



Population Balance Equation Modeling of Crude Oil Demulsification Considering Demulsifier: Modification of Collision Frequency Function Based on Thermodynamic Model

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ABSTRACT

A theoretical model is developed to consider the effect of demulsifier agent on demulsification of water-in-crude oil emulsion. A thermodynamic approach is considered to correlate the critical micelle concentration of a demulsifier to the collision frequency function in population balance equation (PBE). Based on the proposed correlation, the collision frequency function is modified to account the effect of demulsifier agent on water droplets coalescence. The water separation capability of a selected group of demulsifiers is investigated via the conventional bottle test method to obtain the adjustable parameter of the developed equation so that the absolute relative error of predicted demulsification efficiency and experimental data are considered as objective. Comparison between the model simulated results and the experimental data showed that the proposed model could appropriately reproduce the experimental data at different agent concentrations.

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NOMENCLATURE

| | |
|-----------------|------------------------------|
| Bi | Bond number |
| C _i | Concentration |
| d | Droplet diameter |
| e _{ij} | Coalescence efficiency |
| g | Gravity |
| K | Collision frequency constant |
| n | Continuous number density |
| N _i | Discrete number density |
| t | Time |
| u | Velocity |

| | |
|----------------|-------------------|
| $v_{ij}^{(0)}$ | Relative velocity |
| w | Volume |
| z | Length |

Greek Symbols

| | |
|----------|---|
| α | Collision frequency function |
| β | Coalescence coefficient of droplets |
| δ | Ratio of the radius of the small drop to that of the large drop |
| η | Fixed pivot parameter |
| μ | Viscosity |
| ρ | Density |
| σ | Interfacial tension |

1. INTRODUCTION

Demulsification of water-in-crude oil emulsion is a great problem in oilfield industry. The emulsified water contains considerable amount of salts, which should reduce to a distinct concentration since it may cause problems such as corrosion of equipment, fouling in pipelines, catalyst deactivation and etc. The presence of

native surfactants such as asphaltenes, resins, naphthenic acid, etc. make the emulsion stable. The water-in-oil emulsion can be broken by several methods such as chemical demulsification, electrostatic dehydration, gravity sedimentation and heat treatment [1]. Addition of chemical demulsifier is a common method to demulsify water-in-oil emulsion. Demulsifiers are surface-active compounds, which adsorb at water-oil interface and modify the rheological behavior of the existing film. In fact, natural surfactants make a rigid cross-linking film around water droplets,

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which prevent their coalescence. When the demulsifier is injected to the emulsion, the surrounded film thins until reaching a critical thickness that film rupture and drainage happens and so the rate of droplets collision and coalescence accelerates which finally leads to their sedimentation [2].

The effect of demulsifiers on increasing water-oil separation has been investigated in several literatures experimentally, while there are rare papers to model the demulsifier influence in desalination processes. The main role of demulsifiers is to reduce the film interfacial tension. This phenomenon can be explained by Winsor's theory that describes the behavior of oil-water-surfactant system with a ternary diagram. In such a system an optimum case happens when the affinity of surfactant to both oil and water phases is the same and a micro-emulsion rich surfactant phase appears which is in equilibrium with both water and oil excess phases. Thus the maximum phase separation would occur. Therefore, to make the emulsion unstable, the surfactant interaction with both phases of water and oil should be the same [3]. Marques-Silva et al. stated that there is an optimum formulation to attain the maximum dehydration efficiency [4]. They developed an empirical model based on surfactant affinity difference (SAD) model, which correlates the crude oil acidity number, the associated water salinity and relative solubility number of the demulsifier (RSN). Venezuela studied the dehydration process of crude oil emulsion via investigating the factors which cause emulsion stability [5]. He concluded that the most effective mechanism to make the emulsion unstable, is to trap the surfactant in a micro-emulsion phase, so the optimal formulation of the system with low interfacial tension, occurs. Bourrel et al. investigated the behavior of oil-water-surfactant system in the case of using nonionic surfactant [6]. They considered the influence of some parameters such as crude oil nature, type of surfactant, temperature, and water salinity on interfacial tension of the system and developed a correlation between these parameters. Al-Sabagh et al. probed demulsification efficiency of some demulsifiers by considering some parameters such as water oil ratio, molecular weight and concentration of demulsifiers and also their structures [7]. They concluded that increasing water oil ratio, demulsifier concentration and its alkyl chain, enhances demulsification efficiency. They also investigated the relation between interfacial tension and hydrophilic lipophilic balance (HLB) of demulsifiers. Grimes and his co-workers developed a theoretical model based on the population balance to simulate the emulsion separation in a batch gravity settler [8, 9]. They investigated the effect of bulk properties, oil-water interface and surfactants on the average number density of droplets. The simulation results and experimental

data revealed that the degree of poly-dispersity determines the coalescence and separation rate.

