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Modelling of water adsorption–condensation isotherms on beds of nanoparticles

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HIGHLIGHTS

- An adsorption–condensation model was developed.
- This new model is applicable for non-porous and spherical particles.
- Good match between theory and the experimental results.
- Influence of particles diameter, bed porosity and variation of the model constants were studied.
- Particle diameter is the key parameter for the determination of this model.

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ABSTRACT

In this paper, the multimolecular adsorption equation (so-called GAB equation) was modified by adding an amount of condensed water between the particles. This new model was then compared with experimental results obtained on three nanostructured powders of different nature: zinc, amorphous carbon and zinc–aluminium obtained from metallisation fumes. The influence of the particle diameter, the porosity of the sample and the importance of the determination of the GAB constant for the new equation were all studied. We found that the new model corresponds well with experimental data on almost all the range of water activity and thus increases the range of the GAB equation. Finally, the new developed model only uses three fitted GAB parameters and does not require additional adjusting parameters.

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1. Introduction

In recent years, there has been much interest in industrial and research development in the field of nanomaterials. Because of this fast development (e.g., in the metallisation process), a growing part of the population is exposed to this fine and ultrafine particles. While the biological and physico-chemical properties of such fine and ultrafine particles are the subject of numerous scientific publications, there remains a lack of data on the potentially induced toxicological risks.

Institutions use collective protection equipment that relies on, for example, containment or functioning in depression in order to protect people exposed by these particles. These institutions often use High Efficiency Particulate Air Filters (HEPA) placed in the circuits of general ventilation. Almost all the available data corresponds to modes with ambient air (ambient temperature and humidity) but some exceptional conditions of use may result in a high-moisture environment. This is the case with fire where large amount of fumes will trigger anti-fire devices and increase the relative humidity of the air (e.g., fire in a nuclear facility; Mocho and Ouf, 2011). The HEPA filters used in collective protection systems must therefore continue to perform their role even in these extreme conditions.

Laboratory measurements have shown that the presence of moisture greatly modified the behaviour of filters in terms of efficiency and pressure drop (Gupta et al., 1993). Previous studies also indicated that the interaction between particles and water vapour must be taken into account when interpreting the mechanisms which modify the pressure drop of pre-clogged filters in the presence of moisture (Joubert et al., 2010). Indeed, the phenomena governing the variation of the pressure drop seem to correspond to a rearrangement of the particles which make up the sample induced by the sorption of water. It is therefore essential to experimentally and theoretically determine the amount of water collected by the cake formed at the filter surface.

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Previous studies (Popovicheva et al., 2008) have highlighted the important role of water sorption isotherms on nanostructured particles. Carbonaceous aerosols (i.e., soot) from diverse and varied sources (transport systems, industry, industrial heating, and so on) have a strong ability to adsorb air moisture and can therefore fulfil the role of cloud condensation nuclei and ice nuclei. The characterisation of these particles using the water sorption isotherms information is essential since the water sorption of the soot particles is the dominant mechanism defining the residence time of particles in the atmosphere and the cloud droplet nucleation scavenging (Hendricks et al., 2004).

Various models have been developed over the years (Andrade et al., 2011) to mathematically express the relationship between water activity and the equilibrium of the moisture content of a solid. Van den Berg and Bruin (1981) ranked the most important models into three categories – theoretical, semi- theoretical and empirical models. Two multilayer adsorption models can be distinguished among the best-known models namely the BET and GAB equations. These models, which are classified under semi-theoretical category are the most widely used models in food systems.

The BET equation was named after the scientists who developed it, Brunauer, Emmett and Teller (Brunauer, 1938). Only two constants define the BET equation – v_{mG}, the required quantity of sorbate substance needed to cover the solid surface with a monomolecular layer and c_B, a parameter related to the energy difference between the sorbate molecules in the first layer and in the remaining "liquid like" (or pure liquid) layers. The BET equation is usually a sigmoidal-shaped curve and is defined as follows (Rouquerol et al., 2012):

$$v(a_0)_{\mathrm{BET}} = \frac{v_{mG}\, c_B a_0}{(1-a_0)(1+(c_B-1)\, a_0)} \tag{1}$$

where $v(a_0)_{\mathrm{BET}}$ is the amount of sorbate per unit mass of sorbent at sorbate activity, a_0. This activity is defined as the ratio of the experimental (partial) vapour pressure of the sorbate to the vapour pressure at saturation.

