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|1+Emulsions main characteristics and behavior

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Abstract

This review presents the main factors that influence the oil/water emulsion behavior; among of them, three most important ones are the temperature, the water cut and the surfactant concentration; due to the changes produced in the emulsion physicochemical properties and morphology. Aggregation and solvation phenomena change the emulsion characteristics, due to the different modes of interaction between the dispersed phase and the continuous phases. Some equation for correct the viscosity of oils and some others to generate the emulsion viscosity are presented here, highlighting their applicability and their range of use. The piezo viscous effect it is a tool to produce emulsion viscosity data to higher pressures starting from data an atmosphere pressure. A detailed explanation of PIP, the morphology changes and its influence over the emulsion properties is presented here. The mechanism of occurrence of wall slip, and how the components and surface chemistry influence its occurrence of emulsion is explained. The main behavior of emulsion flow through pipes and packed beds making emphasis in the dispersed phase are explained in this review, joined with according to the literature cited, some of the best equations for the pressure drop approximations.

Key words: Emulsion behavior, droplet size, phase inversion, rheology of emulsions, non-Newtonian fluids, and pressure drop.

Emulsiones aceite/agua, características principales y comportamientos.

Resumen

Esta revisión presenta los principales factores de influencia en el comportamiento de emulsiones aceite/agua; entre los cuales, los más importantes son: la temperatura, el porcentaje de agua y la concentración de especies surfactantes; debido a los cambios producidos en las propiedades fisicoquímicas y la morfología de las emulsiones. Los fenómenos de agregación y solvatación cambian las características de las emulsiones debido a los diferentes modos de interacción entre la fase dispersa y la continua. Algunas ecuaciones para corregir la viscosidad de crudos y otras para reproducir la viscosidad de una mezcla son presentadas aquí, resaltando su aplicabilidad y su rango de uso. El efecto piezoviscoso es una herramienta para estimar viscosidad de emulsiones a altas presiones, a partir de datos a presión atmosférica. Una explicación detallada del punto de inversión de fase, los cambios en la morfología y su influencia sobre las propiedades de las emulsiones es presentado aquí. El mecanismo de ocurrencia del deslizamiento en la pared y como sus componentes y la química superficial influencian su ocurrencia en las emulsiones es explicado. El Comportamiento central de emulsiones a través de tuberías y lechos porosos haciendo énfasis en la fase dispersa es descrito en esta revisión, junto con, de acuerdo con la literatura citada, algunas de las mejores ecuaciones para la estimación de la caída de presión en el flujo de emulsiones.

Palabras clave: Comportamiento de la emulsión, tamaño de la gota, inversión de fase, reología de emulsiones, fluidos no newtonianos, caída de presión.

Introduction

Emulsions are fine dispersions of oil in water (O/W) or water in oil (W/O) with droplet sizes usually in the micrometers, formed naturally during flow of oil and water in porous rock formations or promoted in many stages of the oil production and processing, by the mixing with high shear forces in the presence of surface active components such as asphaltenes and resins. For this reason, the knowledge of emulsion behavior is an important task or key factor that can be extremely advantageous, especially as more challenging reservoirs and heavy and extra heavy oils are increasingly being produced [1-53, 56-63].

Emulsion characteristics as others fluid properties, plays an important role for engineering purposes, and is widely used for design calculations, cost estimation and other transport-related properties, as a consequence, a vast number of researches have been done to understand the emulsion behavior, but up to the present, no adequate theory is available that can satisfactorily reproduce the experimental performance of emulsions O/W and W/O [1, 2, 15, 20, 22, 25, 26-32, 34, 44, 48, 49, 54, 55, 58, 60-63].

Engineers are confronted with a large number of emulsion viscosity theories in the literature ranging from highly theoretical models to simple empirical ones; however, many of these are applicable only to a single phase or are only suitable for estimating the emulsion performance over limited ranges of temperatures, pressures and compositions regions [1-28, 34, 50, 60].

For the reasons explained above, this work presents a review of some investigation about the effect of water cut (Φ), temperature (T), pressure (P), share rate (Υ) solid and natural surfactant concentrations or droplet size and distribution (d) among others, over the emulsions behavior; joined with the review of some equation useful to predict emulsion viscosity, pressure drop in pipes, inversion point, wall slip and the flow of emulsion through packed bed. This contribution could help the reader to understand the rheological behavior of emulsions to face the challenge of modeling and predicting emulsion transport properties, it could also be a source of information for developing multiphase flow simulators to optimize oil recovery and it will be an aid for petroleum and chemical engineers through the better the understanding of phenomenon happening in the oil fields, reducing environmental, economic and operational risk [9, 14, 16, 20, 45, 48, 49, 50, 52, 57].

Influence factors in W/O emulsions viscosity

Rheological studies show that temperature, pressure, shear rate, water cut, the presence of indigenous surfactants among others factors, are known to play an important role in the formation and stability of emulsions [1-21].

The viscosity of an emulsion can greatly exceed the crude or the water single phase, it shows an increase of the elasticity and viscosity with the water cut with a Newtonian behavior still maximum water cut; from that point the fluid turns to be non-Newtonian [1-9, 14, 21, 28, 48, 49].

At low water cuts when dilute emulsions are formed, the hydrodynamic forces during droplet collisions govern the viscosity behavior. As the water cut increases, towards highly concentrated emulsions, the resistance to flow can be induced by deformation and rearrangement of the network structure of the thin liquid films between the droplets, with an increase of viscosity much more pronounced when the temperature is low. For instance, for a mixing intensity of 5x106 erg/cm-seg, the maximum value of emulsion viscosity a 50°C is almost 3,5 times the dry oil (without water) viscosity at the same temperature, It is also known that continuous phase controls the viscosity of the emulsion as the temperature is increased or decreased [1-9, 14, 21, 28, 34, 44, 49].

Viscosity of emulsions is typically very large at reservoir temperatures (i.e. below 20°C) but it decreases with an increase in temperature. For example, the viscosity of gas-free Athabasca oil water emulsion at 20°C is greater than 500 cP, and it decreases to about 0.1 cP when the temperature is raised to 130°C. In some cases the reduction of emulsion viscosity can reach half of the initial value for temperature changes of 100°C. This emulsion viscosity reduction could be a result of an increase of Brownian motion with the rise of the temperature; therefore, the external forces such as shear stress and/or pressure are offset by the internal forces, producing additional to a viscosity reduction, and a flow of molecules through the interfaces resulting in a reduction in emulsion stability and viscosity [24, 32, 33, 34, 44, 49].

The stability of emulsions is improved by the concentration of salts and nanoparticles with a particle size below 1 µm, for the adsorption of onto the water–oil interface generating a reduction of surface energy making the emulsion the droplets smaller. In other words, the emulsion droplet size distribution tends to have a narrower range with increasing the nanoparticles and salt concentration. Particles also can form multilayers, and this is considered as a guarantee of good emulsion stability [4, 21, 24, 29, 58].

The water cut has an opposite effect in the emulsion stability; the studies showed that an increase in the water cut decreases the stability of emulsions. By increasing water amount in the continuous phase, the droplet diameter of the emulsion increases, this indicates that droplets could pack closer. Consequently, the separation distance between droplets decreases and the small ones have less free space between the large one, this can intensify coalescence and Ostwald ripening phenomenon (when the dispersed phase is in some extent soluble in the continuous phase, smaller droplet diffuse into bigger ones because of the higher Laplace pressure) described in equation (1) [4, 5, 21 29].

$$V_s = \left(\frac{8\gamma V_m^{\;2} DfC}{9\mathrm{kT}} \right) t^{\frac{1}{3}} \tag{1}$$

Where C is the equilibrium concentration of the molecules of the dispersed phase in the continuous one, Df their diffusion coefficient, Vm the molecular volume γ is the interfacial tension, T is temperature, k is the Boltzmann constant and t is time.

Emulsions often show a shear thinning behavior, this means that the viscosity decreases as the shear rate increases. The share rate can also eliminate the steric or electrostatic barrier that forms a droplet protective film, enhancing the coalesce contributing to the instability of emulsions; but it can also reduce average dispersed droplets size leading to an increase of the viscosity of the emulsion. It also reported that increasing stirring rate favors the emulsion inversion point, because it facilitates the breakup of the dispersed phase into small droplets, promoting the inclusion of the small ones into the continuous phase and the dispersed phase either, both of which improve the formation of multiple emulsions making easier the emulsion inversion point (PIP) [24, 32, 34, 45, 49, 56].

