

Measurement of surface tension by bubble pressure method (exp. 06.)

Important concepts

Definitions for surface tension by interfacial energy and interfacial force, Gibbs surface excess, working principle of bubble pressure measuring apparatus (BPMA), the pressure balance equation for BPMA, the determination of capillary radius of BPMA, Eötvös rule, surface excess.

Objective

In this experiment you will learn one of the methods (the bubble pressure method) used for the determination of the surface tension of liquids. You will also practice how to handle Mohr-Westphal balance used for the density measurement of liquids.

Background:

Qualitatively, the surface tension of liquids is a property that draws a liquid together minimizing its surface. We can also give two quantitative definitions for it:

1. Surface tension is the drawing force acting upon a surface line of unit length. Its dimension therefore is $\text{N/m} = \text{kg} \cdot \text{s}^{-2}$.
2. Surface tension is the work required to produce a new surface of unit area under isothermal and reversible conditions. Its dimension therefore is $\text{J/m}^2 = \text{kg} \cdot \text{s}^{-2}$ (which is the same as above).

Due to definition (2) the surface tension (γ) can be looked upon as the Gibbs free energy of unit surface, and its change is governed by the Gibbs-Helmholtz equation:

$$\gamma = h_\gamma + T \frac{d\gamma}{dT} \quad (1)$$

where h_γ is the enthalpy of unit surface. The derivative $\frac{d\gamma}{dT}$ proves to be negative by experiment and therefore the surface tension of liquids decreases when the temperature increases. The temperature dependence is described by the Eötvös rule:

$$\gamma V^{2/3} = \kappa(T_c - T) \quad (2)$$

where V is the molar volume, T_c the critical temperature and κ is the Eötvös constant. For normal liquids $\kappa = 2.1 \cdot 10^{-7} \text{ J/K}$. For elongated molecules and for liquids whose molecules have a tendency to association the value of κ is different. This fact can be used for the investigation of the structure of liquids.

Another important related quantity is the parachor, P :

$$P = M \frac{\gamma^{1/4}}{d_l - d_v} = M \frac{\gamma^{1/4}}{d_l} \quad (3)$$

where M is the molar mass, d_l and d_v are the densities of the liquid and the vapor, respectively. The parachor is constant over a wide temperature range. The parachor of molecules is additive i.e. it adds up from the atomic parachor values and the structural contributions of the chemical bonds. The structural contributions of single and double bonds are different and so are those of rings consisting of three, four, etc. atoms. This makes the parachor an important source of structural information.

The surface tension of solutions also depends on the concentration. Some solutes (they are called capillary active substances) reduce the surface tension considerably even when they are present in a low concentration. Such capillary active substances are e.g. the alcohols, aldehydes, ketons, fatty acids, and alkyl sulfonates. Capillary inactive substances increase the surface tension to some extent. Such substances are: inorganic compounds, proteins urea, glycerol etc. The concentration of capillary active substances is always much higher on the surface than in the bulk solutions. This is referred to by the expression "positive adsorption". Capillary inactive substances, however, are avoiding the surface (negative adsorption).

Sziszowski (pronounce: Shishkovsky) found the following empirical equation for the concentration dependence of surface tension:

$$\Delta = \gamma_0 - \gamma_c = A \log(1 - Bc) \quad (4)$$

where γ_0 is the surface tension of pure water, and γ_c is that of the solution of concentration c , and A and B are constant characteristic of the solute. Experiments prove that the values of B form geometric series within the homologue series of capillary active substances (e.g., fatty acids: formic acid, acetic acid, propionic acid, etc.). On the average:

$$\frac{B_{n+1}}{B_n} = 3,4 \quad (5)$$

The above relation is known as the Traube rule.

In the following section we give you a short introduction to the theoretical basis of the surface excess of a solute. For a plane surface phase, e.g. a liquid/vapor boundary containing only one solute (n_1) and one solvent (n_2) component an infinitesimally small amount of heat, work or material transfer given to or by the system cause a change in internal energy:

$$dU = T \cdot dS - p \cdot dV + \gamma \cdot dA + \mu_1 \cdot dn_1 + \mu_2 \cdot dn_2 \quad (6)$$

The intensive variables in Eq. (6) are $T, p, \gamma, \mu_1, \mu_2$, and the extensive ones are S, V, A, n_1, n_2 .

