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# Hydration of a natural polyelectrolyte xanthan gum: Comparison with non-ionic carbohydrates

Vitaly Kocherbitov[a,*], Stefan Ulvenlund[b], Lars-Erik Briggner[b], Maria Kober[b], Thomas Arnebrant[a]

[a] *Biomedical Laboratory Science and Technology, Faculty of Health and Society, Malmö University, SE-205 06 Malmö, Sweden*
[b] *AstraZeneca R&D Lund, S-22187 Lund, Sweden*

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ABSTRACT

In dilute solutions, polyelectrolytes exhibit more hydrophilic properties than non-charged polymers do. However, extension of this statement on almost dry systems is questionable. In this study we present sorption calorimetric data on hydration of a natural carbohydrate polyelectrolyte xanthan gum and make comparison with analogous data of three types of cellulose which is a non-charged carbohydrate polymer. An analysis of the sorption isotherm shows that at given relative humidities xanthan gum absorbs greater amount of water than non-charged cellulose does. Nonetheless, the enthalpies of hydration of xanthan gum and of all three considered types of cellulose at zero water content are equal to −18 kJ/mol. Thus, entropy of hydration plays an important role in water sorption behaviour of xanthan gum. The apparent absence of an ion effect on polymer–water interactions can be explained by solvation of ions by OH-groups of the dry xanthan gum. *Ab initio* calculations presented here show that solvation of an ionic group of xanthan gum by a carbohydrate hydroxyl is as strong as hydration of the same group by water. The exothermic heat effect of hydration arises from the loss of the mobility of water on the rigid glassy environment of the polymer. For the first time, the glass transition temperature of dry xanthan gum is reported to be 60 °C.

## 1. Introduction

Hydration of carbohydrate polymers is an important issue for such applied areas of science and technology as food chemistry, pharmacy, textile and paper industry. For applied purposes one has to know how much water a particular polymeric material absorbs at a given relative humidity. The glass transition temperature as a function of water content is also an important parameter of a polymeric material because mechanical properties undergo dramatic changes at the glass transition. However, fundamental mechanisms of hydration of hydrophilic polymers at low water contents are poorly understood. Typically, sorption isotherms of biopolymers are treated using such sorption models as BET (Brunauer, Emmet, & Teller, 1938) or GAB (Anderson, 1946; de Boer, 1968). These and other models provide reasonably good fitting of experimental sorption isotherms, but values of the parameters of the models obtained using fitting procedures do not necessarily correlate with actual physical properties of water–polymer interactions. Recently we showed that multilayer types of models such as BET cannot be used for treatment of sorption isotherms of microcrystalline cellulose (Kocherbitov, Ulvenlund, Kober, Jarring, & Arnebrant, 2008). Formation of multilayers should be expected at solid–gas interface, for example in mesoporous materials like MCM-41 (Kocherbitov & Alfredsson, 2007) but in case of cellulose, water adsorbs at solid–solid interface between microfibrils, therefore monolayer rather than multilayer models better describe processes of sorption of water by cellulose (Kocherbitov et al., 2008) at low hydration levels.

Properties of carbohydrates in aqueous solutions are strongly dependent on the presence of charges: polyelectrolytes are usually more hydrophilic than uncharged polymers. For example, chitosan (Kumar, Muzzarelli, Muzzarelli, Sashiwa, & Domb, 2004) and carboxymethyl cellulose (Kastner, Hoffmann, Donges, & Hilbig, 1997) are not soluble at pH values which correspond to uncharged molecules but soluble in their charged forms.

The fact that ionic groups make the biopolymers more hydrophilic in dilute solutions is often extrapolated to biopolymer–water interactions at low water contents. It is usually assumed that in almost dry state first water molecules bind to ionisable groups of biopolymers (Yang & Rupley, 1979) and at higher water contents to other polar groups. In line with this approach, D'Arcy and Watt (1970) proposed a sorption model that postulates existence strongly and weakly binding sorption sites.

However, direct experimental data on sorption energies of ionic and non-ionic sites of biopolymers are not available. The reasons for that are the difficulty in separation of heat effects arising from hydration of different sorption sites and insufficient accuracy of

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* Corresponding author. Tel.: +46 40 6657946; fax: +46 40 6658100.
*E-mail address:* Vitaly.Kocherbitov@mah.se (V. Kocherbitov).

