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Modeling the influence of temperature on the water vapor sorption by colloidal disperse systems

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Abstract. The influence of temperature on sorption isotherms of water vapor in colloidal disperse systems is investigated in subsoils and natural materials. A new simple mathematical model has been developed for the estimation of the influence of temperature on water sorption isotherms as an alternative approach to Polanyi potential theory that was not able to fit the experimental data

1. Introduction

The relationship between atmosphere relative humidity (**rh**) and equilibrium humidity of a material (**W**) at constant temperature can be displayed graphically by a curve, the so-called water sorption isotherm (**SI**). Usually SI of soils, subsoils, food products, natural and synthetic materials and other colloidal disperse systems are determined at room temperature [1-7]; less often such definitions are carried out at several temperature levels [7-10]. Many known fundamental (Langmuir-type: BET, GAB, MBET, Van-der-Waals, Ion-electrostatic by Deryagin, etc) and empirical (Smith, Caurie, Ferro-Fontan, Oswin, Henderson, Lewicki, Peleg, Polynomial, Double Log Polynomial, etc) models are developed to describe typical S-shaped isotherms [1, 3, 7, 10-13], but none of these models can predict the response of sorption isotherms to temperature changes. However, some studies show that lowering the temperature causes an increase in adsorption and vice versa: at elevated temperatures water vapor adsorption is reduced. [7, 9, 12]. Although a theoretic basis for this effect is quite understandable there are no practical models, with the exception of Dubinin-Polanyi potential theory, that may give us its quantitative estimation [7, 14].

   The aim of our study was to verify the possibility of Polanyi potential theory for a quantitative description of the influence of temperature on sorption isotherms and to develop a new model with the use of proposed early equation [11] for simplified estimation of water vapor sorption by colloidal disperse systems based upon a concept of molecular interactions in these systems.

2. Materials and methods

The main theoretical method for this study was mathematical modeling using the potential theory of Polyani and alternative author's model. For the realization of this approach literature data on the

relationship between SI and temperature in polydisperse capillary porous materials: birch wood, montmorillonite clay and bony (shale) coal from Borovichi deposition (58° 23' 16" N; 33° 54' 55"E) were used from the monograph [13]. It is well known that Dubinin-Polanyi theory is usually applied to nonpolar adsorbents such as activated carbon. But it was also successfully applied to such sorbents as zeolites, silica, metal-organic frameworks to adsorb water vapor from moderate to higher water uptakes [7]. Therefore, we have chosen different materials to test the applicability of this theory.

The methodology for assessing the effect of temperature factor on sorption isotherms was as follows. According Dubinin-Polanyi theory the adsorption potential (ψ_a, [J/mol]) as a quantitative characteristic of field of adsorption force is introduced which is equal the work involved when the volume of one mole of gas is compressed from equilibrium pressure P to saturated pressure P_0 at constant temperature. This potential may be also considered as the work that involved when one mole of adsorbed substances displaces from infinitely distance to the surface of adsorbent. It is obvious that such work for the ideal gaseous adsorbate can be represented in the form (1), as for ideal gas $P/P_0 = rh$ [10]:

$$\psi_a = RT \ln\left(\frac{P_0}{P}\right) = RT \ln\left(\frac{1}{rh}\right) \tag{1}$$

where T – absolute temperature [K], $R=8.31$ J/(mol K) – universal gas constant.

Adsorption potential put in correspondence with the pore volume, where condensation of water vapor V_a, [m^3/mol] takes place, that was determined as:

$$V_a = W \frac{M_\ell}{\rho_\ell}, \tag{2}$$

where $M_\ell = 0.018$ kg/mol – molecular mass and $\rho_\ell = 1000$ kg/m^3 – density of liquid water. V_a as a function of ψ_a is the characteristic Polanyi curve and according Polanyi theory it is considered to be temperature invariant dependency [10, 14]. Consequently constructing a typical characteristic Polanyi curve with the use of (1) and (2) it is possible to make SI corresponded to other temperature, taking into consideration following equations [10]:

$$V_a = W(T)\frac{M_\ell}{\rho_\ell(T)} = W(T_{st})\frac{M_\ell}{\rho_\ell(T_{st})}$$

