Multitemperature fitting of isotherms as a simple method of insight into the thermodynamics of water sorption on building materials

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Water sorption on some building materials is studied. Based on three sets of experimental data, the usefulness of the generalised D'Arcy and Watt (GDW) model for simultaneous multitemperature fitting of isotherms is confirmed. The multitemperature data description not only reduces the number of best-fit parameters, but also makes it possible to analyse the thermodynamics of the process in a simple way. The values of the best-fit parameters are used for calculation of the isosteric enthalpy of sorption (representing the energetics of the process) and the entropy of the sorbed phase (which is connected with the degree of order/disorder). In the case of the studied samples of building materials, sorbed water at initial stages has low entropy and high degree of order. It probably forms a solid-like phase. For higher loadings the behavior of sorbed water is close to that of a liquid.

Key words building materials; water sorption; GDW model; thermodynamics of sorption

INTRODUCTION

Water sorption and desorption on building materials is still a subject of interest to different researchers [1-9]. Moisture is one of the most deteriorating factors of buildings. Moisture also affects many important properties of materials like thermal conductivity. Most building materials are hygroscopic, which means that they absorb water from the environment or desorb water to the environment until equilibrium conditions are reached [10]. Various mathematical models are used to describe sorption - desorption isotherms of water on building materials [8-12]. Sorption isotherms for different materials are usually described separately for each temperature value even if they are measured at different temperatures. It is also possible to describe isotherms for different temperatures simultaneously. The latter procedure (called multitemperature fitting) is often used in practice (see for example [10,13-16]) because it reduces the number of best-fit parameters. Multitemperature data description needs definition of the temperature dependence of the parameters for the sorption isotherm equation. Therefore, the models with strong thermodynamic bases should be favored [14,17]. However, very often, empirical relations are proposed [10,13,16,18] but this does not guarantee thermodynamic correctness. Researchers applying the multitemperature

isotherms fitting usually do not utilize the additional possibility given by this procedure enabling calculation of the isosteric enthalpy of sorption without the need to generate isosteres [17, 18]. The isosteric enthalpy of sorption is related to the energetic state of a sorbed molecule and may be interpreted as the energy released during the sorption of one mole of water (at constant loading) or the energy required for desorption of one mol of water. So the multitemperature isotherms description may be regarded as a simple method of insight into the energetics and thermodynamics of the water sorption process.

The major aim of this communication is to check the applicability of the generalised D'Arcy and Watt model (GDW) [19] to simultaneous multitemperature description of water sorption isotherms on a few building materials. The obtained values of the best-fit parameters are applied for calculating the isosteric enthalpy of sorption. The differences in entropy between sorbed and bulk water molecules are also calculated, basing on fundamental thermodynamic relations. Finally, the mechanism of water sorption and the thermodynamics of the process are discussed.

MATHEMATICAL MODEL

The GDW model assumes a two-step mechanism of a sorption process [19]. At the first step, water molecules are bound by primary sorption sites. Each of these sites can bind only one molecule. The concentration of these sites depends on the nature of the sorbent surface. Water

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molecules bound on the primary centres become secondary sites and are thus able to sorb subsequent molecules. One molecule sorbed on the primary centre may create one secondary site as it is assumed in the Brunauer-Emmett-Teller (BET) [20] or the Guggenheim-Anderson-de Boer (GAB) model [21-23] but the GDW model is an approach that allows assuming any ratio of sorption on the primary and secondary centres [12]. This gives possibility for a better description of real sorption isotherms. In this case, the ratio of sorption on the secondary and primary sites is usually different from unity [24,25]. The mathematical representation of the GDW model is [26]:

$$M = \frac{m_0 K a_w}{1+K a_w} \times \frac{1-k(1-w)a_w}{1-k a_w} \qquad (1)$$

where M is the equilibrium moisture content, a_w is the water activity (i.e. the ratio of the equilibrium vapor pressure to the saturated vapor pressure at a given temperature), m_0 is the concentration of the primary sorption sites (this parameter may be also interpreted as the monolayer capacity), K and k are the kinetic constants connected with sorption on the primary and secondary centres, and w is the parameter determining the ratio of molecules bound to the primary centres and converted into secondary ones.