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experimental methods used for hydration studies. Until recently, the hydration energies were determined only from temperature dependences of sorption isotherms—a method which provided neither high accuracy nor a great number of experimental points at different water contents. Another experimental approach that provides much higher resolution of experimental data and higher accuracy is the method of sorption calorimetry (Kocherbitov & Wadsö, 2004; Wadsö & Markova, 2002) that recently was used for studies of hydration of surfactants (Kocherbitov & Söderman, 2003, 2006; Kocherbitov, Söderman, & Wadsö, 2002), lipids (Kocherbitov, 2005; Sparr, Wadsten, Kocherbitov, & Engström, 2004), proteins (Kocherbitov & Arnebrant, 2006; Kocherbitov, Arnebrant, & Söderman, 2004), cellulose (Kocherbitov et al., 2008) and nanomaterials (Kocherbitov & Alfredsson, 2007). In this work we present a sorption calorimetric study of the natural carbohydrate polyelectrolyte xanthan gum and compare the results with our previously published data on hydration of three types of cellulose (Kocherbitov et al., 2008).

Xanthan gum is a carbohydrate polymer produced by bacteria *Xanthomonas campestris* and is widely used in food, pharmaceutical, cosmetic and technical applications (Dumitriu, 2005; Garcia-Ochoa, Santos, Casas, & Gomez, 2000). Its backbone consists of β-glucose rings and side chains include substituted α-mannose, β-glucose and β-mannose rings. Xanthan gum is an anionic polymer and contains up to two carboxyl groups per repeat unit (Dumitriu, 2005). In the dilute state it forms viscous solutions while in the dry state it is an amorphous powder. Sorption isotherms of xanthan gum at five temperatures and the heat of water sorption calculated from these data were reported (Basu, Shivhare, & Mujumdar, 2007). In aqueous solution xanthan gum has an order–disorder transition at about 50 °C (Dumitriu, 2005). Thermal behaviour of xanthan gum at low water contents is still unclear. In some studies, a glass of transition of wet xanthan gum at subzero temperatures was reported (Basu et al., 2007; Hatakeyama & Hatakeyama, 1998) while in other studies it was not found (Raschip et al., 2008). To the best of our knowledge, the glass transition temperature of dry xanthan gum has not been reported before.

## 2. Materials and methods

### 2.1. Materials

Xanthan gum obtained from Kelco (batch number 3E8468K) was used. Test experiments with xanthan gum obtained from Jungbunzlauer showed that it has very similar water sorption properties to those of xanthan gum obtained from Kelco. The xanthan gum samples were dried in vacuum in contact with 3 Å molecular sieves for 24 h before sorption experiments. The transfer of the dried samples into the calorimetric cell was done in a glove box in dry atmosphere.

### 2.2. Sorption calorimetry

Sorption calorimetric experiments were conducted at 25 °C in a 28 mm two-chamber sorption calorimetric cell inserted in a double-twin microcalorimeter (Wadsö & Markova, 2002; Wadsö & Wadsö, 1996). The samples under study were placed in the upper chamber, while pure water was injected in the lower chamber. In a sorption experiment, water evaporates from the lower chamber, diffuses through the tube that connects the two chambers and is adsorbed by the sample in the upper chamber. The rate of water sorption in a sorption experiment can be controlled by selecting the diameters of the tubes and by choosing the initial mass of the sample. The thermal powers released in the two chambers are monitored simultaneously. The activity of water $a_w$ in the sorption experiments was calculated from the thermal power of vaporization of water in the lower chamber as described in Kocherbitov (2004a). The partial molar enthalpy of mixing of water was calculated using the following equation:

$$H_w^{mix} = H_w^{vap} + H_w^{vap} \frac{P^{sorp}}{P^{vap}} \tag{1}$$

where $P^{vap}$ and $P^{sorp}$ are thermal powers registered in the vaporisation and sorption chambers respectively and $H_w^{vap}$ is the molar enthalpy of evaporation of pure water. For accurate calculation of the partial molar enthalpy of mixing of water the sorption calorimeter was calibrated using magnesium nitrate as a standard substance (Kocherbitov, 2004b).

### 2.3. Gravimetric vapour sorption (GVS)

In addition to the measurements of sorption isotherm using sorption calorimetry, the sorption isotherm of xanthan gum was also measured by gravimetric vapour sorption. The water sorption was determined in the relative humidity range 0–80% at 25 °C using a dynamic vapour sorption system (Surface Measurement Systems). The system consists of a micro balance which records the mass change of the sample when a gas flow ($N_2$) of controlled humidity passes over the sample.

### 2.4. Modulated differential scanning calorimetry

DSC measurements were done using TA Instruments Q2000 calorimeter. Modulated DSC method allows distinguishing between reversing and non-reversing thermal events which is especially useful for detection of glass transitions. The heating rate of 10 °C/min was combined with temperature oscillations with amplitude of ±2 °C and period of 40 s. The xanthan gum samples with masses of about 10 mg were equilibrated for several days at different RH produced by different saturated salt solutions and were then enclosed in hermetically sealed Tzero$^{TM}$ pans at room temperature. In the DSC experiments, the samples were first cooled down to a desired starting temperature, equilibrated for 2 min and then heated up.

