

An easy-to-use modification of the potential theory of adsorption, and its application to different types of adsorbents

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1. Introduction: Dubinin's potential theory of adsorption

The adsorption of condensable gases on porous materials is fundamental to many processes, such as adsorption refrigeration, heat storage, drying processes, water harvesting, and thermal switches. Accurate calculation of adsorption equilibrium data for the adsorbents used in these processes is critical for proper process design and adsorbent selection. Dubinin's potential theory of adsorption has proven to be effective in calculating adsorbent loading from only a few experimental data, even at pressures and temperatures for which no experimental data are available [1, 2]. For this purpose, the adsorption potential

$$\phi_{\text{Dubinin}} = RT \ln \left(\frac{p_s(T)}{p_{ad}(W, T)} \right)$$

and the filled pore volume

$$W = \frac{x}{\rho_{ad}(T)}$$

are calculated from the vapor pressure of the adsorbed phase $p_{ad}(W, T)$ and the corresponding adsorbent loading x , using the vapor pressure $p_s(T)$ of the saturated adsorbent at the same temperature T and the adsorbate density $\rho_{ad}(T)$. If this process results in a single characteristic curve $W(\phi_{\text{Dubinin}})$ that is independent of the temperature of the experimental data, a mathematical fit of this curve can in turn be used to calculate the loading of the adsorbent for different temperatures and adsorbent pressures.

2. The modified version of Dubinin's potential theory of adsorption

The requirement of a temperature-invariant characteristic curve is not always met, as is the case for the adsorption of water on aluminum fumarate (see Figure 1). In some cases it is possible to find a temperature-invariant characteristic curve of adsorption $W(\phi^*)$ using

$$\phi^* = \phi_{\text{Dubinin}} + f_W \cdot \Delta h_{add} \left(\frac{T}{T_0} - 1 \right)$$

with Δh_{add} as an additional fitting parameter and T_0 as the reference temperature 273.16 K [3] (see Figure 1). For the adsorption equilibria documented in [3], $f_W = 1$ was found. So far, this modified version of the potential theory of adsorption has only been applied to the adsorption of water vapor.

Figure 1: Water vapor adsorption on aluminum fumarate- ϕ_{Dubinin} vs. ϕ^*

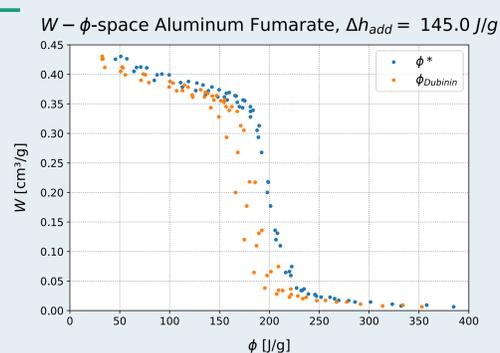


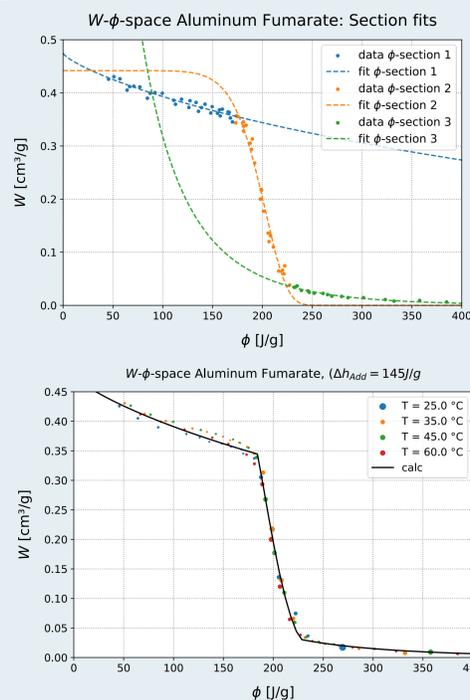
Table 1: Characteristic curves for water and ammonia adsorption

