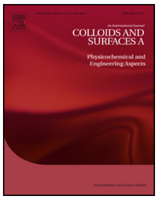
Colloids and Surfaces A: Physicochem. Eng. Aspects 441 (2014) 758–765

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa



# Thermodynamic modeling of water-in-oil emulsions: Implementation for two sizes of droplets

Kaveh Rayat, Farzaneh Feyzi*

*Thermodynamic Research Laboratory, School of Chemical Engineering, Iran University of Science and Technology, Tehran 16846-13114, Iran*

ARTICLE INFO

*Article history:*
Received 14 October 2012
Received in revised form 16 February 2013
Accepted 20 February 2013
Available online 6 April 2013

*Keywords:*
Water-in-oil emulsion
Electric field strength
Droplet deformation
Perturbation theory
Binary mixture

ABSTRACT

A thermodynamic model is proposed for predicting the phase behavior of water in crude oil emulsions while exposed to an external electric field. The model is based on the first order Barker–Henderson perturbation theory using appropriate expressions for interaction potential among water droplets. It is assumed that the emulsion contains two sizes of droplets in contrast to previous work which can handle same size droplets only. The deformation of the droplets during collision is also investigated, which according to results, may be neglected when at least one size of droplets is larger than 1 μm. However when all droplets are small, the deformation makes the emulsion more stable. This phenomenon affects the phase diagram in the whole range of volume fraction and should not be ignored. In order to make the model more realistic, the presence of inorganic salts in water droplets is also considered and the effect on phase diagram is quantified. Existence of electrolytes lowers polarizability of water droplets and decreases the effect of external electric field on saturation curve of the emulsion. Therefore, it leads to a higher value of electric field required to break the emulsion phase. The extra strength of the field required for water droplets containing 5 M NaCl is about 8%.

## 1. Introduction

Water-in-oil emulsion has attracted much consideration in research because of its economic importance and the state of scientific knowledge about it. Most exploited crude oils contain tiny water droplets which show high resistance to coalescence. This leads to special treatment required to separate them from the crude. Although a combination of several practical methods is employed in industry to break this emulsion state, utilizing an external electric field is usually the key process [1–6].

Since the method was introduced in 1911, several research papers have been published which focus on the development, probable mechanisms and modeling of the effect of electric field on the emulsions [1,6–23]. However, because of the complexity of the system, there remains much work in achieving a satisfactory predictive model. In addition to numerous studies, which develop stability models resulting from kinematic relations, a new type of model was introduced by Silva et al. [24] who utilized thermodynamic relations. The origin of their model comes from colloid science, in which based on McMillan–Mayer theory [25], Tavares et al. plotted phase diagrams of some colloid systems based on perturbation theory [26,27]. In the model presented by Silva et al. [24], water droplets in emulsion phase are considered as solute particles which are dispersed in a continuous oil phase. The water phase is assumed as solid particles separated from the solution. Therefore, one can model the system as a fluid–solid equilibrium and find the emulsion stability state from the fluid phase saturation curve.

In our first attempt to improve the model theoretically, we corrected the dipole–dipole interaction potential among droplets. We also introduced a new equation as a factor to the well-known Keesom formula in order to consider mutual induced dipole moments [28]. Then we focused on the deformation of droplets during collision and its effect on the emulsion phase stability. According to the results, the deformation effect for relatively large droplets is negligible. In case of small droplets the deformation leads to higher resistance of the emulsion to phase separation [29].

In all the mentioned studies, droplets are assumed to be of the same size. However, for droplets existing in a real emulsion, a size distribution is always observed. In this work, in order to generalize the existing models to actual samples, we have modified the model for emulsions including two different sizes of droplets. This has been done by changing the expressions for interaction potential among droplets and adjusting the formulas resulting from the perturbation theory. In addition, because of the existence of inorganic solutes in aqueous phase of exploited oils, we have quantified the effect of inorganic salts present in water droplets on the stability of emulsions.

---

* Corresponding author. Tel.: +98 912 1989569; fax: +98 21 77240495.
*E-mail address:* feyzi@iust.ac.ir (F. Feyzi).

0927-7757/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.colsurfa.2013.02.037

## 2. Theory

### 2.1. Interactions between droplets

Following our previous work [28,29], the total potential between two droplets consists of three parts: a steric repulsive term ($u^S$), a vdW attraction expression ($u^H$) and a dipole–dipole attraction potential ($u^D$). Consequently, the total interaction potential between droplets $i$ and $j$ is written as:

$$u_{i,j} = u^S_{i,j} + u^H_{i,j} + u^D_{i,j} \tag{1}$$

vdW attraction for macro-scale objects was formulated by Hamaker [30]. For spheres of two different sizes it gives:

$$u^H_{i,j}(r) = -\frac{A_H}{12}\left(\frac{D_iD_j}{B} + \frac{D_iD_j}{B + D_iD_j} + 2\ln\left(\frac{B}{B + D_iD_j}\right)\right) \tag{2}$$

where $A_H$ is the Hamaker constant, $D_i$ and $D_j$ are diameters of the two droplets and $B$ is defined by the following expression:

$$B \equiv \left(\frac{D_i + D_j}{2}\right)^2 \left(r^2 - 1\right) \tag{3}$$

in which $r$ is the reduced center-to-center distance. It is related to center-to-center distance ($l$) by:

$$r \equiv \left(\frac{2l}{D_i + D_j}\right) \tag{4}$$

The equivalent formula for Hamaker potential between deformed spheres is more complex but the potential value can be calculated with it [31].