The main goal of this paper is developing a mathematical model which takes into account the effect of demulsifier agent on dehydration efficiency of water-in-crude oil emulsion. The rheological behavior of demulsifier agent is modeled based on a thermodynamic approach so that the critical micelle concentration of a demulsifier is correlated to collision frequency function in population balance equation. To obtain the adjustable parameters of the proposed model, a group of demulsifiers is prepared and their demulsification efficiency is detected based on the conventional bottle test method.

2. MATERIALS AND METHOD

2. 1. Materials A group of ionic liquids is considered as demulsifier, which their molecular structure are listed in Table 1. Trioctylmethylammonium chloride (TOMAC) and Trioctylmethylammonium bromide (TOMAB) were supplied by sigma Aldrich and 1-Hexadecyltrimethylammonium bromide (CTAB) was supplied by Merck. N,N-bis(hexaoxyethylene) octadecylammonium tosylate (HEOD-TS) is a synthesized demulsifier by Atta et al. [10].

2. 2. Crude Oil Specification The needed crude oil for experiments was supplied by Sarvestan oil field in Iran.

TABLE 1. Ionic liquids used as a demulsifier

| Ionic Liquid | Cation | Anion |
|---|--------|--------|
| Trioctylmethylammonium chloride (TOMAC) | | Cl^- |
| Trioctylmethylammonium bromide (TOMAB) | | Br^- |
| 1-Hexadecyltrimethylammonium bromide (CTAB) | | Br^- |
| N,N-bis(hexaoxyethylene) octadecylammonium tosylate (HEOD-TS) | | |

The specific gravity of the crude oil was measured through ASTM D-854 test method by pycnometer apparatus. The API is determined as:

$$\text{API} = \frac{141.5}{\text{Specific Gravity}} - 131.5 \quad (1)$$

The viscosity of the crude oil was determined according to ASTM D-2983 test method using Brookfield viscometer. The crude oil was injected to the viscometer tube and a metal spindle was rotated in the crude oil at specific rpm. Water content of the supplied crude oil was measured by centrifuge procedure according to ASTM D 4007-02 method.

The crude oil and toluene were mixed and injected into the centrifuge cone-shaped tube and centrifuged by Eppendorf 5810R Centrifuge for 15 min with 2000 rpm. The physical specifications of the crude oil are listed in Table 2.

To investigate the stability of the crude oil emulsion, a prepared sample of emulsion before bottle test, was placed in oven at temperature of 60°C for 24 hour. It was observed that no water separation occurred so it was concluded that the emulsion is stable. The range of water droplets diameter was detected using Nikon optical microscope. It was revealed that various droplets in the range of 1-50 μm existed in the emulsion before bottle test. Figure 1 exhibits the various droplets diameter of the crude oil emulsion.

TABLE 2. The characteristics of the crude oil

| Physical characterization/ Mass percentage | Value |
|--|-------|
| API gravity at 15°C | 27.5 |
| Viscosity at 15 °C (mPa.s) | 14 |
| Pour point (°C) | -16 |
| Salt content of the crude oil (mg/L) | 1200 |
| Saturates (wt%) | 45 |
| Aromatics (wt%) | 32 |
| Resins (wt%) | 8 |
| Asphaltenes (wt%) | 5 |
| Water and residue (wt%) | 10 |

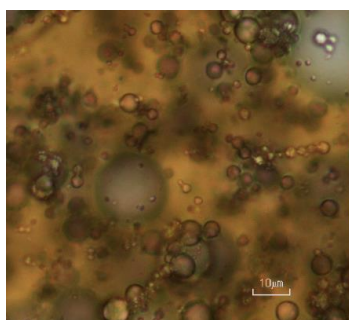


Figure 1. The micrograph of the crude oil emulsion before bottle test

2. 3. Bottle Test Method The capability of selected demulsifiers in breaking water in oil emulsion was investigated via the conventional bottle test method. In the first step, in order to increase salt dissolution and accelerate water separation, the crude oil emulsion was mixed with fresh water in an electric mixer [11]. Then an appropriate amount of demulsifier agent was added to the emulsion and mixed well; the prepared sample was located in an electric oven at the temperature of 80 °C for 12 hours. The phase separation was screened as a function of time and the water separation efficiency was attained as bellow where v is the separated water volume and v_0 is the initial volume of the dispersed phase.