### 2.5. Ab initio calculations

The calculations were done using the MOLCAS software package (Karlstrom et al., 2003) and the B3LYP DFT method. This method is a good compromise between accuracy and calculation speed and is widely used for *ab initio* calculations of relatively large molecules. In calculations of intermolecular interactions using G-types of basis sets one has to take into account the basis set superposition error (BSSE). This error arises from the fact that the basis sets used in calculations do not fully reflect the nature of the real atomic orbitals. Since the ANO-type basis sets more accurately reflect the nature of atomic orbitals, BSSE is much lower when ANO-type basis sets are used, and for large basis sets in DFT calculations it converges to zero. It was shown recently that the use of ANO-type orbitals for description of hydration interactions provides a low BSSE (Kocherbitov, Veryazov, & Söderman, 2007).

## 3. Results and discussion

### 3.1. Sorption isotherm

The sorption isotherm (presented as water activity dependence on water content) of xanthan gum is shown in Fig. 1a. In the same figure, the sorption isotherms of microcrystalline cellulose (MCC), ball-milled MCC and ball-milled recrystallized MCC reported previously (Kocherbitov et al., 2008) are shown. Xanthan gum is clearly most hydrophilic out of the four types of polymeric carbohydrates

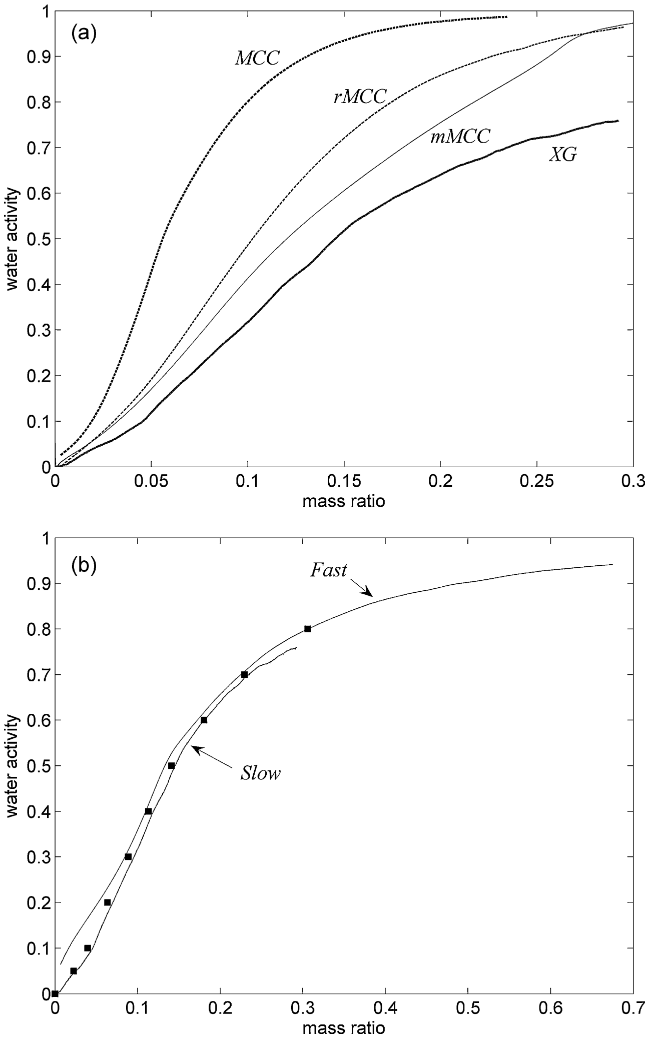

**Fig. 1.** (a) The sorption isotherms of microcrystalline cellulose (MCC), milled recrystallized MCC (rMCC), milled MCC (mMCC) and xanthan gum (XG). (b) The sorption isotherms of xanthan gum in a slow (lower curve) and fast (upper curve) calorimetric experiments together with gravimetric vapour sorption data (squares).

since it absorbs the highest amount of water at given humidity levels (about two and a half times more than the MCC does). This result may seem not surprising because xanthan gum contain ionic groups that can strongly interact with water, while the other three polymers are non-ionic. Below we will show however, that interactions of ionic groups of xanthan gum with water is not the main factor that determines its high hydrophilicity at low water contents. In Fig. 1b two sorption isotherms of xanthan gum obtained using different rates of water sorption are shown. For comparison, the results of gravimetric vapour sorption experiments (squares) are shown. The results of all three experiments are in good agreement, except for the region of lowest water contents, where the “fast” sorption isotherm deviates from both “slow” sorption isotherm and GVS data because of slow diffusion of water molecules in the glassy polymer at low water contents.

