Effect of the precipitation of acid soap and alkanoic acid crystallites on the bulk pH

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1. Introduction

Unilever is one of the world's leading fast-moving consumer goods companies with products sold in over 190 countries. More than 2 billion consumers worldwide use a Unilever product on any given day. The Unilever turnover was €49.8 billion in 2013. More than 174000 people work for Unilever and more than 6000 people work in the global research and development centers (Trumbull, USA; Port Sunlight, UK; Colworth, UK; Vlaardingen, NL; Shanghai, China; Bangalore, India). The quality of the products is challenged with the significant scientific contribution from 7 Universities (Oxford, Cambridge, MIT, Nottingham, Liverpool, Jairpur, Sofia).

One of the strategies for controlling the bulk pH of the products is the usage of fatty acid salts. In the case of one component the mathematical problem is described below. In the products Unilever uses natural substances, which are multi component systems. The developed solution of the described problem can be extended for such kind of mixtures and the precise calculation of the solubility makes the mathematical model applicable for designing of complex materials with given physicochemical properties.

2. Mathematical formulation of the problem

As a basis we will use the theory of the pH of carboxylate soap solutions, which accounts for the presence of NaCl, NaOH, and CO_2. We denote: Z^- the alkanoate ion; M^+ the metal ion (Na^+); HZ is the non-dissociated alkanoic (fatty) acid; MZ is the non-dissociated neutral soap; OH^- is the hydroxyl ion; H+ is the hydrogen ion; HCO_3^- is the hydrogencarbonate ion, which appears because of the solubility of CO_2 from the atmosphere. Five basic equations express the dissociation equilibria of the fatty acid (HZ) and the neutral soap (MZ) molecules, the dissociation of water and CO_2, and the electro-neutrality of the solution:

$$c_{\mathrm{H}} c_{\mathrm{Z}} \gamma_{\pm}^2 = K_{\mathrm{A}} c_{\mathrm{HZ}} \quad \text{and} \quad c_{\mathrm{M}} c_{\mathrm{Z}} \gamma_{\pm}^2 = Q_{\mathrm{MZ}} c_{\mathrm{MZ}} \tag{1}$$

$$c_{\mathrm{H}} c_{\mathrm{OH}} \gamma_{\pm}^2 = K_{\mathrm{W}} \quad \text{and} \quad c_{\mathrm{H}} c_{\mathrm{HCO3}} \gamma_{\pm}^2 = K_{\mathrm{CO2}} \tag{2}$$

$$I = c_{\mathrm{H}} + c_{\mathrm{M}} = c_{\mathrm{OH}} + c_{\mathrm{HCO3}} + c_{\mathrm{Z}} + c_{\mathrm{A}} \tag{3}$$

where c is the concentration of the respective compound, c_{A} is input concentration of salt (NaCl), I is the ionic strength, K_{W}, K_{CO2}, K_{A} and Q_{MZ} are the respective dissociation constants. The activity coefficient, $\gamma_{\pm}$, for this kind of solutions is calculated from the semi-empirical formula:

$$\log_{10} \gamma_{\pm} = 0.055\, I - \frac{0.5115 \sqrt{I}}{1 + 1.316 \sqrt{I}} \tag{4}$$

The amounts of the components M and Z incorporated in the solid phase (in the crystallites) per unit volume are given by the equations:

$$m_{\mathrm{M}} = c_{\mathrm{T}} + c_{\mathrm{A}} + c_{\mathrm{B}} - c_{\mathrm{M}} - c_{\mathrm{MZ}} \quad \text{and} \quad m_{\mathrm{Z}} = c_{\mathrm{T}} - c_{\mathrm{Z}} - c_{\mathrm{HZ}} - c_{\mathrm{MZ}} \tag{5}$$

where c_{T} is the input concentration of MZ and c_{B} is the input base concentration (NaOH).

