimeter can be used to detect the formation of solvate/hydrate and characterize the range of vapor activity where it is thermodynamically stable at a given temperature.

3.5.1. Clathrate formation of polyphenolic compound with acetone

In the present work the sorption calorimetric technique was tested in application to an organic vapor. The absorbent, 2,2′-bis(9-hydroxy-9-fluorenyl)biphenyl (BBP), $M_w = 614.49$ g/mol, >99% purity was obtained from the Institute of Organic Chemistry, Freiberg, Germany. The synthesis and structural details are described in [33,34]. Acetone was p.a. grade from Merck, Germany.

The calorimetrically obtained sorption isotherm (Fig. 10) confirms the formation of the BBP–acetone clathrate with stoichiometric composition 1:2 measured by thermal gravimetric technique (TG) [35].

Seidel et al. [35] reported that the DSC curve and DTG curve for the BBP–acetone system look similar during the whole inclusion process. The constant differential enthalpy of sorption (inclusion) measured by the sorption microcalorimeter supports this observation (Fig. 11). The integral enthalpy of 1:2 solvate formation is −47.8 kJ/mol (C_3H_6O) as measured by DSC [35] and −48.6 kJ/mol (C_3H_6O) as obtained with the sorption microcalorimeter (enthalpy of condensation of acetone is −31.0 kJ/mol).

3.5.2. Hydrate formation

The determination of the critical water activity of a hydration step and of the number of moles of water being sorbed can be problematic. Traditional techniques like storage in desiccators with saturated salt

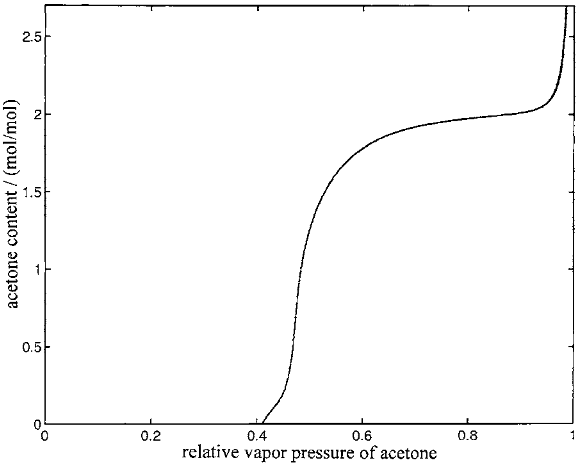

Fig. 10. Calorimetrically obtained sorption isotherm for the system acetone–2,2′-bis(9-hydroxy-9-fluorenyl)biphenyl at 25°C.

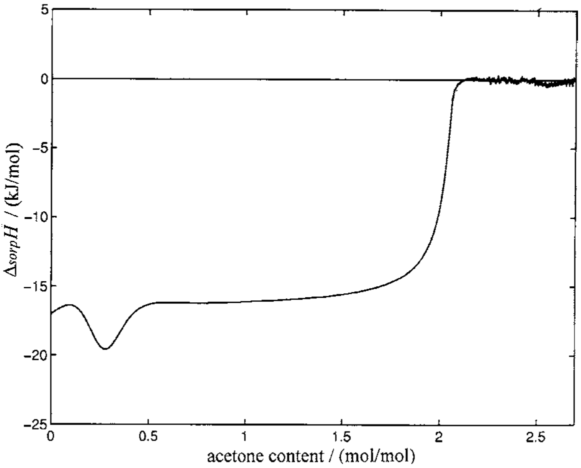

Fig. 11. Differential enthalpies of sorption for the system acetone–2,2′-bis(9-hydroxy-9-fluorenyl)biphenyl at 25°C.

