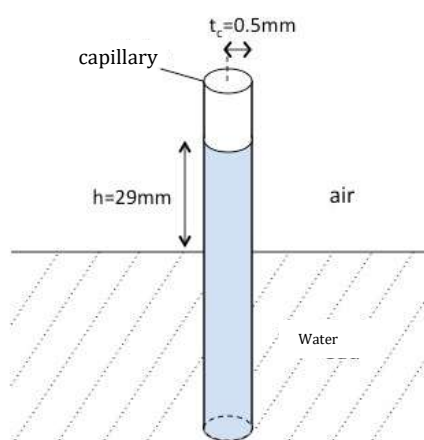


Physical Chemistry of Interfaces: Solutions

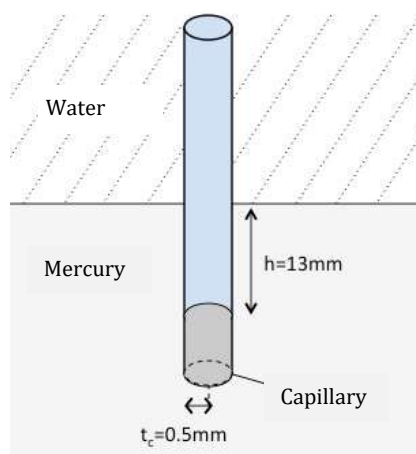
3rd session

3.1 Capillary rise/fall

a) A glass capillary is immersed in water. The water in the capillary rises 29 mm (as demonstrated in the figure below). Suppose that water perfectly wets glass surface and contact angle between water and inside of the capillary is zero. The radius of capillary is 0.5 mm. Estimate the surface tension of water. Tip: Neglect the weight of water meniscus.



b) Consider a water phase on top of mercury phase. The glass capillary is immersed in mercury. This time the capillary fall is observed. The mercury level in capillary is 13 mm lower compared to the plane interface between water and mercury. The radius of capillary is 0.5 mm. Suppose that contact angle between mercury and inner capillary wall is 180° . Calculate the surface tension between water and mercury. The density of mercury is 13.6 g/cm^3 . Tip: Neglect the weight of liquid meniscus.



Solution:

- a) In the equilibrium, the hydrostatic pressure of water in the capillary is equal to the Laplace pressure:

$$p_{HS} = p_{LP}$$

Where

$$p_{HS} = \rho_{H_2O}gh \quad \text{and} \quad p_{LP} = \frac{2\gamma}{r_c}.$$

$\rho_{H_2O} = 1000 \text{ kg/m}^3$ is the water density, $g = 9.81 \text{ m/s}^2$ is gravitational acceleration, $h = 29 \text{ mm}$ is the height of water in the capillary and $r_c = 0.5 \text{ mm}$ is the radius of capillary.

From the equilibrium condition:

$$\gamma = \frac{1}{2} \cdot r_c \rho_{H_2O}gh \approx 0.071 \frac{N}{m}.$$

- b) Laplace pressure is given by $p_{LP} = \frac{2\gamma}{r_c}$. The meniscus in capillary will decrease until the hydrostatic pressure is equal to the Laplace pressure. Hydrostatic pressure is equal $p_{HS} = (\rho_{Hg} - \rho_{H_2O}) \cdot gh$.

From the pressure equality:

$$\gamma_{Hg,H_2O} = \frac{1}{2} \cdot r_c \cdot (\rho_{Hg} - \rho_{H_2O}) \cdot gh \approx 0.402 \frac{N}{m}.$$

3.2 Surface thermodynamics

Surface tension of 1-butanol was measured as a function of temperature at constant pressure $p=1 \text{ atm}$:

T [°C]	10	25	50	75	100
γ [mN/m]	25.28	24.13	22.13	20.03	17.83

Estimate quantities $\gamma = G^s$, S^s , H^s , C_p^s of 1-butanol at $T=50^\circ\text{C}$.

(Data: CRC Handbook of Chemistry & Physics).

Solution.

