Script for Experiment

A42

Determination of the surface tension of a binary mixture employing the maximum bubble pressure method

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1 Abstract

The concentration dependence of the interfacial tension σ of mixtures of water with an organic solvent has to be determined employing the maximum bubble pressure method at constant temperature. Samples with volume concentrations $\phi_B = 0$, 5, 10, 16, 25, 50, 75 and 100% of the organic solvent (acetone, ethanol or methanol) are measured.

2 Introduction

2.1 Theoretical background

The fundamental equation of the free enthalpy G of a system with K components including the contribution of the surface can be written as:

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}p + \sum_{i=A}^{K} \mu_i \mathrm{d}n_i + \sigma \mathrm{d}A \tag{1}$$

The term $\sigma\mathrm{d}A$ is new and refers to the interface. $\sigma = (\partial G/\partial A)_{p,T,n_i}$ is the surface or interfacial tension and $\mathrm{d}A$ is the differential variation of the surface area.

Following Gibbs this expression can be devided into the contributions of the adjoining volume phases liquid (l) and vapour (v) and a contribution of the inhomogeneous inter-“phase“ (superscript σ) lying in between. This inter-phase is regarded as a mathematical two dimensional layer. As for all other extensive quantities we can write for the free enthalpy G of a two phase system:

$$G = G^l + G^v + G^\sigma \tag{2}$$

We can apply equation (1) to G^σ at constant temperature T (for a two dimensional surface $V^\sigma = 0$):

$$\mathrm{d}G^\sigma = \sum_i \mu_i \mathrm{d}n_i^\sigma + \sigma \mathrm{d}A \quad , \tag{3}$$

Integration under the restriction of constant composition yields

$$G^\sigma = \sum_i \mu_i n_i^\sigma + \sigma A \quad . \tag{4}$$

After subsequent differentiation (product rule!) we find:

$$\mathrm{d}G^\sigma = \sum_i \mu_i \mathrm{d}n_i^\sigma + \sum_i n_i^\sigma \mathrm{d}\mu_i + \sigma \mathrm{d}A + A\mathrm{d}\sigma \tag{5}$$

The comparison of equations (3) and (5) yields:

$$0 = \sum_i n_i^\sigma \mathrm{d}\mu_i + A\mathrm{d}\sigma \quad . \tag{6}$$

This derivation is fully analogous to the Gibbs-Duhem equation. For a two component system it reads:

$$A\mathrm{d}\sigma = -n_A^\sigma \mathrm{d}\mu_A - n_B^\sigma \mathrm{d}\mu_B \quad . \tag{7}$$

Introducing now the Gibbs' surface concentration $\Gamma_i = \frac{n_i^\sigma}{A}$ it follows:

$$\mathrm{d}\sigma = -\Gamma_A \mathrm{d}\mu_A - \Gamma_B \mathrm{d}\mu_B \quad . \tag{8}$$

The position of the Gibbs' deviding surface can be fixed arbitraily. In a two component system it is convenient to set $z = 0$ in a way that the surface concentration of the solvent Γ_A becomes zero. The segments denoted $\oplus$ and $\ominus$ in figure 1 cancel.

$$\mathrm{d}\sigma = -\Gamma_{B(A)} \mathrm{d}\mu_B \quad . \tag{9}$$

Now $\Gamma_{B(A)}$ is the relative surface concentration of the solute B after fixing the surface with respect to A. Inserting

$$\mathrm{d}\mu_B = \underbrace{\mathrm{d}\mu_B^\circ}_{=0} + RT \mathrm{d}\ln a_B \tag{10}$$

and rearranging the expression one obtains **Gibbs' adsorption isotherm**:

$$\Gamma_{B(A)} = -\frac{a_B}{RT}\left(\frac{\mathrm{d}\sigma}{\mathrm{d}a_B}\right)_T \tag{11}$$

If the solute is enriched at the surface (e. g. surfactant in water) $\Gamma_{B(A)} > 0$ (in German: kapillaraktiv), if it is depleted (e. g. salt in water) $\Gamma_{B(A)} < 0$ (in German: kapillarinaktiv).

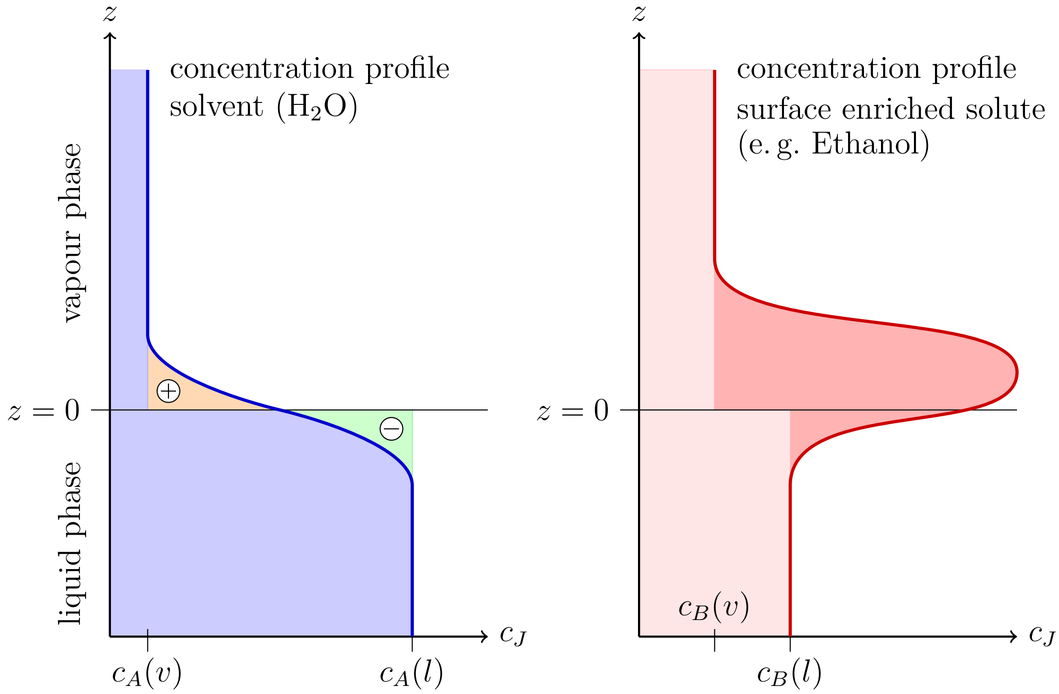

Fig. 1: Fixing Gibbs' dividing surface in a two component system. Concentration profile of the solvent A (left) and of a solut B that is enriched at the interface (right).