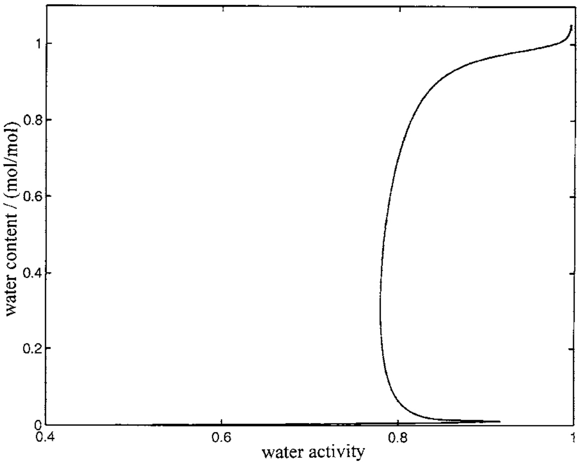

Fig. 12. Calorimetrically obtained sorption isotherm of anhydrous theophylline at 25°C.

solutions can give the hydration stoichiometry, but as there are usually only a few points measured, the corresponding critical activity cannot be accurately determined. Modern automated sorption balances are much more efficient, but a number of measurements with specially designed RH scan programs are usually needed for exact determination of the critical activity of a hydration step [36]. With the present sorption calorimeter we have found that one run in most cases makes it possible to determine the water activities and stoichiometry of all hydration steps of a substance. We have previously published results on morphine sulfate hydration [37] which has rapid hydration kinetics. Here we give results of the hydration on theophylline; the substance that is more challenging due to slow hydration kinetics.

A sample of anhydrous theophylline ($M_W = 180.17$ g/mol) kindly provided by Dr. T. Sokoloski of SmithKline Beecham Pharmaceuticals, was dried in vacuum for 2 days and then exposed to the water vapor in the sorption microcalorimeter. The results of the measurement are shown in Figs. 12 and 13. The sorption isotherm (Fig. 12) of theophylline shows the formation of a monohydrate. However, the measurements of the water activity at the lower limit of the stability range of the hydrate were corrupted, probably, due to the slow hydration kinetics. The water activity is calculated as a function of the rate of water uptake by the sample [15]. After a few minutes at relative humidities above the critical humidity of the hydrate formation (non-equilibrium), the sample starts to sorb, and the calculated activity moves towards the equilibrium value of water activity. The minimum water activity seen during the hydration step is then the one that is closest to the critical activity. At the end of the monohydrate formation, the step on the isotherm is smeared, this is probably due to diffusion resistances within the bed of particles or within the particles.

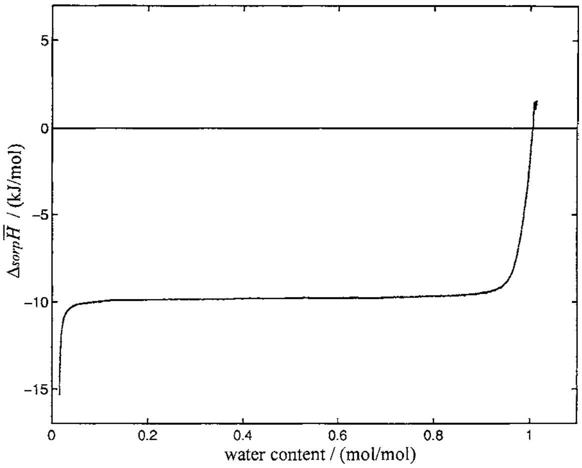

Fig. 13. Differential enthalpies of sorption of anhydrous theophylline vs. water content at 25°C.

An advantage with our simultaneous determination of the sorption isotherm and the differential sorption enthalpy is that the latter is often less disturbed by kinetic problems and can thus help to interprete the sorption isotherm. In this case, the differential sorption enthalpy is constant, −10 kJ/mol (H_2O), from 0 to 1 mole of water per mole theophylline confirming the direct formation of a monohydrate (Fig. 13).

One should note that of the three parameters, water activity, concentration and differential enthalpy of sorption, it is mainly the water activity that is disturbed by kinetic problems. For many substances, a rate-limiting vapor transport or kinetically slow nucleation of a new phase formed upon the hydration can lead to non-equilibrium results. However, the non-equilibrium conditions can be identified from the general appearance of the sorption isotherm and along with the data on differential enthalpy of sorption such a measurement may still provide a valuable information.

