Instruction to experiment A10:

Partial molar excess volume in the water/methanol system.

Task

Basing on precise density measurements one has to determine the mean excess volume in the binary methanol/water system for several different mixtures.

Theoretical Backgrounds

The driving force governing the intermixing of different substances is the pronouncedly increasing disorder in the system. By mixing two substances one observes complex balance between attractive and repulsive interactions of different molecules (mixture of ideal gases represents an exception). Die forces stabilizing the mixture, e.g. the dipole-dipole interactions between adjacent polar molecules, are usually of short range and consequently become more relevant in liquid and solids than in the gas phase. When intermixing two pure liquid substances (A) and (B) consisting of A and B molecules, respectively, three distinct physical states in the resulting phase can be created. The state of the mixture depends on the interaction energy between the A and B molecules, E(A-B), i.e. the following relationships: E(A-B)>E(A-A), E(A-B)<E(A-A), E(A-B)~E(A-A), represent the decisive criterion. These interactions are responsible for the pronounced modifications of the volume ΔV and the enthalpy ΔH observed during the intermixing process.

Case	Volume	Enthalpy	Example
overattracted	$\Delta V < 0$	$\Delta H < 0$	water/sulfuric acid
ideal	$\Delta V = 0$	$\Delta H = 0$	Heptane/Hexane
underattracted	$\Delta V > 0$	$\Delta H > 0$	acetone/carbon disulfide

In this experiment the volume of the real mixed phases (mixtures) and their components will be studied on example of the water/methanol system. The partial molar excess volumes will be derived from the mean excess volume of the H_2O/CH_3OH system. When considering an arbitrary mixture of k different components (1, 2, 3…k), whose composition is defined by the mole number n_i or by the mole ratios $x_i = n_i / \sum n_i$, the following relation applies:

(1)
$$V^{id} = \sum_{i=1}^{k} n_i V_{m,i}^0$$

V^{id} stays for the volume of the mixture, and $V_{m,i}^0$ represents the molar volume of the component i. By dividing the equation (1) by the total mole number of the mixed phase $n = \sum n_i$ one gets the molar volume of the ideal mixture:

(2)

$$V_m^{id}=\frac{V^{id}}{\sum n_i}=\sum_{i=1}^{k} x_i V_{m,i}^0$$

The equation (2) expresses the so called main rule of a mixture: Each component of an ideal mixture contributes to the resulting volume according to its amount. Thus, the specific volume of the ideal mixture, $V_{sp}=1/\rho_{id}$ as a function of the mass fractions ξ_i can be written as follows:

(3)

$$V_{sp}^{id}=\frac{1}{\rho^{id}}=\sum \frac{\xi_i}{\rho_i}$$

whereby ρ_i stays for the density of the component i.

In general the volume of the real mixed phase consisting of several different components can't be predicted precisely. In fact the value V represents a real state function, i.e. it depends on the partial pressure p, temperature T and the composition of the mixture n_i:

$$V=V(p,T,n_1,n_2,\ldots,n_k)=V(p,T,n_i)$$

At constant pressure and temperature the total differential of this function by infinitesimal varied component n_i can be easily calculated as follows:

(4)

$$(dV)_{p,T}=\sum_{i=1}^{k}\left(\frac{\partial V}{\partial n_i}\right)_{p,T} dn_i=\sum_{i=1}^{k} V_{m,i} dn_i$$

The coefficient $V_{m,i} = \left(\frac{\partial V}{\partial n_i}\right)_{p,T}$ is termed by **partial molar volume** of the component i in the mixture. For real mixtures, $V_{m,i}$ depends simply on the composition of the mixture. At constant $V_{m,i}$ value[1], one can integrate the equation (4) simply by replacing the infinitesimal dn_i amounts by finite mole numbers n_i:

(5)

$$V=\sum_{i=1}^{k} n_i V_{m,i} \qquad V_m=\sum_{i=1}^{k} x_i V_{m,i}$$

The difference between the volume of the real mixed phase $V^{~}$ and the volume of the related ideal mixture V^{id} is termed by **excess volume, V^E**.

(6)

$$V^E=V^{real}-V^{id}$$

(1) This requirement can be easily achieved when the small amount dn_i of an individual component is added to the mixture in such a way that the resulting volume dV always corresponds to the final composition of the mixture.