In ideal or dilute solutions the activity coefficient can be set approximately to 1. It follows for Gibbs' adsorption isotherm (using volume concentration ϕ_B as concentrations scale):

$$\Gamma_{B(A)} = -\frac{\phi_B}{RT}\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\phi_B}\right)_T \tag{12}$$

Equation (12) is the main result of the above considerations.[1] Measuring the concentration dependence of the surface tension one has access to the relative surface concentration $\Gamma_{B(A)}$!

2.2 Szyszkowski and Langmuir

The experimental results will be evaluated according to an empirical relation due to Szyszkowski:[2]

$$\sigma(\phi_B) = \sigma_A - a\ln(b\phi_B + 1) \tag{13}$$

with σ_A: surface tension of the pure solvent (here: water), a and b are constants, which have to be evaluated using a nonlinear least square fit. Differentiating σ from equation

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[1] Notice the expression $\frac{\phi_B}{\mathrm{d}\phi_B}$ in equation (12). Since the unit of the concentration is cancelled, the equation can be formulated with any concentration variable.

[2] B. von Szyszkowski, *Z. Phys. Chem.* **64** (1908) 385.

(13) with respect to ϕ_B

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\phi_B} = \frac{ab}{b\phi_B + 1} \tag{14}$$

and inserting the result in equation (12), one obtains:

$$\Gamma_{B(A)} = \frac{a}{RT}\frac{b\phi_B}{b\phi_B + 1} \tag{15}$$

This equation is equivalent to Langmuir's adsorption isotherm[3] (see experiment A45), which describes the adsorption of a gas at a solid surface:

$$n_{ads} = n_{mono}\frac{Kp}{Kp + 1} \tag{16}$$

Analogous to the Langmuir isotherm equation (15) describes the enrichment of a dissolved substance at the liquid-gas-interface. Thus, the term $\frac{a}{RT}$ has the meaning of the maximum number of moles (per unit area) forming a monomolecular layer at the interface. The constant b has the meaning of the equilibrium constant of the following process:

$$B_{\text{dissolved}} \quad \rightleftharpoons \quad B_{\text{interface}} \tag{17}$$

Both quantities a, b as well as $\Gamma_{B(A)}$ are accessible by fitting equation (13) to the data points.

2.3 Experimental principles

Since a liquid system tends to minimize the interface a bubble inside a liquid exhibits an additional pressure. This bubble or capillary pressure p^σ is caused by interfacial tension σ. Restricting to spherical surfaces of radius r it can be quantified by the Laplace equation:

$$p^\sigma = \frac{2\sigma}{r} \tag{18}$$

The bubble pressure is easily accessible since it represents the highest pressure (in addition to the hydrostatic pressure) to create bubbles that stream from a capillary into the liquid. At this highest pressure the radius of the bubble is at its minimum and we have: radius of the bubble ≈ radius of the capillary (see fig. 2):

$$p_{max} = \frac{2\sigma}{r} + \rho_l\left(\phi_B\right)gh' \tag{19}$$

with acceleration of gravity $g = 9{,}807\,\mathrm{ms}^{-2}$, density of the liquid $\rho_l\left(\phi_B\right)$ at concentration ϕ_B (see diagram at the end of this manuscript), immersion depth h' of the capillary into the liquid.

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[3] I. Langmuir, *J. Am. Chem. Soc.* **40** (1918) 1361.

3 Experimental procedure

3.1 Preparation of the solutions

With the help of bulb pipettes and volumetric flasks prepare mixtures of component A (water) and of component B (either methanol, ethanol or acetone; ask the assistant which mixture has to be prepared) with volume concentrations of $\phi_B = 0$, 5, 10, 16, 25, 50, 75 und 100%. For this use the labelled flasks provided with the experiment:

Volume concentration / %	75	50	25	16	10	5
Volumetric flask / ml	20	20	100	50	100	100
Volume to be pipetted / ml	15	10	25	8	10	5

Attention: Never take the components directly from the storage bottles with the pipettes. First fill the estimated volume into a beaker glass. Tabulate the following quantities

- the pipetted volume of component B,
- the kind and size of flasks,
- the respective volume error.

3.2 Getting the apparatus ready

Figure 2 shows a schematic sketch of the apparatus. It consists of a water manometer (=U-tube) which on the left side is connected to the capillary with its grinded end plane, and which on the right side is connected to a supply funnel. The tip of the glass rod connected to the capillary has to be adjusted during the measurement to the liquid surface. This assures a constant immersion depth. The valves H_1, H_2 und H_3 serve for venting the apparatus, filling the manometer with blue coloured water, to build up the pressure p_{max} and for emptying the manometer. All valves and the connection to the capillary have to be checked with respect to leak tightness. Possibly they have to be sealed using vacuum grease.

Now, the manometer fluid has to be poured via the reservoir container (funnel) into the manometer until the liquid reaches the scaled paper. Avoid bubbles, close valve H_2 and fill the blue water until the liquid level is located in the reservoir.