The quality of the products depends considerably on the bulk pH, so that after the numerical solution of the problem one needs to calculate:

$$\mathrm{pH} = -\log_{10}(\gamma_{\pm} c_{\mathrm{H}}) \tag{6}$$

which is measured experimentally for a given composition.

2.1. Solutions with fatty acid precipitates. In this case the concentration of fatty acid is fixed and equal to the equilibrium solubility, S_{HZ}. The amount of the component M incorporated in the solid phase is zero. Therefore, the system of equations is closed and

$$c_{\mathrm{HZ}} = S_{\mathrm{HZ}} \quad \text{and} \quad m_{\mathrm{M}} = 0 \tag{7}$$

2.2. Solutions with precipitate of j:n acid soap. If a precipitate of $(\mathrm{HZ})_j(\mathrm{MZ})_n$ acid soap is present, then one closes the system of equations with the following two conditions: a) mass balance of the amounts m_{M} and m_{Z} with the stoichiometry (j:n):

$$\frac{m_{\mathrm{M}}}{n} = \frac{m_{\mathrm{Z}}}{n + j} \tag{8}$$

b) the solubility relation for a precipitate of j:n acid soap:

$$c_{\mathrm{H}}^{j} c_{\mathrm{M}}^{n} c_{\mathrm{Z}}^{j+n} \gamma_{\pm}^{2j+2n} = K_{jn} \tag{9}$$

where K_{jn} is the respective solubility product.

General mathematical problem: Solve the polynomial equations in more than one variable

$$F_j(x_1, x_2, ..., x_N) = b_j \quad (j = 1, 2, ..., N) \tag{10}$$

in which the coefficients depend slowly on the solution (x_1, x_2, …, x_N) to obtain only the positive solution, that is

$$x_j > 0 \quad (j = 1, 2, ..., N) \tag{11}$$

Note that the difference between concentrations (for example c_H and c_M) can be 10 orders of magnitude.

3. Application of the mathematical model for the characterization of precipitates

In the case of NaMy the values of the following constants are known:

$$K_W = 6.81\times10^{-15}\ \mathrm{M}^2, \quad K_A = 1.995\times10^{-5}\ \mathrm{M}, \quad Q_{MZ} = 2.84\ \mathrm{M} \tag{12}$$

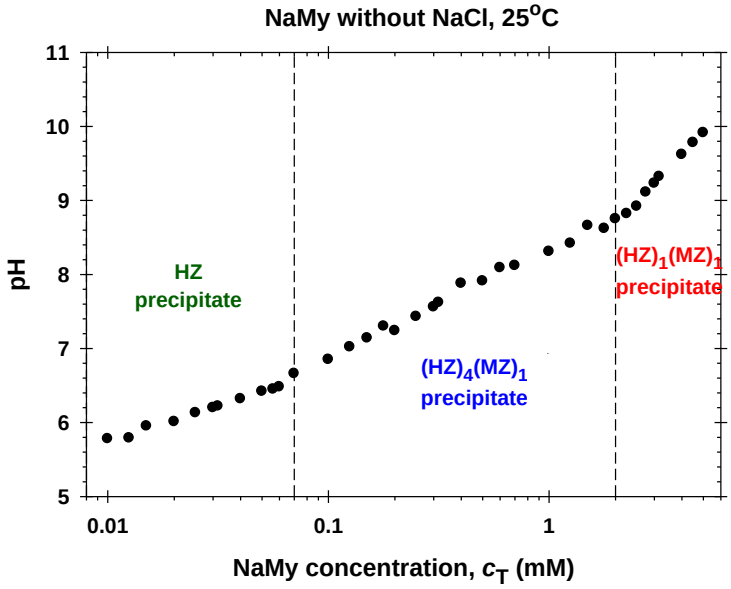

Fig. 1. Dependence of pH on the concentration of MZ (NaMy). Three different regions are measured: fatty acid precipitate; 4:1 precipitate; 1:1 precipitate.