$$x(\%) = \frac{v}{v_0} \times 100 \quad (2)$$

3. THEORY

When surfactant molecules dissolve in an aqueous solution, at a specific concentration of the surfactant, a sharp change in some physico-chemical properties such as interfacial tension, conductivity, osmotic pressure, density, etc occurs. This phenomenon arises from the self-assemble conformation of surfactants that is known as micelles in which the hydrophobic parts of the surfactants are oriented to the interior of the aggregate core. The concentration above which the micelles appear is called critical micelle concentration (CMC) [12]. In a solution which contains surfactant molecules, as they tend to adsorb at the interface of two phases, by increasing the surfactant concentration, the interfacial tension reduces until reaching the CMC where a minimum at interfacial tension occurs and then it would remain constant. In the case of water in crude oil emulsion, due to presence of natural surfactants, which create a strong interfacial tension between two phases, reaching the condition at which the micellization occurs is in favor of water separation process. Actually when interfacial tension reduces to a minimum, the surrounding film rupture happens which accelerates the water droplet collision and so their coalescence and the dehydration efficiency enhances. Therefore, it would be convenient to consider a relation between the critical micelle concentration of a demulsifier and the water collision frequency of water droplets.

Several researchers have determined CMC experimentally while there are few mathematical models to predict the CMC of a surfactant. Nagarajan and Ruckenstein developed a thermodynamic based model to predict the aggregation behavior of surfactants [12]. Via this model, the CMC of all types of surfactants in solution can be estimated if their structural information is available.

3. 1. Free Energy Calculation

According to Nagarajan and Ruckenstein developed model, the chemical potential of the surfactant in micelle aggregate should be equal to those in singly dispersed state. Therefore the Gibbs free energy of the solution which is the difference between standard free energy of surfactant molecules in aggregate and their standard free energy in monomer state, should be a minimum at equilibrium condition [12]:

$$n_g \mu_{i,mon} = \mu_{i,micelle} \quad (3)$$

$$\mu_{i,mon} = \mu_{i,mon}^{\circ} + RT \ln x_{i,mon} \gamma_{i,mon} \quad (4)$$

$$\mu_{i,micelle} = \mu_{i,micelle}^{\circ} + RT \ln x_{i,micelle} \gamma_{i,micelle} \quad (5)$$

$$\Delta_{mic} G_i^{\circ} = \Delta \mu_g^{\circ} = \frac{1}{n_g} \mu_{i,micelle}^{\circ} - \mu_{i,mon}^{\circ} = RT \ln x_{i,mon} \gamma_{i,mon} - \frac{1}{n_g} RT \ln x_{i,micelle} \gamma_{i,micelle} \quad (6)$$

where $\mu_{i,mon}$ and $\mu_{i,micelle}$ are chemical potential of monomer and micelle, respectively and n_g is the number of aggregate. In the case of dilute solution, the surfactant activity of monomer and micelle phase is considered equal to one. In a surfactant solution, CMC is equal to summation of the monomer and micelle phase concentration. By assuming high number of aggregate in the hydrophobic core of the micelle, the second part in right hand side of Equation (6) can be neglected. Therefore, the CMC parameter is calculated as bellow:

$$\Delta_{mic} G_i^{\circ} = RT \ln \phi_{CMC} \quad (7)$$

The standard free energy of micellization consists of some standard free energy contributions, which would be explained as follows:

$$\Delta \mu_g^{\circ} = (\Delta \mu_g^{\circ})_{tr} + (\Delta \mu_g^{\circ})_{def} + (\Delta \mu_g^{\circ})_{int} + (\Delta \mu_g^{\circ})_{steric} + (\Delta \mu_g^{\circ})_{dipole} + (\Delta \mu_g^{\circ})_{ionic} \quad (8)$$

3. 1. 1. Tail Transfer Free Energy

When micellization happens, the hydrophobic tail of the surfactant molecules migrate from aqueous bulk into the aggregate core. Assuming the micelle core is similar to a liquid hydrocarbon, a negative free energy contribution arises due to the transfer of surfactant hydrophobic tail. This energy contribution can be calculated via summing the following correlations, which are developed for methyl and methylene groups of the surfactant tail.

$$\frac{(\Delta \mu_g^{\circ})_{tr}}{KT} = 3.38 \times \ln T + \frac{4064}{T} - 44.13 - 0.02595 \times T \quad (9)$$

$$\frac{(\Delta \mu_g^{\circ})_{tr}}{KT} = 5.85 \times \ln T + \frac{896}{T} - 36.15 - 0.0056 \times T \quad (10)$$