The droplet size distribution of the dispersed phase also has an important effect on the emulsions; particularly for high concentrations of the dispersed phase, this means that the viscosity of emulsion with smaller droplets is always higher than that of the bigger ones. The droplet size distribution of an emulsion is mainly influenced by the interfacial tension between the oil and the aqueous phase, the emulsifying agents, presence of solids and shear rate. It is also clear that emulsions with low water cuts have smaller droplets size diameter, with a tendency to form flocculation under the effect of Van der Waals forces. With an increase in dispersed phase, the droplets tend to collide and coalesce forming larger droplets if the steric or electrostatic barrier is previously eliminated by share forces as it was explained above. It is generally considered that the size of dispersed phase in a stable emulsion is of 10 µm or less [21, 24, 29, 45, 49, 63].

Aging has a significant influence on the rheological behavior of emulsions. The results have demonstrated that precipitated dispersed phase of aged emulsion rises with increasing its volume fraction and decreases with nanoparticle concentration. Aging produces also a droplet size distribution considerably smaller than those fresh emulsions, due to large dispersed phase sedimentation. Consequently, the percentage of dispersed phase in the emulsion is reduced as well the droplet mean diameter and the viscosity. Equation (2) describes the settling velocity (Vs) for the process [4, 21, 24].

$$V_s = \frac{g{D_P}^2\left(\rho_w - \rho_o\right)}{18} \tag{2}$$

Where D is droplet diameter; ($\rho w - \rho o$) is density difference of water and oil respectively and μ is the viscosity of emulsion [23].

The presence of indigenous surfactants in the oils such as naphthenic acids and resins and the total mass of volatile aromatic components are known to play an important role in the formation and stability of emulsions. As with the presence of nanoperticles and salts, natural surfactants will increase the amount of molecules adsorbed at the water/oil interface providing an electrostatic and steric barrier to the coalescence mechanism among the dispersed droplets, enhancing the emulsion stability. In some cases there must be a previous step of activation with acids or other compounds to promote the adsorption of nanoperticles or salts at the droplet interphase [5, 9, 21, 24, 29, 45, 48, 49, 55, 56].

Asphaltenes are polycyclic molecules and contain polar groups (ester, ether, carbonyl) and acidic and basic groups (carboxylic and pyridine functional groups) that can be ionized in at certain range of pH and can also promote emulsion stabilization, as shown in the study of Sandoval (2014), an increase in the concentration of asphaltenes, can produce a smaller droplet size distribution; showing a dispersing effect because they are prone to form mechanically rigid or viscoelastic interfacial films around dispersed phase droplets, this means that hydrophobic particles are attracted to each other in the oil phase and the hydrophilic particles in the aqueous phase, contributing to the high stability of petroleum emulsion [6, 9, 24,29, 45, 48, 49].

As natural surfactants, waxes, primarily consist of alkanes with little tendency to wet the oil–water interface, they, through Van der Waals interactions form a crystal network that stabilizes (W/O) emulsions by physical encasing the dispersed phase. The stabilization, which in the present context refers to the close contact of wax crystals with the oil/water interface, appears of one of two ways: the direct solidification of molten wax at the droplet interface or the migration of previously-formed crystals toward the oil/water interface, both result in the creation of a crystalline sheath around dispersed droplets that confers stability against coalescence by preventing direct droplet coalescence [8, 24, 29, 45, 48, 49].

Resins can lead generally to less stable emulsions because they solubilize asphaltenes in oil, and remove them from the interface. However, if asphaltenes are partly precipitated, resins can resolubilize them and produce and increase in the emulsion stability, but if the resin concentration is too high, the stability is not improved. Oils with A/R ratios higher than 0,6 tend to form stable emulsions, oils with A/R ratios higher than 0,6 tend to form unstable emulsions, while oils with high viscosity ($> 10\ Pa \bullet s$) and asphaltenes content (>10%) or A/R = 0,75 tend to form entrained water-in-oil emulsions, in which the high viscosity of the oil entraps water in its interior. In oils with A/R = 0,5; the formation of a mesostable emulsion is expected, [8, 24, 29, 45, 48, 49].

Density or °API as expected has an inverse relationship with viscosity, the lower API gravity of oil the higher are both dehydrated oil viscosity and emulsion viscosity, but oils with similar API gravity, viscosities, molecular weight and water cut can generate emulsions with different viscosities. As a general rule the emulsion characteristicsare very sensitive to oil composition. Oils with high density tend to form unstable emulsions when subjected to shear. [9, 28, 33, 49].

Pressure also produces a rheology modification, although the viscosity of simple liquids is not affected by moderate pressure increases, it imposed a significant effect on the rheological behavior of emulsions. As the pressure elevates, the emulsion viscosity also increases due to the compression of the free volume inducing greater interaction among molecules and slight density changes. For example, with an increase in pressure from atmospheric to 34,5 Mpa (5000 psi), the viscosity of a high molecular weight hydrocarbon increases by a factor of 4 at the same temperature, and over a similar increase in pressure, the oil emulsion viscosity would increase by a factor of 7. As must be expected, while molecular structure is more complex, larger is the effect of pressure over viscosity [9, 10, 11, 14, 32, 33].

It is also interesting to note that for an Athabasca oil emulsion, an increase in pressure of 10 Mpa resulted in a 49% increase in the emulsion viscosity at 43°C compared with a 33% increase at 120°C. Thus the effect of pressure is more significant at lower temperatures where the oil viscosity is high. Both low temperature and high pressure yield a remarkable increase in the viscosity [11].

Added surfactants plays a major role in the emulsion behavior, because if greater is the emulsifier concentration greater is its stability. As It has been reported that with an increase in emulsifier concentration, droplets become smaller due to lower interfacial tension. With a decrease in droplet size, the overall contacting surface increases and consequently the emulsion viscosity increases [15, 35, 53].

On the other hand, surfactants can also lower viscosity. Emulsions made with surfactants could develop from 5 to 10 times less viscosities than the pure crude oil of the emulsion is made of, this behavior is likely attributed to the efficiency of the surfactant in reducing the interfacial tension of the adsorption film in emulsion, making deformation of the dispersed phase easier. Attention must be paid because the reduction of emulsion viscosity compared with its oil depends on the surfactant kind [44].

Emulsions with low surfactant concentration have larger droplet sizes (range 3-300 μm) compared to those with high surfactant concentration (range 3-140 μm), droplet diameter distributions vary due to the different surfactant/oil ratio [53].

The aggregation and solvation Phenomena.

In emulsions, especially those formed by oils, with high contents of asphaltenes and resins, the formation of aggregates made by this molecules normally usually occurs. These aggregates influence directly the viscosity and rheological behavior of emulsions, and their occurrence is commonly attributed to the Van der Waals intermolecular forces and the polarity difference between the parts of the asphaltenes, which acts as natural surfactants leading to the formation of colloidal suspensions. For these reasons, aggregates such as these retain in their structure a significant part of the continuous phase available, leading to an increase in the effective concentration of the dispersed phase. Consequently, aggregates rise theemulsion viscosity [14, 16, 48].

In the solvation part of the continuous phase is adsorbed onto the surface of the dispersed phase droplets via bond formation, hydrogen bonding, and van der Waals forces mainly due to the presence of natural or added surfactants. This phenomenon also leads to the immobilization of the continuous phase modifying the emulsion viscosity as other properties [14, 16, 48].

Some equations to correct oil viscosity as a function of water cut.

A vast amount of research on the rheological characterization of emulsions has led to a huge numbers of correlations for emulsion viscosity prediction. Here we present the most common of them [16].

