Task VI

PARACHOR

I. Aim of the task

The aim of the task is experimental determination of parachors for chosen liquids and their comparison with those determined by summing of atom and bond parachors.

II. Introduction

1. Cohesive forces, the radius of molecular interaction.
2. Surface energy, surface layer.
3. Definitions of the surface tension:
   a) in terms of force (unit),
   b) in terms of work (unit).
4. Dependence of the liquid surface tension on temperature.
5. Methods of the surface tension measurement:
   a) capillary rise method,
   b) drop weight method (stalagmometric method),
   c) maximum bubble pressure method,
   d) ring method (tensiometric method).
6. Parachor.
7. Additivity.

References:

1. J. Ościk, *Adsorption*, PWN Warszawa, 1982.
2. D. J. Shaw, *Introduction to Colloid and Surface Chemistry*, Butterworth-Heinemann, London 1992.
3. J. Lyklema, *Fundamentals of Interface and Colloid Science*, vol.III: Liquid-Fluid Interfaces, Academic Press, 2000.
4. E. T. Dutkiewicz, *Fizykochemia powierzchni*, WNT Warszawa, 1998, pp. 70–72.
5. Task VIII.
6. J. Demichowicz-Pigoniowa, *Obliczenia fizykochemiczne*, PWN Warszawa, 1984, pp. 259–260.
7. A. Danek, *Chemia fizyczna*, PZWL Warszawa, 1972, pp. 444–445.

III. Theory

III.1. Surface tension of liquids

Molecules liquid state experience strong intermolecular attractive forces. When those forces are between like molecules, they are referred to as **cohesive forces**. The cohesive forces between molecules are unbalanced at a phase boundary. In the case of the liquid/gas interface the resultant force acting on the surface molecules from the liquid side exceeds that from the gas side (Fig. 1).

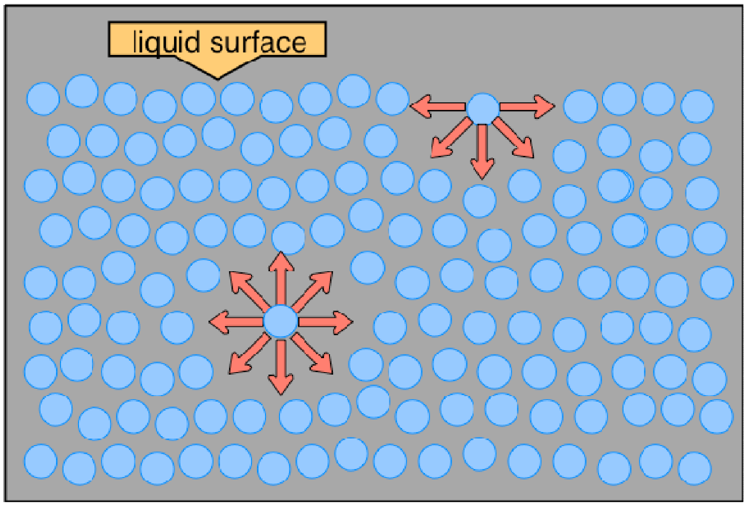


Fig. 1. Surface layer at the liquid/gas interface (http://www.chem1.com).

Surface molecules of the liquid are therefore drawn into the liquid phase, whose surface area tends to diminish. As a consequence of interactions among liquid molecules, the force directed normal to the surface into the liquid is accompanied by another force directed tangentially to the surface and preventing its area from increasing. This latter force per unit length (the cross section of the surface is a line) is a measure of the **surface tension** (denoted by γ or σ).

Since the liquid tends to diminish its surface area, increase of that area requires work against the surface tension. Fig. 2 shows a hypothetical system consisting of a liquid filling a container having a sliding cover. It is assumed that the nature of the lid is such that there is no surface tension between it and the liquid. We shift the lid to uncover a part of the liquid surface of area equal to dA.

