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Excess surface work—A modelless way of getting surface energies and specific surface areas directly from sorption isotherms

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Abstract

Sorption isotherms can be easily transformed into excess surface work (ESW) isotherms, computed as the product of the adsorbed amount and the change in chemical potential. Plotted against the amount adsorbed at least one minimum is yield. Thermodynamically ESW is the sum of the surface free energy and the isobaric isothermal work of sorption. Therefore, ESW is not a model, instead it is just another way of presenting an isotherm. From the amount adsorbed in the first minimum one can obtain a specific surface area similar to the BET surface area. The depth of the ESW in the minimum gives a sorption energy, which corresponds approximately to the loss of degrees of freedom of the sorptive. In this contribution the ESW plots of various sorption isotherms on highly ordered alumina with cylindrical pores of 25 nm width and mesoporous SBA 15 will be presented and discussed.

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1. Introduction

The present state of art for modelling sorption isotherms in porous or dispersed systems is described by the author in a review article [1]. At least there are three variables of interest to be achieved from a sorption isotherm: these are the monolayer capacity for determination of the specific surface area, pore size distribution from the capillary condensation branch and finally sorption energies or energy distributions [2]. All models suffer simply of being a model with assumptions and limited validation ranges. Among all the various models the excess surface work (ESW) concept is different, in its first ideas published in 1996 [3] and later physically explained in 1998 [4]. The objective of this paper is to summarize and point out the fundamental character of this new thermodynamic function ESW and its potential for an energetic characterisation of adsorption phenomena [5].

2. Theory

An adsorption system will be assumed as an open system in mechanical and thermal equilibrium. Thus, the corresponding chemical potentials μ are equal:

$$\mu = \mu_{\mathrm{Gas}} = \mu_{\mathrm{ads}}, \qquad T = T_{\mathrm{Gas}} = T_{\mathrm{ads}}, \qquad \mu = \tilde{\mu}(T + \Delta\mu) \quad \text{and} \quad \Delta\mu = RT\ln\left(\frac{p}{p_{\mathrm{s}}}\right) \tag{1}$$

with the gas constant $R = 8.314\ \mathrm{J\ mol^{-1}\ K^{-1}}$, pressure p, saturation pressure p_{s} and absolute temperature T [K].

The first physical explanation of the excess surface work was derived from the disjoining pressure concept [4] and will be briefly outlined. The thermodynamic parameter disjoining pressure Π was introduced by Derjaguin and Kusakov (see Refs. [6,7]) at the end of the 1930s. It is defined as the difference, accomplished in mechanical equilibrium, between the normal component of the pressure tensor P_{zz} in the interlayer and the pressure P_0 in the phase from which the interlayer was formed by thinning, corresponding to a change in layer thickness h (e.g. desorption) [6]:

$$\Pi(h) = P_{\mathrm{zz}} - P_0 \tag{2}$$

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The following relations hold: $\Delta\mu = -v_{\mathrm{mol}}\Pi$, $\Gamma = h/v_{\mathrm{mol}} = n_{\mathrm{ads}}/A$ and $\Delta\mu = RT \ln p/p_{\mathrm{s}}$ with the molar volume v_{mol}, the surface excess concentration Γ, n_{ads} the surface excess amount and the area A. The Gibbs equation describes the sorption with Γ as the ratio of surface free energy γ_{sv} and change in the chemical potential $\Delta\mu$:

$$\Gamma = -\left(\frac{\mathrm{d}\gamma_{\mathrm{sv}}}{\mathrm{d}\,\Delta\mu}\right) \tag{3}$$

Substitution into the disjoining pressure Π delivers:

$$\Rightarrow \mathrm{d}\gamma_{\mathrm{sv}} = h\,\mathrm{d}\Pi \tag{4}$$

and after integration we yield:

$$\int_{\gamma_{\mathrm{sl}}+\gamma_{\mathrm{lv}}}^{\gamma_{\mathrm{sv}}} \mathrm{d}\gamma_{\mathrm{sv}} = \int_0^{\Pi} h\,\mathrm{d}\Pi = -\int_{\infty}^{h} \Pi\,\mathrm{d}h + \Pi h \tag{5}$$

where s is the solid, l the liquid and v is the vapour.