Benayoune (1998) applied the models of Mooney (1946), Richardson (1958) and Mooney (1961), represented in the equations (3), (4) and (5) respectively to model the emulsion viscosity. In the correlations, μ and μ0 are the emulsion and the dry oil viscosity, Φ is the water cut, a and k are adjustable parameter ranging between 1,35 and 1,91 .

$$\frac{\mu}{\mu_0} = e^{\frac{2,5\,\Phi}{1-k\,\Phi}} \tag{3}$$

$$\frac{\mu}{\mu_0} = e^{a\,\Phi} \tag{4}$$

$$\frac{\mu}{\mu_0} = \frac{\sqrt{1+0,5\,\Phi}}{1-\Phi}\, e^{\frac{1,25\,\Phi}{1-\Phi}} \tag{5}$$

The fitting of the three models gives very good agreements to the experimental data obtained still reaching the inversion point [1].

In the same order of ideas, Johnsen (2002), measured the viscosity of eight oils form the North Sea as a function of water cut finding; as it was first showed by Benayoune (1998), and increase of viscosity due to rise of water cut and more important, the rise of viscosity appears to be quite insensitive to the oil type [3].

The experimental relative viscosities measured here, also were compared with four published correlations of Mooney (1951), Pal and Rhodes (1989), Rønningsen (1993, 1995) and Pal (2000). They showed good agreement with the experimental data, but the Mooney, the P&R and the Pal correlations were oil-specific and have to be tuned to experimental data for each fluid system. Overall, the correlation of Pal and Rhodes, closely followed by the Mooney correlation, and turned out to be the most accurate one and is recommended if experimental data are available for tuning [3].

The Rønningsen correlation does not require any measured values for tuning. Nevertheless, it provides reasonable estimates of the relative viscosity of water-in-oil dispersions for a wide range of oils and conditions. It provides accuracy around 40%. The Pal (2000) correlation is found to be highly sensitive to the choice of tuning value. For most of the systems studied, the Pal (2000) correlation underestimates the relative viscosity at low and medium water cuts when being tuned to the maximum water cut with stable and non-inverted dispersion. When it is tuned at a lower water cut, it strongly overestimates the relative viscosities at high water cuts [3].

Pajouhandeha (2015) fitted his viscosity measurements to the models described below [1, 4, 16]:

Table 1. Models and correlation for emulsion´s relative viscosity

Type	Author	Model or correlation	
Lineal	Einstein (1906)	$\frac{\mu}{\mu_0}=1+1,25\,\Phi$	(6)
	Taylor (1932)	$\frac{\mu}{\mu_0}=1+\left(\frac{5k+2}{2k+1}\right)\Phi$	(7)
	Yaron and Gal-Or (1972)	$\frac{\mu}{\mu_0}=1+\Phi\Bigg[\frac{5,5(4\Phi+10-\frac{84\Phi^{\frac{2}{3}}}{11}+\left(\frac{4}{k}\right)\left(1-\Phi^{\frac{7}{3}}\right)}{10\left(1-\Phi^{\frac{10}{3}}\right)-25\Phi\left(1-\Phi^{\frac{4}{3}}\right)+\frac{10}{k}(10-\Phi)\Big(1-\Phi^{\frac{7}{3}}}$	(8)
	Choi and Schowalter (1975)	$\frac{\mu}{\mu_0}=1+\Phi\Bigg[\frac{2\left[(5k+2)-3(k-1)\Phi^{\frac{7}{3}}\right]}{4(k+1)-5(5k+2)\Phi+42\Phi^{\frac{5}{3}}-5(5k-2)\Phi^{\frac{7}{3}}+4(k-1)}$	10(9)
Power	Guth and Simha (1936)	$\frac{\mu}{\mu_0}=1+2,5\,\Phi+14,1\,\Phi^2$	(10)
	Eilers (1941)	$\frac{\mu}{\mu_0}=\left(1+\frac{1,25\Phi}{1-k\,\Phi}\right)$	(11)
	Roscoe and Brinkman (1952)	$\frac{\mu}{\mu_0}=(1-\Phi)^{-2,5}$	(12)
	Krieger and Dougherty (1959)	$\frac{\mu}{\mu_0}=\left(1-\frac{\Phi}{\Phi_m}\right)^{-2,5\Phi m}$	(13)
	Phan-Thien and Pham (1997)	$\frac{\mu}{\mu_0}\left(\frac{2\frac{\mu}{\mu_0}+5k}{2+5k}\right)^{1,5}=(1-\Phi)^{-2}$	(14)
	Bicerano et al. (1999)	$\frac{\mu}{\mu_0}=\left(1-\frac{\Phi}{\Phi_m}\right)^{-2}\left[1-0,4\left(\frac{\Phi}{\Phi_m}\right)+0,34\left(\frac{\Phi}{\Phi_m}\right)^{2}\right]$	(15)
	Pal (2000)	$\frac{\mu}{\mu_0}\left(\frac{2\frac{\mu}{\mu_0}+5k}{2+5k}\right)=\left(1-\frac{\Phi}{\Phi_m}\right)^{-2}$	(16)
	Pal (2001)	$\frac{\mu}{\mu_0}\left(\frac{2\frac{\mu}{\mu_0}+5k}{2+5k}\right)=\left(1-\frac{\Phi}{\Phi_m}\right)^{-2\,\Phi_m}$	(17)

Exponential	Mooney (1961)	$\frac{\mu}{\mu_0}=e^{\frac{2,5\,\Phi}{1-k\,\Phi}}$	(18)
	Barnea and Mizrahi (1975)	$\frac{\mu}{\mu_0}c\left(\frac{\frac{2C}{3}+K}{c+K}\right) \quad C=e^{\left(\frac{5\,\Phi}{3(1-\Phi)}\right)\left(\frac{0,4+K}{1+K}\right)}$	(19)
	Pal (2001)	$\frac{\mu}{\mu_0}\left(\frac{2\frac{\mu}{\mu_0}+5k}{2+5k}\right)^{1,5}=e^{\frac{2,5\,\Phi}{1-\frac{\Phi}{\Phi_m}}}$	(20)

Where Φ denotes dispersed phase volume fraction, Φm is the dispersed phase volume fraction at maximum packing concentration. K is a constant parameter between 1,28 and 1,30 in Eilers' equation, and between 1,35 and 1,91 in Mooney's equation. K in (12) is the ratio of dispersed phase viscosity to continuous phase viscosity. In (14) K is a factor that takes into account the presence of adsorbed surfactant on the droplets surface [4, 16].

Among all the models tested, Barnea and Mizrahi's correlation (exponential model) is the worst correlation for emulsion viscosity prediction, while Mooney's correlation (exponential model) has given the best results for these fresh emulsions among the mentioned correlations. The two best models after Mooney´s model are Guth-Simha following of Eilers´ [4].

When the authors talk about emulsion with nanoparticles, the fifteen correlations for the relative viscosity failed to take into account the nanoparticle concentration and the results showed the inaccuracy of these correlations. These models provide acceptable results only for the emulsions without nanoparticles [4].

The Hatschek model takes into accounts the influence of adsorbed films onto each dropletin the dispersed phase.The model has a parameter called hydration factor witch as it was already mentioned accounts for the adsorbed film which increases the effective size of each droplet [7]. See equation (21).

$$\frac{\mu}{\mu_0}=\frac{1}{1-\left(h\,\Phi\right)^{\frac{1}{3}}} \tag{21}$$

The *h* goes from 0,25 to 1,25.

The Hatschek model has been tested in emulsions from the Athabasca region in Alberta with an average error of relative viscosity around ±0,2 for low water cut (0%–25%) and 0,5 for high water cut (25–40%) [7].

Dan (2006), propose an equation that contains the effect of hydration and floc, its form is [16]:

$$\frac{\mu}{\mu_0}=\left(1-k_e\right)^{2,5} \tag{22}$$

Ke can be calculated by the the equation

$$k_e=k_e\left(\Upsilon\right)k_e\left(\Phi\right) \tag{23}$$

Ke(Υ) represents the effect of hydration and floc, and is a function of shear rate. The relationship between Ke(Υ) and shear-rate (Υ) can be determined by the experimental relationship between relative viscosity (μr) and shear rate (Υ) at the highest volume fraction of dispersed phase (Φ).

$$k_e\left(\Phi\right) = a\,\Phi^b \tag{24}$$

In equation (24) and b are factors that can be found by power function curve fitting from two points [16].

