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Modeling Ostwald ripening rate of styrene miniemulsions stabilized by a homolog of n-alkane costabilizers

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ABSTRACT

The modified Kabal'nov equation developed by a thermodynamic approach dealing with a regular solution of monomer and costabilizer as the two-component disperse phase adequately describes the Ostwald ripening rate data in a wide range of the volume fraction of costabilizer for styrene miniemulsions stabilized by a homolog of n-alkane costabilizers (C_nH_{2n+2}; $n = 10, 12, 16, 18, 20, 24, 32$) upon aging at 25 °C. The results show that the costabilizer with the shortest chain length ($C_{10}H_{22}$) is not hydrophobic enough to effectively retard the Ostwald ripening process. The effectiveness of n-alkanes as costabilizer in suppressing the Ostwald ripening process increases with increasing n-alkane molecular weight. Nevertheless, further increasing the n-alkane chain length from $C_{24}H_{50}$ to $C_{32}H_{66}$ does not lead to significant improvement in the effectiveness of n-alkane as costabilizer. The major characteristics of the modified Kabal'nov equation are also discussed in this work.

1. Introduction

Monomer miniemulsions are kinetically stable aqueous dispersions of oil droplets (*ca.* 50–500 nm in diameter), prepared by homogenizing a mixture of monomer, water, surfactant and costabilizer. The total droplet surface area of these colloidal systems is very large and most of the surfactant molecules are adsorbed on the monomer droplet surfaces. Subsequently, these monomer miniemulsions can be transformed to latex products via free radical polymerization [1–4]. Thermodynamically unstable fresh miniemulsions tend to undergo Ostwald ripening and/or droplet coalescence processes in order to reduce the total oil–water interfacial area. If miniemulsions are adequately stabilized by surfactants against coalescence, the former would be the predominant mechanism responsible for the substantial degradation of droplets. Ostwald ripening phenomenon is the growth of larger droplets with lower chemical potential at the expense of smaller ones with higher chemical potential via molecular diffusion of monomer from smaller droplets to larger ones [4–7]. However, the presence of an extremely hydrophobic low molecular weight costabilizer in the disperse phase leads to the compensation of the Ostwald ripening effect by the osmotic pressure effect.

Higuchi and Misra [8] were the pioneers to consider Ostwald ripening kinetics in the two-component disperse phase miniemulsion system. They showed that only a small amount of an extremely hydrophobic compound (termed the costabilizer) in the disperse phase dramatically retarded the Ostwald ripening process due to equalization of the concentrations of the major component (*e.g.*, monomer in this work) in droplets of different sizes as a consequence of the osmotic pressure effect. Representative studies were carried out to gain a better understanding of the Ostwald ripening phenomenon associated with miniemulsions in the presence of costabilizer [9,10]. Based on the modified Lifshitz–Slyozov–Wagner (LSW) theory [7], the Ostwald ripening rate (R_O) of the two-component disperse phase miniemulsion system can be expressed as

$$R_O = \frac{d(a_{avg})^3}{dt} = \frac{8\sigma D_2 V_{m1} C_{\infty,2}}{9RT\varphi_2} \tag{1}$$

where a_{avg} is the average oil droplet radius, D_2 the diffusion coefficient of costabilizer in water, $C_{\infty,2}$ the water solubility of the bulk costabilizer, σ the interfacial tension at the oil–water interface, V_{m1} the molar volume of monomer in the droplet, φ_2 the volume fraction of costabilizer in the droplet, T the absolute temperature, and R the gas constant. The pioneering work of Kabal'nov et al. [9] neglected differences in the molar volumes, diffusion coefficients and interfacial tensions between the constituent components 1 (monomer) and 2 (costabilizer) and then developed the following equation to describe the R_O for the two-component disperse phase miniemulsion system.

$$\frac{1}{R_O} = \frac{\varphi_1}{R_{O,1}} + \frac{\varphi_2}{R_{O,2}} \tag{2}$$

where $R_{O,i}$ ($i = 1$ or 2) is the Ostwald ripening rate corresponding to the single component species i and φ_i the volume fraction of the

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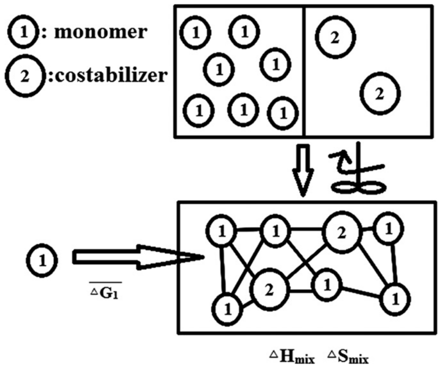


Scheme 1. Mixing of a binary regular solution of monomer (1) and costabilizer (2) accompanied by heat of mixing.

component *i*. When the water solubility of costabilizer ($i = 2$) is nil (*i.e.*, $R_{O,2}$ is extremely small), the first term on the right hand side of Eq. (2) can be neglected. Under the circumstances, it is the costabilizer that governs the Ostwald ripening process.