By comparing equations (2) and (5) one recognizes that the partial molar volume of an ideal mixture $V_{m,i}$ and the molar volume of the pure component $V^0_{m,I}$ are equal. Consequently the partial molar excess volume can be rewritten:

(7)
$$V^E_{m,i}=V_{m,i}-V^\circ_{m,i}$$

By combining the equation (5) and (7) one gets the mean molar excess volume $\overline{V}^E_m$:

(8)
$$\overline{V^E_m}=\sum_{i=1}^{k} x_i V_{m,i} - \sum_{i=1}^{k} x_i V^\circ_{m,i} = \sum_{i=1}^{k} x_i\left(V_{m,i}-V^\circ_{m,i}\right)=\sum_{i=1}^{k} x_i V^E_{m,i}$$

The relationship between the partial molar values of the components and the composition of the mixture is given by the Gibbs-Duhem equation. Differentiation of the equation (5) results in the following equation:

(9)
$$dV=\sum_{i=1}^{k} V_{m,i}\, dn_i+ \sum_{i=1}^{k} n_i dV_{m,i}$$

The total differential of $V=V(p,T,n_i)$:

(10)
$$dV=\frac{\partial V}{\partial p}\,dp+\frac{\partial V}{\partial T}\,dT+\sum_{i=1}^{k} V_{m,i}\, dn_i$$

This expression leads to the general Gibbs-Duhem equation:

(11)
$$\sum_{i=1}^{k} n_i\, dV_{m,i}-\frac{\partial V}{\partial p}\,dp-\frac{\partial V}{\partial T}\,dT=0$$

For isotherm and isobar processes the last formula can be simplified (dT=0 and dp=0):

(12)
$$\left(\sum_{i=1}^{k} n_i dV_{m,i}\right)_{p,T}=0 \qquad \left(\sum_{i=1}^{k} x_i dV_{m,i}\right)_{p,T}=0$$

The molar volume of a pure component , is independent of the mixture composition. Consequently by setting equation (7) into the formula (12):

(13)
$$\left(\sum_{i=1}^{k} n_i dV^E_{m,i}\right)_{n,T}=0 \quad bzw. \quad \left(\sum_{i=1}^{k} x_i dV^E_{m,i}\right)_{n,T}=0$$

Numerical procedure for real binary mixtures

It is recommended first to ignore the ideal amounts of the components (given by the general mixture rule) and continue the work with the excess values. It is convenient to use the mole fraction $x_2=1-x_1$ as the independent concentration variable in a binary system. Consequently, the partial excess volume of the component i:

(14)

$$V_i^E = V_i^E(p,T,x_2) \qquad \left(dV_i^E\right)_{p,T} = \frac{\partial V_i^E}{\partial x_2} dx_2$$

Now the equation (8) can be transformed into the following one:

(15)

$$\overline{V^E} = x_1 V_1^E + x_2 V_2^E$$

and the formula (13) becomes modified as follows:

(16)

$$x_1 \frac{\partial V_1^E}{\partial x_2} + x_2 \frac{\partial V_2^E}{\partial x_2} = 0$$

Finally, we have two mathematical relationships for three values: $V_1^E, V_2^E \ and \ V^E$. Thus, it is possible to determine two values when the third one is known as a function of the mixture composition. By differentiation of the equation (15) (with the condition $x_1 = 1-x_2$) one obtains:

(17)

$$\frac{\partial \overline{V^E}}{\partial x_2} = V_2^E - V_1^E$$

In the next step we calculate first V_1^E from equation (15) and V_2^E from equation (17) and by interlinking both formulae we obtain two relationships expressing V_1^E and V_2^E in terms of $\overline{V^E}$.