Dan model should not be applied for water cut very close to inverse point, because the rigid high dispersed phase fraction will cause some abnormal phenomena such as collision and distortion of the dispersed phase droplets, and that would make the rheological characterization of emulsions more complex [16].

Zhang (2017) in his research titled Viscosity estimation and component identification for an oil-water emulsion with the inversion method used the next equation for the viscosity estimation of an oil water mixture [17, 18].

$$\frac{\mu}{\mu_0} = e^{k\,(1-\varepsilon)} \tag{25}$$

Where ε is the volume content of the continuous phase, dimensionless and k is 2,5. When the emulsion passes from W/O to O/W, Zhang propose the next equation [17]:

$$\frac{\mu}{\mu_0} = \left(1-\Phi\right)^{-2,5}\left(\frac{\mu_d}{\mu_c}\right)^m \tag{26}$$

The index m represents the degree of influence of the dispersed relative emulsion on the apparent viscosity. For light oil emulsions, an m-value of 0,75 is recommended; for heavy oil emulsion, an m-value of 1 is recommended. Mc and μd are the viscosity of the continuous and dispersed phase.

Mukhair (2015) presented a correlation based in the Brinkman model but changing the constant power of Brinkman by a function that incorporates the variation of density and viscosity. The modified correlation can be written including the new factor as follows [23]:

$$\frac{\mu}{\mu_0} = \left(1-h_d\right)^{\frac{\rho_o \mu_o}{\rho_w \mu_w}} \tag{27}$$

Where ρoand ρw are oil and water density. μo and μw are oil and water viscosity. H dis the dispersed phase holdup.

Equation (27) showed fairly good agreement with the experimental data having a mean square error of 27% when it was compared with the present experimental data. However for the same data homogenous model as Pal (2001) and Phan and Pham (1997) have mean square error of 51%.

Piezoviscous coefficient.

The influence of the pressure on the viscosity of crude oils emulsions, also called piezoviscosity, has been widely studied in the literature for monophasic systems. Different rheological models have been proposed to describe this behavior. Most of them take into account the viscosity at atmospheric pressure and a piezoviscous coefficient. Probably the most mentioned one is the empirical Barus model based on the Eyring theory. It assumes that, at a given temperature, the viscosity varies exponentially with pressure, where k is the piezoviscous coefficient (Pa-1), μ0the viscosity (Pa.s) of the fluid at atmospheric pressure and P the pressure (Pa). Barus model is perfectly suitable for the range of pressures encountered in the oil transportation, and also describes accurately the pressure dependence of viscosity and in a large range of temperature [9, 10, 12, 14]:

$$\frac{\mu}{\mu_0} = e^{k\,\Delta P} \tag{28}$$

ΔP is the difference between the measuring pressure and the atmospheric pressure. The experimental results show an exponential increase in viscosity with pressure, and confirm that the Barus model describes accurately the pressure dependence of viscosity and in a large range of temperature [14].

The studies also reveal the unusual temperature dependence observed for the piezoviscosity coefficient. Two domains can be distinguished with an increase or a decrease of k with temperature. In general, it is found that when temperature increases, k decreases. Martin-Alfonso et al (2006) showed that the coefficient for fuel oil decreases when the temperature increases between 10 and 50°C from 5x10-8to 2,25x10-8 Pa-1. However, for temperatures lower than 10°C, their piezoviscous coefficients level off and tend to decrease, they attributed this phenomenon to the solidification of the heaviest components and the resulting microstructural changes. According to Chaudemanche (2009), the non-monotonous variation of the piezoviscosity coefficient with temperature can be related to the viscoelastic properties of the fluid. Actually, the author, assume that the heavy oils behave at low temperature as a solid. When temperature decreases, it gets more and more solid-like and resists much more to the applied pressure. As a result, the coefficient diminishes. At high temperature, we assume that the heavy oil behaves like a liquid with the intrinsic decrease of the piezoviscous coefficient with temperature [12, 13, 14].

The piezoviscous coefficients and viscoelastic properties of a fluid are connected. Actually, the coefficient is an increasing function of temperature for a solid like behavior and a decreasing function of temperature for a liquid-like behavior [14].

By using molecular modelling, it was demonstrated that linear molecules show a lower piezoviscosity coefficient than ramified molecules for the same molecular weight. Linear molecules can move easily compared to ramified molecules. Thus, for linear molecules when a pressure is applied, the structure re-arrangement is facilitated. These observations imply that heavy oil composition might play a major role on the piezoviscosity changes [14].

Equations for predicting emulsion viscosity.

Here there are presented some equations useful to obtain the emulsion viscosity if there is not data of pure oil viscosity and the water cut.

Pal (1998) tried to take into account the effects of shear rate, average droplet size, droplet size distribution, viscosity of continuous phase and viscosity of dispersed phase on the viscosity of emulsions, and proposed a correlation with particle Reynolds number (Rep), volume fraction of dispersed phase, maximum packing concentration of dispersed phase (Φm) and intrinsic viscosity [16].

For concentrated emulsions:

$$\Phi_m^{\frac{1}{2}}\left(1-\mu_r^{\frac{-1}{\eta\Phi_m}}\right)=\left[A_o + A_1 \log_{10}\left(\mathrm{Re}_p\right)\right]+ A_2 \log_{10}\left(\mathrm{Re}_p\right)^2 \tag{29}$$

For low concentrations emulsions:

$$\Phi_m^{\frac{1}{2}}\left(1-\mu_r^{\frac{-1}{\eta}}\right)=\left[A_o+A_1\log_{10}\left(\mathrm{Re}_p\right)\right] \tag{30}$$

Where η is the intrinsic viscosity

$$\eta=2,5\frac{\left(K-0,4\right)}{\left(K+1\right)} \tag{31}$$

K is defined as in equation (15)

Shi (2018) presented a correlation developed by Ronningsen in 1995 based on 110 point of viscosity of a W/O emulsion using different North Sea oil emulsions. This correlation considers the viscosity of the emulsion as a function of temperature and water cut. [18].

$$Ln\left(\frac{\mu}{\mu_0}\right)=a_1+a_2\,T+a_3\,\Phi+a_4\,\Phi\mathrm{T} \tag{32}$$

Where T is temperature and a1, a2, a3, and a4 are empirical coefficients.

Farah (2005) conducted a detailed study on the viscosity of water-in-oil emulsions and presented a model based on temperature and water volume fraction. In Farah´s article, the viscosities of water-in-oil emulsions were measured at atmospheric pressure using a dynamic viscometer at different temperatures and water cut. The following correlation was developed using experimental data mentioned [18, 19].

For a temperature higher than wax appearance temperature

$$\ln\left(\ln\mu+0,7\right)=k_1+k_2\,\Phi+k_3\,\ln\left(T\right)+k_4\,\Phi\ln\left(T\right) \tag{33}$$

For a temperature lower than wax appearance temperature

$$\ln\left(\ln\mu+0,7\right)=k'_1+k'_2\,\Phi+k'_3\,\ln\left(T\right)+k'_4\,\Phi\ln\left(T\right) \tag{34}$$

k1, k2, k3, k4, k´1, k´2, k´3 and k´4 are empirical coefficients.

Azodi (2013) developed an equation for predicting the viscosity of oil–water emulsions, Its form is:

$$\mu=K_1\,\gamma^n\,e^{\left(C_1\,\Phi+\frac{C_2}{T}+C_{3\omega}\right)} \tag{35}$$

K1, n, C1, C2 and C3 are constants and depend on the emulsion kind. ω is the emulsifier concentration, γ is the share rate, T is temperature and Φ is the water cut. The equation (35) was compared with the models of Johnsen and RØnningsen (2003) and Al-Roomi et al (2004) showing a better description of the viscosity data [35].

Al-Roomi et al (2004) presented his correlation for emulsion viscosity prediction based in crudes oil from Kuwait National Petroleum (KNPC). His equation has the form of [44]:

$$\mu=a\gamma^b\left(C\Phi+\frac{d}{T}\right) \tag{36}$$

Where a, b, c and d are constants. T is the temperature (K) and γ is the share rate. The author says that his correlation has high degree of correlation coefficient (98%) indicating the applicability of it to estimate viscosity of oil-in-water emulsion [44].