### 3.2. Enthalpy and entropy of hydration

The most important feature of the method of sorption calorimetry is its ability to measure the enthalpy of hydration simultaneously with the measurement of the sorption isotherm. The enthalpic characteristic of the hydration process measured in sorption calorimetric experiments is the partial molar enthalpy of mixing of water $H_w^m$, which for the sake of brevity can be called the enthalpy of hydration. In Fig. 2, the dependence of $H_w^m$ on the water to carbohydrate mass ratio is shown. According to this figure, the enthalpy of hydration of xanthan gum is not the most exothermic out of hydration enthalpies of the four polymers, but it lies between the hydration enthalpies of MCC and ball-milled MCC.

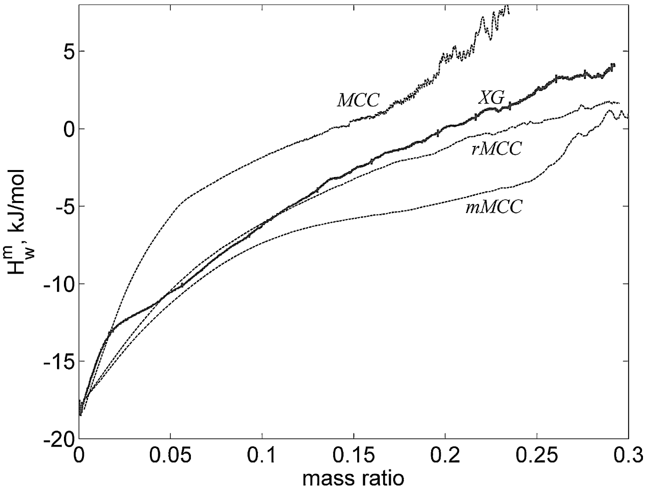

**Fig. 2.** The partial molar enthalpy of mixing of water with xantham gum (XG) and the same parameter for the three types of cellulose: microcrystalline cellulose (MCC), milled recrystallized MCC (rMCC) and milled MCC (mMCC).

The most striking feature of the enthalpy plot is found at water contents approaching zero. Remarkably, all four curves start from approximately the same point: −18 kJ/mol. This clearly contradicts the idea that the energy of interaction of water with a polyelectrolyte should be stronger than that with a non-ionic polymer. Strong water–polymer interactions is thus not the reason for high hydrophilicity of xanthan gum at water contents considered in this article.

Since the enthalpy of hydration alone cannot explain higher hydrophilicity of xanthan gum compared to the three types of cellulose, one should consider entropic contribution to the Gibbs energy of hydration. The partial molar entropy of mixing of water with xanthan gum $S_w^m$ is calculated according to the following equation:

$$TS_w^m = H_w^m - RT \ln a_w \qquad (2)$$

The dependence of $TS_w^m$ on water content is shown in Fig. 3. Comparison of entropy curves of xanthan gum and MCC shows that from a thermodynamic point of view, higher hydrophilicity of xanthan gum is caused by different reasons at different water contents. At low water contents, the enthalpy of hydration is almost identical for both polymers. The entropy of hydration is higher in case of xanthan gum, which leads to a lower water activity in the polyelectrolyte case. At water contents higher than 0.03, the situation is different. The entropy of hydration of xanthan gum is lower than that of MCC, which does not promote hydrophilicity of the former. However, this is overcompensated by lower enthalpy of mixing of xanthan gum compared to MCC (Fig. 2). In short, higher hydrophilicity of xanthan gum compared to MCC is caused by entropy at low water contents and by enthalpy at high water contents.

This behaviour may appear confusing, but it can be easily rationalised if one considers the number of available sorption sites in the two systems. MCC consists of microfibrils that have thickness of about 4 nm. The microfibrils have crystalline structure which prevents water from absorption inside them. Thus, water adsorbs only at interfaces between the microfibrils (Kocherbitov et al., 2008), therefore the number of sorption sites is relatively small. Xanthan gum does not have such crystalline structure, and the number of available sorption sites is higher. At low water contents when water

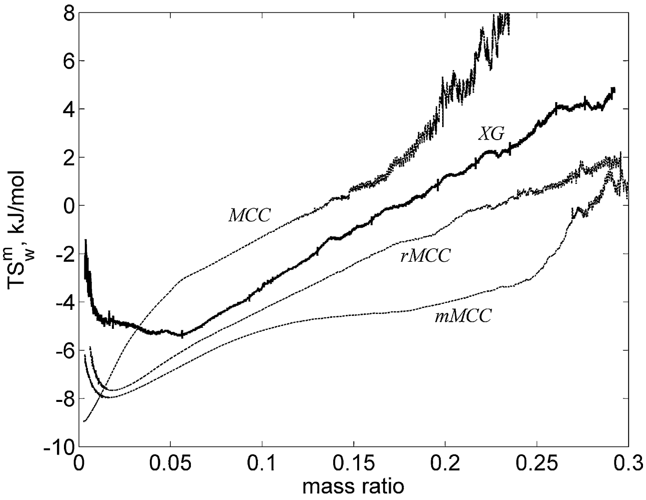

**Fig. 3.** The partial molar entropy of mixing of water with xantham gum (XG) and the same parameter for the three types of cellulose: microcrystalline cellulose (MCC), milled recrystallized MCC (rMCC) and milled MCC (mMCC).