$$\psi_a = RT \ln\left(\frac{P_0(T)}{P(T)}\right) = RT_{st} \ln\left(\frac{P_0(T_{st})}{P(T_{st})}\right), \tag{3}$$

where index «st» is related to parameters of standard SI

Our statements are quite similar to Polanyi ones that sorption of water vapor in porous colloidal dispersed systems is due to action of energetic field of adsorbent and practically all adsorbed water molecules are in liquid state. The SI model was developed by using the modified Van der Waals equation for molecular interactions and the Dubinin-Polanyi theory for the adsorption potential [11]. From the Van der Waals equation, the dependence of the molecular vapor pressure (P [Pa]) on the concentration (C [mol/m^3]) looks as:

$$P = \frac{CRT - aC^2 + abC^3}{1 - bC}, \tag{4}$$

where a [Pa·m^6·mol^{-2}], b [m^3/mol] – modified Van der Waals parameters reflecting the interaction of vapor molecules (attractive and repulsive forces) in energetic field of colloidal disperse system. In the first linear approximation, the adsorption (adsorbed water content W [kg/kg]) should be proportional to the pressure of the adsorbate ($W=K_G P$, K_G [] is Henry's constant). Taking into account that $C=rh \cdot C_0$, where C_0 is the concentration of saturated water vapor, we obtain the following model of SI [11]:

$$W = \frac{n(rh) - m(rh)^2 + k(rh)^3}{1 - p(rh)}, \tag{5}$$

where $n = K_G C_0 RT$, $m = K_G a$, $k = K_G ab C_0^3$, $p = bC_0$ are physically reasonable dimensionless parameters.

The simplify variant fitting for essential range $0 < rh \leq 0.98$, that is usually used for SI analysis is written as third degree polynomial function [11]:

$$W = n(rh) - m(rh)^2 + k(rh)^3, \tag{6}$$

Graphic curves of SI were reproduced on the base of experiential data and models with the use of Microsoft Office Excel 2007 electronic tables. Experimental data were approximated using the built-in algorithm of nonlinear regression «Regression Wizard» in Sigma Plot 9 version software. All obtained parameters were statistically significant at the level of $p < 0.001$ with high reliability ($R^2 > 0.99$), and small standard error ($s = 0.005 - 0.038$ units of rh) of approximation.
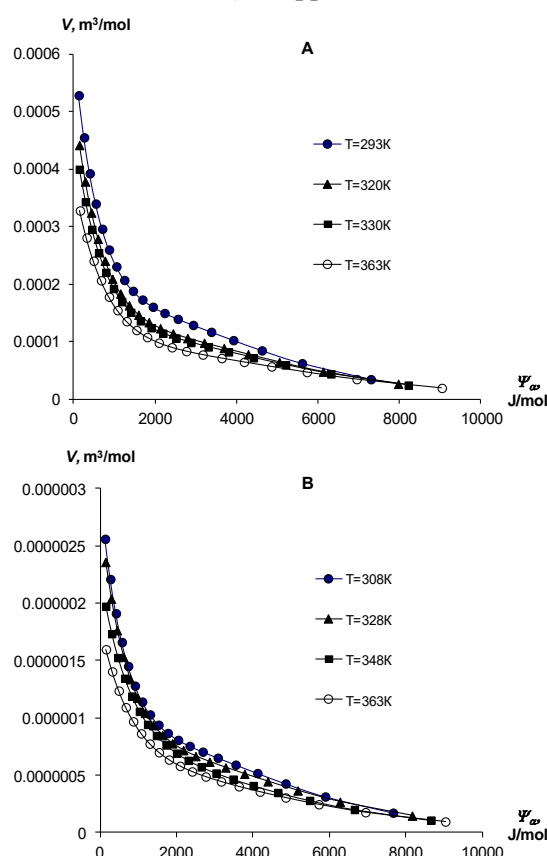

Figure 1. Polanyi characteristic curves for wood (A) and clay (B) based on data [13].

