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Introduction of new functions to speed up sorption measurements

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Abstract The procedure suggested by Jäntti enables estimation or calculation of the values of adsorption parameters in an early stage of adsorption measurements. The procedure may also give information about the validity of models used for the explanation of the measurements. In the present paper new functions are introduced to get results easier.

Keywords Adsorption · Dynamic · Fast measurement · Sorption · Surface

Introduction

In 1970 Jäntti introduced a calculation procedure with the intention to reduce the time necessary for sorption measurements (Jäntti et al., 1970, 1972; Jäntti and Robens, 1981). His method was specially constructed for measurements satisfying:

$$m\,(t) = A + B\,\{1 - \exp(-Ct)\} \tag{1}$$

where m stands for the sorbed mass and where A, B and C are constants (Table 1).

Jäntti introduced the function $J(t)$:

$$J\,(t) = \frac{m_2^2 - m_1 m_3}{2\,m_2 - m_1 - m_3} \tag{2}$$

where $t_2 = t$, $t_2 - t_1 = t_3 - t_2$ and where m_1, m_2 and m_3 are the masses measured at the times t_1, t_2 and t_3 respectively. Jäntti used the fact that when Eq. (1) is satisfied, $J(t)$ is independent of t:

$$J\,(t) = J = A + B \tag{3}$$

Equation (3) implies that the value of A + B can be calculated already soon after the starting of an adsorption measurement which can be helpful as such measurements can well take hours. An other feature of Jäntti's method is that, in the case that $J(t)$ (Eq. (2)), calculated using measured values, proves not to be independent of t, this can be interpreted as a warning of the non-validity of Eq. (1) and that a more complicated molecular model is necessary for the explanation of the measurements. One step further is the possibility that a more complicated molecular model is available and that it allows the possibility to predict the

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Table 1 List of symbols

A, B, C	Constants	$A_{\mathrm{eff}}(t)$, $B_{\mathrm{eff}}(t)$, $C_{\mathrm{eff}}(t)$	Characteristic functions of parallel adsorptions
m	Adsorbed mass	$J(t)$	Jäntti's function (Eq. (2))
t	Time of adsorption	$\mathrm{Index}_{\mathrm{a}}$, $\mathrm{Index}_{\mathrm{b}}$	Indicating two different parallel adsorptions

function $J(t)$. Such a predicted function will generally contain parameters (Poulis et al., 2002, 2004). Comparison with the measured results can lead to estimation of the values of those parameters. In case the comparison between the predicted and the measured $J(t)$ curves leads to too large a discrepancy, an adaptation of the theoretical model might be relevant.

The use of Jäntti's method can result in a gain of time, but can also lead to suggestions about the model to use and to estimations of the values of the parameters. However, the use of Eq. (2) implies a great amplification of measurement errors. The vast increase of sensitivity and accuracy of commercially available balances brings along substantial improvements. The influence of measurement errors can be reduced by increasing the value of $\Delta t = t_2 - t_1$. This however implies a loss ofdetails in the $J(t)$ curve. An optimum of the value of Δt has to be aimed at for each part of the curve. This can easily be accomplished by choosing in advance of the measurements, a number of values of Δt and calculate on line the curves $J(t)$ for each value of Δt.

In order to increase the early warning capacity of $J(t)$ we shall introduce some more functions. The calculation of $J(t)$ during the measurements was from computational point of view very simple, a computer being hardly necessary. The new functions we will introduce here are also of very simple nature. This might be a justification for application also when no guarantee exists for getting additional information by using them.

Introduction of new functions

In the case of values of the adsorbed mass not satisfying Eq. (1), we define the new functions $A_{\mathrm{eff}}(t)$, $B_{\mathrm{eff}}(t)$ and $C_{\mathrm{eff}}(t)$ as a generalisation of the parameters A, B, and C used in Eq. (1).

$$X(t) = (m_2 - m_1)/(m_3 - m_2) \tag{4}$$

$$C_{\mathrm{eff}}(t) = \{1/\Delta t\}\ln X(t) \tag{5}$$

$$B_{\mathrm{eff}}(t) = -\frac{m_3 - m_1}{X^{-t_3/\Delta t} - X^{-t_1/\Delta t}} \tag{6}$$

where (as in Eq. (2)) $\Delta t = t_2 - t_1 = t_3 - t_2$ and m_1, m_2 and m_3 are the masses measured at the times t_1, $t_2 = t$ and t_3 respectively.