3.3 Performing measurements

A 50 mL beaker will be filled with approx. 10 mL of the solution to be measured. It will be placed onto the vertically adjustable (rough and fine) mount. Start the experiment with the pure component B and end with pure water!

Using the rough adjustment of the mount (black screw at the vertical table-track) the tip of the capillary will be positioned as to dip into the solution. Using the fine

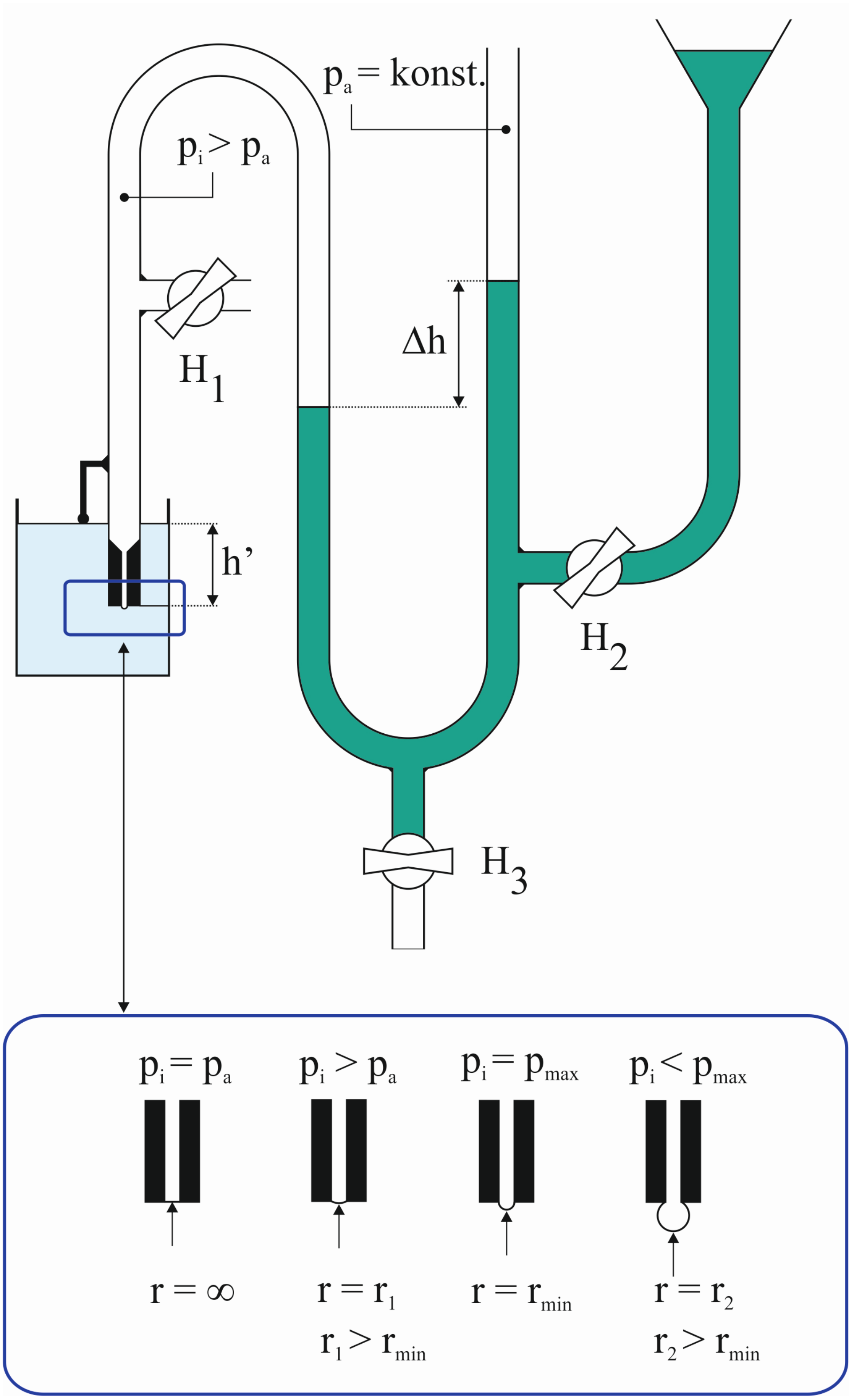


Fig. 2: Sketch of the experimental setup

adjustment (brass screw below the bottom of the mount) retract the tip from the liquid and readjust it until a meniscus is formed between tip and liquid surface.

Now, as valve H_2 is opened carefully, water leaks form the reservoir into the manometer. The air between the meniscus at the end of the capillary an the left manometer tube is compressed. A height difference between the left and right manometer tube will built up. Follow the height difference and read the levels in both tubes just before a series of bubbles is set free into the solution in the beaker. This maximum height level Δh is proportional to the pressure maximum. Each experimenter reads one tube (left or right, change after five readings).

Perform 10 measurements for each solution, calculate the mean value $\overline{\Delta h}$ and its standard deviation $\delta\Delta h$. As the manometer is overfilled with manometer liquid the level can be subsequently lowered by opening valve H_1 and H_3.

After the experiments measure

- the dip depth h' of the capillary with the help of a sliding calliper (use the accuracy of 1/10 mm),
- room temperature.

4 The tasks

1. Calculation of r_K and its error δr_K

   First of all calculate the inner radius of the capillary r_K using the measurement of pure water (equation (19)), with $\rho_l\,(\phi_B = 0) = \rho_{H_2O}$ (density: see appendix). p_{max} can be calculated from the manometer height difference Δh: $p_{max} = \rho_{H_2O}\, g\, \Delta h$.