3. Results of study

The verification of the capability of Dubinin-Polanyi potential theory for the estimation of the temperature effect on SI in the case of studied polydisperse capillary porous materials did not give positive results especially for polar sorbents with hydrophilic surface. Typical characteristic Polanyi curves calculated on the base of experimental SI data at various temperature are shown in the Figure 1. These curves are not invariable ones and display strong dependence on the temperature, so the estimation of the influence of temperature on SI based on Dubinin-Polanyi potential theory is not correct here.

We propose an alternative approach used the model (6) that is based on a modified Van-der-Waals equation for gas phase in which the transformation of gas phase into fluid phase is caused by force field of the adsorbent surface [11]. In this approach the energy of molecular interactions is considered

to be equal to energy of thermal motion of molecules RT, that means the thermodynamic equilibrium in studied hetero-phase system as distribution of molecules between solid, fluid and gas phases at given temperature. From a theoretical point of view it might seem that a decrease of temperature, that is equal to a decrease of molecular-kinetic energy, leads to an increase of adsorption and condensation (ratio of bonded molecules). On the other hand an increase of temperature and thus the thermal velocity of molecule motions leads to the escape of molecules bonded by surface forces with adsorbent into gas phase, that means a decrease of adsorption under the same relative humidity (rh). Using reduced version of SI model as polynomial form (6) and above-mentioned theoretical statements let's try to find the relationship between SI and temperature.

SI obtained at room temperature 20°C (293K) or neighbor temperature of the experiment ($T=T_{st}$) was taken as standard. In this case, SI is going to be higher than the standard curve under temperature $T<T_{st}$ and below it under $T > T_{st}$. When the temperature reaches the critical value $T=T_{cr}$, the water content of adsorbent will be equal 0 ($W=0$), because all molecules having critical energy will be desorbed. It should be mentioned that according classical experiments [15] observed for soil colloids, the temperature 100°C (373K) does not guaranty the total soil dehydratation at the least the colloidal part of soils. That means that the procedure of drying till «an absolute dry state» at 105°C widely used in soil and material science is rather formal one [14]. From thermodynamic point of view this fact is quite obvious because the temperature 100°C is the critical temperature of liquid water vapor phase transition only for unbounded water molecules. The decrease in energy due to bonding of molecules during physicochemical processes leads to a decrease of the freezing point and an increase of the boiling temperature of bound water that provides the basis for well-known cryoscopic and ebullioscopic methods of thermodynamic potential determination [7, 10]. By all appearances, every hetero-phase system depending on a degree of dispersion (surface energy) has own critical temperature (T_{cr}), under which all bound water would be removed. For soil colloidal system this temperature can reach 400–500°C, as was shown in [14, 15].

Quantitative estimation of described above theoretical statements on the influence of temperature on SI may be given by multiplying the right part of equation (6) on the dimension less factor: $\left[1-\dfrac{(T-T_{st})}{(T_{cr}-T_{st})}\right]$. As a result, the model which permits to describe SI in the range $0 \leq rh \leq 0.98$ depending on temperature in contrast to isothermical variant (6) looks as:

$$W(T,rh) = \left[1-\frac{(T-T_{st})}{(T_{cr}-T_{st})}\right] \cdot \left(m(rh) - n(rh)^2 + k(rh)^3\right). \qquad (7)$$