It is worth noting that the GDW model was previously successfully used for fitting water sorption isotherms on different sorbents [16,26-31], including building materials [9,12].

As mentioned above, the multitemperature fitting of sorption isotherms needs definition of the temperature dependence of the model parameters. In the case of the GDW model, the monolayer capacity (m_0) and the w parameter are temperature independent [17]. The kinetic parameters (K and k) depend on temperature according to the basic thermodynamic formulas [17]:

$$K = K_0 \exp\left[\frac{Q}{RT}\right] \qquad (2)$$

$$k = k_0 \exp\left[\frac{q}{RT}\right] \qquad (3)$$

where K_0 and k_0 are almost temperature independent pre-exponential factors, Q and q are the enthalpies of sorption on primary and secondary sites, respectively, and R is the universal gas constant.

The isosteric enthalpy of sorption connected with the GDW model is defined by the equation [32]:

$$q^{st} - L = \frac{\dfrac{K}{(1+K a_w)^2} \times \left(1+\dfrac{wk a_w}{1-k a_w}\right) \times Q + \dfrac{K a_w}{1+K a_w} \times \dfrac{wk}{(1-k a_w)^2} \times q}{\dfrac{K}{(1+K a_w)^2} \times \left(1+\dfrac{wk a_w}{1-k a_w}\right) + \dfrac{K a_w}{1+K a_w} \times \dfrac{wk}{(1-k a_w)^2}}$$

$$(4)$$

where L is the enthalpy of water condensation.

THERMODYNAMICS OF SORPTION

It is well known that the difference in Gibbs free energy between sorbed water and bulk gaseous water is given by the basic thermodynamic equation [33]:

$$\Delta G = RT \ln a_w \qquad (5)$$

On the other hand, there are two factors whose balance determines the changes in free energy: enthalpy (ΔH) and entropy (ΔS):

$$\Delta G = \Delta H - T\Delta S \qquad (6)$$

The difference in enthalpy between sorbed and bulk phases is related to the isosteric enthalpy of sorption/desorption:

$$\Delta H = -q^{st} \qquad (7)$$

The negative sign is a consequence of the signing convention. Combining of Eqns. (5)-(7) allows calculating the difference in entropy between water sorbed in a building material and bulk water:

$$\Delta S = -\frac{q^{st}}{T} - R \ln a_w \qquad (8)$$

EXPERIMENTAL DATA AND THEIR FITTING

Three sets of desorption isotherms (measured at different temperatures) taken from the literature are used. These isotherms are for: (a) concrete (at $T = 293$, 318, 330.5 and 343 K) taken from [11,34], (b) brick (at $T = 288$, 298 and 308 K) taken from [10], and (c) plaster (at $T = 288$, 298 and 308 K) taken from [10].

Experimental data sets were fitted by the GDW model (Eqns. (1)-(3)) using the genetic algorithm proposed by Storn and Price [35], which was previously successfully applied for the description of different experimental data – see for example [19,26]. The applied fitting procedure was described previously [32]. m_0, K_0 (formally $\log K_0$), k_0 (formally $\log k_0$), Q, q, and w are the best-fit parameters. The goodness of fit for isotherms at each temperature is estimated using the determination coefficient defined as:

$$DC_T = 1 - \eta_T \qquad (9)$$

where

$$\eta_T = \frac{\sum_i \left(M_{t,i} - M_{o,i}\right)^2}{\sum_i \left(M_{o,i} - \overline{M}_o\right)^2} \qquad (10)$$

$M_{o,i}$ and $M_{t,i}$ are the observed and the theoretically calculated moisture contents for the *i*-th experimental point and $\overline{M}_o$ is the average observed moisture content. The global parameter defining the quality of the fit for the bunch of isotherms is defined as:

$$DC = 1 - \sqrt{\frac{\sum_T \eta_T^2}{NT}} \qquad (11)$$

where *NT* is the number of considered temperatures.

RESULTS AND DISCUSSION

Table 1 collects the values of the best-fit parameters obtained from the multitemperature description of the considered data sets by the GDW model (Eqns. (1)-(3)).