   The surface tension of water can be calculated as function of the measurement temperature (T in degree celsius)

   $$\sigma_{H_2O}(T) = 0{,}07582\,\frac{\mathrm{N}}{\mathrm{m}} - 1{,}542 \cdot 10^{-4}\,\frac{\mathrm{N}}{\mathrm{K\,m}}\,T \tag{20}$$

   The error δr_K of r_K has to be calculated using Gauß' error propagation from the standard deviation of $\overline{\Delta h}$ (see: `www.ipc.kit.edu/18_2254.php`, either equation 4 or 5).

2. Calculation and representation of $\sigma(\phi_B)$

   Calculate the surface tension for each concentration measured. For the densities $\rho_l(\phi_B)$ of the mixtures see the appendix. For the error calculation consider the error of r_K and the standard deviation of the height measurement $\overline{\Delta h}$. Include in a table: ϕ_B, $\overline{\Delta h}$, $\delta\Delta h$, σ and $\delta\sigma$. Plot σ including error bars ($\pm\delta\sigma$) versus ϕ_B

3. Szyszkowski-Analysis

   Determine the constants a and b of the Szyszkowski equation 13. Fit both parameters using a nonlinear least square routine (e. g. with the help of „Origin 9.1“, which is available in the computer pool at room 406. You can find a short description in the appendix). Plot the fitted curve and the data points in the composition range $0 \leq \phi_B \leq 1$.

4. Determination of Gibbs' relative surface concentration $\Gamma_{B(A)}$

   Determine $\Gamma_{B(A)}$ at compositions $\phi_B = 0{,}2$ and $\phi_B = 0{,}4$ using equation (15). What is the space required by one molecule (either acetone, methanol or ethanol) at the surface? How can that be calculated from $\Gamma_{B(A)}$?

5. Answer the following questions:

   - Explain the difference between volume concentration ϕ_B and volume fraction φ_B. Explain under which experimental conditions one should use which quantity (e. g. consider the sample preparation).
   - Explain the term *wetting*. How can this property be described quantitatively?
   - Where in nature, engineering and daily life does surface tension play an important role? Give some examples.

5 What else should be known

- How do surfactants work?
- Temperature dependence of simple liquids, Eötvös' rule,
- Surface active vs. surface inactive Solutes
- Adsorption isotherm of Gibbs, adsorption isotherm of Langmuir
- Least square method

Appendix

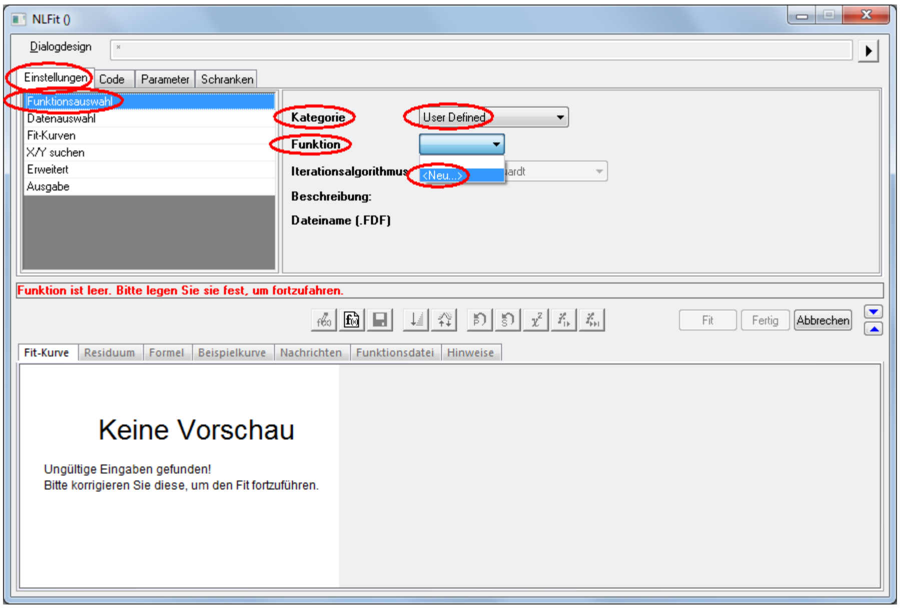
Short description of the program „OriginPro 9.1“

Dieses Produkt ist lizenziert für:
ipc
KIT
Version: 91G
Copyright © 1991-2013 OriginLab Corporation
Diese Software ist durch das US amerikanische Urheber- recht sowie internationale Ver- träge geschützt. Unbefugte Vervielfältigung ist strafbar und wird straf- und zivilrechtlich verfolgt. Alle Rechte vorbehalten.

Creating and plotting data

- Start OriginPro 9.1
- Enter ϕ_B and $\sigma(\phi_B)$ 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 do 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



Kategorie: User Defined

Funktion: <Neu...>

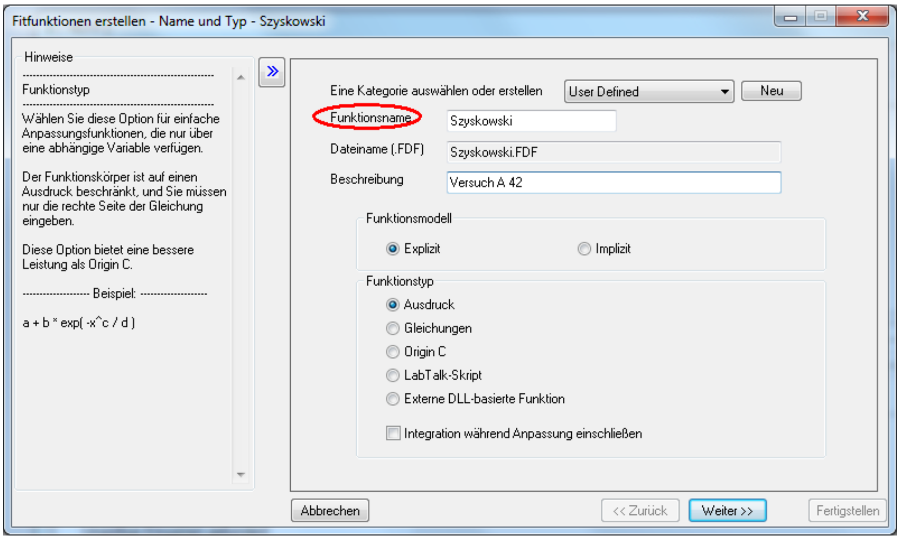
Funktion ist leer. Bitte legen Sie sie fest, um fortzufahren.