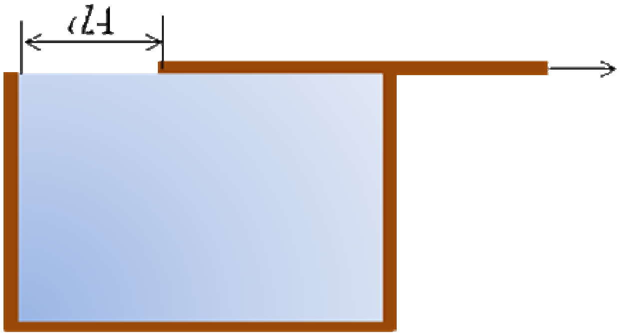


Fig. 2. Formation of a new surface of the liquid.

If the operation is performed quasistatically at constant temperature and pressure, the work will be equal to the increase of Gibbs free energy:

$$dG^s = \gamma dA \tag{1}$$

where G^s is the Gibbs free energy of formation of the new area of surface. In general:

$$G^s = \gamma A \tag{2}$$

or

$$\gamma = \frac{G^s}{A} \tag{3}$$

It follows that the units of surface tension are N/m (newton per meter) or J/m^2 (joules per meter squared) (dyne/cm or erg/cm^2 in the CGS system. The conversions are: 1 dyne = 10^{-5} N, 1 erg = 10^{-7} J; 1 dyne/cm = 1 mN/m; 1 erg/cm^2 = 1 mJ/m^2).

Surface tension represents the work necessary to form unit area of new surface or, equivalently, the increase of Gibbs free energy corresponding to the formation of unit area of surface.

In accordance with the second law of thermodynamics the Gibbs free energy tends to a minimum (under the given conditions of constant temperature and pressure). It follows from equation (2) that the surface free energy may change in two ways:

(I) As a result of changes in surface area A only, as in the case of pure liquids, where the surface tension depends only on the nature of the liquid.

(II) As a result of changes in both surface area and surface tension, as in the case of solutions.

Thermodynamically, the interfacial tension is interpreted as the increase in the Helmholtz or Gibbs energy of the system when the area of the interface under consideration is increased reversibly by an infinitesimal amount dA at constant temperature and composition, and at constant volume or constant pressure, respectively. One can express this as:

$$\gamma = \left(\frac{\partial F}{\partial A}\right)_{V,T,n} \tag{4}$$

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{p,T,n} \tag{5}$$

where n in an abbreviation for the set of amounts n_1, n_2, …, that define the composition of the system. The dimensions of γ are [energy/area]; we shall express them in mJ/m^2. As F and G are in principle measurable, so is γ.

Mechanically, the interfacial tension is the contractive force per unit length, acting in the interface and parallel to it. The dimensions are [force/length], and our usual unit is mN/m = mJ/m^2. Interfacial tensions are mechanically measurable as the forces required to enlarge an interface by an infinitesimal amount. For isotropic interfaces this force is the same in each direction. Since mechanical systems try to find a state of minimum potential energy, a free droplet of liquid naturally assumes a spherical shape, which has the minimum surface area for a given volume.

At equilibrium the thermodynamical and mechanical interpretations should be equivalent.

III. 2. Dependence of the surface tension on temperature

Dependence of the surface tension on temperature was given by Eötvös. This relationship can be written in the following form:

$$\gamma \cdot V_m^{2/3} = k\left(T_C - T\right) \tag{6}$$

where: V_m – the molar volume of liquid; $V_m^{2/3}$ – the sphere surface of 1 mole liquid; T_C – the critical temperature (at this temperature meniscus between the liquid and its vapour disappears); k – the constant of proportionality, which is nearly constant for most not associating liquids and equals $2.1 \cdot 10^{-7}$ J/K (dimension: energy per temperature, joule/kelvin).

In the case of associating liquids, e.g. water, alcohols, organic acids, and amides the constant k is significantly lower. Comparison of these values gives possibility to evaluate the degree of association.

