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Experimental measurement and modeling of nanoparticle-stabilized emulsion rheological behavior

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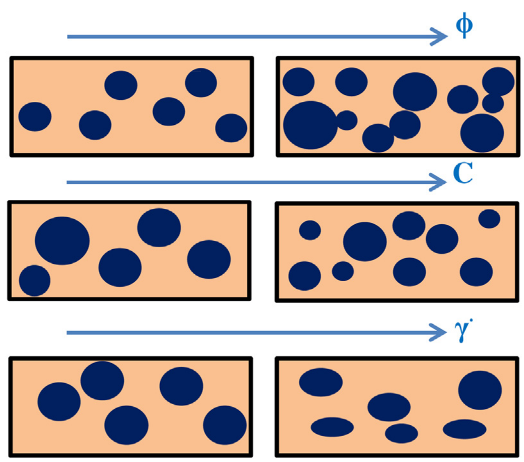
HIGHLIGHTS

- The droplet size of emulsions decreases with the addition of nanoparticles.
- The rheology of water-in-oil emulsions are influenced by the amount of nanoparticles, volume of water fraction, shear rate and angular frequency.
- Based on the experimental data, a new equation was developed to estimate the relative viscosity of solid-free and solid-stabilized emulsions.
- Using the Krieger-Dougherty and Bicerano et al. models, the maximum packing concentration volume fraction were obtained.
- The maximum packing concentration volume fraction increases with shear rate and nanoparticle.

GRAPHICAL ABSTRACT



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ABSTRACT

Emulsions have wide applications in various fields, especially in the petroleum industry. The rheological behavior of water-oil emulsions plays an important role in oil production, transportation and enhanced oil recovery methods Rheology of emulsions is affected by various factors such as dispersed phase fraction, droplet size distribution, a concentration of emulsifying agents, solid concentration, etc. Emulsion stabilization by solids, especially nanoparticles increased the stability, improved the rheological properties and consequently, incrementing the oil recovery from a subterranean formation. It can be pointed out that in very limited cases, the effects of nanoparticles on droplet size distribution of emulsion were investigated and models for prediction of the rheological behavior of solid-stabilized water-in-oil emulsions were not presented. The experiments were carried out using crude oil (petroleum) and fumed silica particle (namely Aerosil R972). In this communication, the effects of different parameters, including water volume fraction, nanoparticle concentration, shear rate, and angular frequency were investigated on the rheological behavior of water-in-oil emulsion. According to the results of rheological experiments, it can be pointed out that the influence of the nanoparticles on the viscosity of water-in-oil emulsions is mainly affected by the water/oil ratio, a number of nanoparticles, shear rate and angular frequency. Nanoparticle decreased water droplet diameter and increased the stability, elasticity and viscosity of the

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emulsion. In addition, for a better understanding of the effect of these parameters on the viscosity of the water-in-oil emulsions, apparent viscosity models were used. Based on the experimental data, a new equation was developed to estimate the relative viscosity of solid-free and solid-stabilized emulsions. The obtained results demonstrated that the proposed model has increased accuracy than previously published correlations.

Nomenclature

ΔG	Energy [kT]
R	Radius [m]
M	Consistency index [-]
N	Flow behavior index [-]
γ_r	Relative viscosity [-]
K	Ratio of dispersed phase viscosity to the continuous phase viscosity [-]
K	Constant parameter [-]
R^2	Regression correlation coefficient [-]
$Inp_{k,i}$	*i*th value of the kth input variable [-]
$Inp_{\bar{k}}$	The average value of the kth input variable [-]
ΔP	Pressure difference [-]
A	Frequency factor [-]
E_a	Activation energy [J/mol]
R	Gas constant [J/mol K]
T	Temperature [K]
C	Nanoparticle concentration [wt%]