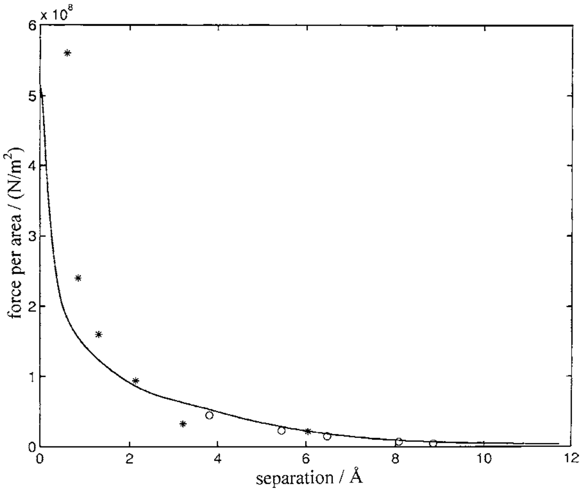

Fig. 14. Swelling of the Bentonite MX-80, force per area vs. separation: (—), calorimetric results at 25°C; (∗), data points obtained with the gravimetric technique in sorption regime at 20°C; (o), data points obtained with the gravimetric technique in desorption regime at 20°C [42].

3.6. Swelling of Bentonite clay

We have used the sorption calorimeter to study the hydration of the sodium form of the montmorillonite clay, Bentonite MX-80. This material is well characterized [38]. It consists of plate like particles, <2 μm in size, which are built up of sheets containing aluminum, silica and oxygen. The hydrophilic character of the Bentonite is due to the charge deficiency introduced by the intracrystalline substitution of isomorphous atoms (e.g. by magnesium) and the acidic OH-groups present on the surface of the clay sheets. The total area of the surface exposed to water vapor in the sodium form of the Bentonite is about 562 m^2/g [38]. The Bentonite has a high surface charge density (around 0.1 C/m^2). It swells when exposed to water vapor accommodating up to four layers of water between the crystalline sheets [38,39].

The calorimetrically obtained sorption isotherm of the Bentonite at 25°C was recalculated assuming planar geometry in terms of the force acting on a unit area of the sheets as a function of separation (Fig. 14). The results were compared with the data obtained by Kahr et al. [38] with McBain type gravimetric apparatus [40] in sorption and desorption regimes for the sample size 0.7–0.8 g at 20°C. The data points reported by Kahr et al. [38] agree well with our continuous measurement of the Bentonite hydration. Experimentally observed force has no oscillating repulsion mode [41,42] in the range of short separations. This may be due to the partial disorder in arrangement of the Bentonite sheets leading to the less ordered water layers between the clay plates as compared to very well defined mica layers.

The results of the direct calorimetric measurement of the differential enthalpy of sorption are consistent with the data points recalculated from the heats of immersion of the Bentonite reported by Kahr et al. [38]. Although, the recalculated data are quite scattered due to the uncertainties introduced by a complex set-up of the immersion calorimetric technique. The differential enthalpy of sorption measured for the Bentonite hydration does not have well resolved plateau regions (Fig. 15) that would indicate the formation of layers of sorbed water with characteristic partial molar enthalpy. Besides the reason mentioned above, this can be due to the presence of energetically heterogeneous sorption sites on the surface of the clay sheets and limitations imposed by the diffusion of water in the clay particles.

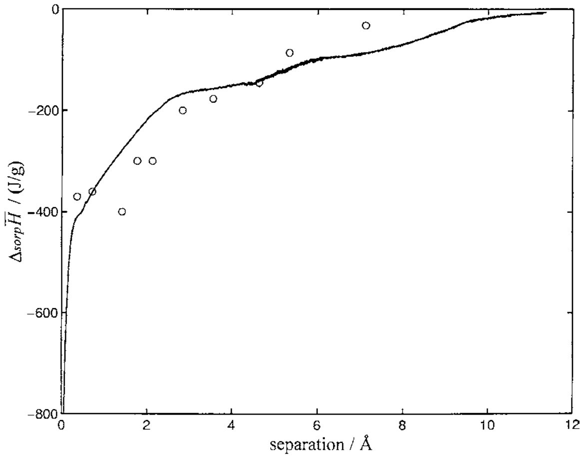

Fig. 15. Differential enthalpies of sorption of Bentonite MX-80 per gram of the clay vs. separation: (—), calorimetrically obtained data at 25°C; (○), data recalculated from the heats of immersion of Bentonite MX-80 at 20°C [42].