Dependence of the surface tension γ on temperature is a linear function with a negative coefficient, i.e. the surface tension of most liquids decreases with the increasing temperature. The surface tension depends on the energy of intermolecular attraction. The kinetic energy of liquid molecules increases with the increasing temperature, that is, more molecules are brought from the interior of the phase into the surface region (from the bulk phase to its surface). It causes an increase of the liquid surface corresponding to a decrease of the surface tension.

Ramsay and Shields claimed that the surface tension disappears near the critical temperature and they modified the Eötvös equation which can be given by:

$$\gamma \cdot V_m^{2/3} = k(T_C - T - 6) \qquad (7)$$

III. 3. Dependence of the surface tension on liquid density

Baczyński and McLeod published an empirical relationship between the liquid surface tension and the liquid density:

$$\gamma = c(d_c - d_p)^4 \qquad (8)$$

where: c – the constant; d_c – the liquid density, and d_p – the vapour density.

III. 4. Parachor

In 1924 Suggden observed the dependence of constant c in equation (8) on the structural properties of a molecule and defined a quantity P that he called the **parachor** P:

$$P = \frac{M \cdot \gamma^{1/4}}{d_c - d_p} \qquad (9)$$

where: M – the molecular weight.

Taking into account the fact, that the vapour density is neglectably small in comparison to the liquid density equation (9) can be expressed in the form:

$$P = \gamma^{1/4} \frac{M}{d_c} \qquad (10)$$

Because

$$\frac{M}{d_c} = V_m \qquad (11)$$

where: V_m – the molar volume of liquid, equation (10) can be given by:

$$P = \gamma^{1/4} \cdot V_m \qquad (12)$$

The parachor can be considered to be a molar volume corrected for the compressive effects of intermolecular forces.

In practice, it is a quantity whose value for a given substance is nearly temperature independent. The parachor is also an approximately additive property of atoms and bonds in a molecule in agreement with the equation:

$$P = \sum nP_a + \sum nP_w + \sum nP_p \tag{13}$$

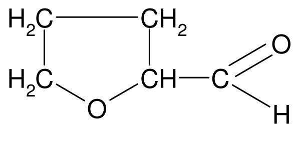
in which: P_a, P_w i P_p denote the parachors of atoms, bonds and rings in a molecule of a given compound, respectively, and n their quantity.

This fact can be used, in some cases, to fix a structure of organic compounds by determination of their parachor from equation (10) or (12) and comparison of the obtained value with that found by summing parachors occurring in the proposed structural formulas for a given compound. The most probable is the structure for which the parachor value calculated from equation (10) is close to that found experimentally from the surface tension measurement, density and molar mass, e.g. the total formula C_2H_6O can be attributed to the formulas: CH_3CH_2OH i CH_3OCH_3, i.e. ethyl alcohol or dimethyl ether. As the parachors $P_{CH_3}, P_{CH_2}, P_{OH}$ and P_O are different, one can attribute the compound to the correct formula by comparing the parachor determined experimentally with that calculated (parachor values are tabularized).

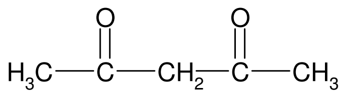
(Example: A. Danek, „Chemia fizyczna")

Knowing the surface tension of a compound of the total chemical formula $C_5H_8O_2$ ($\gamma = 0.0433$ N/m) and density ($d = 1.1094 \cdot 10^3$ kg/m^3), choose which of the structures given below is correct: a) or b)?

a)



b)



$$H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

Calculating the parachor from the experimental data included in equation (10) you obtain:

$$P = (0.0433)^{1/4} \cdot \frac{100}{1.1094 \cdot 10^3} = 411.2 \cdot 10^{-4} \frac{kg^{1/4} \cdot m^3}{kmol \cdot s^{1/2}}$$