molecules interact mostly with sorption sites but not with each other, one of contributions to the partial molar entropy of mixing of water can be expressed as follows:

$$S_w^m = -R \ \ln \frac{N_w}{N_{free}} \tag{3}$$

where $N_w$ is the number of absorbed water molecules, $N_{free}$ is the number of unoccupied sorption sites. Having the same number of absorbed water molecules, a higher number of free sorption sites leads to a higher hydration entropy. A higher number of sorption sites in xanthan gum compared to MCC means higher entropy of mixing and lower water activity at low hydration levels.

At high water contents when most of sorption sites of MCC are occupied and water–water interactions play a major role in the sorption behaviour of cellulose, the enthalpy of hydration of MCC increases and goes through zero ($H_w^m = 0$ means the same enthalpy as in liquid water). At the same water contents, xanthan gum still has enough free sorption sites to accommodate new water molecules, which produces negative values of $H_w^m$. A higher number of sorption sites in xanthan gum compared to MCC means lower enthalpy of mixing and lower water activity at high hydration levels.

### 3.3. Ab initio calculations

As it was above, at low water contents interactions of water with polyelectrolyte xanthan gum are not stronger than interactions with cellulose. The presence of charged groups in xanthan gum does not affect the hydration energy despite of the fact that water–ion interactions are expected to be strong. In order to explain this, we performed *ab initio* quantum mechanics calculations of interactions of ionic groups that present in xanthan gum. Since the only anionic groups of xanthan gum are carboxyl groups and typical counterions are sodium ions, we considered interactions of sodium acetate with water. The results are summarised in Table 1. The energy of interaction of a sodium acetate molecule with a water molecule is below −72 kJ/mol for both the first and the second molecules of water added to sodium acetate. This energy corresponds to interaction of sodium acetate and water in vacuum. In order to compare it with experimentally determined enthalpies of mixing, one has to add the enthalpy of evaporation of liquid water (44 kJ/mol). The obtained value of about −29 kJ/mol indicates that water–ion interactions are strong indeed. Nonetheless, they are not manifested in the hydration experiments, where the strongest interactions were −18 kJ/mol for both ionic xanthan gum and non-ionic cellulose.

To find the reason for this, we performed calculations of interactions of a sodium acetate molecule with a β-glucose molecule. Being a carbohydrate, xanthan gum consists mostly of sugar rings, most of which are glucose rings. In the absence of water, the ionic groups interact with glucose rings and these interactions have to be taken into account. The results of the calculations show that interactions of sodium acetate with glucose are at least as strong as those with water. The interaction energy of the particular configuration shown in Fig. 4 is about −81 kJ/mol, which indicates even stronger interactions than between sodium acetate and water. In the real dry xanthan gum there are of course many other conformations that have different energies, but this example shows that glucose rings can act as good solvents for ionic groups. Glucose rings contain hydroxyl groups that can solvate sodium ions as effectively as water molecules do. Therefore, the net result of hydration of ionic groups of xanthan gum includes not only formation of water–ion bonds, but also disruption of ion–glucose bonds. The values presented here indicate that the net result of hydration of ionic groups of xanthan gum should not involve large energy effects.

### 3.4. The Langmuir and the BET models

Experimentally measured sorption isotherms of natural polymers are usually analysed with various sorption models, such as BET (Brunauer et al., 1938) and GAB (Anderson, 1946; de Boer, 1968). When such models are used in an analysis of porous solids, the BET model provides quantitative information on the surface area of studied objects. In contrast, when the same and other models are used for description of water–biopolymer interactions, their use is normally limited to the fitting of experimental data. The water sorption isotherm of xanthan gum was for example analysed using 12 different models of sorption (Basu et al., 2007) but no attempt to relate the obtained fitting parameters with the physical properties of xanthan gum was presented.

