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Contribution to the study of the combined effects of aqueous solution containing surfactants and biopolymers on some physical and rheological parameters

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ABSTRACT

The study of interactions between micellar systems in the presence of additives (polymer electrolyte) has attracted great scientific interest because of the many practical applications in the food, pharmaceutical, cosmetic, and petroleum industries, especially in enhanced oil recovery. In the latter case, the oil droplets are trapped in porous media and can be moved only under the combined effect of viscous and interfacial forces. This is an aim that can only be achieved with mixed polymer/surfactant systems mixed with other additives. Moreover, in other industries, the formulation of stable emulsions tends increasingly to the use of polymers having significant surface properties alone or mixed with surfactants that provide a medium viscosity and stability to the system. This work is a contribution to the study of the interactions and the effect of these latest on the physicochemical and rheological properties of systems containing soluble biopolymers: Arabic gum, cetomacrogol 1000 and starch, an anionic surfactant, sodium dodecylbenzene sulfonate (LABSNa), and olive oil.

Keywords: Interaction; Surfactant; Biopolymer; Micellar system

1. Introduction

The study of the combined effects of micellar systems with a polymer and an electrolyte has been the subject of several studies for several years because of applications that can be made in several areas: agro food, cosmetic, pharmaceutical, and in oil industry, including enhanced oil recovery (EOR) [1–5]. Indeed, in some practical situations, mixtures of surfactants/polymers/electrolyte solutions are combinations of different types of polymers, surfactants, and electrolytes.

In general, the combination of a low-molecular weight surfactant is used with one or more polymers, which can be surfactants or not. Research on the combined effects and interactions between polymers and surfactants can be done in two ways. In the first case, the polymer is considered to be influenced by the

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surfactant nature. In the second case, the surfactant is considered to be influenced by the polymer substance. In the first case, the surfactant is adsorbed onto the polymer locations, which prevent the formation of micelles. In the second case, the association of the surfactant molecules with macromolecules facilitates the phenomenon of micellization [6].