The BET equation is still used by default to calculate values of water sorbed by monolayers in varied physico-chemical applications although the International Union of Pure and Applied Chemistry (IUPAC) recommends using it only for a very limited range of activity ($0.05 < a_0 < 0.30$) (Everett, 1972). Experimental data does not fit well over the whole range of activity and this has meant that the BET equation's main application is limited to certain specific areas (despite its interesting theoretical basis). Numerous studies have however addressed the shortcomings of this equation (Gregg and Sing, 1991) which resulted in the creation of a new model – the GAB equation.

The GAB equation, created by Guggenheim, Anderson and De Boer (Anderson, 1946; De Boer, 1953; Guggenheim, 1966), can be used to calculate the amount of sorbate captured by the sorbent (Timmermann, 2003). This model's extensive range of activity ($0.05 < a_0 < 0.8$) has made it very popular in the field of food powders technology and led directly to it being recommended by the European Project Group COST 90 (Bizot, 1983) and being awarded the title of fundamental equation for water sorption by compound foods. This equation has also been used in several research areas such as gas sorption (Anderson and Hall, 1948), the adsorption of water vapour, with highly concentrated electrolyte solutions (Stokes and Robinson, 1948) and also with proteins (Gascoyne and Pethig, 1977; Grigera and Berendson, 1979) and other materials (Grigera and Mogilner, 1980).

More recently, Timmermann (1989) improved the GAB equation by introducing three stages to its sorption theory – stage I corresponds to the formation of a monolayer, stage II describes the following layers where the interaction forces are weaker and stage III describes the subsequent layers near a state of "pure liquid". This model, called "Three Sorption Stages (TSS)" differs from the GAB equation in that it introduces a fourth constant (resulting from step III) determined by graphical fitting. The main strength of this model is its wide range of validity of activity (up to 0.95 at least, according to the author) although its main disadvantage is the introduction of another graphically-obtained constant.

In work covered by this paper, we modifed the GAB model by introducing parameters obtained by experimentation which are suitable for almost the whole range of possible activity. The GAB equation underestimates the actual amount of water captured by the solid beyond 0.8 which is due to the fact that, for high activity, the amount of water calculated by the GAB model becomes negligible compared to the amount of water formed by condensation in the space between particles. For this reason the GAB equation was corrected by adding condensed water between the sample's particles Table 1.

Table 1
Particle size analysis.

	Median diameter (nm)	Mean diameter (nm)	Standard deviation (nm)
Zinc–Aluminium	21	21	5
Xe2 PRINTEX	73	71	18
Zinc Inframat Advanced Materials	40	36	10

2. Theoretical part

2.1. GAB equation

The GAB equation is defined as follow:

$$v(a_0)_{\mathrm{GAB}} = \frac{v_{mG}\, c_G a_0 k}{(1-k\, a_0)(1+(c_G-1)k\, a_0)} \tag{2}$$

where $v(a_0)_{\mathrm{GAB}}$ is the amount of sorbate by gram of sorbant at sorbate activity a_0, c_G, the analogue formulation to the BET energy constant c_B (where $c_B \equiv c_G k$) and k a constant. The authors of the GAB equation introduced this constant because they considered the sorption state of sorbed molecules is the same in all the layers beyond the first but nonetheless different from the pure liquid state. In other words, the constant k is the measure of free energy (standard chemical potential) of the sorbed molecules between these two states.

The GAB model is an improvement on the BET equation but shares two of its constants (v_{mG}, the monolayer capacity and c_G, the analogous formulation of the BET constant c_B) and owes its versatility to a third, the constant k. If this third constant is equal to the unit, the GAB model is thus reduced to a BET equation.

It is possible to determine the three characteristic constants of the GAB equation (c_G, v_{mG} and k) by using the following linearization method:

$$F(\mathrm{GAB}) = \frac{a_0}{(1-ka_0)v(a_0)} = \frac{1}{c_G\, k v_{mG}} + \frac{c_G - 1}{c_G v_{mG}} a_0 \tag{3}$$

This equation is the so-called GAB plots, F(GAB) vs. a_0 (first part of Eq. (3) should be linear if the correct value of k is used for the experimental F(GAB)). Then when we have obtained the k-value which best linearises F(GAB) vs. a_0, we can go on to find the two other coefficients by plotting F(GAB) vs. a_0 The second part of

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