3. 1. 2. Tail Deformation Free Energy

The state of hydrocarbons of surfactant tail in the aggregate core differs from the similar liquid hydrocarbon in bulk solution. Actually one end of the surfactant tail is constrained to remain at the interface of water-micelle, while the other end which is in the core of the micelle, should be packed in an aggregate shape with the same density of similar liquid hydrocarbon. Therefore, a positive free energy contribution due to the deformation of surfactants tail would appear as bellow:

$$\frac{(\Delta \mu_g^{\circ})_{def}}{KT} = \frac{9P\pi^2 R_s^3}{80 NL^2} \quad (11)$$

where P is packing factor which is considered to be about 1/3 for spherical micelle, R_s is the core radius, N is the segment number in hydrophobic surfactant tail and L is the segment length.

3. 1. 3. Aggregate Core-water Interfacial Free Energy

A positive free energy contribution occurs due to the creation of an interface between the micelle core and the surrounding medium. The free energy corresponding to this interface generation is as bellow where σ_{agg} is the interfacial tension between aggregate core and bulk phase, a is the micelle core surface area per surfactant molecule and a_0 is the surface area per molecule of surfactant which is shielded from contact with water due to the head of the surfactant.

$$\frac{(\Delta \mu_g^{\circ})_{int}}{KT} = \left(\frac{\sigma_{agg}}{KT} \right) (a - a_0) \quad (12)$$

$$\sigma_{SW} = \sigma_S + \sigma_W - 2\phi(\sigma_S \sigma_W)^{1/2} \quad (13)$$

$$\sigma_S = 35 - 335M^{-2/3} - 0.098(T - 298) \quad (14)$$

$$\sigma_W = 72 - 0.16(T - 298) \quad (15)$$

In the above equation σ_{agg} is considered equal to σ_{SW} which is the interfacial tension between water and the hydrocarbons of the same molecular weight of the surfactant tail, ϕ is equal to 0.55 and M is the molecular weight of surfactant tail.

3. 1. 4. Head Group Steric Interactions

The head groups of surfactants which crowd at the aggregate core surface would cause a steric repulsion in the case of nonionic surfactant, so a positive free energy contribution arises that can be estimated by considering the repulsion term of van der Waals equation of state.

$$\frac{(\Delta \mu_g^{\circ})_{steric}}{KT} = -\ln \left(1 - \frac{a_p}{a} \right) \quad (16)$$

where a_p is the cross sectional area of the surfactant polar head.

3. 1. 5. Head Group Dipole Interactions

In the case of zwitterionic head group, there would be an

interaction between surfactant dipoles at the surface of the aggregate core, which makes a positive contribution to free energy of micellization as follows:

$$\frac{(\Delta\mu_g^{\circ})_{dipole}}{KT} = \frac{2\pi e^2 R_s}{\epsilon a} \left[\frac{d}{d+R_s} \right] \quad (17)$$

where d is the dipole length, e is electronic charge, ϵ is dielectric constant of the solvent and R_s is the radius of spherical micelle core.

3. 1. 6. Head Group Ionic Interactions If the head group of surfactant is cationic or anionic, electrostatic interactions arise at the surface of the micelle and the expression to calculate the produced free energy contribution is as bellow, which is, based on approximate analytical solution of Poisson– Boltzmann equation:

$$\frac{(\Delta\mu_g^{\circ})_{ionic}}{KT} = 2 \left[\ln \left(\frac{s}{2} + \left\{ 1 + \left(\frac{s}{2} \right)^2 \right\}^{1/2} \right) - \left(\frac{2}{s} \right) \left(\left\{ 1 + \left(\frac{s}{2} \right)^2 \right\}^{1/2} - 1 \right) - \left(\frac{2C}{ks} \right) \ln \left(\frac{1}{2} + (1/2) \left\{ 1 + \left(\frac{s}{2} \right)^2 \right\}^{1/2} \right) \right] \quad (18)$$

$$s = \frac{4\pi e^2}{\epsilon k a_8 K T} \quad (19)$$

$$k = \left(\frac{8\pi n_0 e^2}{\epsilon K T} \right)^{1/2} \quad (20)$$

$$n_0 = \frac{(C_1 + C_{add})}{10^3} N_{Av} \quad (21)$$

$$C = \frac{2}{R_s + \delta} \quad (22)$$

In the above equation a_8 is the surface area per head group of surfactant which is calculated at the distance δ from aggregate core. δ is the distance from hydrophobic core of the micelle to the counter ion surface layer center. k is inverse Debye length, C is curvature dependant factor, n_0 is the counter ion number in solution, C_1 is the molar concentration of singly dispersed surfactant in solution and C_{add} is the added salt molar concentration.

