Modeling the role of polymeric costabilizers in retarding Ostwald ripening involved in styrene miniemulsions

Chun-Ta Lin[a], Chorng-Shyan Chern[a],*

[a] Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan

ABSTRACT

A thermodynamic approach dealing with a regular solution of monomer (styrene (ST) herein) and different polymeric costabilizers as the disperse phase of miniemulsion were used to develop a model that describes the Ostwald ripening behavior involved in such a colloidal system. The validity of this model was verified by the Ostwald ripening rate data obtained from ST miniemulsions stabilized by living polystyrene costabilizer (PS_{lc}) or polystyrene costabilizer (PS_c) upon aging at 25 °C. PS_{lc} is more effective in retarding the Ostwald ripening process than PS_c, though PS_{lc} and PS_c have comparable number-average molecular weights. The model can be also used to study the mutual interaction between monomer and polymeric costabilizer. Satisfactory modeling results achieved for ST miniemulsions using polymethyl methacrylate as the costabilizer further verify the general validity of the present model. Finally, the values of heat of mixing and interaction parameter between ST and different polymeric costabilizers were also determined.

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1. Introduction

Emulsions undergo colloidal degradation upon aging primarily via two ways, that is, coalescence and Ostwald ripening. Coalescence among interactive emulsion droplets can be prohibited effectively by an adequate level of surfactant. By contrast, Ostwald ripening is a diffusional degradation process occurring in emulsion with a relatively broad droplet size distribution. It involves the growth of larger droplets with lower excess chemical potential at the expense of smaller ones with higher excess chemical potential *via* the molecular diffusion of oil molecules from smaller droplets to larger ones [1–3]. Ostwald ripening can be greatly retarded by the incorporation of a low molecular weight, water-insoluble species (*e.g.*, long chain alkanes and alcohols, termed as costabilizers) into oil droplets [4–6], and the kinetically stable colloidal product termed the miniemulsion. Reimer and Schork [7,8] used polymer as costabilizer to prepare relatively stable miniemulsions. Recently, we illustrated the effect of polymeric costabilizer molecular weight on the Ostwald ripening behavior of monomer miniemulsions, and established an approach to determine the critical chain length of polymer costabilizer, consistent with those reported in the literature [9].

In our previous work [10], we developed a model based on the thermodynamics approach to quantitatively describe the Ostwald ripening behavior in a wide range of volume fraction of costabilizer (φ_c) for the two-component disperse phase miniemulsions, in which the disperse phase was a regular solution of monomer and costabilizer (*i.e.*, the enthalpy change of mixing ($\triangle H_{mix}$) not equal to zero). A modified Kabal'nov equation was then developed to adequately predict the Ostwald ripening rate (R_O) data and the model is shown below.

$$\frac{1}{R_O} = \frac{\varphi_m}{R_{O,m}} + \frac{\varphi_c \left(1 + C\varphi_c\right)}{R_{O,c}} \tag{1}$$

where $R_{O,i}$ (i = monomer (m) or costabilizer (c)) is the Ostwald ripening rate corresponding to the single component species i, φ_i the volume fraction of the component i, and C a parameter closely related to the intermolecular interactions in the disperse phase. The model is capable of predicting the Ostwald ripening rate data in a wide φ_c range for styrene (ST) miniemulsions stabilized by a homolog of n-alkane costabilizers (C_nH_{2n+2}) upon aging at 25 °C.

The objective of this work was to develop a model via the thermodynamics approach in combination with the Morton equation [11] to quantitatively describe the Ostwald ripening behavior in a wide φ_c range for the two-component disperse phase miniemulsion stabilized by polymeric costabilizer. The validity of this model was then verified by experimental data for various polymeric costabilizers. Furthermore, thermodynamic parameters such as the Flory–Huggins interaction parameter (χ_{mp}) and $\triangle H_{mix}$ between monomer and polymeric costabilizer were determined.

* Corresponding author. Tel.: +886 27376649; fax: +886 27376644.
  E-mail address: cschern@mail.ntust.edu.tw (C.-S. Chern).

2. Model development

2.1. Partial molar free energy of monomer in the presence of polymer in a two-component disperse phase system

Morton et al. [11] considered the equilibrium swelling of emulsion polymer droplets by solvents (e.g., ST) exhibiting a rather limited solubility in the continuous aqueous phase. They derived an expression for partial molar Gibbs free energy of monomer ($\overline{\Delta G_m}$) as follows:

$$\overline{\Delta G_m} = \overline{\Delta G_{mix}} + \overline{\Delta G_{interf}} \tag{2}$$

where $\overline{\Delta G_{mix}}$ represents the contribution from the Gibbs free energy of mixing of monomer and polymer, and $\overline{\Delta G_{interf}}$ the contribution from the droplet-water interfacial energy. Furthermore, $\overline{\Delta G_m}$ was expressed in terms of the classical Flory–Huggins theory [11–13]:

$$\frac{\overline{\Delta G_{mix}}}{RT} = \ln\left(1 - \varphi_p\right) + \varphi_p\left(1 - \frac{1}{n}\right) + \chi_{mp}\varphi_p^2 \tag{3}$$

where φ_p is the volume fraction of polymer in latex droplets, n the number-average degree of polymerization, R the gas constant, T the temperature, and χ_{mp} the Flory–Huggins interaction parameter. As to $\overline{\Delta G_{interf}}$, it was given in terms of the Gibbs–Thomson equation [14].

$$\frac{\overline{\Delta G_{interf}}}{RT} = \frac{2\sigma V_{m,m}}{aRT} = \frac{\alpha}{a} \tag{4}$$

where σ is the droplet-water interfacial tension, $V_{m,m}$ is the molar volume of monomer, a is the radius of monomer droplet, and α is defined as $2\sigma V_{m,m}/RT$. Finally, substituting Eqs. (3) and (4) into Eq. (2) gives the so-called Morton equation:

$$\frac{\overline{\Delta G_m}}{RT} = \ln\left(1 - \varphi_p\right) + \varphi_p\left(1 - \frac{1}{n}\right) + \chi_{mp}\varphi_p^2 + \frac{\alpha}{a} \tag{5}$$

$\overline{\Delta G_m}$ is also termed as 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.