Additionally, Fig. 1 shows the graphical representation of the obtained results. Generally, the fit quality is very good, as proven by the high values of the determination coefficients. This confirms the usefulness of the GDW model for the simultaneous multitemperature description of water sorption on building materials.

The obtained values of the best-fit parameters give some insight into the mechanism of the sorption process. The obtained monolayer capacities (m_0) correspond to the values which may be estimated directly from the isotherms plots. One can also see that the values of enthalpy connected with sorption on the primary sites (*Q*) are high, while those connected with the secondary sites (*q*) are close to zero. The high values of *Q* confirm the hydrophilic character of the considered materials, i.e. the high energy of interaction between water

molecules and their surface. On the other hand, if water molecules are sorbed on the second and higher layers, the H_2O–H_2O interactions are of major importance. Thus, the values of *q* are close to zero (formally, enthalpies in Eqns. (2) and (3) are not absolute values, but they are reduced by the enthalpy of water condensation). It is also interesting that the values of the *w* parameter for all studied samples are lower than 1. This means that not all water molecules sorbed on the primary centres convert into secondary ones. The reason may be steric effects (see Fig. 2 in [17]). Fig. 2 presents the plots of isosteric enthalpy of sorption and of the differences in entropy between sorbed and bulk water. They were calculated on the basis of the obtained values of the best-fit parameters (Table 1) and Eqns. (4) and (8). One can see that the shape of the plots is qualitatively similar for all the samples. The behavior of the isosteric enthalpy of sorption reflects the differences in energetics of sorption on the primary and secondary sites. The q^{st} has high values for small loadings ($M < m_0$) and it decreases as the monolayer is filled, reaching values close to the enthalpy of condensation for the multilayer sorption ($M > m_0$). The highest enthalpy of sorption on the primary centres is observed for the plaster. This is connected with the most pronounced temperature dependence of isotherms for this material (one can wrongly conclude that the influence of temperature is higher for concrete, but the observed changes are caused by the higher differences in temperature).

On the other hand, the shapes of the entropic plots reflect the changes in the degree of order of the sorbed phase. The decrease in entropy of sorbed water in comparison to the gas phase is the highest for small loadings (below monolayer filling). For higher loadings (multilayer sorption) the entropy increases and reaches similar values for all samples

Table 1 Values of the best-fit parameters obtained from the fitting of the studied experimental data by the GDW model (Eqns. (1)-(3)).

Sample	m_0 [%]	K_0	k_0	Q [kJ/mol]	q [kJ/mol]	w	DC_T [*)]	DC
Concrete	2.32	2.73×10^{-6}	0.696	37.2	~0	0.536	0.973 0.986 0.973 0.976	0.977
Brick	0.366	1.17×10^{-6}	0.463	36.9	1.84	0.464	0.995 0.996 0.997	0.996
Plaster	1.01	6.97×10^{-14}	0.223	81.1	3.37	0.484	0.980 0.984 0.975	0.979

