

## Skript zum Versuch

# A45

### Adsorption of 2-Methyl-Butane at Charcoal

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Herausgeber: Institut für Physikalische Chemie

## 1 The task

Measure the adsorption isotherm of 2-methyl-butane (iso-pentane) at charcoal at room temperature. Determine the parameters of the Langmuir and the BET isotherm. Determine the specific surface of charcoal.

## 2 Introduction

Due to attractive molecular interactions and depending on the specific properties of the surface a certain amount of gas molecules sticks at the solid-vapour interface. This is called adsorption. Adsorption is of eminent importance in physics and chemistry, consider e. g. cleaning and drying of gases, heterogeneous catalysis or chromatography etc. At constant temperature free molecules in the gas phase and those adsorbed at the surface are in equilibrium, which strongly depends on the partial pressure  $p_J$  of gas  $J$ . This dependence  $n_{J,ads} = f(p_J)$  is called the adsorption isotherm. (Similar processes can be observed for dissolved substances in a liquid phase that adsorb at the liquid-gas interface, see e. g. experiment A42).

Depending on the nature of the attractive interactions one distinguishes between physical adsorption (physisorption) and chemical adsorption (chemisorption). Usually, the dominating interactions leading to physisorption are van der Waals forces. The respective heat of adsorption is small and comparable in magnitude to the negative heat of evaporation. Several layers can be formed, the adsorption is reversible and the adsorbed molecules keep their chemical identity. In contrast, chemisorption has a high heat of adsorption (comparable to reaction enthalpies) and chemical bonds are formed between

gas molecules and solid surface. In many cases only monomolecular layers are formed; the process can be irreversible and the molecules can lose their chemical identity (e. g. dissociation at the surface). Sometimes it is difficult to distinguish between both scenarios.

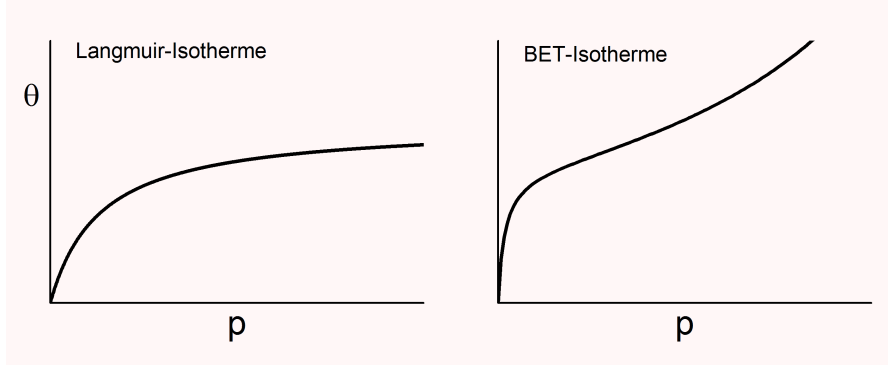


Fig. 1: Adsorption isotherms: left Langmuir, right BET

## 2.1 Langmuir Isotherm

A well known adsorption isotherm is Langmuir's isotherm (see. Fig. 1, left) which obeys the following relation:

$$n_a = \frac{n_{mono}p}{p + a} \quad \text{or} \quad \theta = \frac{n_a}{n_{mono}} = \frac{K_a p}{K_a p + 1} \quad (1)$$

With:  $n_a$  adsorbed numbers of moles,  $\theta$  relative coverage,  $p$  gas pressure,  $n_{mono}$  adsorbed number of moles at complete coverage with a monomolecular layer,  $K_a = 1/a$  adsorption constant, equilibrium constant.

The Langmuir isotherm describes the adsorption at sufficiently low pressures. This model is based on the following assumptions:

1. The adsorption is restricted to a monomolecular layer.
2. All adsorption places at the solid surface are energetically equivalent. That means the adsorption enthalpy is not dependent on the coverage.
3. The interactions between adsorbed molecules are neglected.
4. The adsorbed molecules do not move and diffuse along the surface.
5. The gas phase is regarded as ideal (perfect gas).

