Amphiphilic polymers in disperse systems

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Abstract:

The amphiphilic polymers have a lot of particular physical and chemical properties such as; the aggregation shape and size, the hydrophilic and the lipophilic segments, etc. The researchers on amphiphilic polymers focus on polymers material field. The important theories and signification in using amphiphilic polymers are known to all with its good performances in many fields. In this work initially, the Giesekus model was used to study the rheology of the amphiphilic polymers solution. The Giesekus model includes three parameters that describe any used polymer, and the parameters were selected from the literature data. A mathlab code was created to simulate the Giesekus model. The obtained results showed shear thinning at the shear rate range. Finally, the Hydrophilic-Lipophilic

Deviation (HLD) and Net-Average Curvature (NAC) model was presented. The HLD_NAC model was used to predict the phase behavior of microemulsion and the properties of microemulsion. Depending on microemulsion morphology, some models from literature were presented to predict the microemulsion rheology. The predicted microemulsion morphology and viscosity may be useful in the design of formulations for enhanced oil recovery.

Keywords: Micelle rheology, microemulsion rheology, microemulsion morphology, Giesekus model, HLD_NAC model.

1. Introduction:

There is an increasing interest in the synthesis of amphiphilic polymers, polymeric surfactants, which are use in many diverse areas. These include the preparation of new colloidal nanostructures, latex stabilizers and emulsifiers and various biomedical applications [1]. In addition, polymeric surfactants have surface active properties, so they can be used for the preparation emulsions with controlled stability and with desired rheological behavior as well as nanoparticles with defined surface characteristics. One of the most important applications of polymeric surfactants is in the preparation of oil-in-water (O/W) and water-in-oil (W/O) emulsion, the hydrophobic portion adsorbs at the O/W and dissolves in the oil phase, and the hydrophilic portion dissolves in aqueous medium [2, 3].

Due to the macromolecular entanglement, the molecular structure of these polymeric surfactants should be designed first to get high surface activity copolymers [3]. In addition, the rheological properties of the solutions should be known after the addition of the polymers. However these polymers could be amphiphilic polymeric materials.

The first goal of this article is to investigate the rheological behavior of amphiphilic polymers solution, in aqueous medium, by using the Giesekus model. This model (defined by three material parameters plus the Newtonian viscosity) is one of the most versatile and used differential constitutive relation to model the non-linear viscoelastic behavior in shear. The second goal is to introduce a set of thermodynamic models that used to study the morphology and the rheology of microemulsion aggregates based on their geometrical configuration. The models have been known as HLD-NAC model. HLD referred to Hydrophilic-Lipophilic Deviation, and NAC referred to Net-Average Curvature. The HLD-NAC model is used to predict the phase behaviour of microemulsions, microemulsion properties (e.g. interfacial tension, phase volumes) and the curvature of O/W or W/O interfaces.

The microemulsion phase behavior is very important in many processes, such as microemulsion polymerization and enhanced oil recovery (EOR). Therefore, an understanding of surfactant/oil/brine phase behavior is of fundamental importance to the understanding of any surfactant-based chemical flooding process. As a mixture of oil, water, surfactant, and other components flows through an oil reservoir, the volumes of the phases that form and the properties of those phases dictate the performance of the process.

2. Mathematical description of micellar fluid flow:

2.1Rheological behavior of micellar system:

Many theoretical models have been presented in literature to find the relation between the polymer structure and the rheological behavior of the aqueous solutions. In figure (1), the predictions of the Giesekus model with the nonlinear parameter α=0.15 was shown for an amphiphilic micelle system. It gives an excellent fit to the data over the entire range of shear rates. The Giesekus model is nonlinear constitutive model for viscoelastic fluids based on the concept of anisotropic drag (between the solvent and polymer molecules) [4].