By integrating Eq. (6) we get

$$U = T \cdot S - p \cdot V + \gamma \cdot A + \mu_1 \cdot n_1 + \mu_2 \cdot n_2 \quad (7)$$

The differential of Eq. (7)

$$dU = T \cdot dS + S \cdot dT - p \cdot dV - V \cdot dp + \gamma \cdot dA + A \cdot d\gamma + \mu_1 \cdot dn_1 + n_1 d\mu_1 + \mu_2 \cdot dn_2 + n_2 d\mu_2 \quad (8)$$

Using Eq. (6) and (8)

$$0 = S \cdot dT - V \cdot dp + A \cdot d\gamma + n_1 d\mu_1 + n_2 d\mu_2 \quad (9)$$

For a surface phase at a fixed T and p

$$0 = A \cdot d\gamma + n_1 d\mu_1 + n_2 d\mu_2 \quad (10)$$

The boundary layer is replaced by a surface. In the surface phase for solute component Γ_1 is the amount of chemical substance 1 adsorbed per unit area; i.e. the surface concentration expressed in mol m^{-2} . Solvent is not adsorbed by the surface phase, therefore $n_2 = 0$, and surface excess of solute is

$$\Gamma_1 = \frac{n_1}{A} \quad \Gamma_1 = - \frac{d\gamma}{d\mu_1} \quad (11)$$

$$- \Gamma = \frac{d\gamma}{RT d \ln \frac{c_1}{c_{\text{ref}}}} \quad - \Gamma \cdot RT = \frac{d\gamma}{d \ln \frac{c_1}{c_{\text{ref}}}} \quad (12)$$

Where c_{ref} is 1 mol dm^{-3} . From Eq. (12) it can be seen that the slope of γ vs $\ln c$ function is equal to $- \Gamma \cdot RT$. Positive adsorption is observed when $\Gamma_1 > 0$, i.e. by increasing the bulk concentration of solute surface tension decreases.

Apparatus

Air is pulled (or pressurized) into a liquid through a capillary. The air forms a bubble at the bottom of the capillary then gets released and escapes through a liquid layer into the measuring apparatus (Fig.1.) The apparatus consists of a 200 ml cylindrical vessel furnished with a stopcock on its bottom and funnel on its top (which also has a stopcock). On one side there is a manometer filled with water, on the other side there is the measuring vessel filled with the liquid whose surface tension is to be determined. There are two circular marks on the measuring vessel. The upper mark shows where the meniscus of the measured liquid supposed to be, and the lower one shows the bottom of the capillary (the submerged length of which therefore is always the same). The distance between the two ring marks on the tube is 5 mm. After the measuring vessel is closed, the measured liquid is only connected with the atmosphere through the capillary tube.

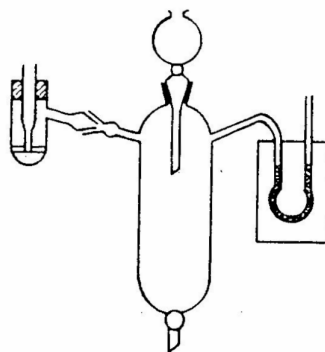


Fig.1.
Apparatus for the measurement of bubble pressure

Tasks to be determined,

1. surface tension of water-iso-buthanol mixtures (new),
2. surface tension of an unknown aqueous solution,
3. mass density of the unknown aqueous solution.

Procedure

1. Prepare water-isobuthanol mixtures from the following table.

series 1. $V(\text{alcohol}) / \text{cm}^3$	series 2. $V(\text{alcohol}) / \text{cm}^3$	series 3. $V(\text{alcohol}) / \text{cm}^3$
1,6	2,0	2,4
0,8	1,0	1,2
0,4	0,5	0,6
0,2	0,25	0,3

One of the series is assigned for you by the instructor. A 5 ml burette is used for filling iso-buthanol into a 25 cm³ volumetric flask and you fill that flask with distilled water up to the ring mark. The surface tension of four samples is determined in the bubble pressure apparatus. Homogenize the solutions very-very carefully!

2. You measure the bubble pressure of water, water-iso-buthanol mixtures and unknown aqueous solution. Note the temperature of laboratory.

For the bubble pressure measurement follow these steps:

- a) Remove the measuring vessel from the equipment. Fill the liquid to be measured into the measuring vessel, and replace the capillary.
- b) Fill the cylindrical vessel half up with water through the funnel.
- c) Close the stopcock of the funnel, and replace the measuring vessel.
- d) Open the stopcock on the bottom of the cylinder and let the water flow out slowly. The pressure will drop inside, pulling outside air through the capillary.
- e) After a while the level difference of the manometer will stabilize. Read this difference, Δh (with 0.1 mm precision).