For very small pressures (  $p \ll 1/K_a$  ) equation (1) simplifies to  $n_a = n_{mono}K_a p$ . Thus, the isotherm is linear with  $p$  at small pressures. At higher pressures ( $p \gg 1/K_a$ ) we find  $n_a = n_{mono}$ , and  $\theta$  asymptotically approaches 1. If one plots  $n_a^{-1}$  versus  $p^{-1}$  equation (1) rearranges to a linear form with intercept  $n_{mono}^{-1}$  and slope  $(K_a n_{mono})^{-1}$ .

From the maximum coverage  $n_{mono}$  the specific surface  $A_s$  of charcoal can be calculated.

$$A_s = n_{mono} N_A \sigma \quad (2)$$

$N_A$  is Avogadro's constant and  $\sigma$  is the area required for one molecule, which can be estimated from the liquid molar volume of the adsorbate (Methyl-Butane) in the liquid state  $V_J(l)$  ( $M_{m,J}$ : molar mass of  $J$ ,  $\rho_J(l)$ : density of the liquid):

$$\sigma = \left( \frac{V_J(l)}{N_A} \right)^{\frac{2}{3}} = \left( \frac{M_{m,J}}{\rho_J(l) N_A} \right)^{\frac{2}{3}} \quad (3)$$

## 2.2 BET-Isotherm

In particular the first three assumptions for the derivation of Langmuir's isotherm are strong restrictions for the description of the adsorption of real systems

- It is probably favourable for a molecule to land in close vicinity to an already adsorbed molecule since it benefits from attractive molecular interactions not only to the substrate but also to that molecule (Langmuir approximation no. 3).
- In addition, it may be reasonable to assume that the adsorption sites are not equivalent (Langmuir approximation no. 2). More favourable sites are covered earlier than others. This leads to an adsorption enthalpy which is not any longer constant: it becomes a function of coverage.
- It may also be possible (violating Langmuir approximation no. 1) that molecules from the gas phase adsorb on top of already adsorbed molecules. This, and only this aspect is discussed in the BET-isotherm introduced in the following.

At high gas pressures and low temperatures the Langmuir model is no longer applicable. One does not observe saturation of the isotherm. Instead, a further increase of the coverage beyond 1 is found in the experiments. This is sketched in fig. (1, right).

Brunauer, Emmett and Teller (BET)<sup>1</sup> showed that this strong increase is due to multilayer adsorption. Assuming a special adsorption enthalpy  $\Delta_{ads}H$  for the first layer and the enthalpy of condensation  $\Delta_{kond}H = -\Delta_{vap}H$  for all other layers. They suggested the following form of an adsorption isotherm (BET isotherm):

$$\begin{aligned} n_a &= n_{mono} \frac{C \cdot S}{(1 - S)(1 + (C - 1)S)} \\ S &= \frac{p}{p_0} \\ C &= \exp \left( \frac{-\Delta_{ads}H - \Delta_{vap}H}{RT} \right) \end{aligned} \quad (4)$$

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<sup>1</sup>S. Brunauer, P. H. Emmett, E. Teller, *J. Am. Chem. Soc.* **60** (1938) 309

with:  $p_0$  vapour pressure of the adsorbing substance at respective temperatures (Methyl-Butane: boiling point at 1013,25 mbar  $T_b = 27,85^\circ\text{C} = 301\text{ K}$ , vaporization enthalpy:  $\Delta_{\text{vap}}H_m(301\text{ K}) = 26,8\text{ kJ/mol}$ ).

The BET-isotherm is able to describe different adsorption or growth modes:

- $|\Delta_{\text{ads}}H| \gg |\Delta_{\text{vap}}H|$ : In this case the first layer is completed before multilayer adsorption sets in and a smooth and flat coverage is expected. In other words: the adsorbate wets the substrate completely.
- $|\Delta_{\text{ads}}H| \ll |\Delta_{\text{vap}}H|$ : In this case the adsorbing molecules tend to land on small adsorbate islands. This results in a rough surface structure. The multilayer islands are precursors of small droplets that wet the substrate only partially.