Wei (2013) Based on the effective medium theory, developed an equation for the emulsion viscosity estimation considering the water fraction (Φ), share rate (γ) and Sauter mean diameter of droplets for the calculation of non-Newtonian factor (kn) and particle Reynolds Number (Nre,p) [45].

$$\left(\frac{\mu}{\mu_0}\right)^{\frac{2}{5}}\left(\frac{\frac{\mu}{\mu_0}+2,5K}{1+2,5\,K}\right)^{\frac{3}{5}}=\left[1-K\left(f_w\right)K\left(N_{re,p}\right)f_w\right]^{-1} \tag{37}$$

Where:

$$N_{re,p}=\frac{\rho_c\,\gamma\,d_{32}{}^2}{4\,\mu_c} \tag{38}$$

The Water fraction factor is:

$$K\left(f_w\right)=\frac{V_o}{V_1}=1+\frac{3\,\Delta\,d_{32}}{d_{32}} \tag{39}$$

Sauter´s mean diameter, µm

$$d_{32}=\frac{\sum_{j=1}^{n}\pi d_j{}^2}{\sum_{j=1}^{n}\frac{1}{6}\pi\,d_j{}^3} \tag{40}$$

Thickness of the absorbed layer at droplet interface is (µm).

$$\Delta d_{32}\approx a_m=\left[\frac{f_{wm}}{f_m}-1\right]d_{32} \tag{41}$$

$$K=\frac{\mu_w}{\mu_o} \tag{42}$$

Non-Newtonian factor

$$K_n=K\left(f_m\gamma d_{32}\right)=K\left(f_w\right)K\left(N_{re,p}\right) \tag{43}$$

The subscript c means continuous phase. Fwm is the maximum packing fraction of the dispersed phase, %, fm real water fraction %. Dj dropletsize (µm).

K(Nre,p), the Particle Reynolds number factor expresses the action counteracting the rise of effective dispersed phase fraction, displaying as the droplet degree of effective dispersed phase fraction when an emulsion is subject to external shear. This factor is mainly affected by shear rate and droplet size distribution. Since oils forming emulsions are different in terms of composition and physical properties, surface active components and their contents, it is recommended that the particle Reynolds number factor is fitted to two experiments at one droplet size but different shear rates. The authors reported that the viscosity predicted by the model is in good agreement with the experimental results, with the maximum relative error of 11% [45].

Inversion Point.

Emulsion phase inversion point (PIP), is the phenomena where by a changing a system property, typically a phase concentration or temperature, causes an abrupt change in emulsion morphology (the dispersed phase becomes the continuous phase and vice versa), in our case corresponds to the water content at which the transition from a water-in-oil (w/o) to an oil-in-water (o/w) emulsion occurs. Emulsion phase inversion is believed to occur because of the complete coalescence of unstable emulsion as they closest packing arrangement condition is approached by addition of the dispersed phase. The PIP corresponds to a critical droplet packing arrangement and typically lies between 50 and 74 vol% of the dispersed phase for monomodal droplets, but can increase up to 85 vol% depending on the droplet size dispersivity [21, 35-56, 61].

Current understanding about this critical point for emulsion phase inversion suggests that it occurs due to some combination of the following mechanisms [21, 36-56, 61]:

1.- Addition of more dispersed phase under shear requires a new dynamic balance between droplet break up and coalescence. The coalescence rate increases more rapidly relative to the break up rate with increasing volume fraction of the dispersed phase. This results in an increase in mean droplet size which diverges to the PIP.

2.- The formation of multiple emulsions prior to phase inversion in the dispersed phase serves to increase the effective droplet phase volume. For example: a w/o emulsion becomes an o/w/o emulsion. Inclusion of smaller continuous phase droplets into the larger dispersed phase droplets increases their effective volume and enhances coalescence.

The dispersed phase addition rate has been reported to have an influence on the PIP value: a slow addition rate of the droplet phase under shear is reported to trigger an early emulsion inversion as a consequence of a high rate of multiple emulsion formation, in contrast to a fast addition rate [21, 36-52, 61].

Rondón (2008) [38] defines the PIP as a phase inversion process in which an emulsion changes its morphology from oil-in-water (O/W) to water-in-oil (W/O) or vice versa, by one of two different paths corresponding to so-called transitional and catastrophic inversions. Generally, catastrophic inversion is produced by the addition of the internal phase by increasing the dispersed phase volume until a critical value is attained at which the dispersed phase droplets are close enough to coalesce upon contact. It can also be induced, although in a lower manner, by the continuous stirring until the swap from water-in-oil to an oil-in-water emulsion (or vice versa) takes place. The inversion takes place through the formation of a multiple morphology, in which the dispersed droplets contain smaller inner droplets of the external phase. The multiple emulsions evolves with the transfer of more external phase as droplets inside the dispersed phase ones; this inclusion increases the dispersed phase volume, whose droplets finally touch one another at some critical value, at which the coalescence happens and the inversion is completed [21, 36-56].

The path of the increment in the mean droplet size when the emulsion conditions approaches to PIP is exponential, but it could be also a lineal path depending of viscosity, interfacial tension and chemistry of continuous phase. As it already known, asphaltenes are generally considered to form a cross-linked, rigid, viscoelastic structure at the oil–water interface and could offer a modification in the path of the emulsion approaching to PIP. Mostly all the emulsions shows a monomodal distribution of droplet diameter while the they get closer to PIP prior to phase inversion point, a bimodal distribution occurs likely indicating a formation of complex W/O/W or O/W/O emulsions [21, 36-52, 61].

During inversion process from W/O the viscosity increases gradually due to dispersed phase inclusion as droplets in the continuous phase leading to a multiple emulsion (W/O/W or O/W/O), in which the droplets of continuous phase contain droplets of the dispersed phase that become somehow inserted inside of them, until an abrupt viscosity fall takes place at moment of the morphology jumps into an O/W emulsion [21, 36-52, 61].

The rise of viscosity when the emulsion approach to PIP could be explained in three stages [37-56]:

1.- In the first one, the emulsion viscosity increases exponentially as the dispersed-phase volume fraction increases, thus corroborating the inclusion of the external continuous phase as droplets inside of the dispersed one.

2.- In the second zone, the emulsion viscosity still increases with the dispersed-phase volume, but with a lower rate of change. The decreasing in the viscosity increases is likely due to the growing probability of a droplets collision coalescence mechanism.

3.- Finally, and just before the inversion point, the observed viscosity reduction indicates that the coalescence takes place and produces a quick gain in dispersed phase connectivity, which is a precursor of inversion.

The increase of oil viscosity has also effects, as the viscosity of continuous phase increases the dispersed-phase mean diameter becomes greater at all times, particularly at the inversion point, which occurs at a much shorter time. With the increase of the dispersed phase viscosity, both, deformation and the breakup of the dispersed phase droplets turn out to be less efficient, under shear flow conditions. A lesser deformation implies an easier droplet interaction enhancing the tendency of coalescence; decreasing the critical dispersed-phase fraction [37-56].

The inversion phenomenon depends on the interactions between the surfactant system and the aqueous and oil phase. It has been shown that an increase in surfactant concentration for low viscosity systems (up to 0,2 cP) favors the multiple emulsions formation. This process contributes to increase the effective dispersed phase to attain a critical packing condition and prompt the inversion phenomena [37-56, 61].

An inversion propagation time is necessary to complete the process, particularly to attain constant viscosity. This inversion propagation time is the period through which the normal morphology propagates through the system, presumably as a result of the fading away of the remnants of the initial multiple morphology [38].

This decrease in the deformability of the droplets is also likely to reduce the formation of multiple morphologies by the reduction the droplet inclusion mechanism by the surfactant molecules at the interphase, as a consequence, the droplet deformation becomes more difficult and this inclusion mechanism fades [37-56, 61].

If the dispersed phase viscosity increases, this lead to a rise of emulsion viscosity when the emulsion get closer to PIP, but this increment more steady than the rise of emulsion viscosity if the continuous phase is more viscous, likely for the formation of an intermediate multiple emulsion with droplets with a pseudo-fibrous structure producing shorter PIP time [37-42].

Pressure drop in W/O emulsions.