Applying the additivity rule and equation (13) one can obtain the parachor in the following way:

for the structure a)

parachor value for 5 carbon atoms	$5 \times 8.5 \cdot 10^{-4} = 42.5 \cdot 10^{-4}$
parachor value for 8 hydrogen atoms	$8 \times 30.4 \cdot 10^{-4} = 243.2 \cdot 10^{-4}$
parachor value for 2 oxygen atoms	$2 \times 35.6 \cdot 10^{-4} = 71.2 \cdot 10^{-4}$
parachor value of double bond	$1 \times 41.3 \cdot 10^{-4} = 41.3 \cdot 10^{-4}$
parachor value of 5-membered ring	$1 \times 15.1 \cdot 10^{-4} = 15.1 \cdot 10^{-4}$

$$P = 413.3 \cdot 10^{-4} \frac{\mathrm{kg}^{1/4} \cdot \mathrm{m}^3}{\mathrm{kmol} \cdot \mathrm{s}^{1/2}}$$

and for the structure b)

parachor value for 5 carbon atoms	$5 \times 8.5 \cdot 10^{-4} = 42.5 \cdot 10^{-4}$
parachor value for 8 hydrogen atoms	$8 \times 30.4 \cdot 10^{-4} = 243.2 \cdot 10^{-4}$
parachor value for 2 oxygen atoms	$2 \times 35.6 \cdot 10^{-4} = 71.2 \cdot 10^{-4}$
parachor value of 2 double bonds	$2 \times 41.3 \cdot 10^{-4} = 82.6 \cdot 10^{-4}$

$$P = 439.5 \cdot 10^{-4} \frac{\mathrm{kg}^{1/4} \cdot \mathrm{m}^3}{\mathrm{kmol} \cdot \mathrm{s}^{1/2}}$$

As follows from the comparison of the theoretical and experimental parachor values the correct structure is the structure a).

III.5. The capillary rise method of the surface tension measurement

Capillary rise techniques are some of the best methods for measuring surface tensions. They provide a bridge to wetting studies and their analysis anticipates that of other techniques of γ measurement.

When an object is partly immersed in a wetting liquid, a concave meniscus is spontaneously formed where solid and liquid meet. The resulting negative capillary pressure Δp may be interpreted as the upward force on the liquid (Fig. 3a). The rise continues until Δp is just balanced by the gravity pressure. So, the surface tension can in principle be obtained from the curvature of the meniscus, the capillary rise, the density difference between the two fluids and the gravitational constant. Similar reasoning can be applied to capillary depression, the situation encountered for non-wetted objects (Fig. 3b).

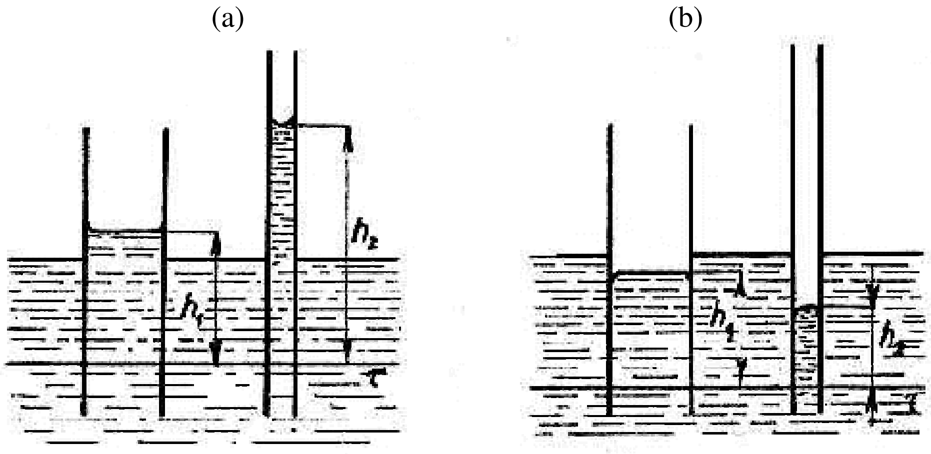


Fig. 3. Capillary rise (a) and depression (b) (www.kekule.science.upjs.sk)

The force of the surface tension can be written:

$$f_1 = 2\pi r\gamma\cos\theta \tag{14}$$

where r is the capillary radius and θ is the contact angle.