4. MODELING

In current research, to investigate the behavior of water droplets in dehydration process, a gravity batch vessel is modeled based on the well-known population balance equation. The general form of the equation is as bellow:

$$\frac{\partial n}{\partial t} + \nabla_x(X_n) + \nabla_r(R_n) - S = 0 \quad (23)$$

In population balance equation the specification of a droplet is defined with internal and external coordinates, where the properties of dispersed phase are displayed with internal coordinate, while the external coordinate exhibits the spatial position of droplet. In Equation (23),

n represents the number density of droplets, X is the rate of change of internal coordinate, R is the rate of external coordinate change and S is the source term which accounts for the rate of droplet production due to death and birth of droplets when coalescence happens. In this study, the axial position, z , is considered as the external coordinate, and the droplet volume, v , as an internal coordinate. The following equation represents the dynamic form of population balance equation:

$$\frac{\partial n(v,z,t)}{\partial t} + u \frac{\partial n(v,z,t)}{\partial z} = \frac{1}{2} \int_{w=0}^v \beta(v-w,w) n(w,z,t) n(v-w,z,t) dw - n(v,z,t) \int_{w=0}^{\infty} \beta(v,w) n(w,z,t) dw \quad (24)$$

In the above equation, u displays the sedimentation velocity of droplets and β is coalescence coefficient of droplets. The birth of droplet class as a consequence of smaller drops coalescence can be illustrated by the first term on the right side of Equation (24), and the second term exhibits the droplets death due to coalescence with other droplets. The following equation shows the coalescence coefficient that is the product of collision frequency function and coalescence efficiency of droplets [13]:

$$\beta(d_i, d_j) = \alpha(d_i, d_j) \times e_{ij} = K \left(\pi(d_i + d_j)^2 v_{ij}^{(0)} e_{ij} \right) \quad (25)$$

$$v_{ij}^{(0)} = \frac{(\mu+1)|\rho_d - \rho_c| g d_i^2 (1-\delta^2) g}{6(3\mu+2)\mu_c} \quad (26)$$

$$e_{ij} = 0.38\delta^{1/2} + \frac{1}{2} B_i \delta^6 \quad (27)$$

$$B_i = \frac{|\rho_d - \rho_c| g d_i^2}{4\sigma} \quad (28)$$

where e_{ij} is coalescence efficiency, $v_{ij}^{(0)}$ is the relative velocity of two droplets when they are only under the effect of gravity force, μ is viscosity ratio of dispersed phase to continuous phase, δ is the diameter ratio of two droplets and B_i is the bond number [14]. It should be pointed that the stock's law is applied to determine the sedimentation velocity of droplets, as below:

$$u = \frac{2|\rho_d - \rho_c| g d_i^2}{9\mu_c} \quad (29)$$

The collision frequency function in population balance equation, α , is for the case of demulsifier absence in the emulsion. Therefore, in order to detect the effect of demulsifiers on water separation efficiency, the collision frequency function should be corrected so as it was mentioned, the equation is correlated to the CMC parameter of demulsifier. Thus, the collision frequency function is modified and the following equation is considered for K parameter in the function (Equation (25)).

$$K = \left(K_0 + \frac{K_1 \ln(C+1)}{CMC} \right) = \left(K_0 + \frac{K_1 \ln(C+1)}{\exp\left(\frac{\Delta\mu_g^{\circ}}{RT}\right)} \right) \quad (30)$$

In the above correlation, K_0 is adjusted in the case of blank state where there is no demulsifier agent in emulsion and K_1 is adjustable parameter that should be fitted with experimental data. The C parameter is the concentration of demulsifier in emulsion.