### 3 Experimental procedure

See fig. (2) for a sketch of the apparatus. The experimental steps are as follows:

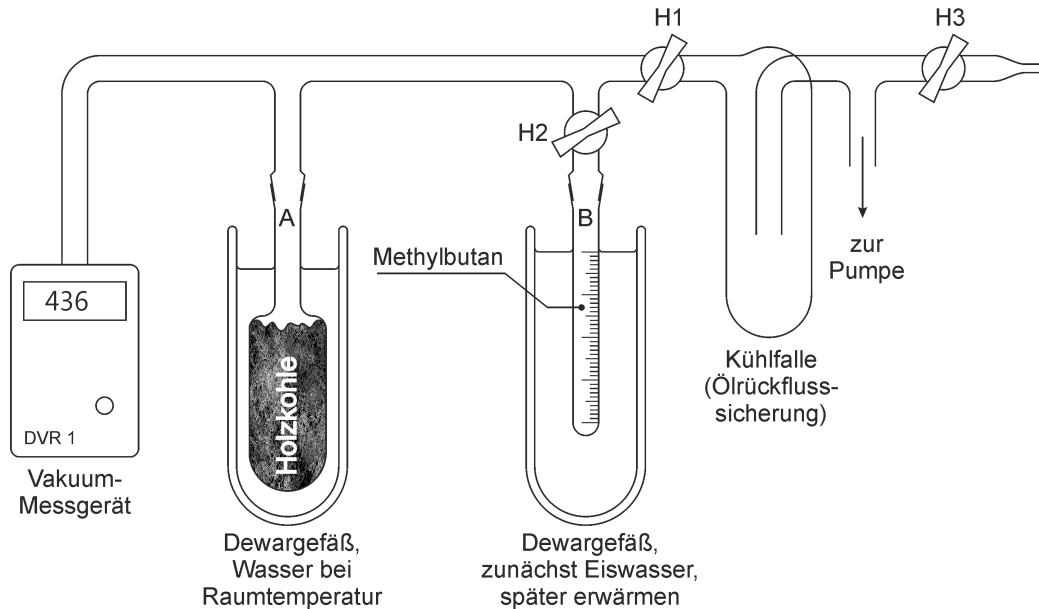


Fig. 2: sketch of the apparatus

#### 1. Filling tube B with methyl butane

Tube B is temperature controlled using a Dewar vessel filled with an ice-water mixture. The tube will be filled by the assistant with methyl butane under the hood. It is then fixed to the apparatus using springs. If necessary use some vacuum grease to seal the conically ground glass joints.

## 2. Evacuation of the apparatus

Switch on the vacuum gauge (switch on the back side). Close valves H1 and H2. Switch on the rotary vane pump (close venting valve H3 of the pump) and evacuate the apparatus via valve H1. Then, for adjusting the meniscus of the methyl butane, open H2 for a short moment until this meniscus drops by evacuation of methyl butane down to the upper most mark of tube B.

## 3. Degassing the charcoal

Carefully move the electrical furnace below tube A and then tube A into the furnace. First set the regulator to 2 A and heat for 2 min and 30 s. Then reduce the heating current to 1 A. This leads to a temperature of roughly 300 °C. Heat for additional 25 min while the apparatus is evacuated via valve H1 (H2 is closed). Then shut down the furnace and remove it from tube A. Let tube A cool down to room temperature.<sup>2</sup> Close valve H1. Open venting valve H3 of the rotary vane pump and switch off the pump.