In the flow of emulsions an increase in the pressure drop with the water cut and with the superficial velocities is found likely due to emulsion crowding at high dispersed phase volume fraction. However, under the same conditions and with no-Newtonian emulsions, the stronger the non-Newtonian characteristics of fluid, the less friction pressure loss increment. This can be attributed to the reducing of effective and apparent viscosity of the fluids. For instance: in pipeline flow, the density of fluid samples is almost constant while the apparent viscosity of power law fluids is reduced due to the wall shearing action, the more deviation from 1 the value of n, the more obvious the shear thinning behavior (reduction of viscosity with share stress), this result must be taken with care because emulsions may remain Newtonian for a wide range of water cuts, and Non-Newtonian behavior may start at relatively high concentrations of the dispersed phase. [61, 62, 67-75].

The drag reduction phenomenon in pipeline flow of emulsions is likely influenced by the droplet size; droplets larger than the size of turbulent eddies can suppress turbulence, leading to drag reduction. The degree of drag reduction generally increases with the increase in the Reynolds number, especially at high dispersed-phase concentrations when a sharp decrease in the effective viscosity of the emulsion if found when the flow changes from laminar to turbulent [62, 69].

It is interesting to observe that the measured friction factors of stable and unstable emulsions, in laminar region, are in a good agreement with the single phase friction factor given by equation (46) as reported by Santos (2017), Plasencia (2013) and Al-Yaair (2014), Zhang (2016) and Metzner (1955) [57-62, 71, 72].

$$f = \frac{16}{\varphi Re} \tag{44}$$

Where the Reynolds is

$$\mathrm{Re} = \left(\frac{D^n V^{2-n}}{V 8^{n-1} K}\right)\left(\frac{4n}{1+3n}\right)^n \tag{45}$$

ε_0 is the dimensionless unsheared plug radius:

$$\varepsilon_0 = \frac{\tau_0}{\tau_w} = \frac{\tau_0}{\left(\frac{f \rho V^2}{2}\right)} \tag{47}$$

n is the rehogical index.

K is the consistency coefficient

When 0 <n < 1the fluid is pseudoplastic, and when n > 1 the fluid is dilatant. V is lineal velocity ρ is the emulsion density.

In transition region the non-Newtonian data deviates appreciably from equation (44), because of the close resemblance between highly non-Newtonian fluids at low shear rates and the true solids, little eddies of the fluid in turbulent motion should behave more nearly like solid particles being the net effect of this phenomenon a more diffuse transition from laminar to turbulent flow, manifested by a much greater transition region than the 2,000 to 3,300 range of Reynolds numbers found for Newtonian fluids [60-73].

In the turbulent region, the unstable emulsion friction factors fall below the Newtonian curve with a deviation of no more than 20% and above an extension of the laminar relationship. The lower values friction factor obtained from turbulent data indicate that pressure drop is less than the value expected on the basis of laminar viscosity for this likely reasons: The first one is that emulsions exhibited drag reduction behavior in turbulent flow, likely due to coalescence and breakup of droplets of unstable, this dynamic process modifies significantly the turbulence of the carrier fluid. The second one is by viscoelastic effects in emulsions, that can arise due to elasticity of either individual droplets or a microstructure formed between the droplets, in this order of ideas, Zakin (1979) explains that droplets under shear are continually flocculating, deflocculating, deforming, breaking, and reforming these modes of distortion in the dispersed phase, and the possibility of various relaxations modes can enhance the viscoelastic effect. The third reason could be the creation of a viscous sub-layer rich in continuous phase making possible the bulk fluid to slip [61, 62, 68, 69, 70-75].

Dodge (1959) proposed a correlation to predict friction factors on turbulent region for non-Newtonians fluids [68, 69, 72]

$$\sqrt{\frac{1}{f}} = \frac{4}{(n)^{0,75}}\left[\log\log N_{\mathrm{Re}}(f)^{1-\frac{n'}{2}}\right] - \frac{0,4}{(n)^{1,2}} \tag{48}$$

Where NReis the generalized Reynolds number defined by the next equation (45)

The authors reported excellent agreement between predicted and experimental friction factors with flow behavior indexes ranging from 0,36 to 0,73 and generalized Reynolds number from 2900 to 36000 [68, 69, 72-75].

Other equation used for predicting the friction factor in emulsion turbulent flow is [72]:

$$f = \frac{0,0791}{n^5 N_{\mathrm{Re}}{}^{P}} \tag{49}$$

$$P = \frac{2,63}{10^n} \tag{50}$$

Equation (49) reproduces values of friction factor silty lower than the experimental, this discrepancy has been attributed to the viscoelastic effect; as mentioned earlier [68, 69, 72-75].

In the flow of unstable emulsions the presence of a dispersed phase may affect the transition from laminar to turbulent conditions. Furthermore, a high concentration of the dispersed phase may delay the transition up to a Reynolds number of 10000. It is also important to highlight that for unstable emulsions there is a decrease in the emulsion friction factor (f) with decreasing pipe diameter at the same Re number.In this sense, Masalova (2013) reports the effect of wall slip increases in flow through tubes of smaller diameters. Furthermore, the degree of drag reduction increases substantially with the increase in the dispersed-phase concentration. The oil in-water emulsion, obtained after inversion, also exhibit drag reduction (as expected) but to a lesser degree [21, 56-63, 68, 69, 70-75].

The degree of drag reduction in unstable water in oil emulsion is much higher, probably due to different stability characteristics of W/O and O/W emulsions. In the case of the unstable oil in water emulsions, resistance to coalescence can occur due to electrical double-layer effect; the double layer may form due to preferential adsorption of ions in the continuous phase. In the case of unstable water in oil emulsions, the continuous phase is nonpolar and the dispersed droplets tend to flocculate rather rapidly due to the diffuse character of the double layer [61, 62, 67, 70-75].

For the surfactant-stabilized emulsions exhibit relatively little drag reduction. In some cases, the drag reduction activity vanishes completely because added surfactant can diminish dynamic coalescence/breakup process. Therefore, the pipeline flow behavior of the surfactant-stabilized emulsions could be predicted reasonably well using the usual equations of single-phase flow and frictions factors calculated by Blasius equation due to the fact that those kind of emulsions do not present coalescence/breakup process [61, 62, 67, 70-75].

$$f=\frac{0,791}{\mathrm{Re}^{0,25}} \tag{51}$$

Flow through long pipes can enhance emulsion formation, the longer mixing period the smaller mean diameter of the droplets is observed at a given liquid velocity and a given intensity of mixing. Furthermore, by increasing the liquid mixture velocity and the intensity of mixing for a constant distance, the size of the droplets decrease to a maximum stable droplet diameter formed before a length of 600 times the internal pipe diameter [74].

There is a critical superficial water velocity in the order around of 0,6 m/s which is required for the onset of emulsification and the formation of unstable oil-water emulsions [74].

In the flow emulsions through long pipes phase inversion is observed in the flow regime of layers of oil-in-water and water-in-oil dispersion indicating that phase inversion takes place within the dispersion layer and only in a restricted part of the cross-sectional area of the pipe [74].

It is recommended that in the case of a lack of knowledge of the behavior of emulsions that the pressure drop should be approximated to the pressure drop of the water phase in the case of oil-in-water emulsions and by the pressure drop of the oil phase in the case of water-in-oil emulsions [74].

Wall Slip Phenomena.

The origin of wall slip can be described by the existence of one lubricating layers located near the walls and composed of continuous phase dragged from the bulk emulsion, this means that most of the deformation occurs near the confining walls whereas the bulk of the material behaves more or less like a solid body or exhibits negligible deformation. In others word, there is a lack of adhesion between the material and the shearing surface because the overall deformation is localize in a low-viscosity lubricating layer (depletion layer) [74-92].

Cloitre (2017) and Chin (2018) explain the wall slip as: In the absence of flow, the soft particles are pressed against the wall by the osmotic pressure of the bulk suspension. Due to the proximity of the particle and the wall, the particles are sensitive to various short-range forces such as dispersive forces, steric hindrance, electrostatic contributions, and hydrophobic-hydrophilic forces, and below the yield stress, there are no large-scale rearrangements, and in first approximation the particles are locked in their position and do not rotate. When a particle slides along the wall during flow, a thin layer of the solvent is created between the particle and the wall allowing the concentrated dispersions to slip [74-89].