Keine Vorschau

Ungültige Eingaben gefunden!
Bitte korrigieren Sie diese, um den Fit fortzuführen.

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).
- Choose as ▶ Funktionskörper ▶ y=[value for σ_{H_2O}]-a*ln(1+b*x) and initialize the parameters by setting under ▶ Parameter ▶ Anfangswerte useful(!) start values for a and b (Fig. 6).
- Click ▶ Fertigstellen, then on the symbol ▶ Fit bis konvergiert (Fig. 7)



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)

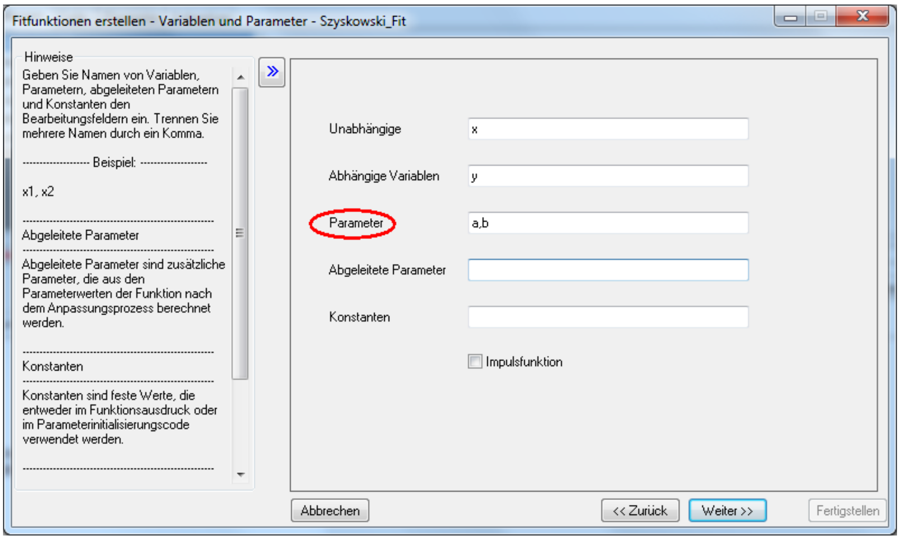
Eine Kategorie auswählen oder erstellen: User Defined
Funktionsname: Szyskowski
Dateiname (.FDF): Szyskowski.FDF
Beschreibung: Versuch A 42

Funktionsmodell
● Explizit ○ Implizit

Funktionstyp
● Ausdruck
○ Gleichungen
○ Origin C
○ LabTalk-Skript
○ Externe DLL-basierte Funktion

☐ Integration während Anpassung einschließen

Fig. 4:



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.

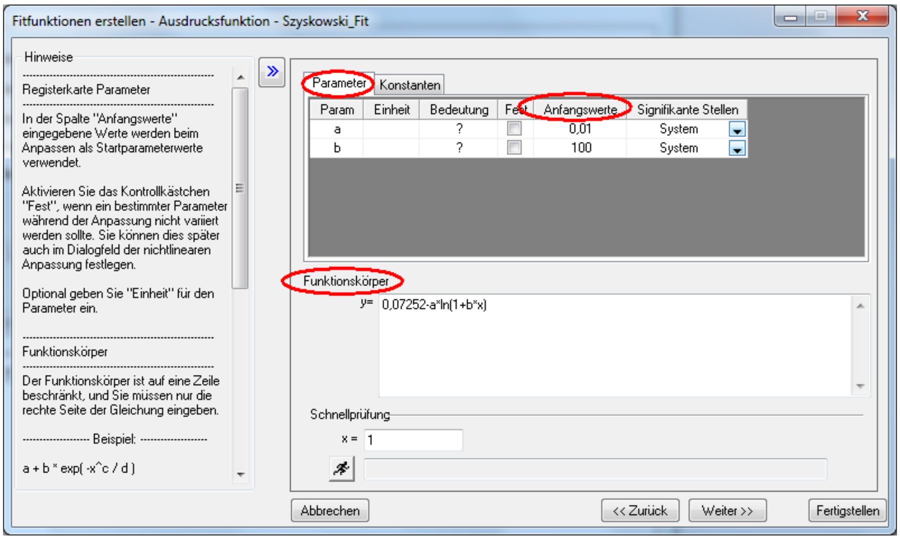
Konstanten

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

Fig. 5:



Fitfunktionen erstellen - Ausdrucksfunktion - Szyskowski_Fit

Hinweise

Registerkarte Parameter

In der Spalte "Anfangswerte" eingegebene Werte werden beim Anpassen als Startparameterwerte verwendet.

Aktivieren Sie das Kontrollkästchen "Fest", wenn ein bestimmter Parameter während der Anpassung nicht variiert werden sollte. Sie können dies später auch im Dialogfeld der nichtlinearen Anpassung festlegen.

Optional geben Sie "Einheit" für den Parameter ein.

Funktionskörper

Der Funktionskörper ist auf eine Zeile beschränkt, und Sie müssen nur die rechte Seite der Gleichung eingeben.