There are several types of intermolecular interactions, which influence the physicochemical and rheological properties of aqueous solutions, among which are electrodynamic interactions involving the attractions between atoms. They are also called Lifshitz-Van Der Waals forces [7]. The interaction between a dipole and a permanent other permanent dipole (or forces orientation) was described by Keesom. Interactions between a permanent dipole and an induced dipole (or induction forces) were described by Debye. Polar interactions are also cited: polar and Coulomb interactions. One of the surfactant characteristics is its tendency to reduce the surface tension between two immiscible fluids. In particular, ionic surfactants, this property is modified by the presence of a polymer in solution, this last has also an effect on the critical micelle concentration (CMC). For low concentrations of surfactant, it may be that there is no influence of the surface activity of the polymer on the lowering of the surface tension [8]. A study of polyethylene glycol (PEG modified) and sodium dodecyl sulfate (SDS), the formation of spherical micelles having the same size for concentrations above the CMC [9]. Research activities in the field of interactions between polymer, surfactant, and electrolyte are classified according to the nature of the surfactant and polymer in several types [10]. There are: the ion/polymer interactions ionic surfactant (nonionic)/ electrolyte and following the surfactant concentration, the mixtures were ranked by the value of the CMC in three cases: surfactants complex polymers before, at and above the CMC [11]. The rheological properties are important in study of the combined effects polymer/ surfactant/electrolyte/oil. In fact, the determination of these lasts is used to identify the system. The polymers are used in systems to increase the viscosity of the solutions, for this reason, they are known as thickening agents. It is therefore important to determine the influence of the polymer and the surfactant concentrations in mixtures by measuring the rheological parameters. The rheological study should provide a better understanding of the relationships between the properties of a material and its structure, and to deal with practical situations implementing this type of fluid [12]. The polymer/surfactant systems have numerous industrial applications. In the field agribusiness, e.g. certain food emulsions (such as canned sauces), a low shelf life is often sufficient, while others (such as creams liqueurs) should remain stable for several years. Therefore, a food emulsion is stable if the number and organization of droplets change only slowly and over time imperceptible [13]. In food industry, several additives are recommended, to make a stable food colloid, among them the polymers are the most important. In the pharmaceutical field, the active ingredient must be in usable form, applicable or manageable, this format is particularly important for applied products to the skin and mucous membranes. Formulators have raw materials more efficient for the production of forms adapted to strictly pharmacological parameters of the active ingredient, i.e. allowing it to perform its role in the best conditions. This shaping will therefore depend on the nature and composition of the transporter [14]. Among the forms or pharmaceutical systems, emulsions, microemulsions, multiple emulsions, and vesicular systems (liposomes) occupy a prominent place in their innovative performance. These systems are proving to be rich potentialities: chronoliberation, protection of sensitive and fragile molecules. The combined effects of surfactant/polymer such systems may increase their stability and/or improve its rheological characteristics, but the viscosity imparted is accompanied by a slowdown in the rate of diffusion of the active ingredient in the vehicle [15]. For microemulsions, it is possible to modify their viscosities, while maintaining their rheological characteristics by gelation. For example, in the case of microemulsion/water, silicon oxide can be used as gelling, but in microemulsions/oil/water, the xanthan gum and carbopol can be used. This moderate increase in viscosity may allow better skin application, but will change the penetration options microemulsions. In oil area, it is well known that the primary recovery phase during which allowed the oil flow, taking advantage of the only natural energy field only produces 5–15% of oil present in the deposit. The need to increase performance has imposed the development of new operating methods called "EOR" [16–18]. Viscosity, temperature, pressure, and speed are the specific characteristics of the deposit. Among thermal, mechanical, and chemical processes used in EOR, chemical means can significantly improve the recovery efficiency. The most additives used in these processes are surfactants, polymers, and alkali [19]. Typically, in EOR, water is used with soluble high-molecular weight polymers, such as polyacrylamides and polysaccharides that significantly increase the viscosity in the reservoir and allowing drainage of the mobility control solution of the solution, which seeks to pass through the more permeable zones of the reservoir [20]. The surfactant/alkali/polymer systems can complete successfully the two conditions necessary to increase the recovery efficiency with minimal expenditure, these conditions are: a low-interfacial tension between water and crude oil and mobility. The injected solution should be greater than that of the crude. The use of surfactant combined with alkali in the presence of polymers has attracted great importance in several countries, including the USA and China. The surfactant/polymer/electrolyte/oil system has a synergistic effect resulting from the combined effects of these three compounds on the content of the deposit. This effect allows achieving an ultralow interfacial tension water/oil and controls the mobility of the injected solutions. This has resulted in an increase in production efficiency with minimum cost of chemicals products [21]. Thus, polymer/surfactant interactions, represents an important role in improving and interfacial rheological properties of systems. The interfacial tension of mixture containing alkaline and polymer depend so highly of these two compounds concentrations. However, the polymer added to increase the viscosity of polymer/surfactant/alkaline weakly affect the value of the interfacial tension system [22].

2. Experimental

2.1. Products

In this study, the anionic surfactant used is the sodium dodecylbenzene sulfonate (LABSNa) [23–26]. It comes from Fluka, its chemical formula is:

$C_{12}H_{25}(C_6H_4)\ SO_3Na$, and its purity is 90%.

The polymers used are: starch, Arabic gum, and cetomacrogol. Starch is a polysaccharide of crude formula $(C_6H_{10}O_5)_n$, is from Fluka, cetomacrogol 1000 is of the PEG family of formula $H(OCH_2CH_2)n$ of molecular weight (950-1,055) purchased from Panreac; and Arabic gum is a polysaccharide of molecular weight 240,000 from Fluka. The oil used is from algeria olive oil (IFRI) with density: $0.88\ g\ L^{-1}$, its composition is estimated on average that it has 14% saturated fatty acids, 11% unsaturated and poly 60-80% oleic acid. Moreover it contains polyphenols, vitamin E flavonoids, provitamin A, minerals and micro-elements.

2.2. Material

The conductivity measurements were performed using a conductivity meter LF 191 of the German company WTW kind. The range of measurement of the electrical conductivity is between 1 and 999 $mSiemans\ cm^{-1}$.