(18)

$$V_1^E = \overline{V^E} - x_2 \frac{\partial \overline{V^E}}{\partial x_2} \quad und \quad V_2^E = \overline{V^E} + x_1 \frac{\partial \overline{V^E}}{\partial x_2}$$

Application

The mean molar excess volume V_E can be determined by measuring the density ρ of the resulting mixture as well as the densities of the pure components ρ_i. When the mixture composition is given by weight dues ξ_i and the mole mass M_i of each component is known, then the $\overline{V^E}$ can be calculated by means of the following expression:

(19)

$$\overline{V^E} = \overline{V} - \overline{V^{id}} = \frac{V - V^{id}}{\Sigma n_i} = \frac{(1/\rho) - \Sigma\left(\xi_i/\rho_i\right)}{\Sigma\left(\xi_i/M_i\right)}$$

For a binary mixture the plot of the function $V^E(x_2)$ represents a parabola-like curve which crosses the x_2 axis at $x_2 = 0$ and $x_2 = 1$ (points A_1 and A_2, see Fig. 1). Basing on the curve of the integral excess volume one can derive both partial volumes, V_1^E and V_2^E, on a numerical or graphical way.

Graphical Evaluation

We plot first the measured values V^E as a function of x_2 in a diagram. All data points belonging to the plot will be fit by hand with a smooth function within the whole range, $x_2[0-1]$.
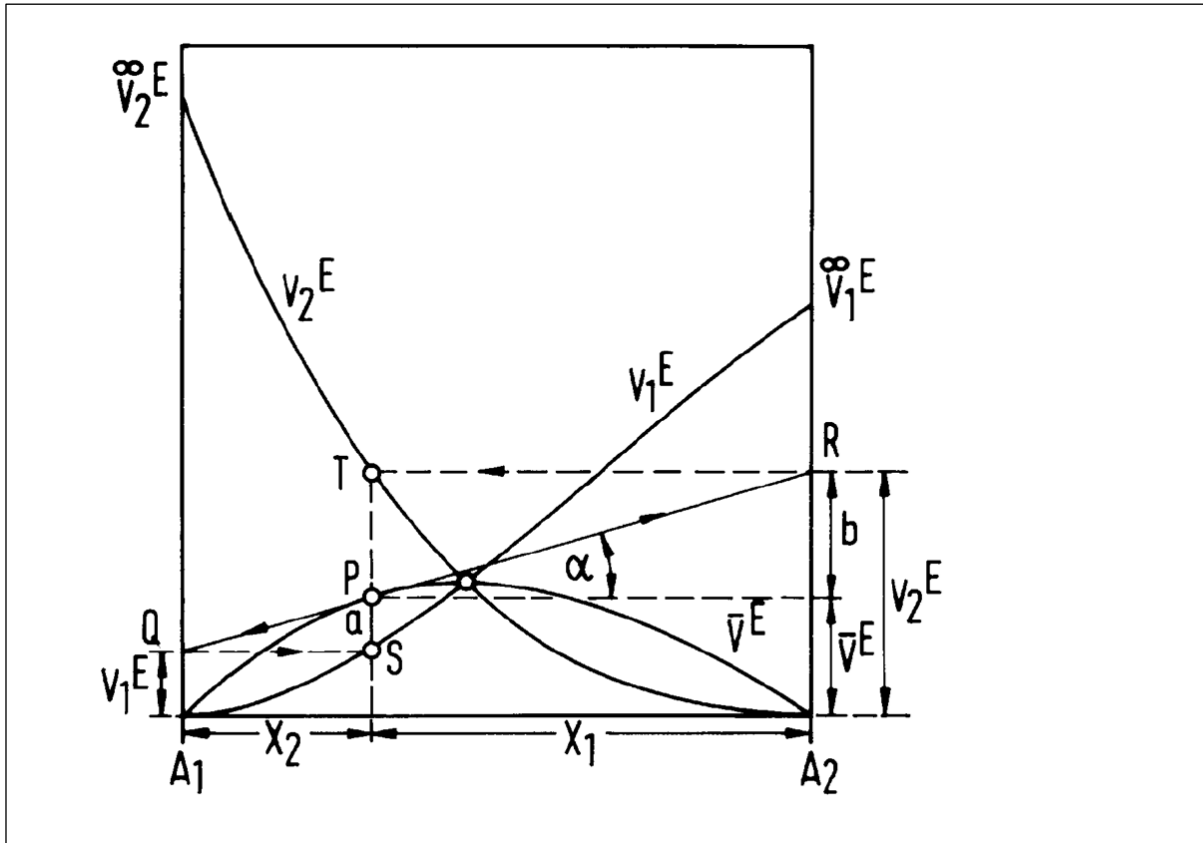
Fig. 1 Scheme supporting the graphical evaluation of the partial molar excess volumes.