Some authors describes the wall slip as a liquid layer separating soft suspended objects from the wall, that are maintained by the balance between the lubrication flow in the slip layer, which creates a lifting force that pushes the suspended particles away from the solid surface. Although the elastic force induced by particle deformation and related to the osmotic pressure in the concentrated system tends to reduce the slip layer thickness [74-92].

Depletion layer arises from steric, hydrodynamic, viscoelastic and chemical forces and constraints acting on the disperse phase immediately adjacent to the walls. The enrichment of the boundary near the wall with the continuous (and usually low-viscosity) phase means that any flow of the fluid over the boundary is easier because of the lubrication effect, this leads to an apparent decrease in the measured bulk viscosity. In the case of emulsions the deformability of the droplets and creaming enhance this effect. This is usually confined to a very narrow layer-with typical thickness of 0,1 - 10µm [74-92].

In emulsions, migration of the droplets away from the walls could be due to the deformability of them, repulsive and attractive forces and osmotic pressure witch can occur even if no transverse gradient of shear rates is present. Consequently, a thin depletion layer can be formed, which gives rise to slippage when the sample is sheared [74-92].

Wall depletion phenomena are generally confined to a certain range of shear rates associated with constant values of shear stress or, in other words, around a critical stress at which a sudden drop in viscosity takes place. As some of the authors have previously pointed out the shear rate (or stress) range in which wall slip phenomena appear coincides with the region where the applied shear produces a continuous deflocculation of droplets. This deflocculation process, at least in concentrated emulsions, is associated with a dramatic decrease in viscosity in a short range of applied stresses [74-92].

Slip manifests itself in way that viscosity measured in different size geometries gives different answers if it is calculated by the normal way. In particular, the apparent viscosity decreases with decrease in geometry (size tube radius). Large particles of the disperse one and a large dependence of viscosity with the concentration of the dispersed phase are the circumstances which can give slip, especially if coupled with smooth walls and small flow dimensions. The effect is usually greatest at low speeds/flow rates and when the particles carry electrostatic charges and the continuous phase is electrically conductive. Walls themselves can repel adjacent particles because of various physicochemical forces arising between the particles and the walls [74-92].

The formation of the depletion layer is mainly controlled by the volume fraction of the system coupled to the particle size of the dispersed phase; this means that as the volume fraction continuous phase increases droplet-wall repulsions dominate. However, as the amount of dispersed phase, and therefore, the number of droplets, present in the sample increases, the repulsion between the droplets due to packing restrictions starts to dominate over the droplet-wall repulsion ensuring that the depletion layer thickness decreases up to a maximum volume fraction where the formation of a depletion layer is no longer possible[74-92].

Two-phase dispersed systems often show slip effects under steady-flow conditions or even during oscillatory measurements. Slip takes place because of the displacement of the disperse phase away from solid boundaries. In the case of emulsions this effect is even more dramatic due to the deformability of the droplets and by creaming. Thus, slip is often more pronounced when an emulsion is formed by large droplets, or when it is weakly flocculated and the flocs behave as individual large droplets under the action of gravity [74-92].

Slip is usually more significant at low shear rates. It has been shown that emulsions show a low-shear rate-limiting viscosity and above a critical shear-rate/shear-stress a large decrease in viscosity is noticed. Normally the flow of an emulsion shows very high viscosity in the Newtonian region at low shear stresses and then a shear-thinning region characterized by a drop in the viscosity. This flow behavior is related to a dramatic structural breakdown and rearrangement induced by shear stress viscosity [74-92].

The most important factor to be considered in relation to wall slip is the emulsion composition, probably the existence of different interparticle interactions influence emulsion lubricating layer formation. For instance, a very structured continuous phase (gel-like) seems to reduce or damp the wall slip phenomena, but in the wall slip regime, this phenomenon seems to be independent of the dispersed phase concentration, but strongly dependent of surface characteristics and chemistry. As a general rule, wall slip decreases with the rise in the dispersed phase concentration because more collisions between particles and between particles and wall take place, which results in the increases of frictional force [74-92].

Wall slip increases as the particle size increases. This is because it is harder for particles with a larger size to fill the space around the solid boundary, leading to the formation of thicker slip layer and causing the rise of slip velocity. This means, the larger the particle size, the thicker the slip layer, the higher the wall slip velocity [74-92].

Temperature or thermal effects near walls can, in principle, result in what looks like slip, because heat generation in very viscous materials due to high shear rate is near the wall of pipes, would lead to a decrease in viscosity; however, if the heat transfer in the wall is good enough, the effect is mitigated. Said in others words, the reduction in viscosity makes it is easier for the particles to slip and move away from the wall. In the same orders of ideas, the viscosity is one of the major factors affecting the wall slip. As the viscosity increases, it will be more difficult for the particles in the suspension to slip near the wall [74-92].

Gravity also modifies wall slip because it pushes the particles against the wall modifying the surface roughness. Gas cushions on the solid interface may appear under the influence of thermal fluctuations near a solid wall or due to the release of a gas dissolved in a fluid also promotes wall slip. It is well established that large particles or flocs, the appearance of creaming enhance slip effects [74-92].

It is known that the amount of slip clearly decreases as the emulsifier concentration increase. In addition to this, a higher agitation speed imposed during emulsification reduces wall slip, for instance; when a very low value of droplet diameter is obtained, wall depletion is practically eliminated, due to the stronger interparticle interactions which enhance the formation of a structural network and its stability against creaming. However, it was also noticed that emulsions with similar droplet diameter but different composition might show very different values of wall slip because the magnitude of the interdroplet interactions [74-92].

Wall slip and it is highly dependent on the properties of surfaces. Depending on their chemical nature, shearing surfaces can be made either attractive or repulsive with respect to the particles of the dispersion. Surfaces which are totally wetted by the continuous phase are responsible for the formation of a continuous lubricating film: the particles of the dispersed phase are depleted from the wall which is in favor of wall slip. On the opposite, if the surface is wetted by dispersed phase particles, they tend to stick on it contributing to create some artificial roughness and delay the slip [74-92].

If a continuous-rich layer establishes near the wall, and covers the rough surface of the pipe, the roughness of the surface may not play a significant role. However, if the liquid-rich layer is not thick enough to cover the surface roughness, slip may take place [74-92].

Wall slip velocity consistently increases with increasing the wall shear stress and, at a constant wall shear stress; it increases with decreasing pipe diameter. As the diameter of the pipes decreases, the surface area to volume ratio increases, implying that smaller channels have a relatively larger interfacial area, making them more pronounced to the slippage [74-92].

Wall slip velocities are less sensitive to changes in pipe size, at low values of the shear stress; but when the shear stress increases, wall slip velocities are more sensitive [74-92].

Flow of emulsions through packed beds.

The issues related to emulsion transport in porous media can be found in many industrial processes, and understanding the phenomena occurring during the flow of emulsion through porous deposit has a significant importance in engineering [93-110, 112].

During the O/W emulsion flow in porous structure, it is important to determine whether the dispersed system can be treated as homogenous fluid or not. If the dispersed phase droplets are small enough, compared to the flow channels, it is possible to state that the fluid is a homogenous medium with complex a rheology. However, in most practical cases, the dispersed phase droplets are significantly bigger than pores, which mean that their presence cannot be neglected, in this case it is necessary to consider how other emulsion properties such as droplets sizes influences the flow [96-99, 101, 102, 110-114].

During the emulsion flow through porous media, a reduction in the permeability can be observed. In the case where the pore radius is similar or greater than the particle radius, the droplet can flow periodically varying diameter due to pore configuration, but some of them entering the pore deform significantly and generate a lower radius in the front than the radius of the droplet back, If the actual pressure difference along the pore is lower than the flow pressure, the droplet is trapped within the pore, if the drag forces produced by the continuous phase fluid flow, become large enough to overcome the capillary pressure threshold the droplet trapped in the pore will flow,This critical velocity is a function of surface properties such as adhesion or zeta potential value of the system and the droplet size to pore size ratio. Large flow velocities can result in droplet breakup, if the capillarynumber is equal or exceeds unity.[96-99, 101, 102, 110-114].