The definitions given by Eqs. (4)–(6) can be elucidated by using into Eq. (1) the values of t_1 and m_1, this results into an equation with three unknowns A, B and C. Repeating that procedure for the values t_2 and m_2 and once more for t_3 and m_3 we get three equations which allow us to solve the three parameters A, B and C. By repeating this procedure for different values of t, we get the time dependency of $A_{\mathrm{eff}}(t)$, $B_{\mathrm{eff}}(t)$ and $C_{\mathrm{eff}}(t)$.

The function $A_{\mathrm{eff}}(t)$ will not be dealt with in the below, but instead we will use $J(t)$ as defined by Eq. (2). When we chose a small value for Δt, we can use the relation

$$J(t) = A_{\mathrm{eff}} + B_{eff} \quad (\Delta t \text{ small}).$$

Application of the new functions

As an example we shall deal with a computer simulation. This has the advantage that the discussion about the fit between measured results and theoretical model is not relevant. We acknowledge the fact that this fitting should be the most important part of a paper on adsorption, but in the present paper we restrict ourselves to the way of presentation of measured adsorptions and we will therefore avoid the fitting discussion (Poulis et al., 2006) by simply using a computer simulation. In our example we will deal with parallel adsorption. The words parallel adsorption we shall use for the simultaneous and independent occurrence of two or more adsorptions each satisfying the Eq. (1), but with different values of the parameters (Massen et al., 2000). The simplest example of parallel adsorption is of course the simultaneous and independent occurrence of adsorptions on different adsorbents both being present in the sample. To illustrate another example of parallel adsorption we return to Eq. (1). In the discussion of the model used for the explanation of measured results, Eq. (1) usually appears as the solution of a simple

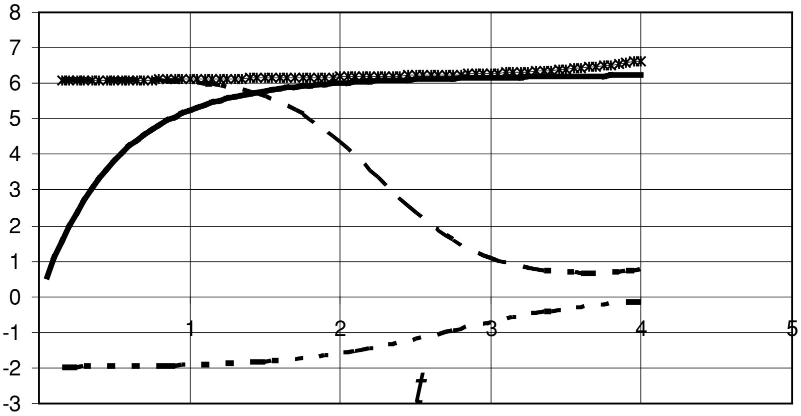

Fig. 1 The difference between C_a and C_b is so large that when only the curves of $m(t)$ and $J(t)$ were used, it would have been possible to overlook the second adsorption. So this figure is a demonstration of the usefulness of the $B_{\text{eff}}(t)$ and – $C_{\text{eff}}(t)$ curves. ___ $= m(t)$, _ _ _ _ $= B_{\text{eff}}(t)$, _ ·· _ ·· _ ·· $= -C_{\text{eff}}(t)$, xxxxxxxxxx $= J(t)$. $A = 0$, $B_a = B_b = 6$, $C_a = 0.01$, $C_b = 2$

first order linear differential equation. In case the fitting between theory and experiment is not satisfying, this model will have to be adjusted. This will often lead to a linear differential equation of a higher order. The solution will be a summation of different functions of the shape of Eq. (1) and can so be described as parallel adsorption.

