Exercise 18

LIQUID-VAPOR INTERFACE ADSORPTION.
GIBBS ISOTHERM

Key concepts: Adsorption, adsorption isotherms. Gibbs isotherm. Surface excess and methods of its determination. Extend of surface coverage. Surface tension: definition, ring measuring with ring method, contact angle.

The thermodynamics of an adsorption process at the liquid-vapor interface was studied by Gibbs in 1978. As a results of his work the equation, called Gibbs isotherm was determined, which is the basis of the physicochemical studies on surface phenomena. Gibbs isotherm shows the dependency of surface excess of adsorbed molecules or ions of particular substance (Γ_J), its chemical potential (μ_J) and surface tension (γ). At constant temperature and constant pressure, Gibbs isotherm can be written as:

$$\Gamma_J = -\left(\frac{d\gamma}{d\mu_J}\right)_{T,p} \qquad (1)$$

Knowing that $d\mu_J = RT d\ln a_J$, where a_J is activity of substance J, and assuming that for diluted solution a_J is approximately equal to its concentration c_J, the equation (1) can be written as:

$$\Gamma_J = -\frac{1}{RT}\left(\frac{d\gamma}{d\ln c_J}\right)_{T,p} \qquad (2)$$

The experimental determination of the surface excess Γ_J for a given substance is to determine the $\left(\frac{d\gamma}{d\ln c_J}\right)$ coefficient for a solution of a given concentration. To do this, the surface tension is measured for a series of solutions of successively increasing concentration (Figure 1). The obtained dependence of the surface tension on the concentration of a particular substance can be described by the empirical equation:

$$\gamma = z_0 + z_1 \ln c_J + z_2 (\ln c_J)^2 \qquad (3)$$

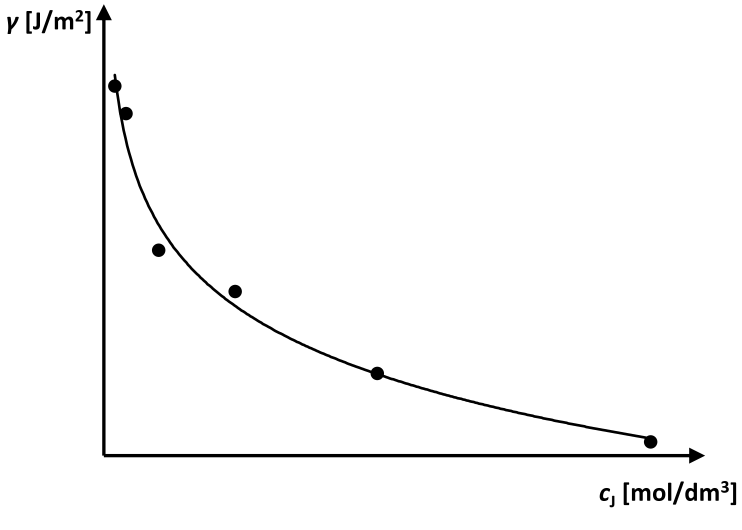

Figure 1. Dependence of surface tension on the concentration of a substance.

Differentiating equation (3) with respect to $\ln c_J$ we obtain:

$$\frac{d\gamma}{d\ln c_J} = z_1 + 2z_2\ln c_J \qquad (4)$$

After substituting equation (4) into equation (2), we obtain:

$$\Gamma_i = -\frac{1}{RT}(z_1 + 2z_2\ln c_J) \qquad (5)$$

The plot of the dependence of Γ_J on c_J is a graphical representation of Gibbs isotherm (Figure 2). he adsorption curve asymptotically tends to the surface excess limit $\Gamma_{J,\infty}$. The value of $\Gamma_{J,\infty}$ can be determined from equation (6):

$$\Gamma_{J,\infty} = -\frac{1}{RT}\lim_{c_J\to c_{max}}(z_1 + 2z_2\ln c_J) \qquad (6)$$

where c_{max} is the concentration of the substance read from Figure 2, from which the Γ_J values are almost constant. The $\Gamma_{J,\infty}$ corresponds to the maximum covering of the surface with the surface-active-agent. This value, multiplied by the Avogadro constant (N_A), is equal to number of units (n_J) located on the 1 m^2 of surface:

$$n_J = \Gamma_{J,\infty}N_A \qquad (7)$$

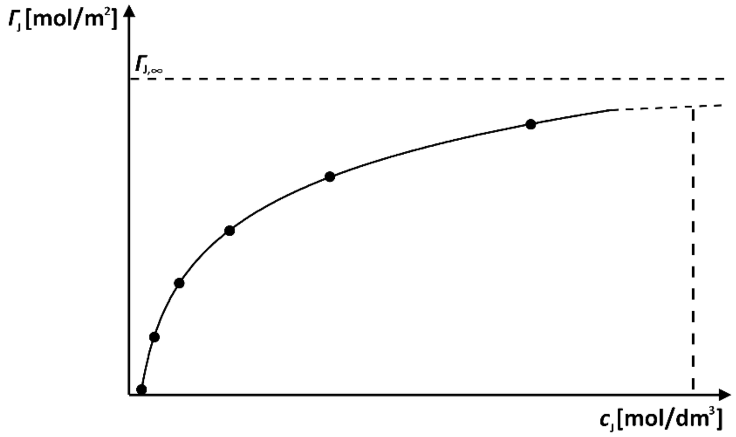

Figure 2. Gibbs isotherm: the dependence of the surface excess on the concentration of a substance. The limiting surface excess and concentration, c_{max}, are also marked on the chart.

From the number of molecules located on 1 m^2, the area (A_m) occupied by one molecule can be calculated:

$$A_m = \frac{1}{n_J} = \frac{1}{\Gamma_{J,\infty}N_A} \qquad (8)$$

Knowing the molar volume of the adsorbed substance ($V_{\mathrm{m,J}}$), one can also calculate the thickness of the adsorption layer (d_{J}) from the relation:

$$d_{\mathrm{J}} = \frac{V_{\mathrm{m,J}}}{A_{\mathrm{m}} N_{\mathrm{A}}} \qquad (9)$$

Experiment method

The aim of the exercise is to determine the adsorption isotherm of acetic acid $\Gamma_J = f(c_J)$ and $\Gamma_{J,\infty}$ value, as well as to calculate n_J, A_m, d_J. The subscript "J" means acetic acid and can be omitted in further formulas.

In the exercise, surface tension is measured by using the ring method. Since Lecomte du Noüy described the first ring tensiometer in 1919, the ring method has been a method often used to measure surface tension. In this method, the measuring probe is a platinum ring horizontally suspended on a balance bar. The ring is immersed in the studied liquid until it is completely wetted and then slowly lift form the surface of a liquid. The force, F, required to raise the ring from the liquid's surface is measured. In the pulled ring, the surface tension acts along its wetted perimeter, the so-called wetted length l. The surface tension can be described by the equation:

$$\gamma = F/l$$

The wetted length l of the ring is related to its dimensions and $l = 4\pi R$, where R is the average value of the inner and outer radius of the ring. A standard ring is made of wire with radius $r = 0.185$ mm, the average value of its radius is $R = 9.545$ mm and the wetted length $l = 119.95$ mm.

When the ring is pulled out of the liquid, not only the force associated with the surface tension acts on it, but also the gravitational force of the liquid (that is, the weight of the liquid) lifted by the ring above the level of the liquid surface. During the measurement, both of these forces are measured and the measured value of surface tension, γ^* is increased by the gravitational force. Thus, in order to obtain the true value of γ, it is necessary to introduce a correction factor, Ψ:

$$\gamma = (F/l)\Psi = \gamma^*\Psi$$

In the exercise, surface tension measurements are made with a K6 tensiometer (Figure 3), which is linearly compensated so that the correction factor for measurements of pure water at 20 °C is equal to unity. For aqueous dilute solutions of substances for which $a \approx c$, one can assume that $\Psi \approx 1$.

The surface tension should be determined for solutions with concentrations of 0.0625, 0.125, 0.25, 0.50, 1.00, 2.00 M, which are prepared from a starting solution with a concentration of 2 M. Measurements should be started with water, and then the solutions should be studied from the lowest to the highest concentration.

Procedure

(a) prepare the studied solutions;

(b) level the device using the set screws located in the base of the tensiometer;

(c) before measurements, both the ring and the measuring vessel should be thoroughly washed with distilled water and then with acetone. Wait for a while until the measuring ring is dry. At this time, fill the measuring vessel to ½-¾ of its height with the studied solution and place it on the measuring table;

(d) the height of the table with the measuring vessel is adjusted with the screw (1) - henceforth, all numbers in the brackets refer to Figure 3. *Note*: The distance of the ring from the surface of the studied liquid in the measuring vessel should be about 1 cm and must not be greater than 1.5 cm. The ring should be exactly centered with respect to the measuring vessel;