Giesekus model gives reasonable shapes for most material functions, and the analytical expression on the case of steady shear flow is shown as follows [5]:

$$\frac{\eta}{\eta_o} = \frac{(1-f)^2}{1+(1-2\alpha)f} \qquad (1)$$

Where:

$$f = \frac{1-\chi}{1+(1-2\alpha)\chi} \qquad (2)$$

and

$$\chi^2 = \frac{[1+16\alpha(1-\alpha)(\lambda\dot{\gamma})^2]^{1/2}-1}{8\alpha(1-\alpha)(\lambda\dot{\gamma})^2} \qquad (3)$$

Here λ is the time constant (relaxation time), $\dot{\gamma}$ is the shear rate, η_o is the zero shear rate viscosity, and α is a dimensionless parameter (Giesekus parameters) and is responsible for non-linearity of the constitutive model.

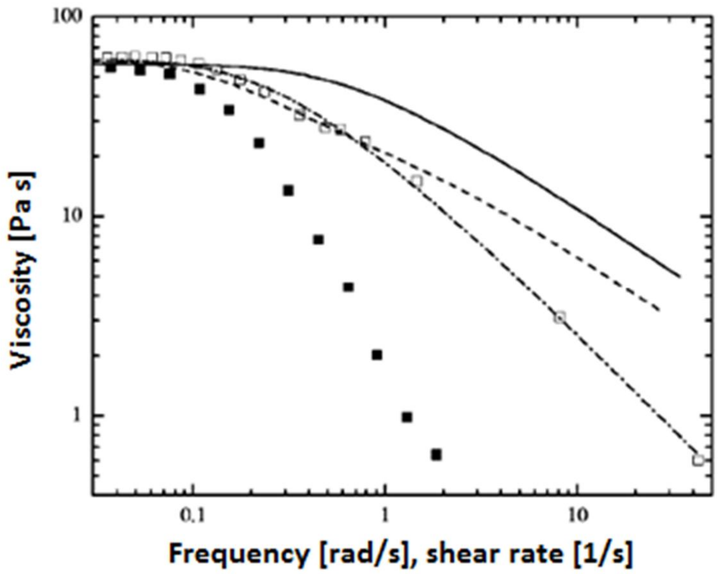

Figure (1): Viscosity as a function of shear rate and frequency for a 0.05 M CTAB wormlike micelle solutions. ■: the dynamic viscosity; □: the viscosity; solid line: the FENE_P model prediction; dashed line: the Bird-DEAguiar model prediction; and dash-dot line: the Giesekus model prediction.

2.2 Microemulsion morphology :

Microemulsion properties, such as composition, interfacial tension, specific phase transitions, and phase volumes, as a function of phase behavior were studied in literature [6]. Three different structure types of microemulsion were presented; oil-in-water (O/W) (Winsor Type I), water-in-oil (W/O) (Winsor Type II), and bicontinuous in oil and water (Winsor Type III). The corresponding relationship between microemulsion viscosity and phase behavior, for a surfactant (sodium dihexyl sulfosuccinate (SDHS))-oil (mixture of 20 wt% naphthalene and 80 wt% toluene)-water (SOW) system in the presence of various concentrations of added electrolyte, was previously reported [6, 7], and the effect of the electrolyte concentration on the phase behavior and on the interfacial tension (IFT) was investigated, figure (2). The ultralow IFT value obtained when the same volumes of oil and water are solubilized in the middle phase to give net zero curvature is referred to the optimal salinity [6, 7]. The phase behavior of this system and other surfactant-oil-water systems are usually obtained based on experimental data. The Fish phase diagram and the ternary phase diagram are usually used to show the microemulsion regions of types I, II, and III as a function of surfactant concentration and an independent variable such as temperature, salinity, pH, etc.