## 4. Measuring the adsorption isotherm

Cool down tube A with a Dewar to room temperature. The Dewar is filled with VE-water<sup>3</sup> from the big plastic bottles which are thermally equilibrated to room temperature. Measure the room temperature. Carefully open valve H2 to evaporate a small amount (about 0,2 ml) of methyl butane into the evacuated part of the apparatus. Then close H2. Wait for 10 min to obtain equilibrium and read the equilibrium pressure and the evaporated volume of methyl butane. Repeat this in approximately 0,2-ml-steps until a pressure of about 100 mbar is achieved, then evaporate in steps of about 0,1 ml. From the volume-pressure pairs calculate the total volume evaporated from tube B according:

$$n_a = \frac{\rho(t)}{M_m} \sum_i V_i(l) \quad (5)$$
$$\rho(t) = \frac{0,6406}{1 + 1,527 \cdot 10^{-3} t + 3,21 \cdot 10^{-6} t^2} \cdot \frac{\text{g}}{\text{cm}^3}$$

with:  $M_m = 72,15 \text{ g mol}^{-1}$  molar mass of Methyl-Butane,  $t$  temperatur in °C.  $\rho(t)$  is the temperature dependent density of liquid Methyl-Butane and  $V_i(l)$  are the volume increments of liquid Methyl-Butane evaporated into the apparatus

If the evaporation of methyl butane takes to long, one can heat up tube B to room temperature or above using warm water. Don't forget to consider the temperature dependence of the density! Draw volume  $V$  versus pressure  $p$  as draft sketch.

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<sup>2</sup>After 5 min cooling can be accelerated with a water filled beaker.

<sup>3</sup>VE = voll entsalzt, deionized

5. Shut down of the apparatus

Open carefully H1, then H2. Dismount tube B, empty and clean it. Leave H1 open to atmospheric pressure.

## 4 Safety considerations

Include in your safety considerations the methods (vacuum, furnace) and substances used in the experiment. Explain:

- What kind of administrative and organizational rules should be considered to perform the experiment safely?
- What kind of technical rules and procedures should be obeyed?
- What kind of personal protective equipment do you recommend?

## 5 What you should know

Chemical and physical adsorption, ionosorption, Lenard-Jones-potential, heat of adsorption, dynamic equilibrium, Langmuir-isotherm and its kinetic derivation, BET isotherm, application of adsorption.

## 6 Additional questions (to be discussed by the students in their reports)

1. Which forces are responsible for physical adsorption?
2. Plot qualitatively the potential energy of an adsorbing molecule in the force field of the absorbing surface as function of the distance  $r$ . What is the difference between physical and chemical adsorption?
3. Discuss how one can measure the heat of adsorption.

## Appendix

### Short description of the program „OriginPro 9.1“ and higher

This is a short description for experiment A42. Please use it for fitting the isotherms of Langmuir and BET correspondingly.

Creating and plotting data

- Start OriginPro 9.1



- Enter  $p$  and  $V$  in columns A(X) and B(Y)
- Create two new columns (right mouseclick aside the table ► **Neue Spalte**) and enter the errors in x- and y-direction. These columns have to be declared as error columns (right mouseclick on the head of the respective column marks the column ► **Setzen als** ► e. g. x-Fehlerbalken).