At equilibrium this force is equal to the weight of the liquid column f_2 increased or decreased in the capillary till the height h:

$$f_2 = \pi r^2 h\rho g \tag{15}$$

where ρ denotes the liquid density and *g* is acceleration of free fall.

At equilibrium f_1=f_2, thus:

$$2\pi r\gamma\cos\theta = \pi r^2 h\rho g \tag{16}$$

hence:

$$\gamma = \frac{1}{2}\frac{rh\rho g}{2\cos\theta} \tag{17}$$

In the case of liquids wetting capillary walls, the contact angle θ is practically equal to zero, then cosθ = 1 and one can use the following equation:

$$\gamma = \frac{1}{2}rh\rho g \tag{18}$$

III.6. The drop weight (stalagmometric) method of the surface tension measurement

This is a fairly accurate method and perhaps the most convenient laboratory one for measuring the surface tension. This method is based on determining the weight of a drop (or its volume) flowing out from a capillary of a stalagmometer ended with a flat or a conical tip (Fig.4).

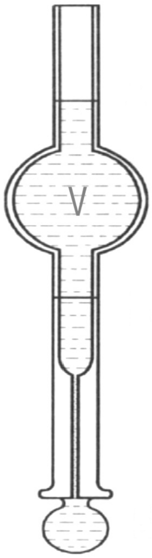


Fig. 4. Stalagmometer (www.magiste.republika.pl).

The method is based on the Tate's formula associating the drop weight W with the liquid surface tension γ:

$$W = 2\pi r\gamma \tag{19}$$

where: r – the inner capillary radius.

Actually, the weight W' is obtained, which is less than the „ideal" value W, which results from the process of drop formation at the end of a capillary. Harkins and Brown introduced a correction factor f, which is a function of the inner capillary radius, the falling drop volume (v) and a constant (a) characteristic of a given stalagmometer. Accordingly, f = f (r, a, v), and W' can be given by:

$$W' = 2\pi r\gamma f \tag{20}$$

Simultaneously, W' = m·g (m – the drop weight, g – acceleration of free fall), and then:

$$\gamma = \frac{m \cdot g}{2\pi r \cdot f} \tag{21}$$

Because $m = v \cdot d$, and $k = 2\pi r \cdot f$ (constant for a given stalagmometer), this equation can be written in the form:

$$\gamma = \frac{v \cdot d \cdot g}{k} \tag{22}$$

If V cm^3 liquid leaks out from the stalagmometer giving n drops of liquid, the mass of one drop equals $m = \frac{V \cdot d}{n}$, or:

$$\gamma = \frac{V \cdot d \cdot g}{n \cdot k} \tag{23}$$

The surface tension measurements are often performed as relative ones, taking water as a reference liquid, because its surface tension was measured in a wide range of temperatures.

Thus, the surface tension of water is:

$$\gamma_w = \frac{V \cdot d_w \cdot g}{n_w \cdot k} \tag{24}$$

$$\frac{\gamma}{\gamma_w} = \frac{\frac{V \cdot d \cdot g}{n \cdot k}}{\frac{V \cdot d_w \cdot g}{n_w \cdot k}} = \frac{d \cdot n_w}{n \cdot d_w} \tag{25}$$

hence:

$$\gamma = \gamma_w \cdot \frac{d \cdot n_w}{d_w \cdot n} \tag{26}$$

where: n_w, d_w and γ_w denote the number of drops, the density and the surface tension of the standard liquid – water, respectively, n, d and γ are the number of drops, the density and the surface tension of the studied liquid, respectively.

III.7. The maximum bubble pressure method of the surface tension measurement

This method is very attractive because it attempts to measure the capillary pressure directly. So, if the radii of curvature are known in one point of the interface, the interfacial tension can be computed. By applying an internal pressure, the meniscus can be pushed down till at $p = p_{max}$ the bubble starts to grow spontaneously. The principle is sketched in Fig. 5. The gas bubbles are produced and enter the liquid through a capillary whose radius is known. During this process the pressure passes through a maximum (Fig. 5). The bubble finally escapes from the capillary and rises. The cycle begins again with the formation of the next bubble.