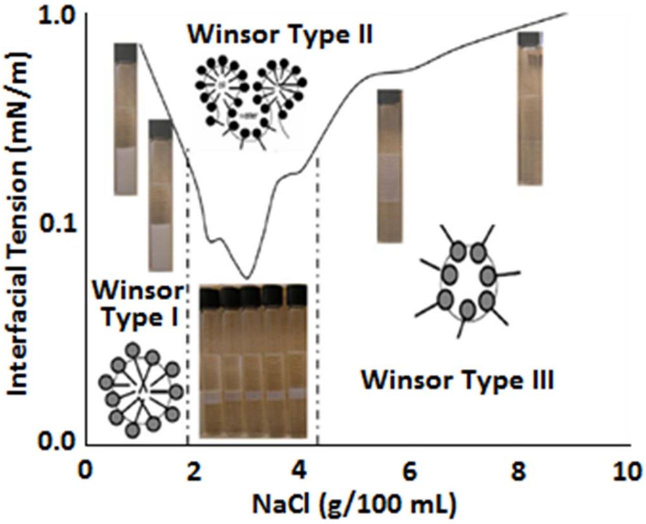

Figure (2): Microemulsion phase behavior and the corresponding interfacial tension

Because of the complexity of these systems and the difficulty in observing the actual process mechanisms experimentally, mathematical models have been used to simulate the processes. Various theories concerning microemulsion phase behavior have been proposed in literature [8, 9]. Some of them explained the thermodynamic stability of O/W dispersion to the surfactant film presents at the interface, which affects the curvature and the rigidity of the interface [10]. Temperature, salinity, and surfactant structure are the most important parameters that considered in the microemulsion phase behavior theories. They may be used to delineate the region where three coexisting phases occur. The interfacial tension of the microemulsion with a coexisting oil or aqueous phase are also often of special focus and may sometimes be used to guide their formulation [8]. For systems prepared using an ionic surfactant the hydrophilic-lipophilic deviation (HLD) model was proposed [9]. The HLD is a semi-empirical equation describes the change in chemical potential when a surfactant molecule is transferred from the oil phase to the aqueous phase [10].

The HLD equation for ionic surfactants is:

$$\frac{\mu_w^s - \mu_o^s}{RT} = HLD = \ln(S) - K \times N_{C,O} - f(A) - a_T \Delta T + C_c \qquad (4)$$

In this expression;

μ_w^s ; The water phase viscosity, and μ_o^s ; represents the oil phase viscosity (both at T).

R; is gas constant, and T; is the system temperature.

S; represents the electrolyte concentration within the aqueous phase (in g/100 mL).

$f(A)$; depends on the type and concentration of the cosurfactant added to the system; $f(A) = 0$ if no cosurfactant is used.

K; in the range from 0.1 to 0.2 (0.17 for most surfactants).

$N_{C,O}$; represents the number of carbons in the alkane oil phase (also known as alkane carbon number or ACN) for non-alkane oil is approximately zero.

a_T; temperature factor, is typically 0.01 K^{-1}

ΔT; is $T - T_{ref}$, where T is the temperature of the system and T_{ref} is the reference temperature (25 ^{o}C).

C_c; is the characteristic curvature of the surfactant which reflects the hydrophilic/lipophilic nature of the surfactant.

For modeling purposes, it is assumed that a shift in the HLD from HLD < 0 → HLD ≈ 0 →HLD > 0 reflects a sharp transition in the microemulsion phase behavior from type I → type III → type II [10, 11].

The curvature of the oil-surfactant-water interface using the HLD model was scaled by using the net-average curvature (NAC) model. The NAC model uses the point of net zero curvature as the critical point in the phase transition from O/W to W/O microemulsions. In addition, the NAC model uses HLD model to calculate the chemical potential difference of transferring a surfactant from the oil to the aqueous phase, and the value is used as a scaling parameter to calculate the net and average curvatures (NAC) of the surfactant at the W/O interface [6, 10, 11].

The net curvature (H_n) is scaled the HLD as follows [6]:

$$H_n = \left|\frac{1}{R_o}\right| - \left|\frac{1}{R_w}\right| = -\frac{HLD}{L} \qquad (5)$$

Where R_o and R_w are the radii of coexisting hypothetical droplets of oil and water, L is a length scaling parameter proportional to the length of the surfactant tail (≈1.2 times).

$$H_n = 0 \quad for\ bicontinuous\ (R_{o\approx}R_w)$$
$$H_n > 0 \quad for\ \ Type\ I \quad (R_w \gg R_o)$$
$$H_n < 0 \quad for\ \ Type\ II \quad (R_o \gg R_w)$$

For type I;

$$R_w = \frac{3 \times V_w}{A_s} \qquad (6)$$

$$A_s = \sum_i C_{Si} \times V_w \times 6.023 \times 10^{23} \times a_i \qquad (7)$$

V_w; the volume of water in the system

A_s; the total surfactant interfacial area

C_{Si}; the concentration of the surfactant “i” in the aqueous phase

a_i ; the surface area per molecule of the surfactant

The same calculations are used for the type II.