Set a small drop time and measure the maximum level difference on manometer.

Take at least 5 readings at a drop time. Use three different drop times!

When changing solution, use water aspirator to rinse the capillary with the new liquid.

3. Measure the mass density of the unknown solution using the Mohr-Westphal balance (MWB). The MWB (Fig.2) comes with a glass rod and a series of weights (riders). The mass of the largest rider (U shaped brass wire) is equal to that of 15 °C water occupying the same volume as the glass rod. The smaller riders are 1/10 and 1/100 of the largest one. The MWB directly measures the density of a liquid by giving the weight loss of the glass rod completely submerged in that liquid. There is a scale on the beam of the balance for measuring the tenths of the nominal values represented by each rider. The nominal values are: 1 g/cm^3 (large brass rider), 0.1 g/cm^3 , and 0.001 g/cm^3 . Thus a typical reading is like this 1.526 or 0.865.

NOTE: When measuring, the glass rod must be completely submerged and it must not touch the wall of the vessel.

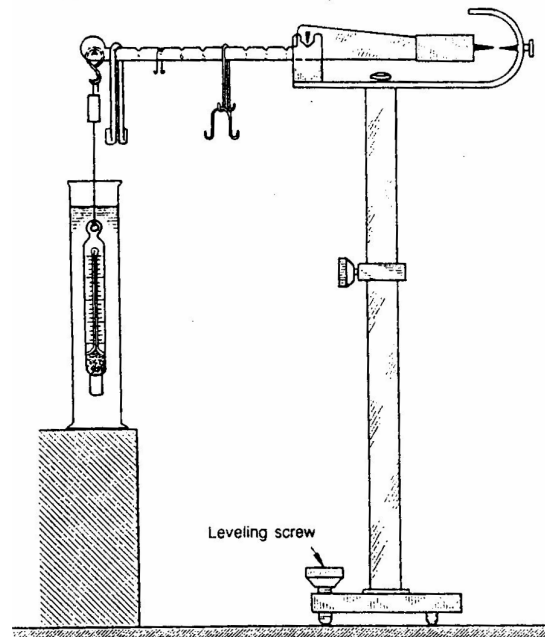


Fig.2.
A typical Mohr-Westphal balance

- a) Before taking the first measurement, the balance has to be zeroed. Measure the temperature in the lab, and find the density data of water from the table at that temperature (see below). Set the balance for MWB by using the appropriate weights (riders) on arm, while the glass body is immersed totally in distilled water without touching the wall of graduated cylinder. Rotate the counterbalance to obtain the horizontal position of arm (the index pointer on the end of the beam lines up with the point on the frame). Now MWB is calibrated to distilled water at lab temperature.
- b) Set the MWB with unknown solution. Replace distilled water in the graduated cylinder by unknown solution. Set the balance with placing riders on the nine equally spaced notches on the beam. Read the position of riders, and add them up. Density of liquids may be obtained to four decimal places.

Scale:

1 g/cm^3 rider is worth on the hook 1 g/cm^3 , on notches 9. - 1. $0.9 - 0.1\text{ g/cm}^3$.

0.1 g/cm^3 rider is worth on the hook 0.1 g/cm^3 , on notches 9. - 1. $0.09 - 0.01\text{ g/cm}^3$.

0.01 g/cm^3 rider is worth on the hook 0.01 g/cm^3 , on notches 9. - 1. $0.009 - 0.001\text{ g/cm}^3$.

Table. The temperature dependence of mass density of water

$T / ^\circ\text{C}$	$\rho / \text{kg/m}^3$	$T / ^\circ\text{C}$	$\rho / \text{kg/m}^3$
16,0	998,95	22,0	997,77
17,0	998,78	23,0	997,54
18,0	998,60	24,0	997,30
19,0	998,41	25,0	997,05
20,0	998,21	26,0	996,79
21,0	998,00	27,0	996,52

Evaluation of the data

1. The radius of capillary, r :

$$r = \frac{2 \cdot \gamma_v}{\rho_v \cdot g \cdot (\Delta h - h_1)},$$

where $h_1 = 0,005$ m, $\gamma_w = 0,07253$ N/m, $g = 9,81$ m/s² and ρ_w the density of water at the temperature of measurement.