By drawing tangents at several selected points P of the curve one enables to directly apply equation (18). The intercept point between the tangent and the V^E-axis at $x_2=0$ corresponds to V_1^E and the intercept at $x_2=1$ corresponds to V_2^E at the partial mole fraction x(P), at which the tangent approaches the curve (point P in Fig. 1). The resulting values establish the functions $V_1^E(x_2)$ and $V_2^E(x_2)$, i.e. the partial molar excess volumes wanted here. The two curves should cross each other in the maximum or minimum of the main V^E curve.

Numerical Evaluation

The function $V^E(x_2)$ will be fit by an analytic polynomial (the coefficients of this polynomial will be derived from the best fit to the experimental points). The details of the applied fit procedure are given in supplement. The analytic polynomial should fulfill two requirements: $V^E(0) =0$ and $V^E(1) =0$, for $x_2=0$ and $x_2=1$, respectively. Thus, the polynomial is given by a following formula:

(20)
$$V^E(x_2)=x_2(1-x_2)\left(a+bx_2+cx_2^2+\ldots\right)$$

The accuracy of the experimental data (mean standard deviation) governs the number of the relevant terms in this expansion. In the case of binary mixtures usually the expression can be interrupted after the fourth term. After performing the multiplication one obtains an expression which fulfills the aforementioned requirements:

(21)
$$V^E(x_2)=ax_2+(b-a)x_2^2+(c-b)x_2^3+cx_2^4$$

The first derivative of this expression yields:

(22)
$$\frac{\partial V^E}{\partial x_2}=a+2(b\text{-}a)x_2+3(c\text{-}b)x_2^2\text{-}4cx_2^3$$

Now, when knowing the fit parameters a, b and c, one can use directly this expression for calculating the V_1^E and V_2^E according to equation (18).

Instruction Sheet
Operation of the density measuring device

The density ρ of the mixture (see equation (19)) will be determined by means of a digital densitometer (Modell DMA 38, Heraus/Paar). The mixture will be placed into a U-shaped glass tube and via an electronic coupling excited to undamped oscillations. The resonance frequency (or oscillation period) of the glass tube depends on the mass of the filled mixture. The volume involved in oscillations is limited and precisely defined by clumped support of the glass tube (localized swelling on the U-tube). Consequently, the mass of the sample is proportional to its density, M=V ρ. The oscillator can be considered as a harmonic one with an oscillation period T_S:

(23)
$$T_S=2\pi\sqrt{\frac{m_{ges}}{c}}=2\pi\sqrt{\frac{m+\rho V}{c}}$$

where m_{ges} is the total mass of the system (the oscillator mass + the mass of the filled substance).

When taking into account the constants characteristic for the specific set-up of the densitometer: $A=\frac{4\pi^2 V}{c}$ and $B=\frac{4\pi^2 m}{c}$ one obtains directly the density:

(24)
$$\rho=\frac{1}{A}\left(T_S^2\text{-}B\right)$$

The two constants, A and B, can be simply determined by measuring the densities of two pure substances with known densities, e.g. water and air. The difference of the resulting densities ρ_1 and ρ_2 enables to calculate the constant A:

(25)
$$\rho_1\text{-}\rho_2=\frac{1}{A}\left(T_{S,1}^2\text{-}T_{S,2}^2\right)$$

When setting the A and ρ_1 values into equation (24) one obtains the second constant B. Both constants have to be stored into the device memory and the densitometer shows on the display the current density value of the sample.

Calibration

1. The calibration procedure can be activated by turning on the densitometer (the switch on the backside of the instrument). The related switch on the back side, marked by "cal", has to be activated together with a plastic nozzle attached.
2. On the display appear two options: "at temp" and "full range". One has to choose "at temp". The cursor jumps periodically between the two options: The choice proceeds by pressing the "print/set" button at the moment where the cursor marks the desired option (function).