5. MODEL SOLUTION

The population balance equation is solved based on the popular class method of Kumar and Ramakrishna which applies the fixed pivot technique for solving the equation [15]. In this paper, $n(v, z, t)$ in Equation (24) is discrete to 110 classes, where $N_i(z, t)$ illustrates the number of water droplets in i^{th} class:

$$N_i(z, t) = \int_{v_i}^{v_{i+1}} n(v, z, t) dv \quad (31)$$

The following equation represents the discrete form of PBE:

$$\frac{\partial N_i(z,t)}{\partial t} + u \frac{\partial N_i(z,t)}{\partial z} = \sum_{j,k}^{j \geq k} \left(1 - \frac{1}{2} \delta_{j,k}\right) \eta \beta_{j,k} N_j N_k - N_i \sum_{k=1}^M \beta_{i,k} N_k \quad (32)$$

The distribution among the classes is defined by the term η where x_{i+1} is the mean of v_i and v_{i+1} .

$$\eta = \begin{cases} \frac{x_{i+1}-v}{x_{i+1}-x_i} & x_i \leq v \leq x_{i+1} \\ \frac{v-x_{i-1}}{x_i-x_{i-1}} & x_{i-1} \leq v \leq x_i \end{cases} \quad (33)$$

6. RESULTS AND DISCUSSION

In this survey, an effort is made to develop a mathematical model to account the effect of demulsifier compounds on crude oil dehydration. Generally, demulsifier agents tend to adsorb at the interface of two phases so they would substitute the natural emulsifier molecules and decrease the water-oil interfacial tension, which leads to separation of the phases. When the interface of two phases saturates with demulsifier molecules, the critical micelle concentration occurs which causes the interfacial tension to be minimum so film rupture happens and droplets collision frequency increases. Thus, the dispersed phase separation accelerates. Therefore, to construct the model, it is tried to relate the collision frequency of water droplets in population balance equation and the CMC parameter of the demulsifier. Actually, the critical micelle concentration of the surfactant in water-in-crude oil emulsion corresponds to minimum of Gibbs free energy of micellization, in which the interfacial tension between two phases reaches to a minimum that leads to separation of two phases. Therefore, the best performance of demulsifier agents on dehydration efficiency was attained by Equation (30). It should be

noted that the behavior of water droplets in lab scale is investigated in two cases of blank and demulsified crude oil. At first, the system is modeled based on the one-dimensional population balance equation. Then, the conventional collision frequency function in population balance equation, which is for the case of absence of demulsifier is modified to account for the effect of demulsifier agent. The proposed model consists of adjustable parameters, which should be fitted with experimental data. The accuracy of proposed model is investigated through the bottle test method in which the water separation efficiency is determined experimentally. A group of surfactants is considered as demulsifier and their performance in water separation is detected. It should be pointed that the experimental data of demulsifier HEOD-TS was adopted from Atta et al. paper [10]. Table 3 presents the calculated adjustable parameter of the developed correlation to predict the collision frequency of water droplets, the R-square of the model and the predicted CMC of demulsifiers. R-square is calculated via fitting the dehydration efficiency results of population balance equation in presence of demulsifier agent and the ones from experimental results.

As it was declared, the system was modeled in two cases of absence and presence of demulsifier agents. Therefore, at first, the population balance equation is solved with the conventional collision frequency function in the absence of demulsifier. Figures 2(a-b) show the predicted droplet size distribution at top and bottom of the vessel versus time in the case of blank system. It is observed that the water content of the emulsion decreases by time, however, the rate of change is not too much which indicates that in the absence of demulsifier the collision frequency of droplets are too small to cause coalescence. Actually, in this case, the large droplets move down from top of the vessel to the bottom section only due to the gravitational force.

It is observed in Figure 2(b) that the rate of change in droplets number is not sensible which can be described such that at the bottom section of the vessel at a specified section, the large water droplets are moving

TABLE 3. Calculated adjustable parameter of developed model

| Demulsifier | K_1 | CMC (Mm) | R^2 |
|-------------|---------|------------------|--------|
| CTAB | 2395.11 | 1.005 (300 ppm) | 0.9932 |
| | | 1.019 (500 ppm) | |
| TOMAB | 424.66 | 0.222 (1000 ppm) | 0.9805 |
| | | 0.229 (1500 ppm) | |
| TOMAC | 366.24 | 0.111 (1000 ppm) | 0.9841 |
| | | 0.115 (1500 ppm) | |
| HEOD-TS | 2513.21 | 0.61 (250 ppm) | 0.9896 |

down while droplets from upper section are flowing toward this part, so the droplet size distribution remains constant. Figures 3, 4, 5 and 6 show the demulsification ratio versus time for considered demulsifiers which are plotted based on the predicted results of population balance modeling and the experimental data. It is observed that the proposed model can predict the demulsification efficiency well. Figures 7 and 8 exhibit a comparison between droplets size distribution at top and bottom of the vessel for two demulsifiers of TOMAC and CTAB that are plotted based of the simulated results of population balance in which the developed model for collision frequency function is applied. It is appeared that at a specified section of the vessel, the amount of water decreases with time and the picks of curves are moved toward the smaller drops, which indicates that the large droplets are settled while the small droplets still have remained in the vessel. However, the demulsifier agent increases small droplets collision and so accelerates their coalescence, which

causes generation of large droplets that would settle down. The higher amount of water and presence of large droplets at the bottom of the vessel, enhances the droplets collision rate that leads to smaller droplets coalescence.