Fitting the parameter of the Szyszkowski function

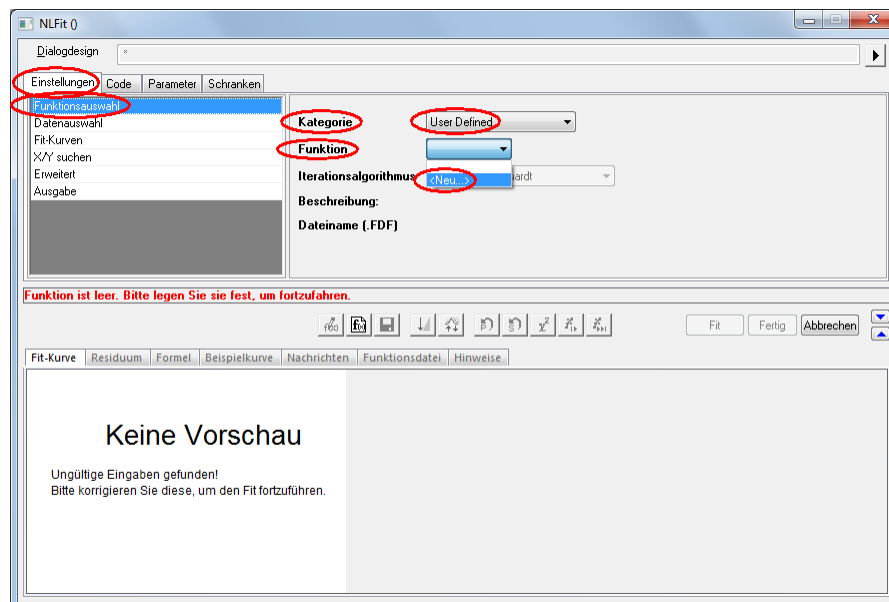


Fig. 3:

- Mark all columns ► **Analyse** ► **Anpassen** ► **Nichtlinearer Fit**.
- In the Fitdialogfenster (Builder) under ► **Einstellungen** ► **Funktionsauswahl** ► **Kategorie** ► **User Defined**, then select ► **Funktion** ► **<Neu...>** (Fig. 3).
- In the following Fit-Dialogfenster under ► **Funktionsname** choose a function name and leave all other settings unchanged (Fig. 4).
- Choose the independent (e. g. x) and the dependent variable (e. g. y) and list in the field ► **Parameter** the fitting parameters ( $a$  and  $b$ ) (separated by a comma) (Fig. 5).

Fitfunktionen erstellen - Name und Typ - Szyskowski

Hinweise  
 Funktionstyp  
 Wählen Sie diese Option für einfache Anpassungsfunktionen, die nur über eine abhängige Variable verfügen.  
 Der Funktionskörper ist auf einen Ausdruck beschränkt, und Sie müssen nur die rechte Seite der Gleichung eingeben.  
 Diese Option bietet eine bessere Leistung als Origin C.  
 ----- Beispiel: -----  
 $a + b * \exp(-x^c / d)$

Eine Kategorie auswählen oder erstellen: User Defined [Neu]

Funktionsname: Szyskowski

Dateiname (.FDF): Szyskowski.FDF

Beschreibung: Versuch A 42

Funktionsmodell  
☒ Explizit ☐ Implizit

Funktionstyp  
☒ Ausdruck  
☐ Gleichungen  
☐ Origin C  
☐ LabTalk-Skript  
☐ Externe DLL-basierte Funktion  
☐ Integration während Anpassung einschließen

Abbrechen << Zurück Weiter >> Fertigstellen

Fig. 4:

Fitfunktionen erstellen - Variablen und Parameter - Szyskowski\_Fit

Hinweise  
 Geben Sie Namen von Variablen, Parametern, abgeleiteten Parametern und Konstanten den Bearbeitungsfeldern ein. Trennen Sie mehrere Namen durch ein Komma.  
 ----- Beispiel: -----  
 x1, x2  
 Abgeleitete Parameter  
 Abgeleitete Parameter sind zusätzliche Parameter, die aus den Parameterwerten der Funktion nach dem Anpassungsprozess berechnet werden.  
 Konstanten  
 Konstanten sind feste Werte, die entweder im Funktionsausdruck oder im Parameterinitialisierungscode verwendet werden.

Unabhängige: x

Abhängige Variablen: y

Parameter: a,b

Abgeleitete Parameter:

Konstanten:

☐ Impulsfunktion

Abbrechen << Zurück Weiter >> Fertigstellen

Fig. 5:



- Choose as ► Funktionskörper ►  $y=[\text{code for the isotherm}]$  and initialize the parameters by setting under ► Parameter ► Anfangswerte useful(!) start values for  $a$  and  $b$  (Fig. 6).