If $T = T_{cr}$, the dimension less factor in square brackets will be reduced to 0 (1–1=0) and thus, $W(T,rh) = 0$. When $T = T_{st} = 293K$, this factor will be equal to 1, because a numerator in the fraction ($T = T_{st} - T_{st}$) is equal to 0, and function $W(T,rh)$ represents «standard» isotherm, obtained at the temperature of experiment $T = T_{st.}$. If $T<T_{st}$, a numerator $(T - T_{st})$ will take negative values, and the factor in square brackets will take a value >1, that means the promotion of adsorption. Otherwise if $T > T_{st}$, the factor will be <1, that means a decrease of adsorption. A unique «fitting» parameter, responsible for the shift of SI above or below the «standard» SI at given temperature is index of critical temperature varying in the range of $100 \leq T_{cr} \leq 500$°C ($373 \leq T_{cr} \leq 773K$). In such a manner rather simple model (5) based upon the known «standard» IS, obtained experimentally at room temperature, allows to predict a response of vapor sorption on the temperature change in the hetero-phase physical system.
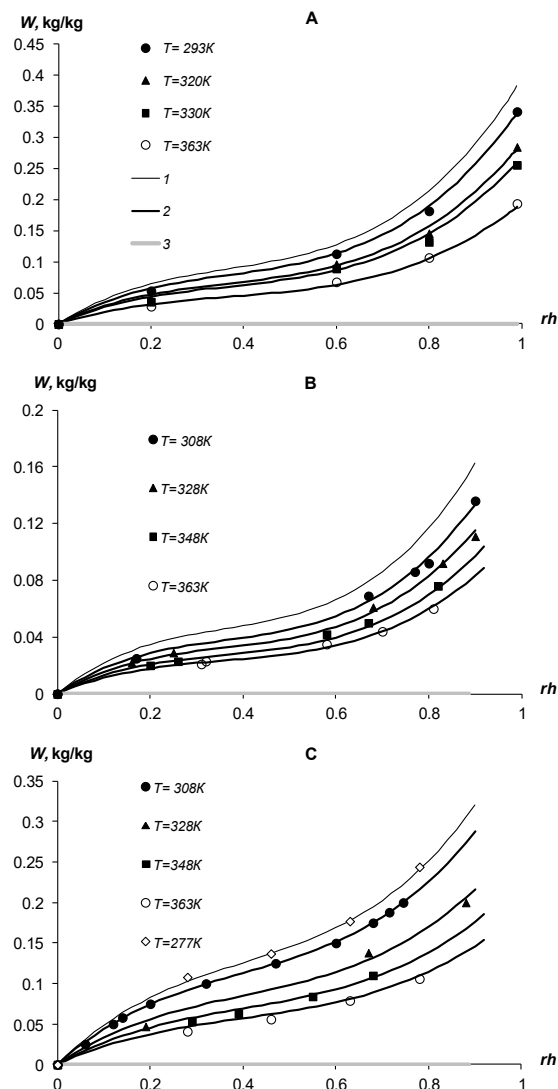
Figure 2. Modeling the influence of temperature on SI in colloidal disperse systems.
A – wood, T_{st} = 293K, T_{cr} = 450 K, **B** – clay, T_{st} = 308K, T_{cr} = 453 K, **C** – bony coal T_{st} = 308K, T_{cr} = 435 K; symbols are real data [13], curves – model (7): 1– T=273K, 2 – variable temperatures, 3 – T = T_{cr}.

Given approximated equations (6) for «standard» temperatures:
A. W=0.4319 rh – 0.8894 rh^2 + 0.8077 rh^3, R^2 =0.999;
B. W=0.2139 rh – 0.4229 rh^2 + 0.3729 rh^3, R^2 =0.999;
C.. W=0.5191 rh – 0.8894 rh^2 + 0.7418 rh^3, R^2 =0.999.

As we can see from the Figure 2, curves that are counted according to the standard SI fit experimental symboled points so our model works quite adequately. As standard, SI for wood at 293K, and for clay and bony coal at 308K were chosen Fitting parameters in term of critical temperatures were 450K (wood), 453K (clay) and 435K (coal). At this the absence of adsorption (zero moisture) was shown at critical temperatures as it follows from the formula (5). Unfortunately, there are no data on sorption at temperatures below than standard ones in [13], except the data for shale peat at a temperature of 277 K. To illustrate the capability of the model (5) the calculation of SI at temperature 277K was performed. This SI is predictably located above «standard» curves (thin line in Figure 2).

All that shows that proposed model (5) is quite suitable for the description of the influence of the temperature factor on SI in colloidal disperse systems and may be considered as an alternative to calculated data obtained with the use of Polanyi potential theory.

4. Conclusions
Calculations of water vapor sorption isotherms on the basis of the potential theory of Dubinin-Polanyi do not give satisfactory results to describe the effect of the temperature on the water vapor sorption in colloidal-dispersed porous systems, represented by polar sorbents with hydrophilic surface.

The alternative is a simple mathematical model of molecular interactions based on the modified Van der Waals equation and containing, along with the variables of relative humidity and air temperature, a critical temperature parameter at which the surface adsorption becomes impracticable.

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