Below we shall try to compare the use two classical models of sorption—the BET and the Langmuir models for description of water sorption by xanthan gum. The water sorption isotherm of xanthan gum has a so-called sigmoidal shape, i.e. the same shape as a BET sorption isotherm has, which may justify the application of the latter for the treatment of xanthan gum sorption data. The nature of the systems for which the BET model was designed is however different from the carbohydrate–water systems. The BET model assumes solid–gas interface where gas molecules are adsorbed on

**Table 1**
*Ab initio* results.

| System | n(Na-OH)[a] | Total energy (atomic units) | Solvation energy, kJ/mol | Solvation energy per n(Na-OH), kJ/mol |
|---|---|---|---|---|
| $H_2O$ | 0 | 76.4617075041 | – | – |
| Glucose | 0 | 687.4313817527 | – | – |
| AcNa | 0 | 390.9394520439 | – | – |
| AcNa + $H_2O$ | 1 | 467.4289199552 | −72.88 | −72.88 |
| AcNa + $2H_2O$ | 2 | 543.9180761558 | −144.94 | −72.47 |
| AcNa + Glucose | 1 | 1078.40171481 | −81.07 | −81.07 |

[a] *n*(Na–OH) denotes the number of OH groups of water or glucose in contact with the $Na^+$ ion.

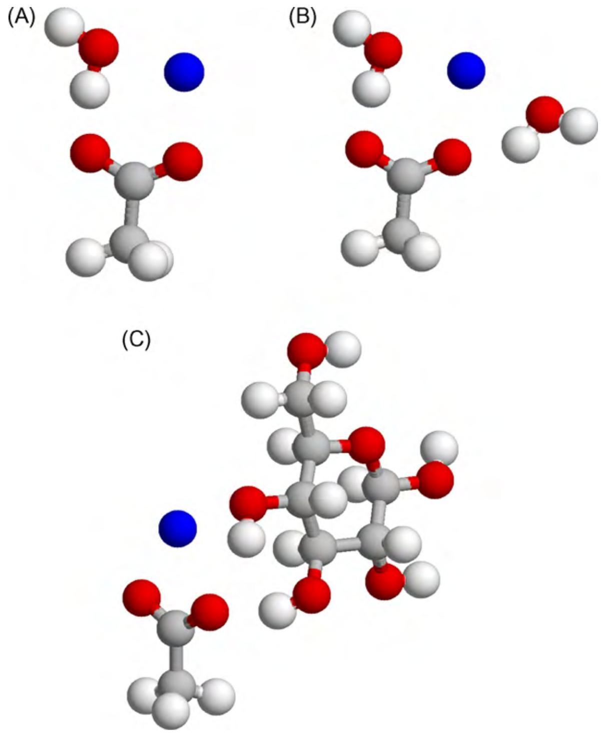

**Fig. 4.** Structures: a sodium acetate molecule with one (a) and two (b) water molecules; a sodium acetate molecule with a glucose molecule (c).

the solid surface and in addition, more gas molecules are adsorbed on those molecules, forming multilayers on the solid–gas interface. The amount of water adsorbed on the surface at a given water activity depends on the monolayer capacity $r_w^{\max}$ and a constant $C$ that describes the energy if interactions of the adsorbate and the surface:

$$r_w = r_w^{\max}\frac{Ca_w}{(1-a_w)(1-a_w+Ca_w)} \quad (4)$$

If the BET equation is used for characterisation of biopolymer–water interactions, then the monolayer capacity should have the meaning of the amount of water molecules that is able to adsorb on the existing sorption sites with 1:1 stoichiometry. The sorption sites in xanthan gum may be hydroxyl groups, or in particular their hydrogen atoms and oxygen electron pairs that can form hydrogen bonds with water molecules. The multilayers of the BET model would then correspond to water molecules adsorbed on water molecules adsorbed on the polymer OH groups.

Unlike the BET model, the Langmuir model postulates formation of only monolayers of adsorbate. It includes parameters that have similar meaning to those in BET model and it has the following form:

$$r_w = r_w^{\max}\frac{Ca_w}{1+Ca_w} \quad (5)$$

In contrast to the BET model, the Langmuir model allows only limited adsorption at $a_w = 1$ limit, and therefore it cannot reproduce the sigmoidal shape of the sorption isotherm. The main difference between the Langmuir and the BET model is that the former assumes that all adsorbate molecules adsorb on the adsorbent's sorption sites, while the latter assumes that a part of the molecules is adsorbed on pre-adsorbed adsorbate molecules. One can expect therefore that the fitting of the same experimental data will produce a greater number of the sorption sites in case of the Langmuir model compared to the BET model. Results shown in Table 2 confirm that this is the case. It is worth to note also that the constant $C$ has greater values when the BET equation is used. The logarithm of the constant is related to the free energy of adsorption, not to the enthalpy of adsorption (Kocherbitov & Arnebrant, 2010), therefore its comparison with $H_w^{mix}$ data cannot be used as a simple criterion of applicability of one of the models.