Fig. 1 shows the experimental dependence of pH on the concentration, c_T, for NaMy solution without added salt and base, that is for

$$c_A = 0\ \mathrm{M} \quad \text{and} \quad c_B = 0\ \mathrm{M} \tag{13}$$

For convenience the experimental concentrations are given in mM, so that for example 10 mM (experimental value) corresponds to 0.01 M (for numerical calculations). The strategy of modeling is the following:

a) For concentrations below 0.07 mM one uses Section 2.1 (fatty acid precipitate) with the equilibrium solubility:

$$S_{HZ} = 5.25\times10^{-7}\ \mathrm{M} \tag{14}$$

to fit the experimental data with one adjustable parameter, K_{CO2}.

b) With the obtained value of K_{CO2} one studies the concentration region from 0.07 to 2 mM. In this region the stoichiometry of the precipitate is known:

$$j = 4 \quad \text{and} \quad n = 1 \tag{15}$$

and one uses Section 2.2. The fit of experimental data gives the most probable value of the solubility product K_{41}.

c) Finally, for concentrations larger than 2 mM the stoichiometry of the precipitate is

$$j = 1 \quad \text{and} \quad n = 1 \tag{16}$$

and again the model described in Section 2.2 should be applied. From the fit of experimental data one obtains the solubility product K_{11}.

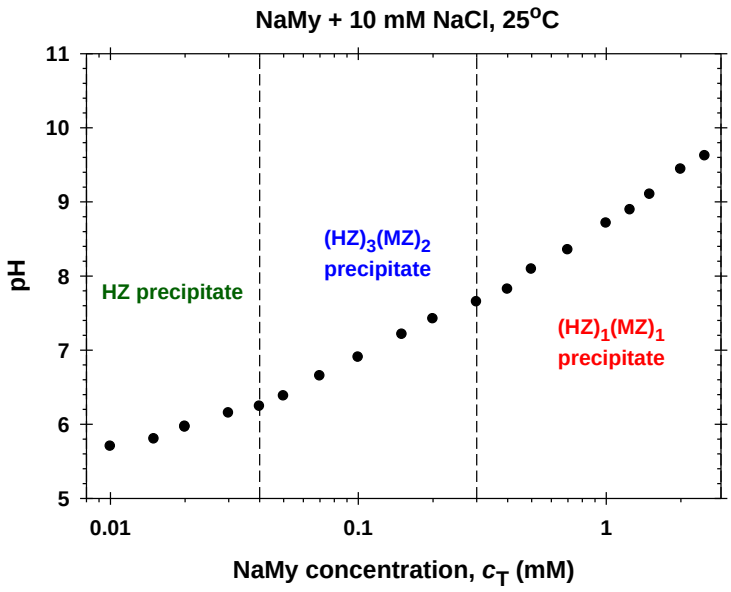

Fig. 2. Dependence of pH on the concentration of MZ (NaMy) in the presence of 10 mM NaCl. Three different regions are measured: fatty acid precipitate; 3:2 precipitate; 1:1 precipitate.

Fig. 2 shows the experimental dependence of pH on the concentration, c_T, for NaMy solution in the presence of 10 mM NaCl:

$$c_A = 0.01\ \text{M} \quad \text{and} \quad c_B = 0\ \text{M} \tag{17}$$

In this case:

a) For concentrations below 0.04 mM HZ precipitate is observed. The fit of experimental data with the model from Section 2.1 gives K_{CO2}.

b) For concentrations in the region from 0.04 to 0.3 mM the stoichiometry of the precipitates is j:n = 3:2, that is from the fit of experimental data with the model from Section 2.2 one obtains K_{32}.

c) Finally, for c_T > 0.3 mM the stoichiometry of the precipitate is j:n = 1:1. Thus the most probable value of the solubility limit K_{11} can be obtained.

Note, that K_{CO2} and K_{11} calculated from the two sets of experimental data (Figs. 1 and 2) should be close each others.