For type III microemulsion the average curvature (H_a) term is used [6]:

$$H_a = \frac{1}{2}\left(\frac{1}{R_o} + \frac{1}{R_w}\right) \leq \frac{1}{\xi} \qquad (8)$$

$$\xi = \frac{6\phi_o\phi_w V_m}{A_s} \qquad (9)$$

ξ; characteristic length to limit the size of the microemulsion aggregates

ϕ_o *and* ϕ_w; the volume fractions of oil and water

V_m; the volume of the microemulsion phase

The HLD-NAC model was successfully used in the past to predict the microemulsions properties such as; phase volumes [6], interfacial tensions [10], oil-water solubilization capacities [6], phase transitions, and droplet size of nonionic and ionic surfactant microemulsions.

2.3Microemulsion rheology :

The viscosity of the microemulsion phase is function of both the microemulsion morphology and electrolyte concentration as shown in figure (3). The viscosity of the microemulsion phase depends on the shape and interactions of the dispersed particles. Shape changes as a function of several independent variables such as; salinity, temperature, surfactant concentration or structure etc. and the interaction between the dispersed particles increase by increasing their volume fraction and this lead to an increase in the bulk viscosity. Microemulsion contains anisometric particles, such as sphere, prolate, oblate, or rodlike micrpemulsion. The following models predict the microemulsion viscosity relating to the drops shape and the volume fraction [7];

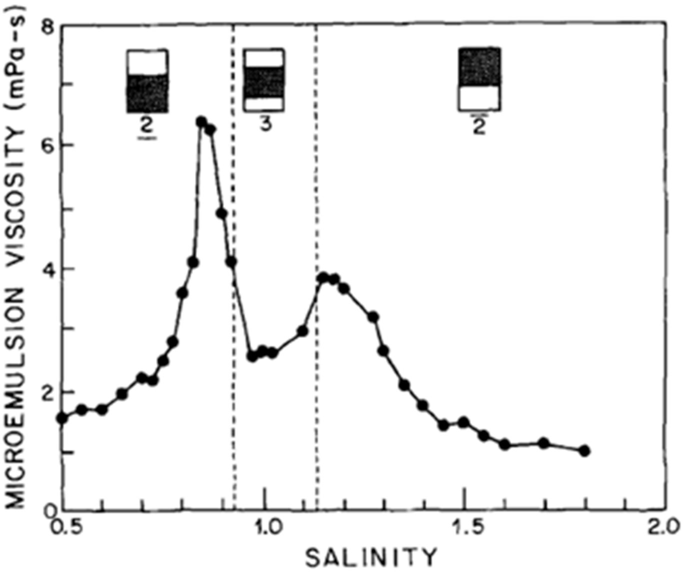

Figure (3): Microemulsion viscosity as a function of salinity [7].

For liquid spheres dispersed in another liquid medium:

$$\eta_r = 1 + \phi\left(\frac{\eta_s + 2.5\eta_d}{\eta_s + \eta_d}\right); \qquad (\phi < 0.02) \qquad (10)$$

$$\eta_r = \frac{(1 + 1.5\phi)}{(1 - \phi)}; \qquad (\phi > 0.02) \qquad (11)$$

For prolate, oblate, or rodlike microemulsions (axial to radial ratio < 10):

$$\eta_r = 1 + N \times L^3 = 1 + \left(\frac{4c_g L^2}{\pi d^2 \rho}\right); \qquad \left(N < \frac{1}{L^3}\right) \qquad (12)$$

$$\eta_r = \frac{96 \times c_g^3 \times L^6}{(5\pi^2 \rho^3 d^6 \ln\left(\frac{L}{d}\right))}; \qquad \left(N > \frac{1}{L^3}\right) \qquad (13)$$

For prolate, oblate, or rodlike microemulsions (axial to radial ratio > 10):

$$\eta_r = 1 + \upsilon\phi \qquad (14)$$

Where η_r = relative viscosity $= \frac{\eta}{\eta_s}$

η is the system viscosity, η_s is the viscosity of the continuous phase.