3.7. *Determination of the diffusion coefficients of organic vapors*

The sorption microcalorimeter can be used to assess a diffusion coefficient of a vapor provided that the boundary conditions in the top and bottom chambers of the calorimetric cell are known and can be kept constant and the mass transport of the vapor in the cell is well controlled.

When the evaporating system attains a steady state, there is a net flow of vapor to the sample while the nitrogen gas (second component of the gas phase in the cell) is stationary. During this main part of a measurement, the vaporization and the sorption processes take place at near-equilibrium conditions and a constant value of thermal power of vaporization, P_v, is measured. The vapor flow can be calculated directly from the measured thermal power of vaporization

$$q = \left(\frac{P_v}{\Delta_v H}\right) M_w \qquad (1)$$

In the absence of significant gradients in pressure, temperature and density the rate of vapor transfer is also described by the equation [43]

$$q = \left(\frac{p_{tot}}{RT}\right) \varkappa D_c M_w \ln\left(\frac{p_{tot} - p_{sat} a_s}{p_{tot} - p_{sat} a_v}\right) \qquad (2)$$

where p_{tot} is the total pressure in the cell (Pa), D_c denotes the diffusion coefficient of the vapor in N_2 (m^2/s), $\varkappa$ a constant characterizing the effective geometry of the cell (m), $\Delta_v H$ the enthalpy of vaporization (J/mol), M_w the molar mass of the vapor (g/mol), p_{sat} denotes the saturation vapor pressure at the conditions of the experiment (Pa), and a_s and a_v are the vapor activities in the sorption and vaporization chambers.

The geometrical constant of the cell, $\varkappa$, calculated once from Eqs. (1) and (2) for a vapor with a known diffusion coefficient may be applied to calculate the diffusion coefficients of other vapors. The constant has been determined in experiments [15] with water vapor sorption on molecular sieves, 3 Å, as an absorbent maintaining water activity 0 in the sorption chamber. Similar experiments conducted with methanol vapor and molecular sieves, pore size 4 Å, gave the diffusion coefficient of 0.161×10^{-4} m^2/s at 25°C and atmospheric pressure in the range of molar fractions of methanol in the gas phase from 0 to 0.17 ($\Delta_v H =$ 37.28 kJ/mol (CH_3OH) [44] and $p_{sat} = 16946.6$ Pa [45]). The experimental result is consistent with the value of diffusion coefficient of methanol in air, 0.159×10^{-4} m^2/s, reported in [46].

4. Conclusions

The new microcalorimetric technique to measure vapor sorption can be successfully applied to the study of a variety of systems and phenomena associated with a vapor uptake. Different kinds of vapor-forming liquids can also be used.

The method provides a continuous isothermal scan of a system in a broad range of relative vapor pressures at near-equilibrium conditions and gives reproducible sorption isotherms and differential enthalpies of sorption. The calorimetric results agree well with data from other established techniques.

The method has been proved to be useful in application to systems where vapor sorption can initiate physical and chemical changes, e.g. capillary condensation, hydrate and solvate formation, crystallization and lyotropic phase transitions. Critical vapor pressures and phase boundaries of the lyotropic phase transitions can be determined together with corresponding differential enthalpies of sorption. Sorption isotherms and differential enthalpies of sorption are obtained simultaneously for one and the same sample. The sorption process can be characterized thermodynamically. The technique can be used to study the vapor transport phenomena as well.

The method is especially useful for substances that are sensitive to temperature changes when application of Clausius–Clapeyron equation for calculation of $\Delta_{\mathrm{sorp}}\overline{H}$ is not feasible.

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