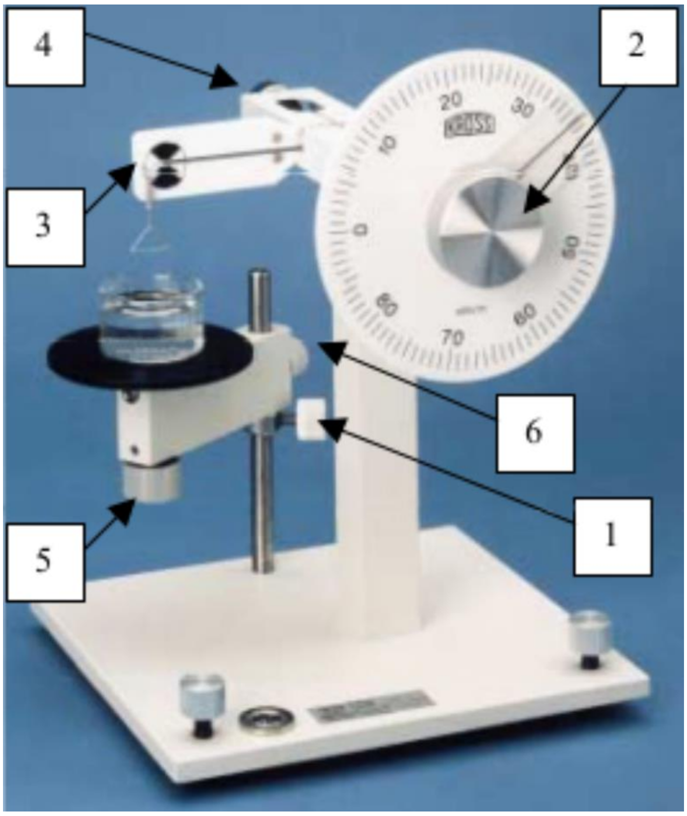

Figure 3. Tensiometer K6

(e) before each measurement, the scale of the tensiometer should be zeroed with the dial (2). The weighing bar holding the ring should, in its zero position, overlap the white mark field (3). If this cannot be done, then the zero position should be adjusted with the screw (4);

(f) with the screw (5) turned clockwise, the measuring table is slowly raised until the ring is immersed in the studied liquid to a depth of about 5 mm. The table is then immobilized by lightly tightening the screw (6) as far as it will go. Wait a while until the surface of the liquid is smooth and stabilized. Turning the screw (5) counterclockwise lowers the measuring table until the weighing bar moves downward beyond the white mark area (3);

(g) by turning the screw (2) clockwise very slowly, the twist of the belt increases and the ring begins to pull out. This leads to an upward movement of the weighing bar beyond the white area of the mark (3). At this point, the liquid membrane between the ring and the liquid surface may break. If not, the weighing beam is now moved back to the "zero position" by lowering the measuring table with a counterclockwise rotation of the screw (5). The steps described in this section should be repeated until the liquid film between the ring and the liquid surface is broken, that is, until the surface tension forces are overcome. Then read the value of the surface tension from the tensiometer scale;

(h) after the measurement, unscrew (release from resistance) the screw (6), and then lower the measuring table down by turning the screw (5) counterclockwise until there is a slight resistance;

(i) repeat the measurement three times for each solution, starting from point (e). Average the obtained values of surface tension (γ);

(j) before changing the solution in the measuring vessel, lower the table using the screw (1). For the new studied solution, carry out measurements starting from point (d);

(k) after the measurements are completed, both the ring and the measuring vessel should be thoroughly washed with distilled water and then with acetone.

Calculations

(a) from the obtained surface tension results for different concentrations of solutions, plot the dependence: $\gamma = f(\ln c)$;
(b) from equation (3), determine the coefficients z_0, z_1 i z_2, disregarding the solution of zero concentration;
(c) from equation (5) calculate Γ for each concentration;
(d) the dependence of Γ on c should be plotted on a graph, from which the $c_{\max}$ value is determined. Reasonable $c_{\max}$ values should be selected from the concentration range from 2 to 5 M.
(e) calculate Γ_∞, n, A_m and d using equations (6), (7), (8) and (9), respectively;
(f) write down the obtained results in Table 1.

Table 1. Results

c M	0.000	0.0625	0.125	0.250	0.500	1.000	2.000
γ_1 [J m^{-2}] γ_2 γ_3 $\gamma_{śr}$							
Γ [mol m^{-2}]							

z_0 =
z_1 =
z_2 =

Γ_∞ =
n =
A_{cz} =
d =