The repulsion force is considered to be proportional to the inverse of seventh power of separation distance according to Wu et al. [32]. As a result, the repulsive potential can be found from the following formula (for details see [28]):

$$u^S = \frac{c}{6(r-1)^6}, \qquad c = \frac{A_H D_i D_j B'_{r_0}(r_0 - 1)^7}{12}\left(\frac{1}{B^2_{r_0}} + \frac{1}{\left(B_{r_0} + D_iD_j\right)^2} - \frac{2}{B_{r_0}\left(B_{r_0} + D_iD_j\right)}\right) \tag{5}$$

If we consider the adsorption layer thickness around droplets as $L$, the parameters $B_{r0}$ and $B'_{r0}$ are evaluated in the touch point of droplets $\left(r_0 = 1 + 2(L_i + L_j)/(D_i + D_j)\right)$:

$$B_{r_0} = \left(\frac{D_i + D_j}{2}\right)^2 \left(r_0^2 - 1\right) \tag{6}$$

$$B'_{r_0} = \frac{r_0\left(D_i + D_j\right)^2}{2} \tag{7}$$

In order to find the dipole–dipole interaction for the same size droplets, the simple relation introduced in [28] can be used. However, for different size droplets, there is no equivalent formula due to the complexity of the system. Therefore, in case of different size droplets, at the first step, longitudinal and transverse components of induced dipole moments inside droplets are found from the following relations [33,34]:

$$p_{i,L} = \cos\,\theta(\sinh\gamma)^3 \times \sum_{n=1}^{\infty}\left[\frac{p_{i,0}R_j^3\left(2\beta\right)^{2n-2}}{\left(R_j\sinh(n\gamma) + R_i\sinh((n-1)\gamma)\right)^3} + \frac{p_{j,0}R_i^3\left(2\beta\right)^{2n-1}}{(l\sinh(n\gamma))^3}\right] \tag{8}$$

$$p_{i,T} = \sin\,\theta(\sinh\gamma)^3 \times \sum_{n=1}^{\infty}\left[\frac{p_{i,0}R_j^3\left(-\beta\right)^{2n-2}}{\left(R_j\sinh(n\gamma) + R_i\sinh((n-1)\gamma)\right)^3} + \frac{p_{j,0}R_i^3\left(-\beta\right)^{2n-1}}{(l\sinh(n\gamma))^3}\right] \tag{9}$$

where $p_i$ is the dipole moment of droplets which have a radius of $R_i$ ($D_i = 2R_i$), $\theta$ is the angle between center-to-center line and the external electric field direction, $p_{i,0}$ and $p_{j,0}$ are point dipoles of droplets $i$ and $j$, defined by Eqs. (12) and (13), and parameters $\gamma$ and $\beta$ are defined by the following equations:

$$\cosh\,\gamma = \frac{l^2 - R_i^2 - R_j^2}{2R_iR_j} \tag{10}$$

$$\beta \equiv \left(\frac{\varepsilon_w - \varepsilon_{oil}}{\varepsilon_w + 2\varepsilon_{oil}}\right) \tag{11}$$

$$p_{i,0} = 4\pi\beta\varepsilon_0\varepsilon_{oil}ER_i^3 \tag{12}$$

$$p_{j,0} = 4\pi\beta\varepsilon_0\varepsilon_{oil}ER_j^3 \tag{13}$$

in which $\varepsilon_0$ is the vacuum permittivity, $E$ is the magnitude of external electric field and $\varepsilon_{oil}$ and $\varepsilon_w$ are relative permittivities of oil and water, respectively. Considering Eqs. (8) and (9) similar equations can be written to calculate the dipole moment of droplet $j$.

Having dipole moment values, the dipole interaction potential is written as [35]:

$$u^D_{i,j}(r,\theta) = -\frac{4p_{i,L}p_{j,L} - 2p_{i,T}p_{j,T}}{\pi\varepsilon_0\varepsilon_{oil}r^3\left(D_i + D_j\right)^3} \tag{14}$$

The dependence on $\theta$ is eliminated using the potential distribution theorem [36]:

$$\exp\left(-\frac{u^D_{i,j}(r)}{kT}\right) = \frac{1}{2}\int_0^{\pi}\exp\left(-\frac{u^D_{i,j}(r,\theta)}{kT}\right)d\theta \tag{15}$$

In order to find dipole interaction potential in each value of center-to-center distance, the integral in Eq. (15) should be evaluated numerically.

### 2.2. Phase modeling

As described above, in this model the emulsion and the separated water phases are treated as fluid phase and solid phase, respectively. Regarding the presence of two different sizes of droplets in the emulsion, the fluid model has to cover the binary size mixtures, which is modeled and treated in this work. Meanwhile, it is assumed that when the distance from equilibrium is very small, only droplets of one size separate from the emulsion and their equilibrium will determine the saturation state. Therefore, in order to find the saturation curves, the separated phase will be one component which needs a one component solid phase model to represent the phase.

Following our previous works, we have employed perturbation theory to reach the required equation of state for both fluid and solid phases. The repulsion part is considered as the reference and the remainder as the perturbation. For details we refer readers to Refs. [28,29].

$$u^{ref} = u^S \tag{16}$$

$$u^{pert} = u^H + u^D \tag{17}$$