In our previous work [11], it was shown that Kabal'nov equation failed to describe the R_O data in the whole φ_2 range 0.01–0.05 for the two-component disperse phase miniemulsions. This is primarily because Kabal'nov et al. [9] assumed that the solution of constituent components in the disperse phase was ideal (*i.e.*, enthalpy change of mixing ($\triangle H_{mix}$) = 0). An empirical equation with two adjustable parameters (K_1 and K_2) was developed to adequately predict the R_O data and the model is shown below [11].

$$\frac{1}{R_O} = \left(\frac{1}{R_{O,1}}\right)(1 + K_1\varphi_2 + K_2\varphi_2^2) \tag{3}$$

where $K_1 = (R_{O,1} - R_{O,2})/R_{O,2}$ and $K_2 = R_{O,1}[1/(R_O\varphi_2) - 1/R_{O,2}]/\varphi_2$. The objective of this work was to develop a model via the thermodynamics approach to quantitatively describe the Ostwald ripening behavior in a wide φ_2 range for the two-component disperse phase miniemulsions, in which the disperse phase was regular ($\triangle H_{mix} \neq 0$). The validity of this theoretical model was then evaluated by experimental data taken from the literature [12].

2. Model development

2.1. Partial molar Gibbs free energy of a regular solution

It is necessary to take into account the effect of $\triangle H_{mix}$ for a regular solution (Scheme 1) and the Gibbs free energy change of mixing ($\triangle G_{mix}$) can be expressed as

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \tag{4}$$

where $\triangle S_{mix}$ (> 0) is the entropy change of mixing. The mixing process is endothermic when $\triangle H_{mix} > 0$, whereas it is exothermic when $\triangle H_{mix} < 0$.

In this work, a statistical or quasi-chemical model was used to treat the effect of $\triangle H_{mix}$ [13]. In this model, $\triangle H_{mix}$ was assumed only related to bound energies between adjacent atoms. Another assumption involved is that the interatomic distance and bound energy are independent of composition. Thus, $\triangle H_{mix}$ can be calculated according to the following equations:

$$\Delta H_{mix} = \Omega x_1 x_2 \tag{5}$$

where $\Omega = zN_{tot}[E_{12} - (E_{11} + E_{22})/2]$ that is closely related to the intermolecular interactions, z is the coordination number of an atom in a crystal, N_{tot} is the total number of atoms, and E_{11}, E_{22} and E_{12} are energies associated with 1–1 bond, 2–2 bond and 1–2 bond, respectively, and x_i is the molar fraction of component *i* and $x_1 + x_2 = 1$. In addition, $\triangle S_{mix}$ can be expressed by the following equation [13].

$$\Delta S_{mix} = -R(x_1 \ln x_1 + x_2 \ln x_2) \tag{6}$$

When the solution is regular the partial molar Gibbs free energy of mixing (*i.e.*, excess chemical potential ($\Delta\mu_1$)) for component 1 ($\overline{\triangle G_1}$) can be expressed as

$$\overline{\Delta G_1} = \Delta G_{mix} - x_2\left(\frac{d\Delta G_{mix}}{dx_2}\right) \tag{7}$$

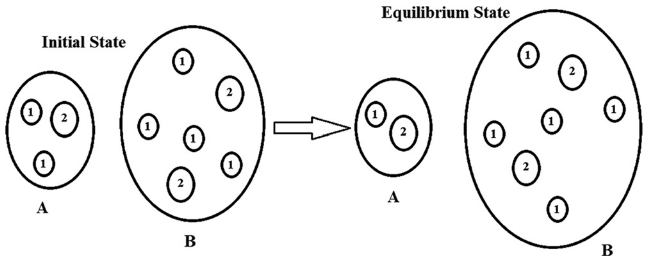
Substituting Eqs. (4)–(6) into Eq. (7) then results in the following equation.

$$\begin{aligned}\overline{\Delta G_1} &= \Delta G_{mix} - x_2(d\Delta G_{mix}/dx_2)\\ &= \Omega x_2^2 + RT\ln(1 - x_2)\end{aligned} \tag{8}$$

$\overline{\Delta G_1}$ (or $\triangle\mu_1$) is the excess chemical potential that determines the internal energy change for a change in composition arising from the addition of a small amount of monomer into the regular solution, as shown schematically in Scheme 1.

2.2. Excess chemical potential of component 1 (e.g., monomer) in the two-component disperse phase system for the case of zero solubility of component 2 (e.g., costabilizer) in water

Formation of a two-component disperse phase system (*e.g.*, miniemulsion) comprising a large population of microdroplets suspended in the continuous aqueous phase generates an extremely large total oil–water interfacial area. Therefore, interfacial phenomenon naturally comes into play in the stability of the colloidal product upon aging. These droplets consist of the major component monomer and costabilizer that is completely insoluble in water ($C_{\infty,2} = 0$), which form a regular solution therein. This colloidal system is the focus of this work. Kabal'nov et al. [9] considered such a system (except for the assumption of an ideal solution used in their work) to be very similar to a semipermeable membrane since costabilizer was insoluble in the continuous aqueous phase. At equilibrium, the chemical potential of solvent (a permeating component) is the same on both sides of the membrane, whereas that of solute (a nonpermeating component) exhibits different values when crossing the membrane. For a two-component disperse phase system with a relatively narrow droplet size distribution initially, mass transfer of component 1 from the smaller droplet to the larger one occurs in consequence of the difference in the capillary pressures (Scheme 2). This will then result in a concentration gradient for component 2 between the even smaller droplet and the even larger one, thereby leading to the suppression of the Ostwald ripening process. This is simply because insoluble component 2 is not allowed to transport between two droplets of different sizes. Eventually, Ostwald ripening is terminated and, therefore, equilibrium is achieved when the capillary pressure is effectively compensated by the osmotic pressure. Based on this scenario, Kabal'nov et al. [9] then established the equilibrium condition for $\triangle\mu_1$. In a similar manner, we derived the following expressions for the equilibrium condition for $\triangle\mu_1$.



Scheme 2. Changes in the radii of two droplets (labeled as A and B) comprising monomer (1) and costabilizer (2) from the initial state to the equilibrium state in a two-component disperse phase system.