We will discuss the situation where two parallel adsorptions play a part. As we take the parallel adsorptions (index$_a$ and index$_b$) to be mutually independent, we apply:

$$m(t) = A + B_a[1 - \exp(-C_a t)] + B_b[1 - \exp(-C_b t)] \tag{7}$$

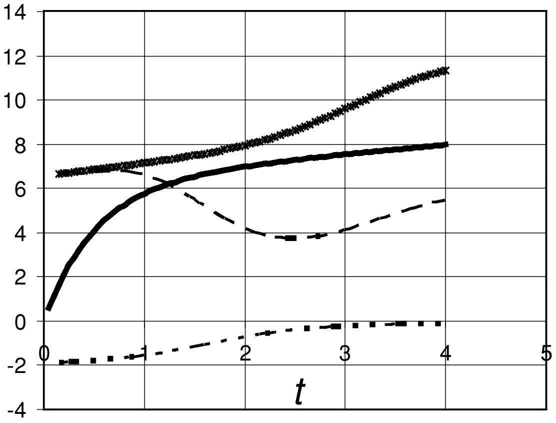

Fig. 2 The use of the plots $m(t)$ and $J(t)$ would suffice for the estimation of the vales of B_a and B_b. The plots however might give a welcome support to the conclusions. Note that the apparent minimum in the $B_{\text{eff}}(t)$ curve adds to the suggestibility. ___ $= m(t)$, _ _ _ _ $= B_{\text{eff}}(t)$, _ ·· _ ·· _ ·· $= -C_{\text{eff}}(t)$, xxxxxxxxxx $= J(t)$. $A = 0$, $B_a = B_b = 6$, $C_a = 0.1$, $C_b = 2$

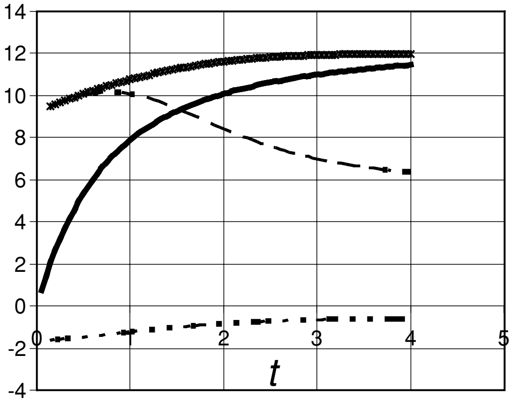

Fig. 3 The values of C_a and C_b so close to one another that an estimate of the value of B_a is not acceptable from the plots of $m(t)$ and the $J(t)$. The $B_{\text{eff}}(t)$ curve however gives a reasonable estimate of the value of B_b. Combining this with the estimate of the value of the sum of B_a and B_b from the $J(t)$ curve leads to an acceptable result. ___ $= m(t)$, _ _ _ _ $= B_{\text{eff}}(t)$, _ ·· _ ·· _ ·· $= -C_{\text{eff}}(t)$, xxxxxxxxxx $= J(t)$. $A = 0$, $B_a = B_b = 6$, $C_a = 0.6$, $C_b = 2$

The advantage of using the new functions is that, particularly when combined with the plots of $m(t)$ and of $J(t)$, they can contribute to the drawing of conclusions, often already at an early stage of the measurements.

As demonstration a computer simulation has been set up, see Figs. 1–4. Through these figures we show the dependency of the functions $J(t)$, $C_{\text{eff}}(t)$ and $B_{\text{eff}}(t)$ on the values of the parameters C_a, C_b, B_a and B_b. For simplicity the parameter A is chosen to be zero throughout. We concentrate on the warning of the existence of two parallel adsorptions instead of a single adsorption. The four figures show the dependency of the functions $J(t)$, $C_{\text{eff}}(t)$ and $B_{\text{eff}}(t)$ on the values of