3. On the display appears "fill air". The tube has to be connected to the upper valve and subsequently the measuring tube should be drayed/evacuated for ~4 minutes by activating the "pump" function. Afterwards press the button "print/set".
4. After completing the measurement of the oscillating period $T_{s,1}$ for air one has to press the button "print/set". Afterward the display shows a request: The measuring tube should be filled with water.
5. Thus, the U-shaped glass tube will be filled with distilled water according to the instruction and the button "print/set" will be activated (please, avoid the bubbles formation!).
6. After completing the measurement of the oscillating period for water, $T_{s,1}$, press two times the "print/set" button and remove the water from the measuring tube (draying /evacuation for ~4 minutes by activating the "pump" function). Now, the calibration of the instrument is completed and the densitometer is ready for the measurement of the mixture density.

Test

It is aimed to measure the density of distilled water at 20°C. The measurement becomes completed when in the value appearing on the display only the last digit blinks. The density measured is given here by the upper value shown on the display (units: g/cm^3). The lower value is irrelevant for this experiment. According to the literature the density of distilled water at 20°C reaches a level of 0.9982 g/cm^3. The calibration procedure performed here was successful when the discrepancy between the experimental and literature data is lower than 0.001 g/cm^3.

The measurements

It is aimed to determine the densities if six different methanol/water mixtures kept at 20°C. For each mixture the density measurement should be repeated three times. The results which exhibit striking deviations can be simply ignored. The mixtures will be prepared by means of six clean and drayed snap-on lid glasses. The components will be dosed according to the amount ratios summarized in Table II. From the weighted mass one can derive the mass fraction for both substances.

Table II.

Mixture	1	2	3	4	5	6
m_{H_2O} [g]	0,3	1	2	3,5	5	6
m_{CH_3OH} [g]	6,7	6	5	3,5	2	1

Evaluation of the results

1. Basing on equation (19) one has to determine the mean molar excess volume $\overline{V^E}$.
2. The molar excess volume will be plotted as a function of the mole fraction x.
3. By applying the graphical procedure to the curve of the molar excess volume the partial molar excess volume for both components of the mixture should be determined (at least by six points).

4. Basing on equations (18) and (22) the partial molar excess volumes of water and methanol should be determined by exploiting the numerical procedure described above. The results should be presented by a graph.
5. The results obtained by means of the two methods (numerical and graphical method) should be compared and the possible deviations discussed.
6. A mathematical analysis of the experimental errors is not necessary. Only a short discussion of the possible error sources and their influence on the final results will be expected.

Practical hints to the work

1. The samples will be filled via the lower valve by means of a syringe without the cannula.
2. Attention should be paid to excluding the possible formation of bubbles in the U-shaped glass tube as well as to the fact that the whole visible region of the glass tube should be filled with water or methanol. An experiment with bubbles is nugatory.
3. After completing the injection the syringe must remain plunged in the valve (otherwise the substance drops out from the measuring U-tube).
4. In order to avoid the bubbles formation it is recommended to perform the injection of the fluid substance slowly with constant speed.
5. After completing the measurement the fluid substance has to be removed by means of the syringe. After this step the syringe will be trashed.
6. Before starting the preparation of the next mixture the measuring U-shaped glass tube should by drayed for ~4 minutes. For this purpose the tube should be connected with the upper valve and by pressing the button "pump" the evacuating pump should be turned on or off. Afterward the tube has to be disconnected again.
7. Before preparing a new mixture the syringe should be flushed with acetone.
8. Methanol can penetrate the skin as a toxic agent. Consequently, one has to avoid the contact with the skin.

Recommended Literature

1. Riedel, L. Physikalische Chemie: Eine Einführung für Ingenieure; Bibliographisches Institut Ag: Zürich, **1974**.
2. Prigogine, I.; Defay, R. Chemische Thermodynamik, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig **1962**.
3. Atkins, P. W.; de Paula, J. Physikalische Chemie; 4., vollständig überarbeitete Auflage; Wiley-VCH: Weinheim, **2006**.