ϕ is the volume fraction of the dispersed phase, $\eta_d$is the viscosity of the dispersed phase, N is the number density of the dispersed droplets, L is the length of the dispersed droplets, c_g is the concentration of dispersed droplets in mass per unit volume, d is the diameter of the dispersed droplets, ρ is the density of the microemulsion phase, and υ is a parameter that varies according to the axial and radial axes of the dispersed droplets. The axial length (L) and the radial radius (R=d/2) are related to the H_n and H_a as follows [11];

$$H_n = \left[\frac{4}{(L+2R)}\right] + \left[\frac{\left(\frac{2L}{R}\right)}{(2L+4R)}\right] \tag{15}$$

$$H_a = \frac{(6L+12R)}{(9LR+12R^2)} \tag{16}$$

H_n and H_a can be determined by using the NAC model.

To predict the microemulsion viscosity it is important to know the microemulsion type. A shift from the type I of the spherical shape to type III of the cylindrical shape are predicted when the aggregates get a cylindrical shape of length L and radius R, and L/R>10 [11].

3. Results and discussions:

3.1Rheological behavior of amphiphilic polymer solutions:

The rheological properties of solutions have been modified by using polymer additives, which have many applications in industry. An important application in use the amphiphilic polymer solutions are enhanced oil recovery (EOR), where the viscosity is an important factor that controls the production process. The viscosity of a polymer solution depends on the polymer-solvent interactions [12]. In an aqueous medium and above a certain concentration, these amphiphilic polymers tends to form aggregates that lead to the formation of a physical network that effect on the rheological properties of the medium [3].

The morphologies of these aggregates can range in shape and size from spherical micelles, to wormlike micelles, figure (4), to lamellae depending on surfactant and counterion concentration. The rheology of different surfactant solutions has been investigated by many researches [12, 13]. Under the right conditions, the micelles can entangle and impart viscoelasticity to the fluid. The behavior of wormlike micelles solutions is similar to that of polymer solutions. The essential difference between the two is on the backbone of the polymer. However, micelles are in a state of thermodynamic equilibrium with the solvent and are always broken and reformed under Brownian fluctuations, and this leads to a broad and dynamic distribution of micelle lengths, which can change under an imposed shear or extensional flow [4].

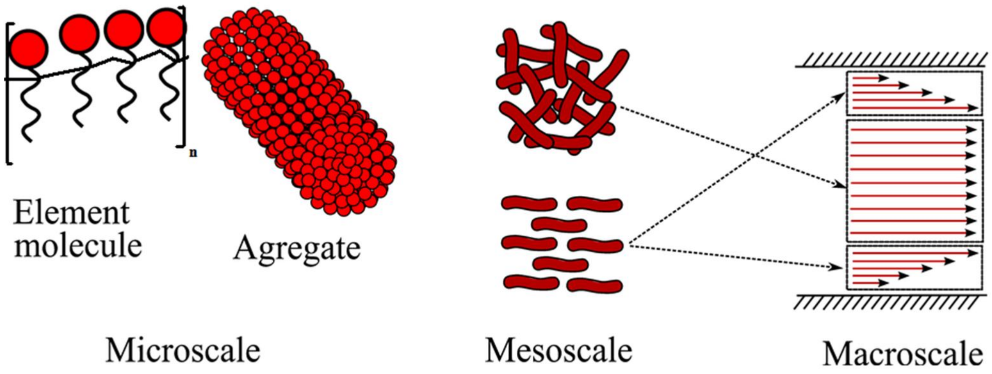

Figure (4): Wormlike micelles, from microscopic structure to the macroscopic flow behavior.