[*)] – the values are arranged according to the rise in temperature

($\Delta S \approx -150$ J/mol/K). The difference in standard entropy between liquid water and water vapour is equal to -119 J/mol/K [36]. Thus, the obtained results suggest that water sorbed in the multilayer has a slightly higher degree of order than liquid water. In the case of water bound in the monolayer, its entropy is lower. This suggests a high order of the initially sorbed molecules. The high energy of interaction with the surface and the loss of degrees of freedom may suggest formation of quasi-solid state of water sorbed in the monolayer.
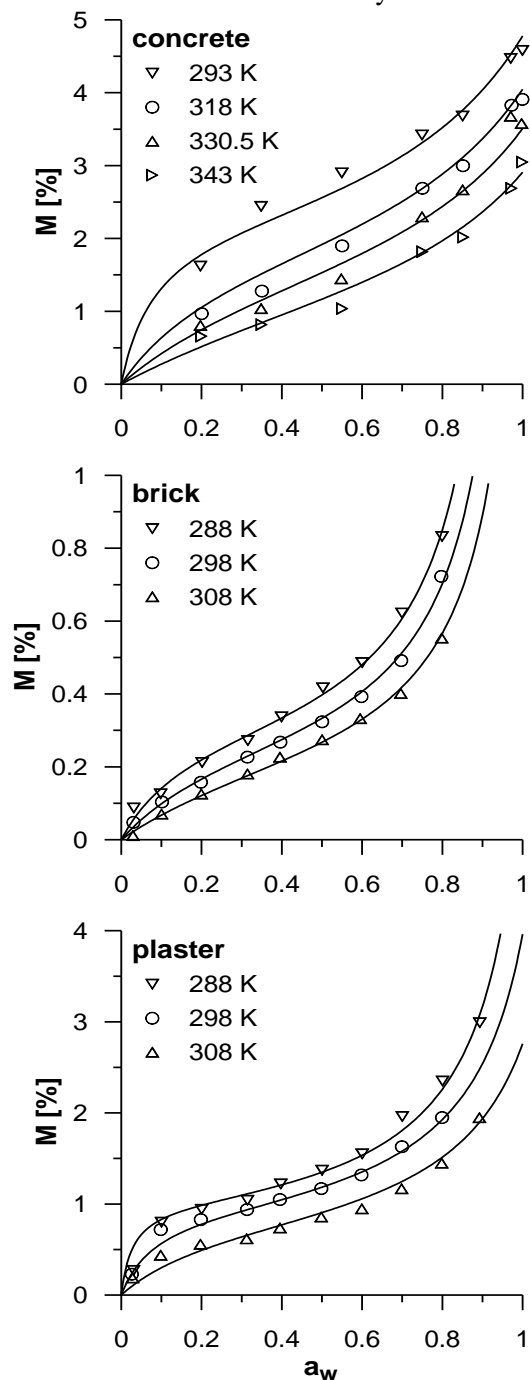

Fig. 1. Results of the simultaneous mutlitemperature fitting of desorption isotherms by the GDW model (Eqns. (1)-(3)) for all the studied experimental data sets.

CONCLUSIONS

The presented results confirm the usefulness of the GDW model for simultaneous multitemperature description of water sorption isotherms on building materials. The multitemperature fitting not only reduces the number of best-fit parameters, but it also makes it possible to analyse the thermodynamics of the process in a simple way. The obtained values of the best-fit parameters allow calculating the isosteric enthalpy of sorption (representing the energetics of the process) and the entropy of the sorbed phase (connected with a degree of order). In the case of the considered samples of building materials, similar qualitative behavior is observed. Sorption of water at low activities takes place on high-energetic surface sites and the enthalpy is high. Initially bound H_2O molecules exhibit a high, even solid-like degree of order. In the next stages, molecules are mainly sorbed due to H_2O–H_2O interactions. Thus, the enthalpy of sorption reaches values close to the enthalpy of water condensation. Entropy of H_2O bound in the multilayer is close to the entropy of liquid water, so the packing of these molecules is similar to that of the liquid phase.