Origin 8.6 G-based fit procedure

All data pairs (x_2, V^E) of the $V^E(x_2)$ function measured will be inserted into two columns of a new worksheet. Both columns will be marked and via "Zeichnen", "Symbol" the "Punktdiagramm" the desired graph will be plotted. The fit curve will be created by choosing: Menü „Analyse" „Anpassen" „Nichtlinearer Fit". Next, the window „NLFit" becomes activated (see Fig. 2). One hast to choose in Dropdown-Menü: <Neu>. This step opens two new windows. The foremost window stays for the proper name of the new function. Analogous proceeds when entry the name of the function. In the window „Anpassungsfunktionsbuilder" one has to select the type of the function: „Gleichung", afterward press the button „weiter". Under "Parameter" the parameters a, b and c should be inserted and the button "weiter" pressed. In the field „Funktionskörper" one sets $y = a*x + (b-a)*x^2 + (c-b)*x^3 - c*x^4$ as a fit function proposed. For all three parameters the initial value 1 should be inserted. The check of the correctness of the function proposed can be performed by clicking the icon "Männchen". When the function proposed was wrong or defective the corresponding message appears. Afterward again press the button "weiter". When the function is correct then click the button "Fertig". When necessary in the window „NLFit" a new fit function has to be inserted. Afterward press the button „Fit". You find the resulting fit parameters, a, b and c as well as the fit errors and the calculated fit function in a new window.
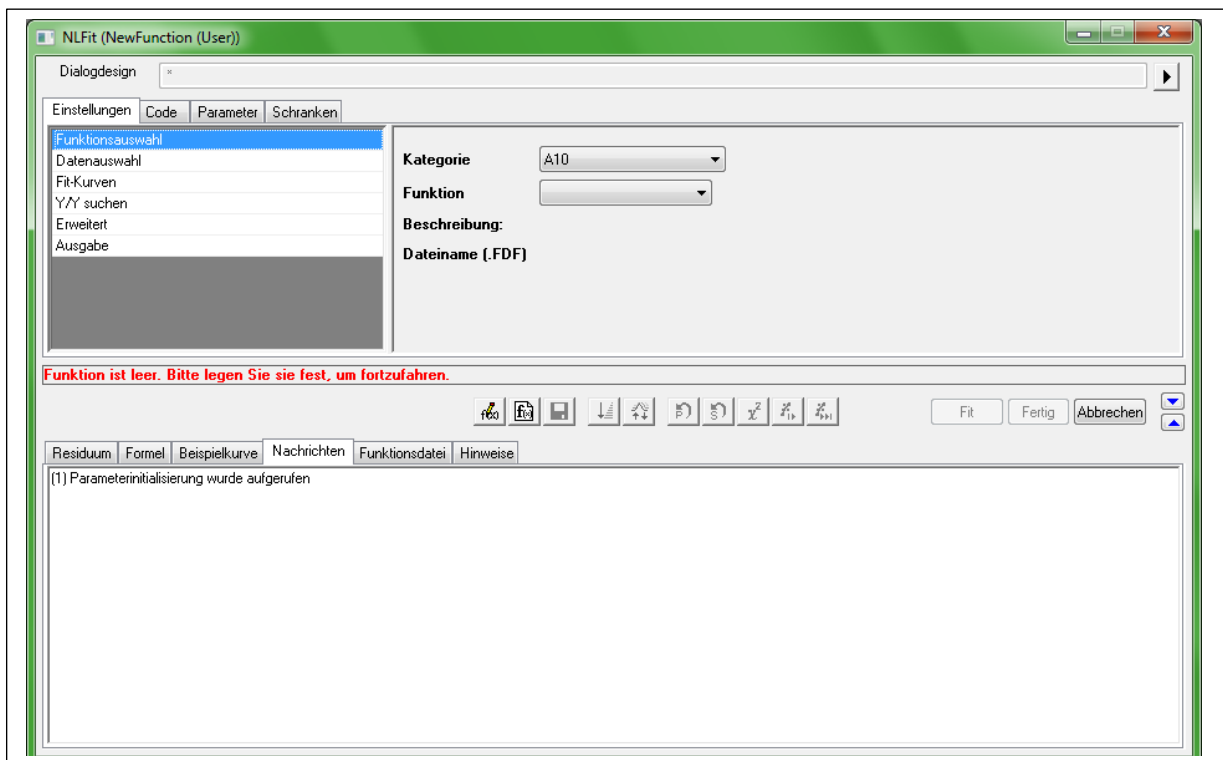

Fig. 2 Origin window for non-linear fit of the experimental data