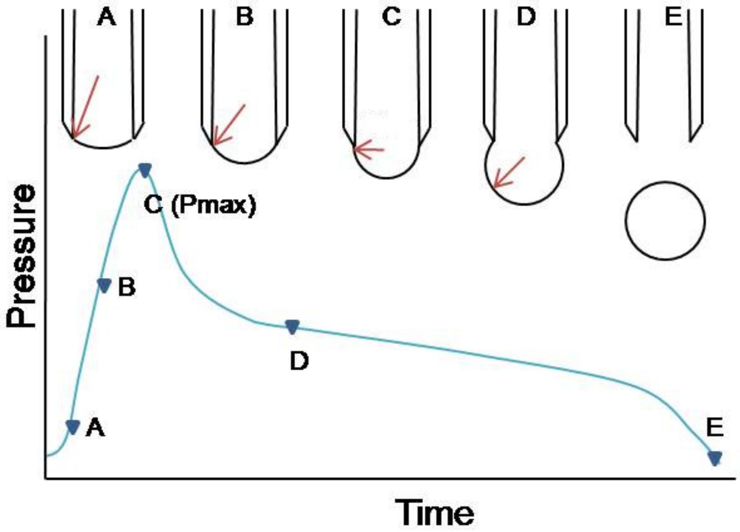


Fig. 5. Principle of the method of maximum bubble pressure (www.en.wikipedia.org).

There is a relationship between the liquid surface tension and the minimum pressure needed to pick the bubble from the capillary dipped in the liquid. According to the Cantor equation:

$$\gamma = \frac{rp}{2} \tag{27}$$

where r denotes the capillary radius and p is the minimum pressure (in mN/m^2), at which the bubble is released.
This technique is often applied to liquid-liquid interfaces if the density of the liquid to be measured is lower than that of the external one.

III.8. The ring (tensiometric) method of the surface tension measurement

This method is based on directly measuring the force needed to keep an object (a ring) at an interface and pull it upward from a liquid (Fig. 6). The force has a gravity and a capillary contribution, the latter depending on surface tension and contact angle. So, if the former is accounted for, the product of surface tension and contact angle can be obtained. When the object is completely wetted by the liquid, the surface tension is accessible. Instruments by which such forces are measured are called tensiometers. The ring method got its name through the work of Du Noüy, who described a convenient apparatus for the surface tension measurement.

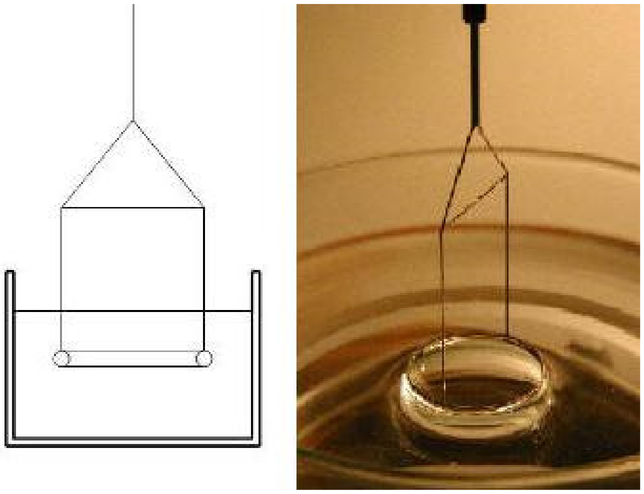


Fig. 6. Du Noüy ring for the surface tension measurement (www.maist.com.cn).

The force required to detach the ring from the liquid can be expressed by the equation:

$$f = 2l\gamma \tag{28}$$

where l is the ring perimeter.