Recently we showed that for description of water sorption by microcrystalline cellulose, the Langmuir rather than the BET model should be used (Kocherbitov et al., 2008). The parameters of the Langmuir model for microcrystalline cellulose are shown in Table 2. Comparison of the parameters of the Langmuir model of xanthan gum and microcrystalline cellulose shows a large difference in the number of the sorption sites but a small difference in the free energy of interactions. This is in agreement with our observations of enthalpies and entropies of hydration of cellulose and xanthan gum. Application of the BET model indicates a lower number of sorption sites in MCC compared to xanthan gum and a higher free energy of interactions, which contradicts our enthalpy and entropy data. The free energy of sorption (related to the constant $C$) includes enthalpic and entropic contributions. The former is similar for both systems at low water contents, the latter includes a contribution from mixing (Eq. (3)). In principle, a greater value of $C$ in the BET case could be the result of the entropic contribution, but in order to achieve this, the number of sorption sites in xanthan gum calculated using the BET model should be higher than the number of sorption sites in MCC calculated using Langmuir model, which is not the case.

This comparison shows that application of the Langmuir model provides a better estimate of the monolayer capacity in xanthan gum. However, being mathematically more flexible, the BET model provides better fitting of experimental data. Moreover, the Langmuir model is more sensitive to the range of water activities where it is applied. Table 2 shows that at higher water activities the number of sorption sites calculated using the Langmuir model is significantly higher, while $C$ is lower. This fact has a simple physical meaning: at high water activities water adsorbs on wider range of sorption sites, including those with lower sorption energy, which is reflected by the value of parameter $C$.

It is of interest to compare the number of sorption sites calculated using sorption models with the structure of xanthan gum. A repeating unit of xanthan gum contains 29 oxygen atoms, most of them are highly hydrophilic OH or COO$^-$ oxygen atoms and can accept at least two hydrogen bonds. The number of hydrogen bond acceptors can thus be estimated as about 60. In dry xanthan gum, the polar oxygen atoms can form intramolecular bonds with OH hydrogen atoms and with counterions such as sodium. If water molecules are present in the system, they disrupt intramolecular hydrogen bonds and bind to the sorption sites. In this model, intramolecular hydrogen and ion-dipole bonds correspond to free binding sites, disrupted (hydrated) intramolecular bonds correspond to occupied sorption sites. Since every water molecule can donate two hydrogen bonds, the maximum number of sorption sites can be estimated as the number of hydrogen bond acceptors divided by two, i.e. it is close to the number of oxygen atoms in the monomeric unit. A comparison with Table 2 shows that this value is close to the number of sorption sites obtained from the Langmuir model at higher water activities. One should note that this value is

**Table 2**
Comparison of the Langmuir and the BET sorption models for description of water sorption isotherms of xanthan gum (XG) and microcrystalline cellulose (MCC). Letters *m* and *n* denote masses and moles respectively.

| | $m_w/m_x$ | $C$ | $n_w/n_x$ | $a_w$ range |
|---|---|---|---|---|
| Langmuir (XG) | 0.245 | 2.16 | 14 | 0.05–0.4 |
| Langmuir (XG) | 0.430 | 0.95 | 24 | 0.20–0.4 |
| BET (XG) | 0.086 | 7.64 | 5 | 0.05–0.4 |
| Langmuir (MCC) | 0.095 | 2.43 | – | 0.05–0.4 |

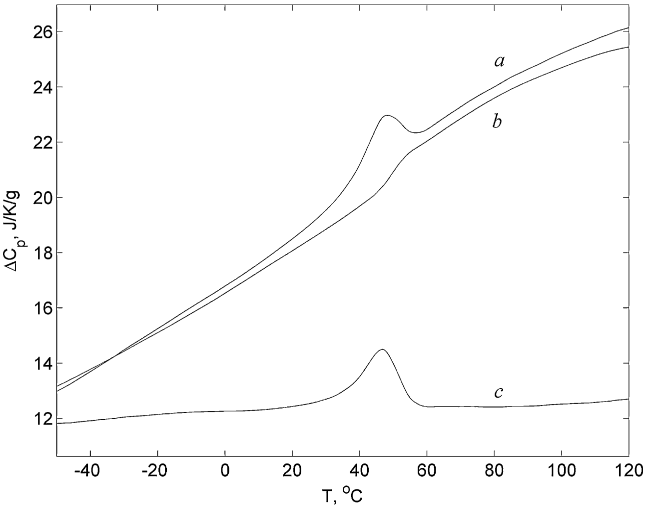

**Fig. 5.** DSC scan of xanthan gum–water mixture equilibrated at 53%RH. (a) The total heat flow, (b) reversing heat flow, and (c) non-reversing heat flow (shifted upwards by 12 J/K/g for illustrative purposes). The scan rate is 10 °C/min.