2.2. Excess chemical potential of monomer in the two-component disperse phase system for the case of zero solubility of polymeric costabilizer in water

Formation of a two-component disperse phase system (e.g., miniemulsion) comprising a large population of submicron droplets 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 colloidal products upon aging. These droplets consist of the major component (monomer) and polymeric costabilizer that is completely insoluble in water ($C_{\infty,p} = 0$), which form a regular solution therein. This colloidal system is the focus of this work. Kabal'nov et al. [1] considered a two-component disperse phase system with an ideal solution ($\Delta H_{mix} = 0$) of monomer and costabilizer as the disperse phase to be very similar to a semipermeable membrane since costabilizer was essentially insoluble in water. At equilibrium, the excess 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. In a similar manner, for a two-component disperse phase system with a relatively narrow droplet size distribution initially, mass transfer of monomer from a smaller droplet to a larger one occurs in consequence of the difference in the capillary pressures. This will then result in a concentration gradient for polymeric costabilizer between the shrinking droplet and the expanding one, thereby leading to the suppression of the Ostwald ripening process. This is simply because insoluble polymeric costabilizer 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 and coworkers [1] then established the equilibrium condition for ΔG_m. Similarly, we derived the following expressions for the equilibrium condition for $\overline{\Delta G_m}$.

$$\frac{\overline{\Delta G_m}}{RT} = \frac{\overline{\Delta G_{me}}}{RT} = \ln\left(1 - \varphi_{pe}\right) + \left(1 - \frac{1}{n}\right)\varphi_{pe} + \chi_{mp}\varphi_{pe}^2 + \frac{\alpha}{a_e}$$

$$\approx -\varphi_{pe} - \frac{\varphi_{pe}^2}{2} + \left(1 - \frac{1}{n}\right)\varphi_{pe} + \chi_{mp}\varphi_{pe}^2 + \frac{\alpha}{a_e}$$

$$= -\frac{1}{n}\varphi_{pe} - \left(\frac{1}{2} - \chi_{mp}\right)\varphi_{pe}^2 + \frac{\alpha}{a_e} = \text{constant} \tag{6}$$

where the subscript e represents a certain parameter at equilibrium. For example, a_e is the equilibrium droplet radius. Note that, in the above derivation, the terms of third order and higher were neglected in expanding the function $\ln(1-\varphi_{pe})$ in a Taylor series. The term α/a_e on the right hand side of Eq. (6) represents the Laplace pressure effect [15], and the remaining terms the competitive osmotic pressure effect. In addition, similar to the Kabal'nov approach [1], Eq. (6) can be expressed equivalently as follows:

$$\left(\varphi'_{pe} - \varphi''_{pe}\right) + \left(\frac{1}{n} + \left(\frac{1}{2} - \chi_{mp}\right)\left(\varphi'_{pe} + \varphi''_{pe}\right)\right) = \alpha\left(\frac{1}{a'_e} - \frac{1}{a''_e}\right) \tag{7}$$

where φ_{pe}' and φ_{pe}'', and a_e' and a_e'' are the volume fractions of polymeric costabilizer and the radii of two arbitrary droplets with different sizes brought into equilibrium, respectively.

Fig. 1 shows the influence of polymeric costabilizer molecular weight (= $n\times$molecular weight of repeating unit) on ΔG_m. To
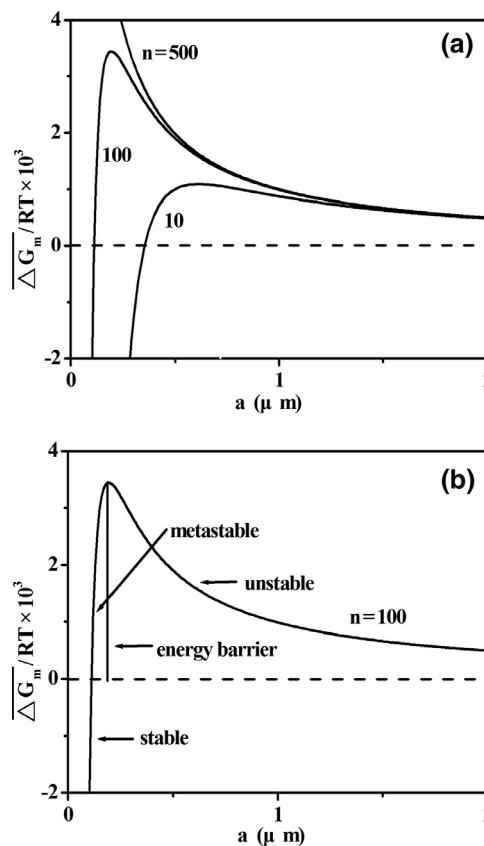

Fig. 1. (a) Profiles of dimensionless excess chemical potential as a function of droplet radius calculated by Eq. (5) with $n = 10$, 100 and 500 and (b) a representative example of thermodynamic colloidal instability ($\Delta G_m/RT > 0$ and $d(\Delta G_m/RT)/da < 0$), stability ($\Delta G_m/RT \leqq 0$) and metastability ($\Delta G_m/RT > 0$ and $d(\Delta G_m/RT)/da \geqq 0$).