IV Experimental

A. Apparatus and materials

1. Apparatus: stalagmometer.
2. Equipment:
   - hair drier,
   - attachment for pipettes,
   - vessel for liquid,
   - filter paper.
3. Substances:
   - acetone,
   - octane,
   - C_6H_{12},
   - ethyl acetate,
   - $C_4H_8O_2$,
   - isobuthylmethylketone,
   - methanol,
   - water.

B. Program

1. Determination of the surface tension of the studied organic liquids by means of the comparative stalagmometric method.
2. Calculation of experimental parachor values of the studied liquids on the basis of the measured values of the surface tension.
3. Calculation of theoretical parachor values for given liquids by summing of the atom and bond parachors in molecules of these liquids.
4. Establishing the correct structure of the compound on the basis of the measured surface tensions.

C. Methods

The surface tension should be measured by the stalagmometric method for the following liquids: acetone, octane, C_6H_{12}, ethyl acetate, $C_4H_8O_2$, methanol, isobuthylmethylketone and water.

For this case it is needed to:

- dip a tip of the stalagmometer in liquid and fill the stalagmometer with liquid 1 cm above the bulb vessel,
- put a vessel under the tip of the stalagmometer,
- determine **three times** the number of drops released from the stalagmometer for the same volume of liquid.

Before putting liquid the stalagmometer must be thoroughly washed, rinsed with acetone and dried.

D. Results and conclusions

1. Calculate the surface tensions of the studied liquids using equation (26). Densities of the studied liquids at 20^0C are listed in Table I. The surface tension of water at 20^0C is $\gamma_w = 72.75$ mN/m.
2. Calculate the parachors of the studied liquids applying equation (10) and compare with the values obtained by summing the atom and bond parachors in molecules of these liquids (equation (13)), using the data from Table II.

Table I. Densities of the studied liquids at 20^0C.

Liquid	**Density, $d^{20} \cdot 10^3$ kg/m^3**
acetone	0.7899
octane	0.7027
C_6H_{12}	0,7791
ethyl acetate	0.9010
$C_4H_8O_2$	1.0337
methanol	0.7915
isobuthylmethylketone	0.8000
water	0.9992

Table II. Atom parachors and bond parachors, [P] – in $10^{-4}\ \frac{kg^{1/4}\cdot m^3}{kmol\cdot s^{1/2}}$

Atom	**P**	**Atom**	**P**	**Atom**	**P**	**Bond**	**P**
C	8.5	P	67.0	Se	111.1	single	0
H	30.4	F	45.7	Si	44.5	double	41.3
H in OH	20.1	Cl	96.5	As	89.1	triple	82.9
O	35.6	Br	120.9	Sb	117.3	ring 3-membered	29.7
N	22.2	I	161.8	Sn	102.9	4-membered	20.6
S	85.7	B	29.2	Hg	122.2	5-membered	15.1
						6-membered	10.8
						O_2 in esters and acids	106.7

3. Put the measurement results together with those calculated in Table:

Substance name	Drop number	Surface tension [N/m]	Parachor $\left[\frac{\mathrm{kg}^{1/4}\cdot \mathrm{m}^3}{\mathrm{kmol}\cdot \mathrm{s}^{1/2}}\right]$	
			experimental	calculated

4. Draw conclusions about additivity of the studied liquid parachors.
5. On the basis of the measured values of surface tension of the compounds characterized by the chemical formulas:

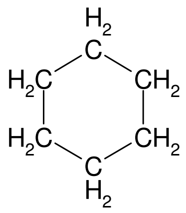
   a) C_6H_{12} b) $C_4H_8O_2$

   choose which of the structures given below is correct:

C_6H_{12}

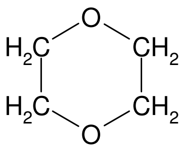
a) $CH_3-CH_2-CH_2-CH_2-CH=CH_2$

b)



$C_4H_8O_2$

a)



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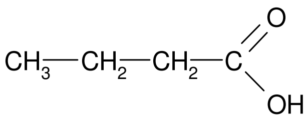

$CH_3-CH_2-CH_2-C(=O)OH$