Beispiel:

a + b * exp(-x^c / d)

Param	Einheit	Bedeutung	Fest	Anfangswerte	Signifikante Stellen
a		?	☐	0,01	System
b		?	☐	100	System

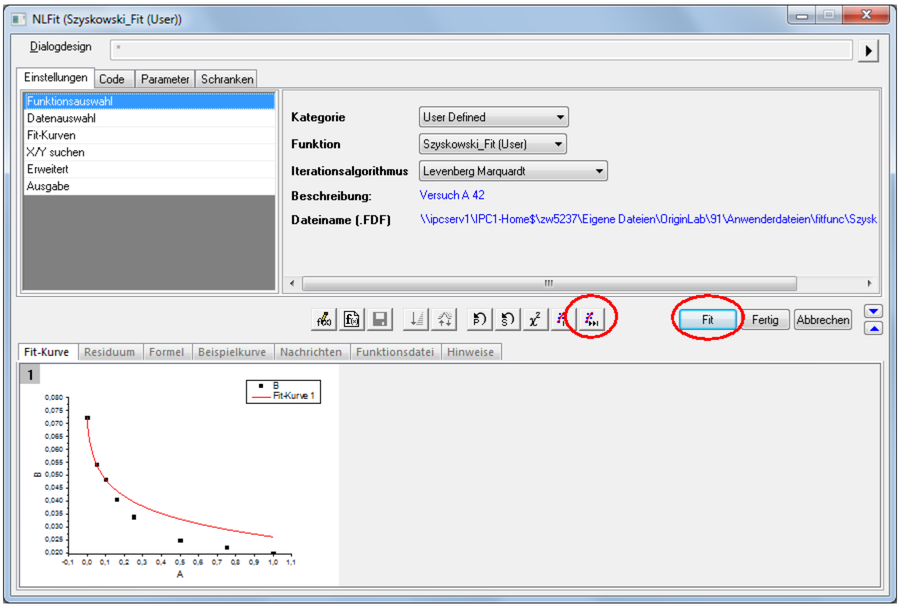
Funktionskörper

y= 0,07252-a*ln(1+b*x)

Schnellprüfung

x = 1

Fig. 6:



NLFit (Szyskowski_Fit (User))

Kategorie: User Defined

Funktion: Szyskowski_Fit (User)

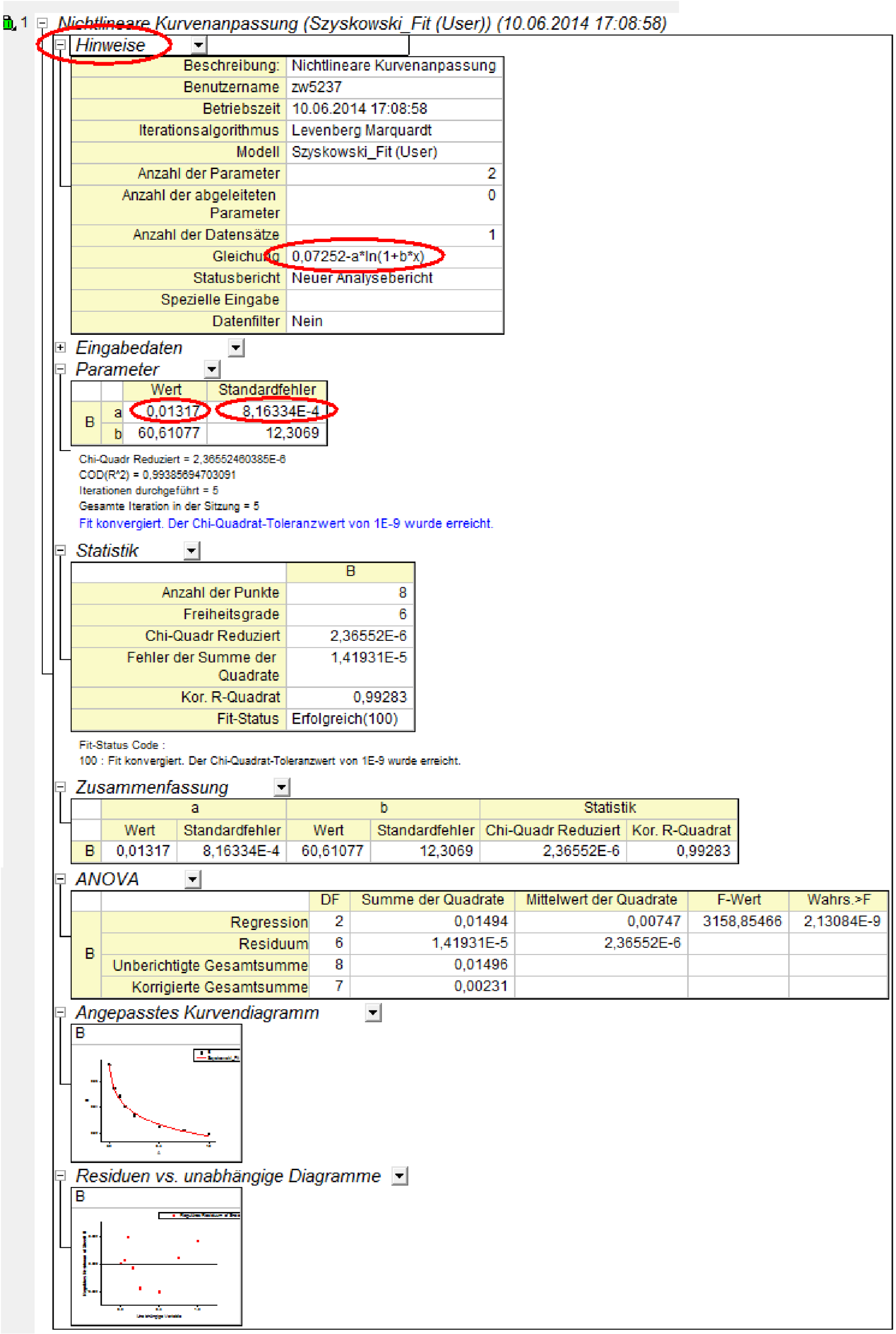
Iterationsalgorithmus: Levenberg Marquardt

Beschreibung: Versuch A 42

Dateiname (.FDF): \\ipcserv1\IPC1-Home$\zw5237\Eigene Dateien\OriginLab\91\Anwenderdateien\fitfunc\Szysk

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 menue ▶ **Hinweise**, to disply the fit function. Below that you find a graph, which can be magnified bei double clicking (Fig. 8).