3.1.1 Case study of micelles rheology

Figure (5) shows the predicted result from Giesekus model. Mathlab code was created to simulate the model, the code on the appendix. The data is for an amphiphilic polymer solution [4], with $\eta_o = 10\ PaS$, and λ=0.4 S.

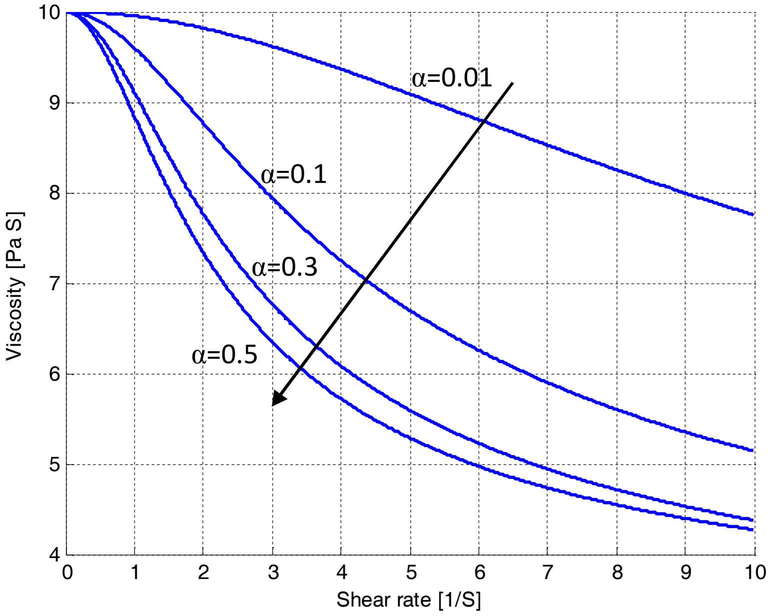

Figure (5): Influence of the Giesekus parameters on the viscosity curve.

The Giesekus model presents shear-thinning viscosities at the shown shear rate range for all the Giesekus parameters. The micelle solution is shown as a function of shear rate. At small shear rates, less than 0.03 S^{-1}, the micelle solution behaves like a rheologically simple fluid; the viscosity approximately the same value. The shear thinning behavior is due to the breakdown of the micelles in the system upon application of shear. As the applied shear stress is increased, the fluid begins to shear thin. According to the figure (5) results, it should be mentioned that when the Giesekus parameter equal zero ($\alpha = 0$) the viscosity becomes constant.

3.2Microemulsion rheology

At a fixed shear rate or shear stress, microemulsion viscosity goes through a sharp maximum, a local minimum, and a second maximum as the salinity of the mixing brine increases, figure (3) [7]. Near these maxima, microemulsions exhibit non-Newtonian behavior. Away from these maxima, microemulsion appeared to be Newtonian, [14, 7]. These viscosity maximums are related to the hydrophobic interactions between the surfactant tails. However, the first maxima is higher than the second maxima because of the type III microemulsion onset where the surfactant takes lamellar shape at this point the hydrophobic interaction at the highest value. In addition, the second maxima where the inverse microemulsion onset the hydrophobic interaction becomes lower that leads to decrease the solution viscosity.

3.2.1 Case study of microemulsion rheology

Equations 10 and 11 are used to calculate the relative viscosity η_r of the surfactant/decane/water system at 20 ^{o}C as a function of the volume fraction ϕ (of surfactant plus decane) the range of the ϕ is presented. Mathlab code was created to solve the previous equations, and the code is on the appendix. The predicted results are shown in figure (6). The reference viscosities of water and decane at 20 ^{o}C are 1.00 CP and 0.92 CP, respectively.