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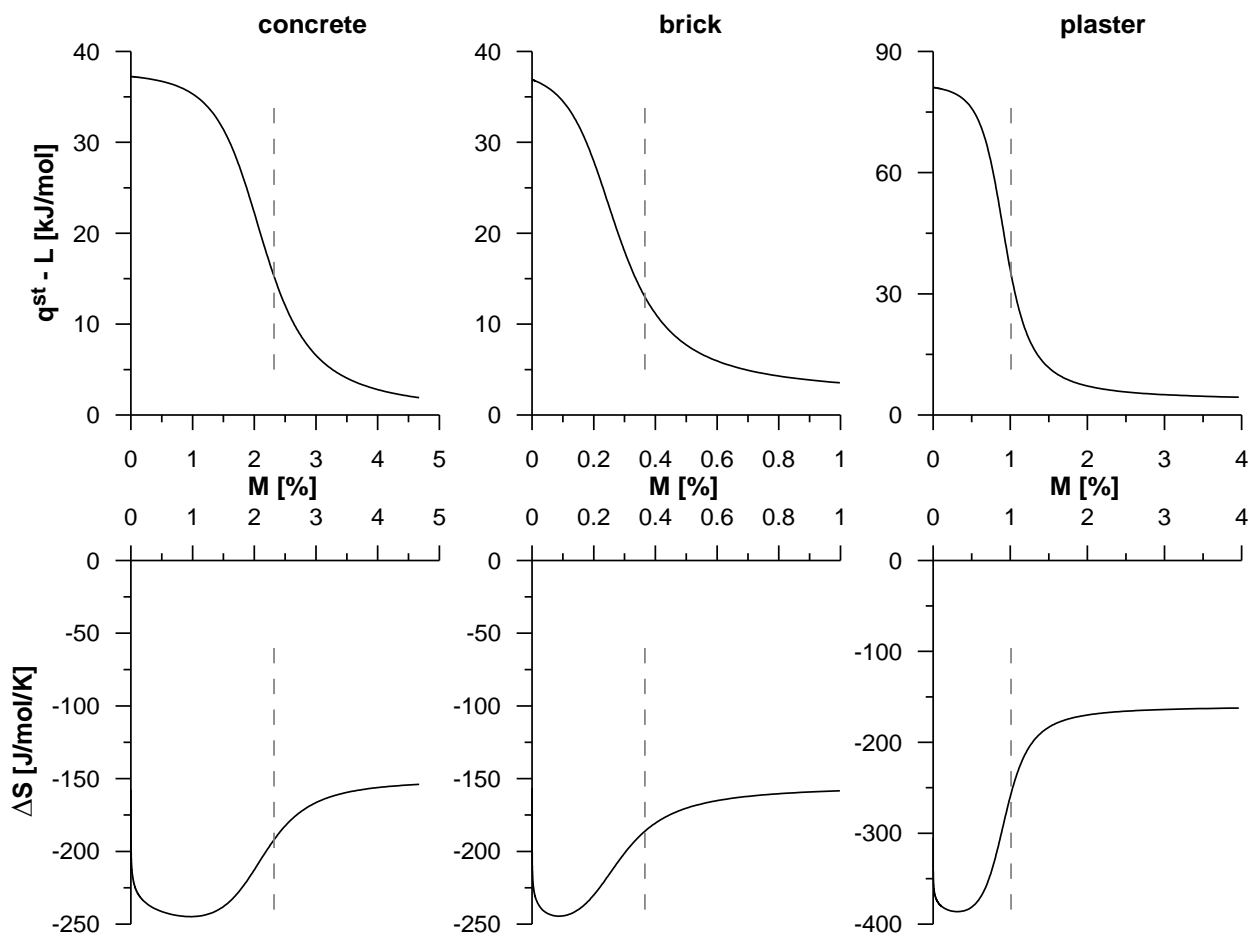
Fig. 2. Plots of isosteric sorption enthalpy and related difference in entropy for water desorption on the studied materials. The data are generated for T = 298 K by Eqns. (4) and (8). The dashed lines represent the monolayer capacities (see Table 1).

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МНОГО-ТЕМПЕРАТУРНО НАПАСВАНЕ НА ИЗОТЕРМИ КАТО ПРОСТ МЕТОД ЗА ИЗУЧАВАНЕ НА ТЕРМОДИНАМИКАТА НА СОРБЦИЯТА НА ВОДА В СТРОИТЕЛНИ МАТЕРИАЛИ

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(Резюме)

Изследвана е сорбцията на вода в някои строителни материали. Потвърден е обобщен модел на D'Arcy и Watt (GDW) за едновременното напасване на изотермите на базата на три групи от експериментални данни. Много-температурното описание на опитните данни не само намалява броя на търсените параметри, но и позволява простия анализ на термодинамиката на процеса. Стойностите на най-добрите параметри са използвани за пресмятане на изостеричната енталпия на сорбция (представляваща енергетиката на процеса) и на ентропията на сорбираната фаза (свързана със степента ред/безпорядък). При изследваните проби от строителни материали сорбираната вода в началото има ниска ентропия и висока степен на порядък, вероятно заради формирането на твърдо-подобна фаза. При високи натоварвания сорбираната вода се отнася повече като течна.