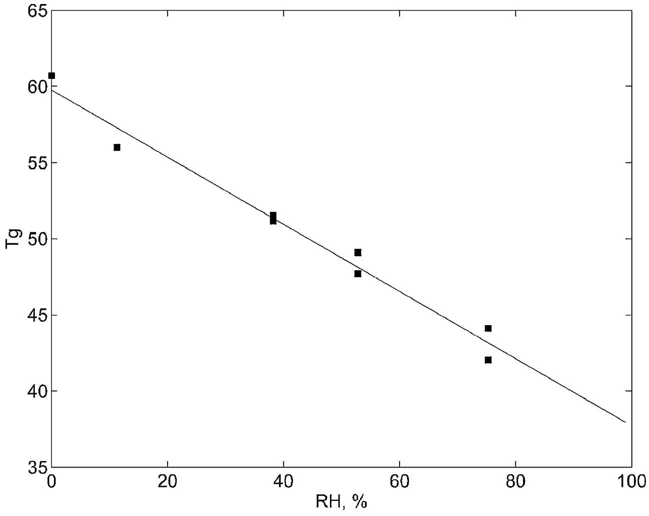

**Fig. 6.** Dependence of the glass transition temperature of xanthan gum on relative humidity.

related to semi-dry xanthan gum, not to the solution of xanthan gum. In a dilute solution, the number of polymer-water contacts should be estimated by addition of the numbers of hydrogen bond donors and acceptors.

## 4. DSC and the glass transition

Fig. 5 shows a typical DSC scan of a humid xanthan gum sample. The moisture was added to the sample by sorption of vapour from a saturated salt solution. The total heat flow curve has a maximum, therefore the transition might be interpreted as a first order phase transition. A similar transition in wet xanthan gum was reported before (Raschip et al., 2008), but the nature of the transition was not unambiguously determined. In the present work we used modulated DSC technique that allows separation of reversing and non-reversing heat flows in a DSC experiment. As one can clearly see from Fig. 5, the reversing heat flow has a step, not a peak at the temperature of the considered thermal event. The thermal event is thus a glass transition.

A similar thermal behaviour was observed in all samples obtained by sorption of water from vapours that have humidities below 80%. When the samples were saturated in vapours with higher humidities, the glass transition was not as clearly observed as in Fig. 5. We suggest that the reason for this is the release of molecular stress during equilibration process. At high humidity conditions the samples are not in the glassy but in the elastic (rubbery) state at room temperature which allows the samples to achieve a more equilibrium state compared to the glassy samples that can retain the molecular stress obtained during manufacturing process. In samples with high water contents, in addition to the glass transition, melting of ice at temperatures −10 to 20 °C was observed (data not shown).

The glass transition temperature of xanthan gum as function of relative humidity (water activity multiplied by 100%) is shown in Fig. 6. A linear dependence of glass transition on water activity is observed up to 75%RH. Water acts as a plasticizer, decreasing the glass transition temperature of xanthan gum from about 60 °C in the dry state to about 43 °C when the sample was equilibrated at 75% RH. At higher humidities however, one should not expect to find continuation of the linear dependence because at high humidities the uptake of water increases dramatically (Fig. 1). The dependence of $T_g$ on RH is therefore expected to be stronger at high humidities.

The DSC data show that dry xanthan gum is in the glassy state at room temperature. As it was shown in several calorimetric studies (Kocherbitov & Arnebrant, 2006; Kocherbitov & Söderman, 2004; Kocherbitov et al., 2004; Kocherbitov et al., 2008), sorption of water by glassy materials is accompanied by an exothermic heat effect. The heat effect is not strongly dependent on the presence of charged groups in the system and caused by release of the kinetic energy of water molecules that occur upon integration of water molecules into the solid matrix.

## 5. Conclusions

We have studied hydration of a natural carbohydrate polyelectrolyte xanthan gum using the method of sorption calorimetry. Comparison with our previously published data on microcrystalline cellulose, ball-milled cellulose and recrystallized cellulose shows that:

- At given levels of relative humidity xanathan gum absorbs more water than the cellulose does.
- The enthalpy of hydration of xanthan gum and all studied types of cellulose at zero water content is −18 kJ/mol.
- High energy interactions of water with ionic groups of xanthan gum are not seen in calorimetric experiments due to solvation of ions by hydroxyl groups of the carbohydrate (confirmed by *ab initio* calculations).
- A greater number of sorption sites in xanthan gum is the reason for its higher water sorption capacity.
- The Langmuir sorption isotherm provides a better estimate of the number of sorption sites in xanthan gum than the BET sorption isotherm does.
- As seen from DSC experiments, xanthan gum is in the glassy state at room temperature. The glass transition temperature of dry xanthan gum is 60 °C.
- The loss of the mobility of water upon absorption in the glassy material is the major contribution to the exothermic heat effect of sorption of water by carbohydrates.

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