2. The calculation of surface tension of i-butanol containing solutions:

It is supposed the density of solution to be equal to density of water at the same temperature,

$$\gamma_{sol} = \frac{\rho_{sol} \cdot r \cdot g (\Delta h - h_1)}{2},$$

3. The surface excess, Γ determination

The piling up of one of the components in a solution causes surface excess to the bulk of solution. This Gibbs type interfacial excess concentration is greater than the bulk concentration, and they referred to exactly the same volume.

a) The concentrations of dilution series are calculated. Data: $M(\text{i-butanol}) = 74,12$ g/mol, $\rho_{\text{ib}}(25^\circ\text{C}) = 0,798$ g/cm³. The unit of concentration is mol/dm³.

b) The function of $\gamma = f(\Gamma)$ is $\gamma = -\Gamma RT \cdot \ln c + \text{const.}$

You construct the graph of functions (i) γ - c , and (ii) γ - $\ln c$. The γ vs. $\ln c$ function can be fitted by a straight line the slope of which is $-RT$. From slope Γ can be calculated.

4. The calculation of surface tension of unknown solution

The surface tension of unknown solution described in calculation step 2 above is calculated. *The density, ρ_{sol} will be equal to the one you measured with MWB)*

Graphs, results, data to be reported

1. The level differences of manometer and their average, $\Delta h(\text{average})$ / meter, for distilled water, and the radius of capillary, r / meter.

2. Make a table for i-butanol containing solutions, use column headings like given below.

$V(\text{i-but.}) / \text{cm}^3$	$c \text{ mol/dm}^3$	$\Delta h(\text{aver.}) / \text{m}$	$\gamma_{\text{b.}} / \text{N/m}$
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- plotting γ vs. c , and γ vs. $\ln c$ functions,
- calculation of the value of Γ from the slope of function γ vs. $\ln c$.

3. For unknown solution: its mass density in kg/m³, $\Delta h(\text{average})$ / m, the temperature of measurement and the surface tension of solution.

Sample questions and answers for the minimum level tests (MLT).

MLT is devoted for practicing and preparing to labs at home, and its topical list covers the problems we discuss at the beginning of the lab.

MLT Q.and A

Q1. Give definition for: mass density.

A1. The mass of a system (solid, liquid or gas state) divided by its volume is called mass density. Mass density is an intensive property which does not depend on the extension of the substance. Unit: g/cm^3 . Mass density is temperature dependent.

Q2. Give definition for: hydrostatic pressure.

A2. The hydrostatic pressure $P_w = \Delta P = \Delta h \cdot d_{\text{water}} g$. Where Δh is the level difference in m, $g=9.81 \text{ m/s}^2$, and d_w is the mass density of water at the temperature of manometer. Unit: Pa, or N m^{-2} . (Both in Q2. and Q1. about hydrostatic pressure was asked.)

Q3. Give definition for capillary pressure (explain your notation).

A3. Surface tension in the surface layer of a liquid acts as a tangential force to the liquid/air interface and tries to lessen the surface area of liquid. The pressure proportional to this force can be given as $P_\gamma = 2\gamma/r$. Here r is the radius of capillary.

Q4. Give the working principle: manometer.

A4. Manometer is used for pressure determination. It is an U-shaped glass tube containing a liquid of known mass density. The liquid is usually water, ethanol or mercury. Manometer shows a liquid level difference which is proportional to the pressure to the system to be studied. The manometer pressure is proportional to the level difference of manometer liquid,

$$\Delta P = \Delta h \cdot d_{\text{water}} g$$

Q5. Give definition for: molar volume.

A5. The molar volume of the i^{th} component V_i is a partial molar quantity, in a mixture it is defined as

$$V_i = \left(\frac{\partial V_{\text{mix}}}{\partial n_i} \right)_{T,p,n}, \text{ but for a pure liquid, it is the volume of one mole material. Unit: } \text{m}^3/\text{mol}$$

Q6. Define the surface excess concentration. Discuss the sign of Γ .

A6. The surface excess given in mol m^{-2} is a two dimensional concentration at the boundary of different phases, and can be given as:

$$-\Gamma = \frac{d\gamma}{RT d \ln \frac{c_1}{c_{\text{ref}}}}$$

The sign of surface tension concentration derivative will adjust the sign of Γ . If

$$\frac{d\gamma}{d \ln \frac{c_1}{c_{\text{ref}}}} < 0, \text{ i.e. increasing the solute concentration the surface tension decreases } \Gamma \text{ is positive. It}$$

happens when solute is an organic molecule. If

$\frac{d\gamma}{d \ln \frac{c_1}{c_{\text{ref}}}} > 0$, i.e. increasing the solute concentration the surface tension increases Γ is negative. It

happens when solute is an inorganic salt.