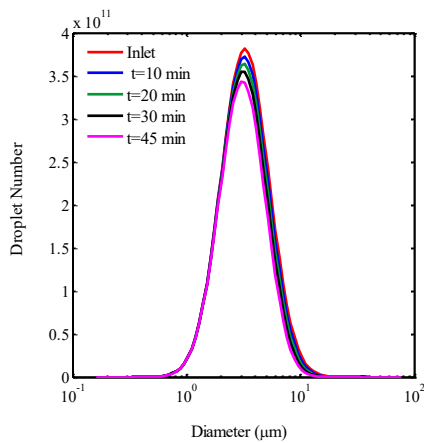


Figure 2(a). Droplet size distribution at top of the blank system

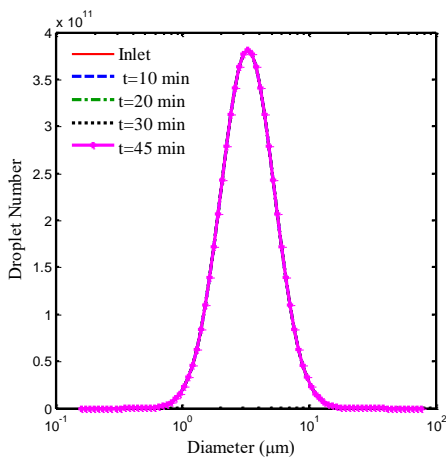


Figure 2(b). Droplet size distribution at bottom of the blank system

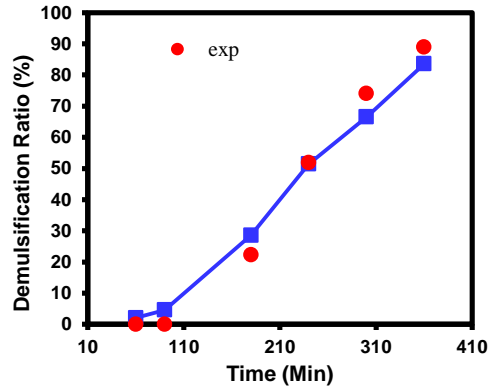


Figure 3. Demulsification ratio versus time for 500 ppm CTAB

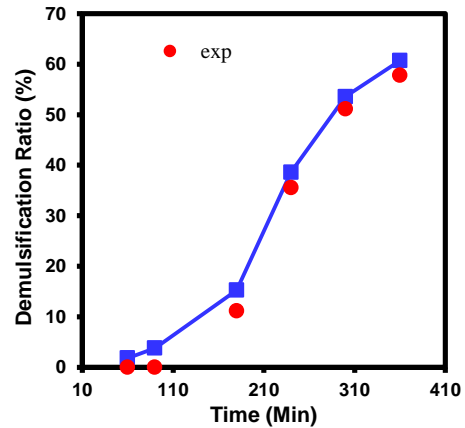


Figure 4. Demulsification ratio versus time for 1000 ppm TOMAB

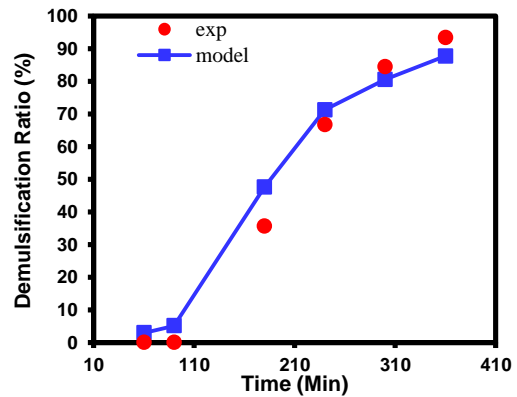


Figure 5. Demulsification ratio versus time for 1000 ppm TOMAC

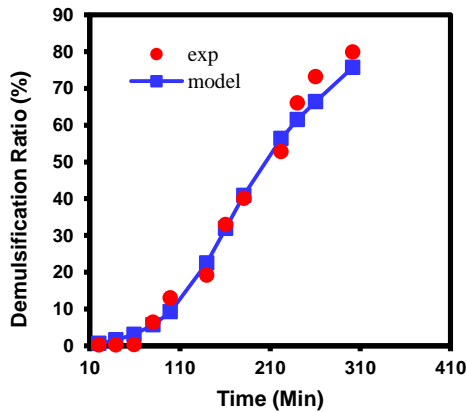


Figure 6. Demulsification ratio versus time for 500 ppm HEOD-TS

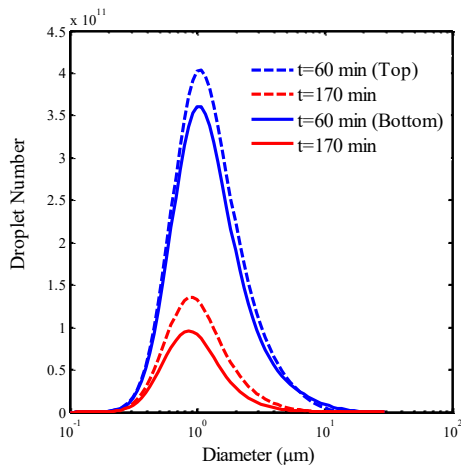


Figure 7. Droplet size distribution at top and bottom of the system in the presence of 1000 ppm demulsifier TOMAC

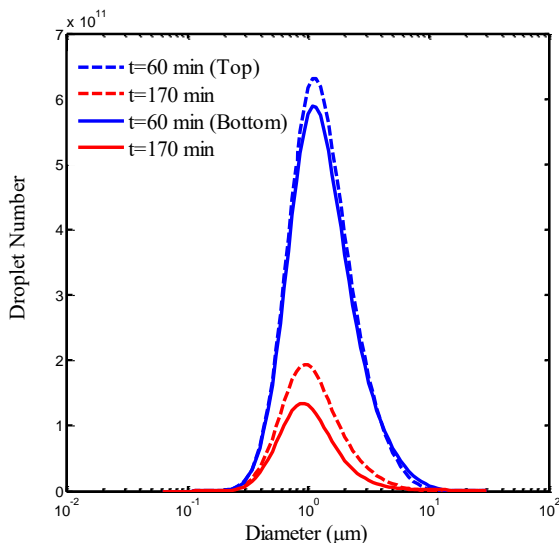


Figure 8. Droplet size distribution at top and bottom of the system in the presence of 300 ppm demulsifier CTAB

Thus, the number of small droplets is less while the large ones are more at this section when compared to top section of the vessel.

7. CONCLUSION

In this research, the collision frequency function in population balance equation was corrected so that the effect of demulsifier agents at various concentrations on dehydration efficiency of water-in-oil emulsion was investigated. The demulsification of water-in-oil emulsion was modeled via correlating the critical micelle concentration of the demulsifier to collision frequency function in population balance equation. The results of predicted demulsification