adsorbent	adsorbent	Δh_{add}	f_W	ρ_{ad} (see [3])	$W(\phi^*)$	RMSEP	raw data from
Aluminum fumarate	Water	145 J/g	1	Nikolaev-Dubinin	$\begin{cases} 0.478 \frac{\text{cm}^3}{\text{g}} \exp \left(- \left(\frac{\phi^*}{743.92 \frac{\text{J}}{\text{g}}} \right)^{0.7994} \right), 45 \frac{\text{J}}{\text{g}} < \phi^* < 184.4 \frac{\text{J}}{\text{g}} \\ 0.737 \frac{\text{cm}^3}{\text{g}} \exp \left(- \left(\frac{\phi^*}{191.89 \frac{\text{J}}{\text{g}}} \right)^{6.8468} \right), 184.4 \frac{\text{J}}{\text{g}} < \phi^* < 227.2 \frac{\text{J}}{\text{g}} \\ 3.606 \frac{\text{cm}^3}{\text{g}} \exp \left(- \left(\frac{\phi^*}{10.10 \frac{\text{J}}{\text{g}}} \right)^{0.5016} \right), 227.2 \frac{\text{J}}{\text{g}} < \phi^* < 1391.7 \frac{\text{J}}{\text{g}} \end{cases}$	0.008 cm³/g	<ul style="list-style-type: none"> • 25 °C • 35 °C • 45 °C • 60 °C [4]
CAU-23	Water	100 J/g	1	Mugele	$\begin{cases} 51.425 + 36.346 \left(\frac{\phi^*}{\text{J/g}} \right) - 0.15125 \left(\frac{\phi^*}{\text{J/g}} \right)^2 \frac{\text{cm}^3}{\text{g}}, 11.4 \frac{\text{J}}{\text{g}} < \phi^* < 177.9 \frac{\text{J}}{\text{g}} \\ 1 + 93.792 \left(\frac{\phi^*}{\text{J/g}} \right) - 0.36458 \left(\frac{\phi^*}{\text{J/g}} \right)^2 \frac{\text{cm}^3}{\text{g}}, 177.9 \frac{\text{J}}{\text{g}} < \phi^* < 196.1 \frac{\text{J}}{\text{g}} \\ 0.473 \frac{\text{cm}^3}{\text{g}} \exp \left(- \left(\frac{\phi^*}{187.73 \frac{\text{J}}{\text{g}}} \right)^{13.9176} \right), 177.9 \frac{\text{J}}{\text{g}} < \phi^* < 196.1 \frac{\text{J}}{\text{g}} \\ 2.881 \frac{\text{cm}^3}{\text{g}} \exp \left(- \left(\frac{\phi^*}{9.99 \frac{\text{J}}{\text{g}}} \right)^{0.4814} \right), 196.1 \frac{\text{J}}{\text{g}} < \phi^* < 853.8 \frac{\text{J}}{\text{g}} \end{cases}$	0.033 cm³/g	<ul style="list-style-type: none"> • 25 °C • 40 °C • 60 °C [5]
MIL-101	Ammonia	-420 J/g	1	Nikolaev-Dubinin	$0.376 \frac{\text{cm}^3}{\text{g}} \exp \left(- \left(\frac{\phi^*}{462.54 \frac{\text{J}}{\text{g}}} \right)^2 \right) + 0.915 \frac{\text{cm}^3}{\text{g}} \exp \left(- \left(\frac{\phi^*}{131.23 \frac{\text{J}}{\text{g}}} \right)^{0.7994} \right)$	0.023 cm³/g	<ul style="list-style-type: none"> • 30 °C • 120 °C [6]

3. Practical application of the modified potential theory of adsorption

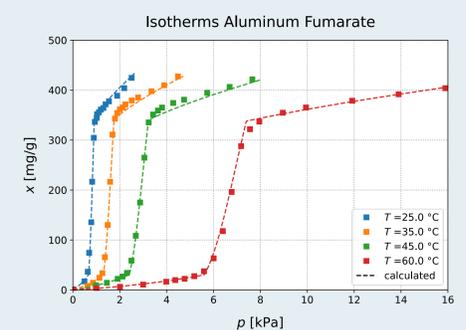
In this project we applied the modified potential theory to the adsorption of water vapor on aluminum fumarate and CAU-23, and to the adsorption of ammonia on MIL-101. In a first step Δh_{add} , f_W and the adsorbate density model were manually chosen so that all the experimental data best coincide into a single characteristic curve. The parameters of appropriate mathematical functions detailed in [3] to describe the characteristic curve were then determined using a two-step optimization procedure to minimize the root mean square error of prediction (RMSEP) of the curve fit (see Figure 2).

Figure 2: Two-step optimization procedure to determine the characteristic curve of adsorption



In a first step, the characteristic curve is divided into up to three sections, and an initial local curve fit is performed. In a second step, a global optimization is carried out, which also adjusts the limits of the individual curve sections. The resulting curves are shown in Table 1. Finally, the calculated equilibrium data are compared with the measured data for validation (see Figure 3).

Figure 3: Validation of calculated adsorption equilibrium data



4. Summary and outlook

The adsorption of water vapor on aluminum fumarate and CAU-23, as well as the adsorption of ammonia on MIL-101, can be well described by the modified potential theory of adsorption, while the results are very inaccurate using only the original version of the potential theory. In the future, more adsorption equilibria will be investigated, and a third optimization step will be introduced which also finds the optimal adsorbate density model, Δh_{add} and f_W automatically. The theory will also be extended for multicomponent adsorption.

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