In terms of the more familiar chemical potential we can rewrite the integrals as:

$$\begin{aligned}\Delta\gamma_{\mathrm{sv}} &= -\int_{-\infty}^{0} \Gamma\,\mathrm{d}\,\Delta\mu = \Delta\mu\Gamma - \int_0^{\Gamma} \Delta\mu\,\mathrm{d}\Gamma \Rightarrow \Phi =: \Delta\mu\Gamma \\ &= \Delta\gamma_{\mathrm{sv}} + \int_0^{\Gamma} \Delta\mu\,\mathrm{d}\Gamma \end{aligned} \tag{6}$$

The term Πh is equivalent to the expression $\Delta\mu\Gamma$, this was introduced by Adolphs and Setzer [3] as a new thermodynamic function called the excess surface work Φ, defined as [4]:

excess surface work =

: surface free energy + isothermal isobaric work of sorption

Physically, it means that each adsorbed molecule decreases the surface free energy and at the same time increases the isothermal isobaric work of sorption, abbreviated in the following as work of sorption.

3. Interpretation of the excess surface work minimum

The excess surface work results from the counter acting process between the surface free energy and the work of sorption. If these two are balanced, we observe a minimum in the ESW plot against the adsorbed amount. Before this minimum the surface free energy is dominating and afterwards at higher sorption capacities the work of sorption. Starting from a free surface covered step by step with adsorbed molecules, after completion of a monolayer the surface–adsorbate interaction changes into an adsorbate–adsorbate interaction and consequently the influence of the surface must be reduced. This does not necessarily mean that the influence vanishes like in the BET model [8], where already in the second adsorbed layer bulk conditions are assumed. However, the work of sorption should be dominant after completion of a monolayer and thus, we may define the ESW minimum as the location of a monolayer. Fig. 1 describes such a transformation of an isotherm into an ESW plot. Like in the standard BET analysis [8] it is possible to compute a specific surface area. A comparison of BET and ESW specific surface areas in the range of some cm^2/g up to 1000 and more m^2/g is given for over 300 isotherms in [4], where the ESW surface areas were about 10% lower than the BET values. We observed also in [5] that the depth of the minimum Φ_{min} is approximately of the same size as the loss of degree of freedom of an adsorbed molecule according to the rule of Dulong–Petite. Again, we find a strong argument for the completion of a monolayer at the ESW minimum. With the last adsorbed molecule which finishes the completion of a monolayer the maximum of interaction is reached between the adsorbed molecules and the surface and thus the maximum loss of degrees of freedom.

4. Interpretation of the Zwicker–de Boer model with the excess surface work concept

At its minimum the derivative of the excess surface work $\mathrm{d}\Phi$ vanishes:

$$\mathrm{d}\Phi = \Delta\mu\,\mathrm{d}\Gamma_{\mathrm{ads}} + \Gamma_{\mathrm{ads}}\,\mathrm{d}(\Delta\mu) = 0 \tag{7}$$

A solution is the Zwicker–de Boer model [9]:

$$\Delta\mu = \Delta\mu_0 \exp\left(-\frac{\Gamma_{\mathrm{ads}}}{\Gamma_{\mathrm{mono}}}\right) \Rightarrow \ln(|\Delta\mu|) = -\frac{\Gamma_{\mathrm{ads}}}{\Gamma_{\mathrm{mono}}}\ln(|\Delta\mu_0|) \tag{8}$$

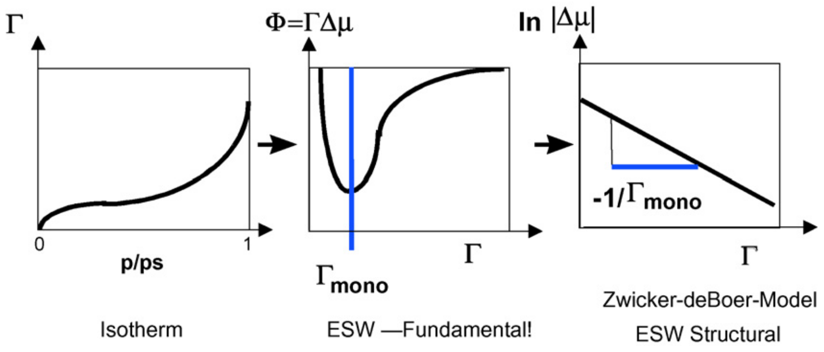

Fig. 1. Scheme of the transition of an isotherm into a fundamental ESW plot and according to the Zwicker–de Boer model the linearization with new interpretation of constants (ESW structural component).