The viscosity of the solutions was measured using a Haake viscosimetric type VT5R (Germany) rotating at mobile to measure the viscosity of Newtonian and non-Newtonian liquids. It consists of a cylinder driven by a motor rotation speed to be switched by means of a calibrated spring. The range of viscosity and shear rate is from 0.3 to $200\ s^{-1}$.

2.3. Preparation of mixtures

Solutions of surfactant (LABSNa) are prepared at concentrations under, at and above the CMC. The CMC, the value of this last is $0.523\ g\ L^{-1}$. These concentrations are chosen in the main to cover a wide range of concentrations. For polymers, concentrations were chosen based on previous studies [8,10,23–25].

3. Results and discussions

3.1. Conductivimetric study

In order to study the combined effects between polymers and surfactants in mixtures, we performed measurements of conductivity for evaluating the electrostatic interactions, particularly, when these substances are (ionic surfactant, charged polymer, and electrolyte). This method was used by Goddard [8] to study the effect of salt on the interaction between poly (ethylene oxide), by Nedjhioui et al. [23–25] to study the influence of interactions of hydroxypropyl methylcellulose and SDS, and the interaction between polymers (xanthan gum, and surfactants (SDS and LABSNa)), by Moulai-Mostefa et al. [25] to study the interactions between PEG, carboxymethyl cellulose, and two surfactants: SDS and polysorbate 20 (tween 20), by Minatti and Zanette [27] to determine the critical aggregation concentrations (CACs) and the saturation point of the polymer in SDS/Poly(ethylene glycol) system, by Hou et al. [28] and finally by Sovilj and Petrovic [29] to study the interaction of polyethylene oxide and the sodium dodecyl sulfonate.

3.1.1. LABSNa/starch system

The conductivity of solution is the contribution of the total conductivity of each free ion. According to this assumption, the total specific conductivity of a solution containing sodium K^{+}_{Na} (in the LABSNa $(C_{18}H_{24}SO_3Na)$); ions dodecyl sulfonate ions $C_{18}H_{24}SO_3^-$ (DBS^-), $K_{\mathrm{DBS}}{}^-$; and the contribution of the conductivity of the polymer (Starch): (K_{ST}), since the latter is a charged polyelectrolyte, is given by Eq. (1):

$$K = K^{+}_{\mathrm{Na}} + K^{-}_{\mathrm{DBS}} + K_{\mathrm{ST}} \qquad (1)$$

For this system, the specific conductivity presents, for the concentrations domain of LABSNa and starch considered, two break points (Fig. 1). In the presence of

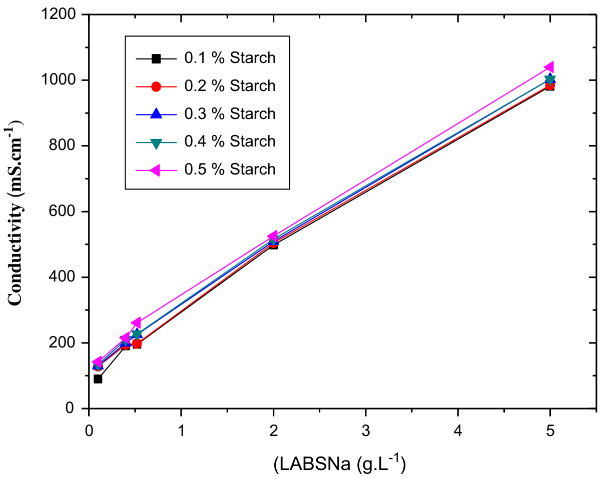

Fig. 1. Effect of starch concentration on the conductivity.

surfactant alone [23], the behavior of the conductivity is also characteristic of this later, it rapidly rises to the "CMC" of LABSNa (first break point) in the vicinity of 0.523 g L^{-1}. In the presence of polymer, Fig. 1 shows that the values of the conductivity of the solution are above that of the surfactant alone. In this case also, it appears that increasing the ionic strength of the solution due to the polymer in addition to surfactant-loaded influenced conductivity. The change in slopes of the curves after the first break point, the CAC explains the beginning of the association of molecules and starch LABSNa adjacent the surfactant concentration of 2 g L^{-1}. There is then a change of slope of the conductivity as a function of the concentration. From this point, it is considered that the molecules of the surfactant adsorbed on the polymer chains, and the conductivity increases slightly with increased concentrations of surfactant until at saturation point or polymer (PSP).