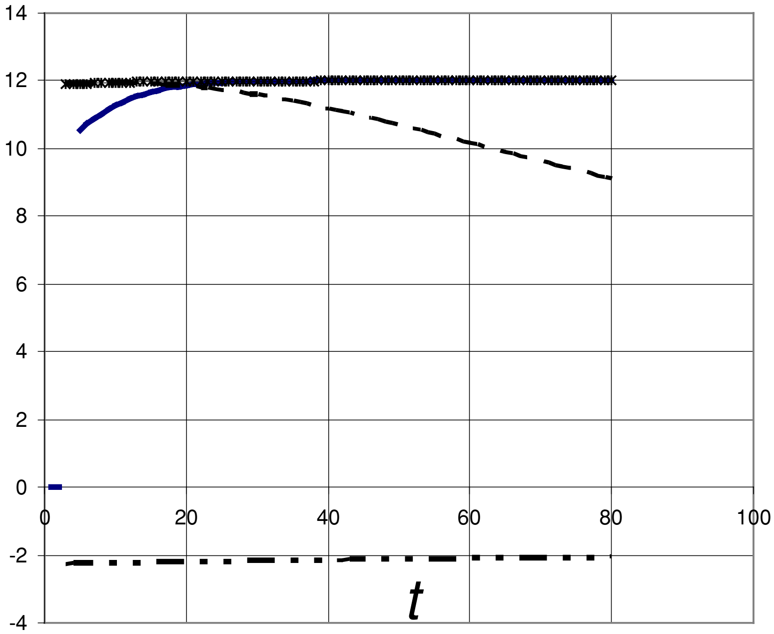

Fig. 4 The values of C_a and C_b are almost equal to one another. Only the $B_\mathrm{eff}(t)$ curve gives an indication of the existence of two adsorptions. ___ = $m(t)$, ---- = $B_\mathrm{eff}(t)$, _ ·· _ ·· _ ·· = $-C_\mathrm{eff}(t)$, xxxxxxxxxx = $J(t)$. $A = 0$, $B_\mathrm{a} = B_\mathrm{b} = 6$, $C_\mathrm{a} = 2.5$, $C_\mathrm{b} = 2$

the parameters C_a, C_b, B_a and B_b. In these figures the values of $C_\mathrm{b} - C_\mathrm{a}$ are chosen such that they increase fromFigs. 1 to 4. It is clear that, when C_a equals C_b, we may not expect to find any indication of a difference between the values of B_a and B_b. Indeed the figures show a decreasing resolution for B. This demonstrates that the level of applicability of the new functions strongly depends upon the conditions.

In Fig. 1 we have to do with $C_\mathrm{a} \ll C_b$ and with measurements in a time interval where the a adsorption could hardly play a part. We see that at small values of t the $J(t)$, the $C_\mathrm{eff}(t)$ and the $B_\mathrm{eff}(t)$ curves do not distinguish themselves from horizontal straight lines, so indicating a single adsorption. But at larger values of t, the $C_\mathrm{eff}(t)$ and the $B_\mathrm{eff}(t)$ curves prove their applicability much earlier by showing pronounced deviations from horizontal lines. The $C_\mathrm{eff}(t)$ curve even gives already an estimate of the value of C_a.

In Fig. 2 the $m(t)$ curve shows deviations from a simple adsorption curve in so far that the horizontal asymptote seems not to be completed. The $J(t)$ curve shows at small values of t that only one of the substrates contributes, while at large values of t the contribution of the other is obvious, all be it that the value of $B_\mathrm{a} + B_\mathrm{b}$ is not completely attained. The $B_\mathrm{eff}(t)$ curve shows a pronounced minimum, which could only be ascribed to the existence of parallel adsorption.

In Fig. 3 the values of C_a and C_b are far enough apart so the $J(t)$ curve gives a reasonable indication of the existence of parallel adsorptions. The $B_\mathrm{eff}(t)$ curve gives only a reasonable estimation of the value of B_b, but combining this with the asymptotical value of $J(t)$ we might estimate of the value of B_a.

In Fig. 4 the value of $C_\mathrm{b} - C_\mathrm{a}$ is so small that only the $B_\mathrm{eff}(t)$ curve gives an indication that a single adsorption could not be the basis of the experimental results.

Another advantage of the use of $C_\mathrm{eff}(t)$ is that it can be applied for extrapolation purposes in order to reduce time consumption of sorption measurements. An extra advantage of combination of Jäntti's method with the new functions is that near the end of a conventional measurement, the measurement time can still be shortened as the exponential function with the smallest value of C does not contribute to the time necessary for the measurement.

Conclusion

The three options of Jännti‘s method are

1. Gain of time
2. Suggestions about the sorption model
3. Estimate of values of parameters

The new functions $B_{\mathrm{eff}}(t)$ and $C_{\mathrm{eff}}(t)$ support the options 2 and 3, there exist situations where, when using the three functions one obtains better suggestions and estimates than would be the case when considering $J(t)$ only.

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