Different thermodynamic properties of interface are given by:

Gibbs free energy of surface: $G^s = \gamma$

Surface enthalpy: $H^s = \gamma - T \left(\frac{\partial \gamma}{\partial T} \right)_{P,S}$

Surface entropy: $S^s = - \left(\frac{\partial \gamma}{\partial T} \right)_{P,S}$

Surface heat capacity: $C_p^s = -T \left(\frac{\partial^2 \gamma}{\partial T^2} \right)_{P,S}$

Since we need to know the second derivative of γ with respect to T , we convert the units to K and Nm^{-1} and find the second order equation by the least squares method:

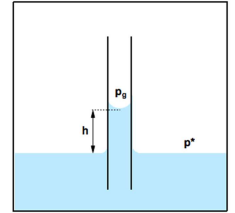
$$\gamma = 0.040211 - 2.9922 \cdot 10^{-5} T - 8.0546 \cdot 10^{-8} T^2$$

3.3 Capillary ascension and Kelvin equation.

A cylindrical capillary is immersed of radius r_c in a wetting liquid.

In this case the height of capillary rise h is expressed by the following relation:

$$h = \frac{2 \gamma \cos \theta}{\rho g r_c}$$



According to simplified Kelvin equation the pressure above flat interface between liquid p^* and gas and the pressure above curved interface (meniscus) p_g are not equal. The relation between these pressures is expressed as follows:

$$p_g = p^* \exp \left(\pm \frac{2 \gamma \cos \theta V_{m,l}}{R T r_c} \right)$$

here γ is the surface tension, ρ is liquid density, $V_{m,l}$ is molar volume of liquid and θ contact angle between solid/liquid/gas).

a) What is the correct sign in the equation above? What is the relation between sign and contact angle θ ?

c) Express the relation between h and $\frac{p^* - p_g}{p^*}$.

d) Estimate the h and $\frac{p^* - p_g}{p^*}$ for quartz capillary immersed in water :

$T = 25^\circ\text{C}$, $\gamma = 72.7 \text{ mNm}^{-1}$, $\theta = 0^\circ$, $\rho = 997 \text{ kg m}^{-3}$, $M_{\text{H}_2\text{O}} = 18 \text{ g mol}^{-1}$, $r_c = 0.2 \text{ mm}$, $R = 8.314 \text{ Jmol}^{-1}\text{K}^{-1}$, $g = 9.81 \text{ ms}^{-2}$.

Solution:

a) The sign of the radius of curvature depends on the convexity or concavity of the liquid / gas interface in the capillary, the radius of the capillary r_c is being chosen as positive.

If the liquid is wetting ($\theta < \pi/2$), as in the drawing, the interface is concave, the radius of curvature is equal $r_{\text{curvature}} = r_c / \cos(\theta)$ and $p_g < p^*$ with a minus sign in the argument of the exponential. If the liquid is non-wetting ($\theta > \pi/2$, $\cos(\theta) < 0$), the interface is convex, the radius of curvature is $r_{\text{curvature}} = r_c / \cos(\pi - \theta) = -r_c / \cos(\theta)$, $p_g > p^*$ and the sign in the exponential is also negative.

c) If we replace the expression for h in the Kelvin equation, we receive:

$$\frac{p^* - p_g}{p_g} = 1 - \exp\left(-\frac{2 \gamma \cos \theta V_{m,l}}{R T r_c}\right) = 1 - \exp\left(-\frac{h \rho g V_{m,l}}{R T}\right).$$

Since the argument in the exponential is small, we can approximate it using $e^{-x} \approx 1-x$, and the equation is then equal to

$$\frac{p^* - p_g}{p_g} \approx \frac{h \rho g V_{m,l}}{R T}.$$

d) Numerically:

$$h = \frac{2 \cdot 7.27 \cdot 10^{-2}}{997 \cdot 9.81 \cdot 2 \cdot 10^{-4}} = 7.43 \cdot 10^{-2} \text{ m} = 7.43 \text{ cm}$$

$$V_{m,l} = \frac{1.8 \cdot 10^{-2}}{997} = 1.805 \text{ m}^3 \text{ mol}^{-1}$$

$$\frac{p^* - p_g}{p_g} = \frac{7.43 \cdot 10^{-2} \cdot 997 \cdot 9.81 \cdot 1.805}{8.314 \cdot 298} = 5.3 \cdot 10^{-6}$$