3.1.2. LABSNa/cetomacrogol system

The cetomacrogol being also a charged polymer, its contribution in terms of conductivity is not negligible and calculating the conductivity of the solution can be determined in the same manner as the preceding cases i.e. assuming that it is the sum of contributions to the total conductivity of the free ions. The overall specific conductivity can be determined taking into account the contribution of the conductivity of the polymer (cetomacrogol): (K_{CETOM}), since the latter is a charged polyelectrolyte. This conductivity is then given by:

$$K = K^{+}_{\text{Na}} + K^{-}_{\text{DBS}} + \kappa_{\text{CETOM}} \qquad (2)$$

For this system, the specific conductivity presents, for areas of LABSNa and cetomacrogol concentrations considered, two break points (Fig. 2). The first point is located near the CMC: 0.523 g L^{-1}, in the presence of the surfactant alone, the behavior of the conductivity is also characteristic of this later; it increases rapidly under the CMC LABSNa (first break point). In the presence of polymer, changing slopes of the curves after the first break point, the CAC explains the beginning of the association of molecules LABSNa and Cetomacrogol (second break point).

3.1.3. LABSNa/Arabic gum system

Arabic gum contributes also in the solution in terms of conductivity. The determination of the conductivity can be given by assuming that it is the sum of contributions of the total conductivity of each free ion. The values can be determined taking into account the contribution of the conductivity of the polymer (Arabic gum: GA) (K_{GA}). This conductivity is then given by:

$$K = K^{+}_{\text{Na}} + K^{-}_{\text{DBS}} + K_{\text{GA}} \qquad (3)$$

For this system, the specific conductivity presents, for areas of LABSNa concentrations and Arabic gum has two break points (Fig. 3), the first point is located in the vicinity of the CMC that is to say 0.523 g L^{-1}. In the case of Arabic gum, the break points are less visible than in the two previous cases and we see that all the curves have the same paces.

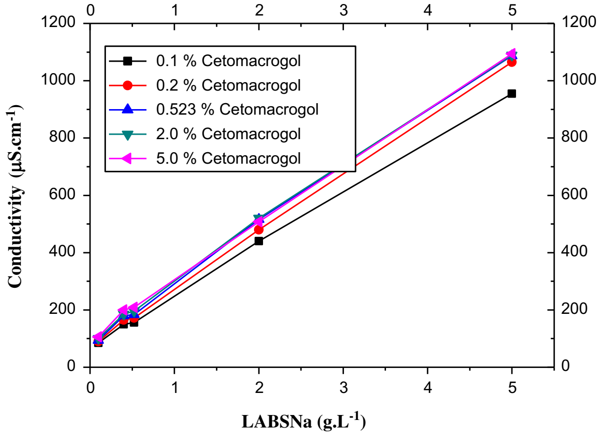

Fig. 2. Effect of cetomacrogol concentration on the conductivity.

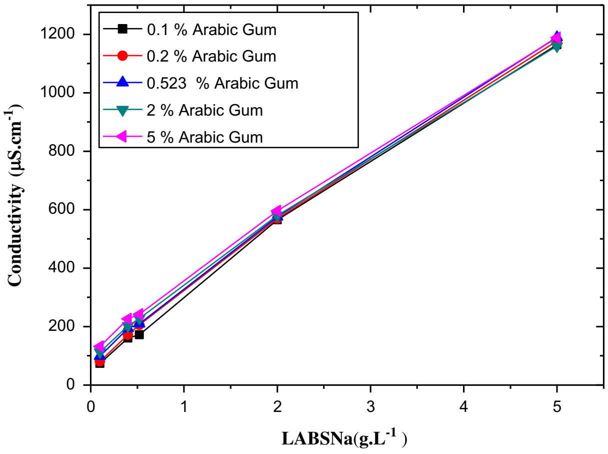

Fig. 3. Effect of Arabic gum concentration on the conductivity.