1 Nichtlineare Kurvenanpassung (Szyskowski_Fit (User)) (10.06.2014 17:08:58)

Hinweise

Beschreibung:	Nichtlineare Kurvenanpassung
Benutzername	zw5237
Betriebszeit	10.06.2014 17:08:58
Iterationsalgorithmus	Levenberg Marquardt
Modell	Szyskowski_Fit (User)
Anzahl der Parameter	2
Anzahl der abgeleiteten Parameter	0
Anzahl der Datensätze	1
Gleichung	0,07252-a*ln(1+b*x)
Statusbericht	Neuer Analysebericht
Spezielle Eingabe	
Datenfilter	Nein

Eingabedaten

Parameter

		Wert	Standardfehler
B	a	0,01317	8,16334E-4
	b	60,61077	12,3069

```
Chi-Quadr Reduziert = 2,36552460385E-6
COD(R^2) = 0,99385694703091
Iterationen durchgeführt = 5
Gesamte Iteration in der Sitzung = 5
Fit konvergiert. Der Chi-Quadrat-Toleranzwert von 1E-9 wurde erreicht.
```

Statistik

	B
Anzahl der Punkte	8
Freiheitsgrade	6
Chi-Quadr Reduziert	2,36552E-6
Fehler der Summe der Quadrate	1,41931E-5
Kor. R-Quadrat	0,99283
Fit-Status	Erfolgreich(100)

```
Fit-Status Code :
100 : Fit konvergiert. Der Chi-Quadrat-Toleranzwert von 1E-9 wurde erreicht.
```

Zusammenfassung

	a		b		Statistik	
	Wert	Standardfehler	Wert	Standardfehler	Chi-Quadr Reduziert	Kor. R-Quadrat
B	0,01317	8,16334E-4	60,61077	12,3069	2,36552E-6	0,99283

ANOVA

		DF	Summe der Quadrate	Mittelwert der Quadrate	F-Wert	Wahrs.>F
B	Regression	2	0,01494	0,00747	3158,85466	2,13084E-9
	Residuum	6	1,41931E-5	2,36552E-6		
	Unberichtigte Gesamtsumme	8	0,01496			
	Korrigierte Gesamtsumme	7	0,00231			