Greek symbols

G'	Storage modulus [Pa]
G"	Loss modulus [Pa]
Ω	Angular frequency [rad/s]
'H	Dynamic viscosity [Pa S]
$\lvert\eta^*\rvert$	Complex viscosity [Pa S]
F	Frequency [Hz]
λ	Time constant [Sec]
η	Viscosity [Pa S]
η_{ri}	Predicted emulsion relative viscosity [Pa S]
$\overline{\gamma_r}$	Average value of the predicted emulsion relative viscosity [Pa S]
ϕ	Dispersed phase volume fraction [%]
ϕ_m	Maximum packing concentration volume fraction [%]
τ_0	Apparent yield stress [dynes/cm^2]
η_P	Apparent viscosity [Pa S]
γ_{ow}	Interfacial tension [N m^{-1}]
θ_{ow}	Contact angle [°]
T	Shear stress [dynes/cm^2]
$\dot{\gamma}$	Shear rate [Sec^{-1}]

1. Introduction

Emulsion (water-in-oil and oil-in-water) is a disperse system consisting of at least two immiscible liquids in which liquid droplets finely suspended in a second immiscible liquid. As a matter of fact, emulsions are composed of two main phases, continuous and dispersed. Moreover, emulsions contain a surface-active agent (surfactants or emulsifiers). the Surface-active agent may be derived from the oil itself or can be added manually. Surface-active agent has two main functions: (1) to decrease the interfacial tension between phases; consequently, the energy required for emulsification is reduced, and (2) adsorbed on the droplet surfaces and create an interfacial film, which prevents coalescence between the water droplets; thus, stabilize the formed emulsion [1–4].

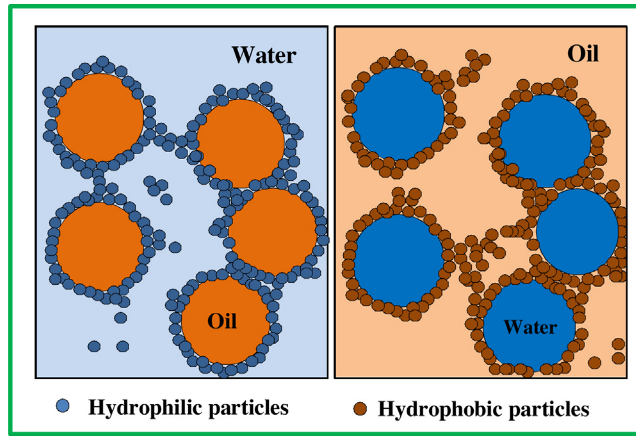

Fig. 1. Sketch of structure of oil- in-water emulsion stabilized by hydrophilic particles (left) and water-in-oil emulsion stabilized by hydrophobic particles (right).

Emulsions may contain solid particles in addition to gas [5]. Solids in emulsions cover the droplet surface and hindering coalescence. In other words, the added solids decrease the droplet diameter [6,7]. The added solid should remain undissolved in both the continuous and disperse phases, have high surface area and their particle size should be small [8]. The performance of this particle as a stabilizer depends on the particle size, interparticle interactions and particle-oil-water contact angle (θ_{ow}). To find the best contact angle (θ_{ow}), Eq. (1) can be used.

$$-\Delta G = \pi r^2 \gamma_{ow} \ (1 + \cos\theta_{ow})^2 \quad (1)$$

In this equation, ΔG is the energy required to separate the particle with a radius r from the oil-water interface of tension γ_{ow} into oil. The maximum value of this equation occurs at the contact angle (θ_{ow}) of 90°. Hydrophilic particles with contact angles less than 90° stabilize oil-in-water emulsions while hydrophobic particles with contact angles more than 90° stabilize water-in-oil emulsions. Therefore, an emulsion type can be altered from oil-in-water to water-in-oil or reverse by changing the contact angle (with surface modification) [9]. Fig. 1 indicates the structure of water-in-oil emulsion and oil-in-water emulsion, which have been stabilized by hydrophobic and hydrophilic particles, respectively. The nanoparticle is the best choice for solid-stabilized emulsion due to their small size and high surface area [10].

Emulsions have wide applications in various fields such as food product, pharmaceutical, cosmetic, paints, adhesives, inks, pulp and paper, biological fluids, agricultural product, explosives, petroleum industry (drilling, production, enhanced oil recovery, transportation and process) and so on as a result of their highly variable physical properties [11–14].

Different criteria can be used to classify the emulsions. Based on the classic classification, water and oil play the main roles. Typically, the emulsions are divided into four groups namely water-in-oil, oil-in-water, oil-in-water-in-oil and water-in-oil-in-water