rate by the modified population balance equation was compared with the obtained experimental data of conventional bottle test method for the selected group of demulsifiers and the R-square lies between 0.98 and 0.99. Comparison between model results and the experimental data revealed that the developed model could appropriately predict the effect of demulsifier on dehydration efficiency.

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Population Balance Equation Modeling of Crude Oil Demulsification Considering Demulsifier: Modification of Collision Frequency Function Based on Thermodynamic Model

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در این مقاله، مدلی تئوری به منظور بررسی اثر مواد تعلیق‌شکن بر روی راندمان جداسازی آب از امولسیون نفت خام پیشنهاد داده شده است. بر اساس اصول تعادل ترمودینامیکی، رابطه‌ای بین غلظت بحرانی مواد تعلیق‌شکن با تابع فرکانس برخورد در معادله موازنه جمعیت، ارائه داده شده است. بر اساس رابطه پیشنهادی، تابع فرکانس برخورد به‌نحوی تصحیح شده است که تاثیر مواد تعلیق‌شکن در به‌هم چسبیدن قطرات آب در نظر گرفته شود. به منظور تعیین پارامتر تنظیم شدنی مدل پیشنهاد داده شده، گروهی از مواد تعلیق‌شکن در نظر گرفته شده و با انجام آزمایش‌های بطری کارایی آن‌ها در جداسازی آب از نفت، از طریق محاسبه خطای مطلق نسبی بین نتایج راندمان جداسازی آب حاصل از مدل پیشنهادی و نتایج داده‌های آزمایشگاهی، بررسی شده است. مقایسه بین نتایج حاصل از شبیه‌سازی و نتایج آزمایشگاهی، مناسب بودن مدل را در پیش بینی راندمان جداسازی قطرات آب از امولسیون نفت خام در غلظت‌های مختلف تعلیق‌شکن، به‌خوبی نشان می‌دهد.

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