Equation (52) can be used to determinate the pressure necessary to push a dispersed phase droplet through the pore. If Actual pressure differential across the pore is less than that predicted by equation (52), the emulsion droplet plugs the pore throat. If it higher the dispersed phase droplet undergoes distortions to pass through the pore constriction [96-99, 101, 102, 110].

$$\Delta P = 2\sigma\left[\frac{1}{r_1} - \frac{1}{r_2}\right] \tag{52}$$

Where:

σ: Superficial tension

r1: Pore radii

r2: Droplet radii

In emulsions with droplets with sizes smaller than the pores, the particles can flow easily through the structure, but can also be captured in porous bed or pockets due to its interception to porous walls, which is related to the acting of Van der Waals and hydrodynamic forces, reducing the permeability. Physicochemical attachment and detachment of the dispersed phase can be attributed to small scale heterogeneities of the pore-surface dispersed-phase properties. In particular, surface charge heterogeneities on both the dispersed and solid phases play a fundamental role in the dispersed phase transportation [96-99, 101, 102, 110-114].

Another parameter, which essentially affects the emulsion flow through porous media, is the concentration of dispersed phase. This factor strongly influences the fluid rheological properties. When emulsion phases are Newtonian, they still show non-Newtonian behavior, presenting a rapid rise in the apparent viscosity for the elastic instability. It is normally assumed that, the higherthe concentration is, the longer the flow time through the porous medium [93, 98, 111].

The elastic instability is associated with the formation of apparent stagnation zones (dead zones) around stagnation points, and the latter is linked to the instability of dead zones and their violent disintegration into small eddies, but the rise in emulsion viscosity caused by the flocculation of droplets counteracts elastic flow instability [93, 98].

During the emulsion flow through porous media it was also observed that, at the beginning of the process, the concentration of emulsion that flows out from the porous bed is lower than the concentration of emulsion injected into the porous structure. However, during the process, the concentration of emulsion leaving the bed increases, and finally reaches the value similar to the concentration of emulsion entering the porous medium; this shows that droplets in the dispersed phase are temporarily trapped and then released after some time (sticky time). This phenomenon is caused by the "straining" mechanism, in which the dispersed phase is retained inside the porous bed and only the continuous phase flows. When small pores are blocked by dispersed phase droplets, it leads to a situation when flow occurs only through the main large paths. In such pores emulsion is not captured and its structure does not change, which explains the invariable concentration of dispersed phase after some time [96-98, 100, 101, 112].

The structure of emulsion changes, during its flow through porous structure. It has been observed that, at the beginning of the flow, the droplets leaving the porous bed are smaller than the ones that are initially injected; however, during the process their size changed and bigger onesare presented in outflow. Finally the droplets size distribution is similar to the droplets size distribution in emulsion entering the bed. This change is less noticeable in the case of lower concentrated emulsions. In case of high concentrated emulsions, the amount of bigger droplets is so significant that all available spaces are filled instantly, which results in the situation where only the slight changes in diameters can be observed. Big droplets, during flow through the structure of the bed, are not only stopped, but also sometimes being ripped into smaller ones [96-98, 102, 112].

The pressure fluctuations seem in the emulsion flow through porous media can be explained as: with the passage of a single large droplet through the capillary throat. As the tip of the droplet passes through the smallest diameter section, pressure reaches a local maximum value and then it drops as the front of the droplet moves into the diverging portion of the constriction. A new pressure rise occurs whenever a large droplet starts to protrude the capillary throat [101, 102, 112].

Pores media wettability plays an important role in the flow of emulsions in porous media. If the structure is wetted by the continuous phase, it will capture some amount of carrier leading to a purer flow of dispersed phase. A medium wetted by the dispersed phase will plug the porous structure by the hindrance effect, enhancing the formation of free droplets phase [110].

Most workers have used the definition of Reynolds (Re´) proposed by Ergun (1953) of friction factor for the flow of Newtonian liquids through packed bed modified by Kemblowski and Michniewicz (1979) for non-Newtonian liquids, and presented by Chhabra (1991) [103-107]. The Re´ is described as follows.

$$\mathrm{Re}' = \frac{\rho V_o^{2-n} Dp^n}{K\left(1-\epsilon\right)^n}\left(\frac{4n}{3n-1}\right)^n\left(\frac{15\sqrt{2}}{3\epsilon^3}\right)^{1-n} \tag{53}$$

Where:

Dp is volume equivalent diameter,

Vo is superficial liquid velocity,

n is power law flow behavior index

K is power law consistency coefficient (0,02 up to 1,3)

Є is the porosity

Ergun have shown that equation (53) it is applicable to determinate the friction factor for the flow of non-Newtonian liquids through packed for Re´ between 0,0016 and 2,5 and n between 0,4 and 0,7 [103-107].

$$f = \frac{150}{\mathrm{Re}'} + 1,75 \tag{54}$$

Here is important to mention that considerable confusion exists in the literature regarding the numerical constants appearing in equation (53), especially the value of 150. Indeed, the values ranging from 115 to 180 have been suggested in the literature, for beds of uniform size spherical particles. Even wider variations in the values of constants in equation (53) have been observed for beds of non-spherical particles. This correlation predicts results of pressure drop measurements with an average error of 13% for Re´ form 0,001 up to 100 [103-110].

Some evidence suggests strongly that emulsions can be produced in the porous media. Emulsions could be formed within the pore-throat structure where the velocity gradients or shear rates are very high because the disruptions of the bulk interface between the two liquids, leading to the initial formation of the dispersed phase. Interfacial tension and viscosity ratio of the immiscible liquids play a dominant role in the emulsification of these liquids in porous media [110, 111, 112, 113].

Conclusions

The most important factor of influence in the behavior of oil/water emulsion is the temperature for all de changes produced when and emulsion is submitted to it property, among them, the reduction of continuous phase viscosity followed by the emulsion viscosity and the rise in the Brownian motion of molecules leading to a destabilization of the dispersed phase, enhancing the elimination of surfactants layers making easier the coalescence of droplets into bigger ones, ending in the two phase separation.

Surfactant concentration added or not, play according to our knowledge, the second of the more important factors influencing the emulsion behavior; because the morphological changes that a surfactant can make; like reducing the mean droplet diameter distribution, stabilize the droplets with a protecting layer preventing them to coalesce with others droplets; in some cases, if the emulsion is well stabilized, the emulsion can behave as a homogenous fluid. The surfactant can make possible solvation and aggregation phenomena, leading to deep changes in the emulsion microstructure.

A series equation for correcting oil phase viscosity as a function of water cut (Ø) and other variables as a temperature are presented in this small review, but due to the fact that most of them have parameters that must be determined from experimental data, the usage of each one of the equation should pass through a previous stage of validation with experimental data. Precaution must be taken if one of these equations would be used without this validation stage.

PIP or phase inversion point, is triggered by a series of morphological changes in the emulsion for the share rate, adding of dispersed phase or other mechanism that aids the coalescence of dispersed phase and the formation of multiple emulsions (O/W/O or W/O/W) still the inversion is complete.

The transition from laminar flow to turbulent flow in emulsions is delayed up to Reynolds numbers above 10000 for the viscoelastic effects. Unstable emulsions in pipes or channels, usually shows a drag reduction due to wall slip, coalescence and breakup of droplets or by viscoelastic effects in the emulsion in the turbulent region. When the emulsions are stables, the mechanisms of drag reduction vanish.

Wall slip phenomena occurs in the flow of emulsions basically for the appearance of a less viscous layer made of mostly continuous phase, created by a series of short-range forces and is triggered after a critical stress associated with a continuous deflocculation of droplets.

The flow of emulsions in packed beds is highly influenced by the droplets diameter distribution, this parameter determines if the fluid should be treated as a homogenous or as dispersion. Droplets bigger than the pore throat will plug it reducing the permeability, droplets smaller than the pore throat could pass free through the pore. A variety of interaction pore wall/droplet can be found, and they can be responsible for the reduction in the flow through the porous structure. Instead of all written above, the flow of emulsion in porous media is a very complex task because all the chemical interactions and the emulsion rheological performance.

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