Angepasstes Kurvendiagramm

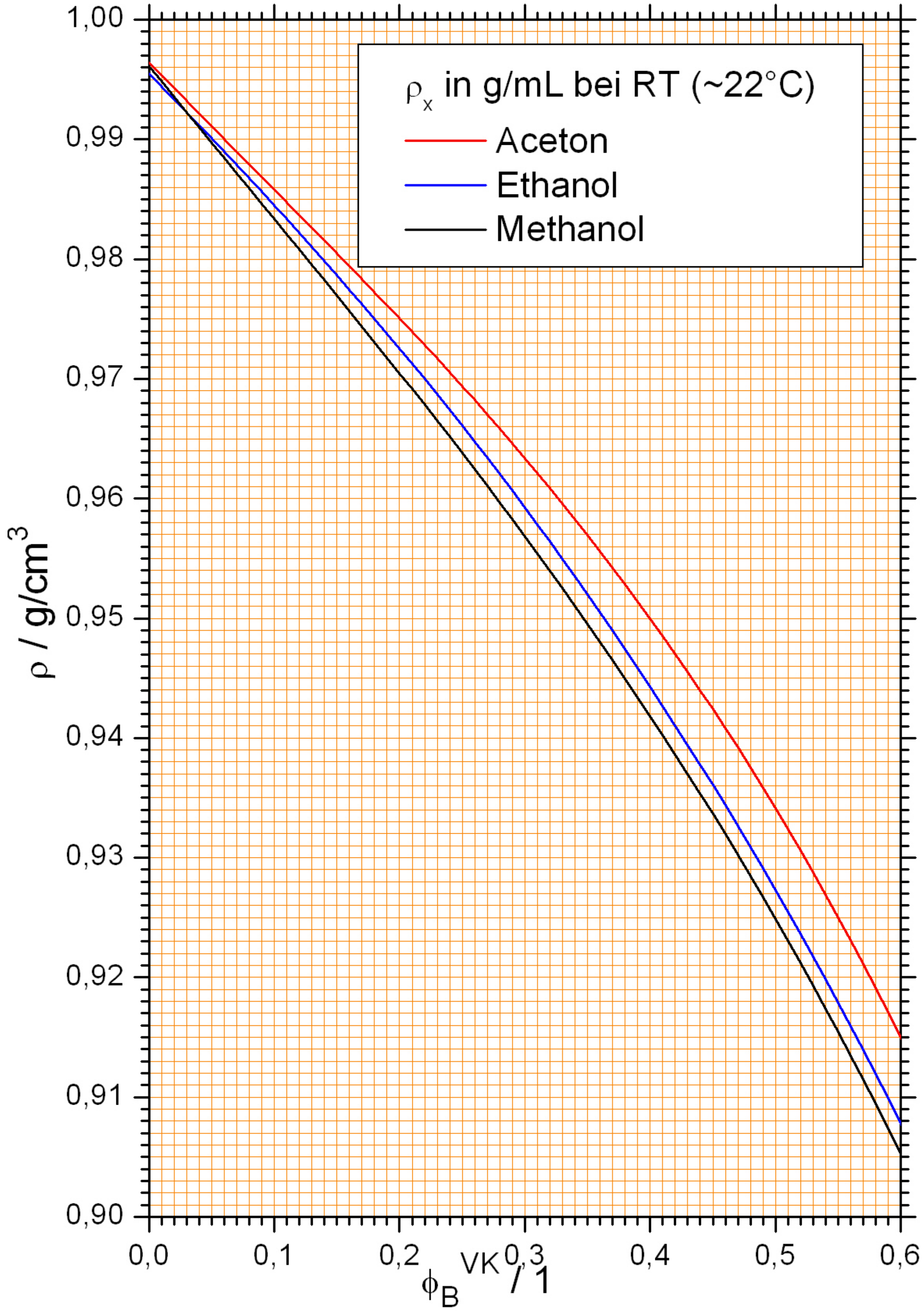
B

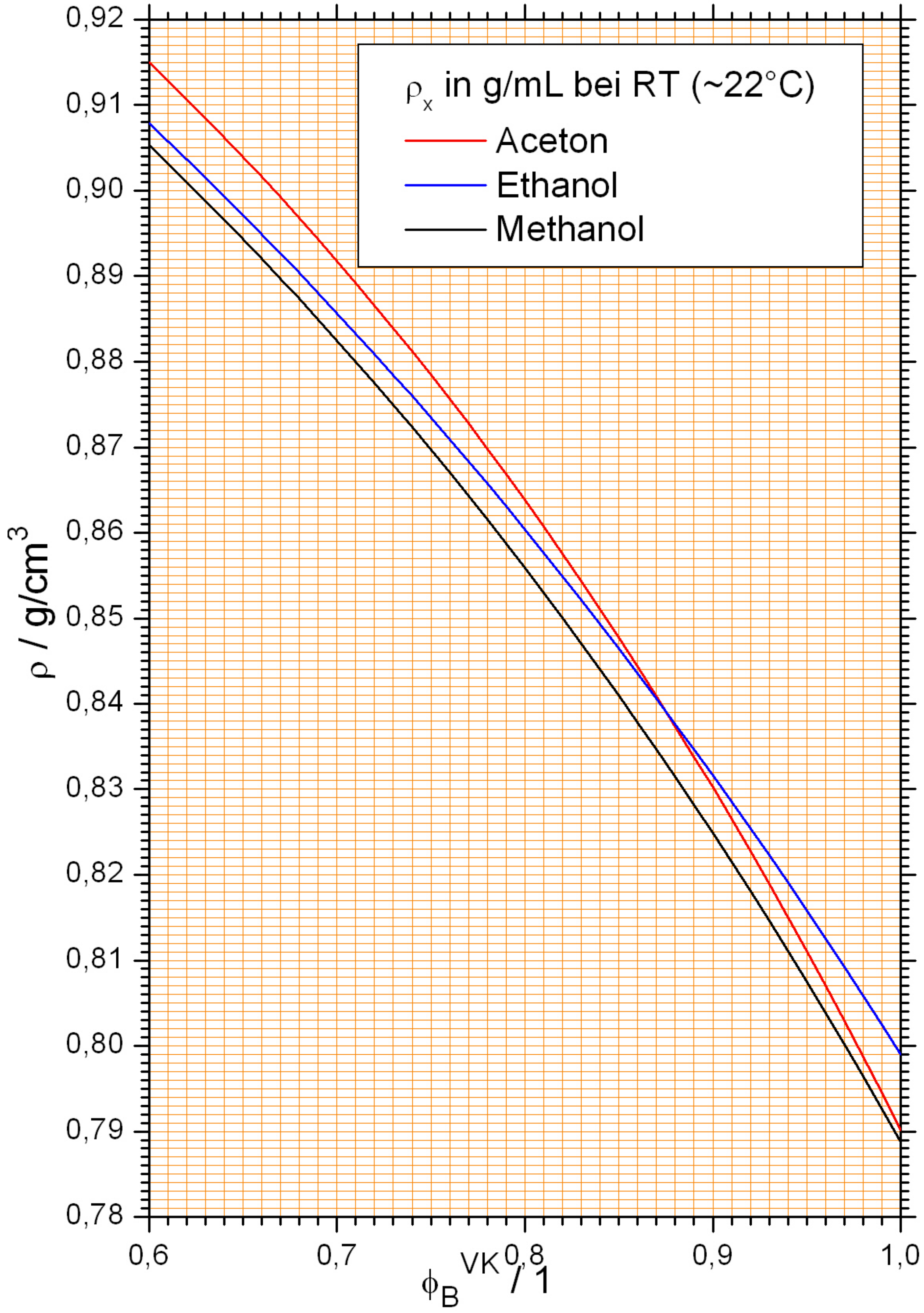
Residuen vs. unabhängige Diagramme

B

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).


ρ_x in g/mL bei RT (~22°C)
Aceton
Ethanol
Methanol
ρ / g/cm³
1,00
0,99
0,98
0,97
0,96
0,95
0,94
0,93
0,92
0,91
0,90
0,0
0,1
0,2
0,3
0,4
0,5
0,6
ϕ_B^{VK} / 1


ρx in g/mL bei RT (~22°C)
Aceton
Ethanol
Methanol
ρ / g/cm3
0,92
0,91
0,90
0,89
0,88
0,87
0,86
0,85
0,84
0,83
0,82
0,81
0,80
0,79
0,78
0,6
0,7
0,8
0,9
1,0
ϕB VK / 1