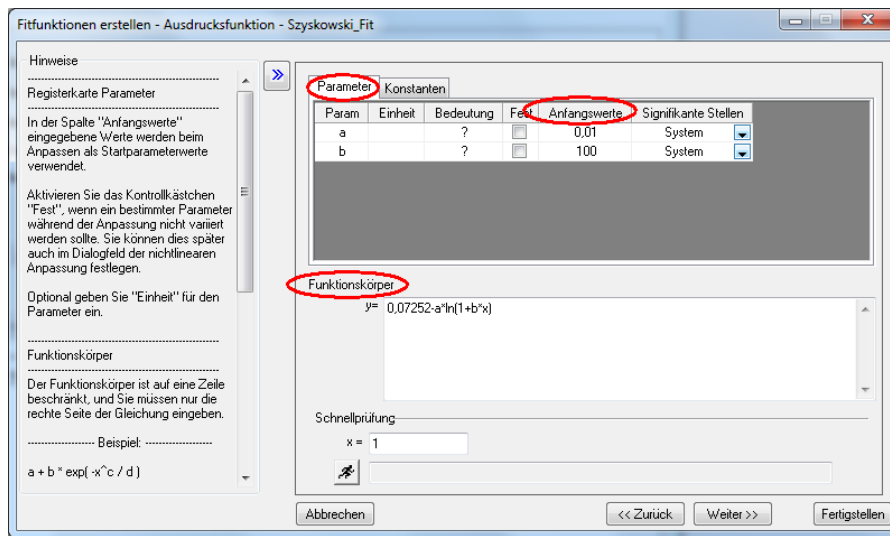


Fig. 6:

- Click ► Fertigstellen, then on the symbol ► Fit bis konvergiert (Fig. 7 )

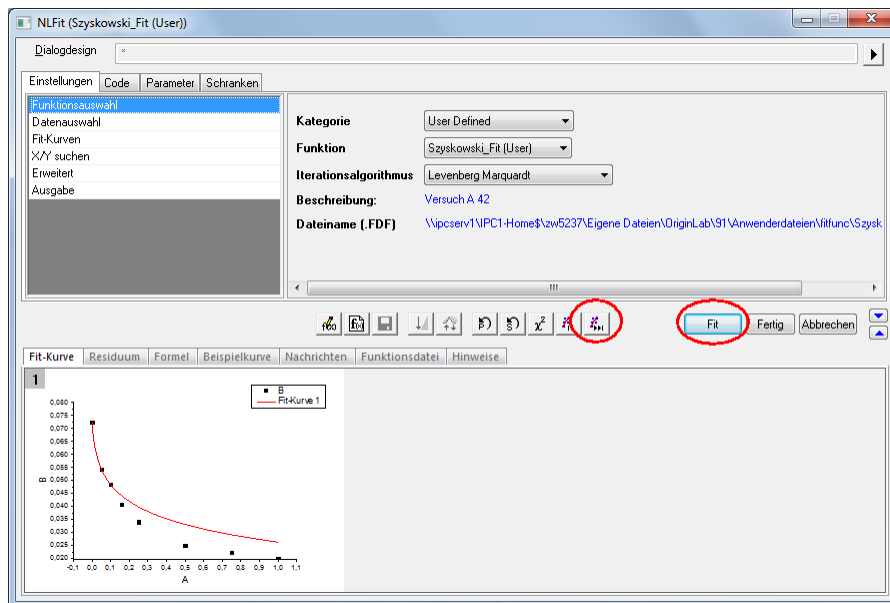


Fig. 7:

- As the fit converged successfully Fit konvergiert press ► OK. You proceed to the fit results with parameters  $a$  and  $b$  with their errors. Open in the menu ► Hinweise,

to display the fit function. Below that you find a graph, which can be magnified bei double clicking (Fig. 8).