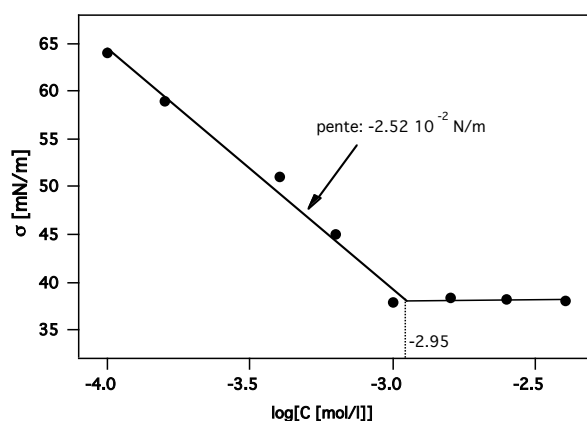
3.4 The surface tension of aqueous solutions of surfactant CTAB (hexadecyltrimethylammonium bromide) at 25 ° C. was measured:

C [M]	1.0×10^{-4}	1.6×10^{-4}	4.0×10^{-4}	6.3×10^{-4}	1.0×10^{-3}	1.6×10^{-3}	2.5×10^{-3}	4.0×10^{-3}
γ [mN/m]	64	59	51	45	37.8	38.3	38.2	38

Estimate for this surfactant the critical micelle concentration (CMC), the surface excess for concentrations close to the CMC, as well as the effective area occupied by a molecule at the air / solution interface. Considering that the aggregation number is $\nu = 93$ for this surfactant, what are the fractions of the surfactant molecules that are on the surface, and in the form of monomer or micelle in the solution, for a total concentration of $C = 2 \cdot 10^{-3}$ M. Assume that the system is of the form of a 10cm x 10cm x 10cm cube, so that the area of the gas-liquid interface is 100cm².

Solution:

From the plot of dependency γ on $\log C$, we receive:



The value of the critical micelle concentration (CMC) is given from the extrapolation of two linear regions of the plot: $C_{CMC} \approx 1.1 \times 10^{-3} M$

The surfactant is a monovalent salt which is completely dissociated in the water, we can therefore apply the Gibbs equation:

$$\Gamma_2^{(1)} = -\frac{1}{2 \cdot RT} \cdot \left(\frac{\partial \gamma}{\partial \ln c} \right)_{p,T} = -\frac{1}{2 \cdot 2.303 \cdot RT} \cdot \left(\frac{\partial \gamma}{\partial \log c} \right)_{p,T}$$

$$\Gamma_2^{(1)} = -\frac{1}{2 \cdot 2.303 \cdot 8.31 \cdot 298} \cdot (-2.52 \cdot 10^{-2})_{p,T} = 2.2 \cdot 10^{-6} \text{ mol m}^{-2}$$

Effective area occupied by one molecule on the gas/solution interface is estimated by:

$$a = \frac{1}{N_{av} \Gamma_2^{(1)}} = \frac{1}{6.022 \cdot 10^{23} \cdot 2.2 \cdot 10^{-6}} = 7.5 \cdot 10^{-19} \text{ m}^2 = 75 \text{ \AA}^2$$

Assume we have one liter of the solution, for example in the form of cube. The area of gas/solution interface is $1 \text{ dm}^2 = 10^{-2} \text{ m}^2$. The concentration of molecules on the surface is

$$c_{surf} = \frac{a \cdot \Gamma^{excès}}{V} = 2.2 \times 10^{-8} M.$$

$$f_{surf} = \frac{c_{surf}}{c} = \frac{2.2 \times 10^{-8} \text{ mol}}{2 \times 10^{-3} \text{ mol}} = 1.1 \times 10^{-5}$$

Concentration of the molecules in the monomeric form is $c_{monomer} \approx c_{CMC} = 1.1 \times 10^{-3} M$, where $c = 2 \cdot 10^{-3} M > C_{CMC}$.

$$f_{monomer} = \frac{c_{monomer}}{c} = \frac{1.1 \times 10^{-3} M}{2 \times 10^{-3} M} = 0.55$$

The fraction of the molecules present in the form of micelles is:

$$f_{micelle} = \frac{c_{micelle}}{c} = \frac{(2-1.1) \times 10^{-3} M}{2 \times 10^{-3} M} = 0.45.$$

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