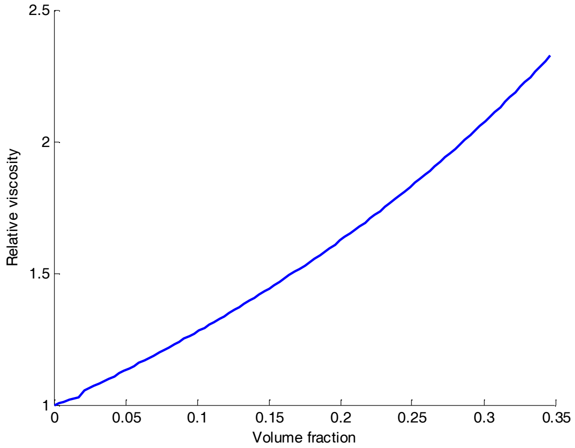

Figure (6): Relative viscosity as a function of the volume fraction.

Comparing the predicted data with the experimental data from the literature [7] gives acceptable result. However, it has observed that the O/W microemulsion has viscosity behavior similar to the W/O microemulsion and both microemulsion types (I&II) are considered contain individual aggregates. At low volume fractions, it is sufficient to assume the viscosity behavior of type I and type II microemulsions similar to colloidal hard-sphere system. The microemulsion viscosity was calculated by substituting the predicted volume fractions of the dispersed phases as well as the viscosities of the contineous and dispersed phases. The relative viscosity goes up as the volume fraction increases. The viscosity deviation happens at critical volume fraction. This probably happens because intermolecular hydrophobic interactions, leading to an increase in the viscosity. It has reported that adding salt to microemulsion, its viscosity reaches a maximum value [7], and this fact is of great importance when the application in oil wells is sought, because the oil reservoirs have high salinity.

4. Conclusion:

The Giesekus model was used to study the micelles rheology, this model used for viscoelastic fluids. The Giesekus model presents shear-thinning viscosities for all the Giesekus parameters. The shear thinning behavior is due to the breakdown of the micelles in the system upon application of shear. The HLD-NAC model was presented. The HLD_NAC model was used to predict the phase behavior of microemulsion and the properties of microemulsion. It has not reported using this model for studying the behavior of polymeric surfactant/oil/water system. The predicted microemulsion rheology was studied, the O/W and W/O microemulsions were assumed have similarly viscosity behavior and it was sufficient to consider them as a colloidal hard-sphere system. The relative viscosity of the microemulsion goes up as the volume fraction increases. It may be useful in the design of formulations for enhanced oil recovery to study the micelles rheology, and microemulsion rheology and morphology using the presented models.

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5. References:

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6. Appendix:

A.1 Mathlab code to solve the Giesekus model

```
clear
Thao=10
lamda=0.4
alpha=[.5 .3 .1 .01]
shrate(1)=.01
delta=.05
N=100000
for k=2:N
   shrate(k)=shrate(k-1)+delta
end
for i=1:4
   for j=1:N
      A1=sqrt(1+16*alpha(i)*(1-alpha(i))*(lamda*shrate(j))^2)
```

```
    A2=8*alpha(i)*(1-alpha(i))*(lamda*shrate(j))^2

x=sqrt((A1-1)/A2)
f=(1-x)/(1+(1-2*alpha(i)*x))
visco(j)=Thao*((1-f)^2/(1+(1-2*alpha(i))*f))
  end
  figure(1)
  hold on
  plot(shrate,visco,'b-','Linewidth',2)
  hold off
  grid on
  xlabel('Shear rate [1/S]')
  ylabel('Viscosity [Pa S]')
end
```

A.2 Mathlab code to solve the Equation 10 and 11

```
clear
fai(1)=0
N=100
del=.35/100
ThauS=1.002 % water viscosity (cP)
Thaud=0.92  % decane viscosity (cP)
for i=1:N
```

```
if fai(i)>0.02
    Thaur(i)=(1+1.5*fai(i))/(1-fai(i))
    fa(i)=fai(i)
else
    if fai(i)<0.02
        Thaur(i)=1+fai(i)*((ThauS+2.5*Thaud)/(ThauS+Thaud))
        fa(i)=fai(i)
    end
    fai(i+1)=fai(i)+del
end
fai(i+1)=fai(i)+del
end
figure(1)
hold on
    plot(fa,Thaur,'b-','Linewidth',2)
    hold off
    xlabel('Volume fraction')
    ylabel('Relative viscosity')
```