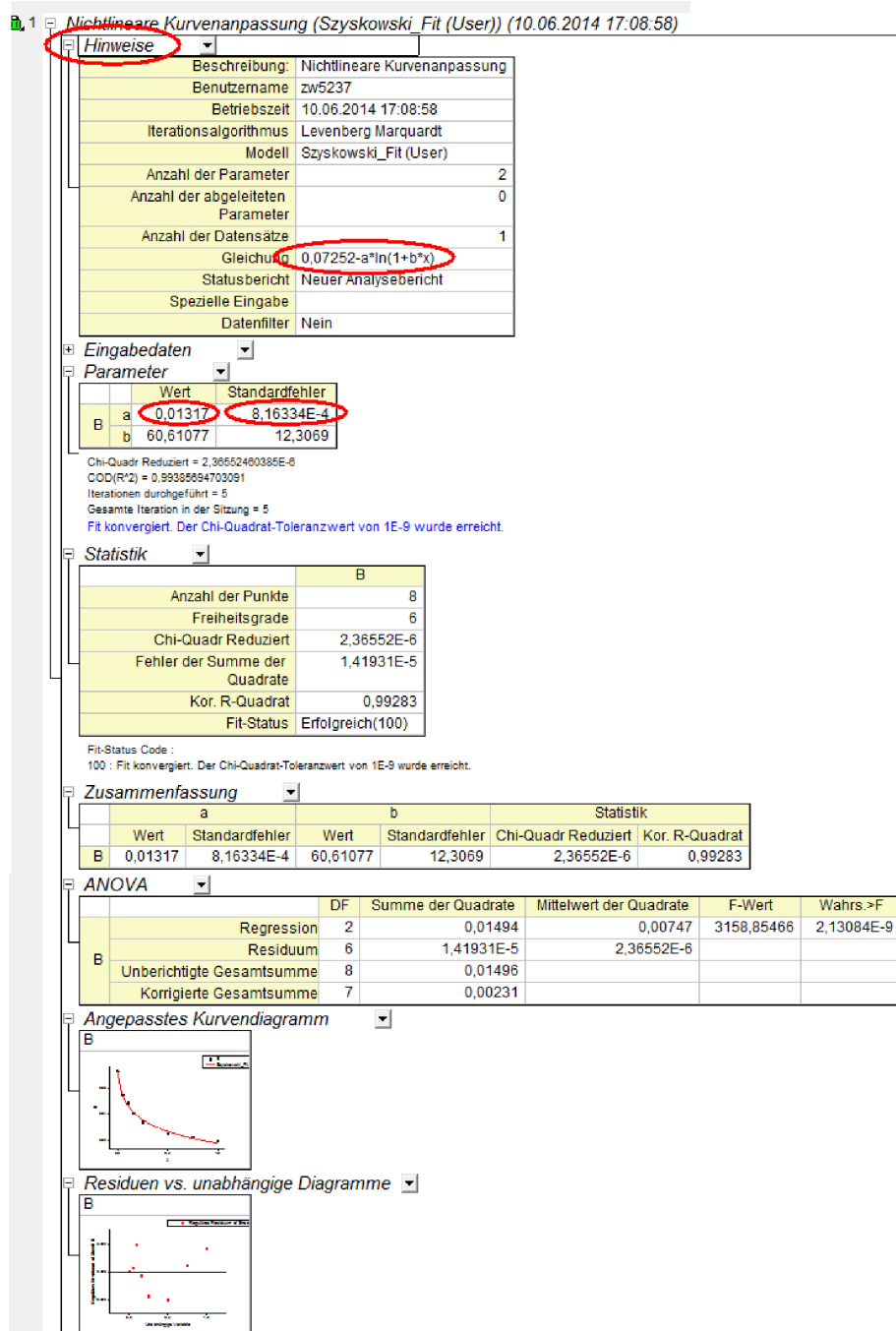


Fig. 8:

- If the fit did not converge (z.B. Funktion konvergiert nicht, try different starting values for parameters  $a$  and  $b$ . Check the formular (e.g. for the correct delimiter symbol: dot or comma).