3.2. Viscometric study

The polymers are usually used in various applications to increase the viscosity of the solutions, for this reason, they are known as thickening agents. In order to determine the influence of the surfactants on polymers in aqueous solutions, we measured the viscosity of the last depending on the polymer concentrations. The determination of the rheological properties of aqueous solutions containing a polymer, a surfactant, and an oil system is used to identify and classify them according to its use in formulations, in this part of the work; we focused on the characterization of a viscometric study of polymer/surfactant/oil mixtures.

3.2.1. SDBS/starch/oil system

Fig. 4 shows the variation of the viscosity versus shear rate of system containing polymer, surfactant, and oil. When the shear rate is minimum (30 rpm s^{-1}), the viscosity of the solution containing the starch is maximum for all concentrations. Increasing the speed causes a decrease in the viscosity of a rapid manner to the speed value (50 rpm s^{-1}), beyond this value, the viscosity remains substantially constant until it reaches its minimum value corresponding to speed (200 rpm s^{-1}).

During the flow of a fluid, the apparent viscosity of the fluid gradually decreases as the shear rate increases. The curves in Fig. 4 have the same speed and decrease with increase in polymer concentration. The decrease in viscosity with increasing shear rate is normal because this last cause the dispersion of the molecules of the compounds present in the solution may result in the decrease of the viscosity.

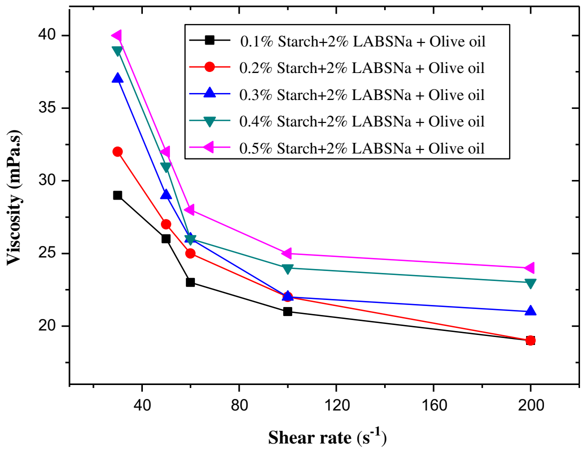

Fig. 4 Effect of starch concentration on the viscosity.

3.2.2. LABSNa/cetomacrogol system

Fig. 5 shows the variation of the viscosity versus shear rate of a system containing cetomacrogol, surfactant, and oil.

The interpretation of these curves shows that for the same speed (30 rpm s^{-1}) as in Fig. 3, the viscosity of the solution containing cetomacrogol, show maximum values for all concentrations of the polymer. In this case also, an increase in the shear rate results in a rapid decrease in viscosity. Above a value of 50 rpm s^{-1}, the viscosity is not too much influenced by the increase of the shear rate.

3.2.3. LABSNa/Arabic gum system

Fig. 6 is another representation of the curves of the viscosity versus shear rate of a system containing the

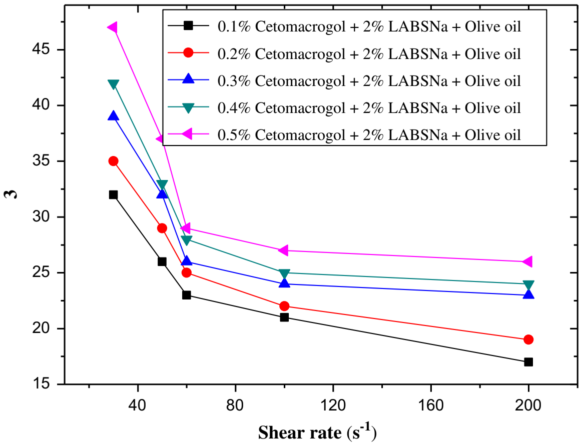

Fig. 5. Effect of cetomacrogol concentration on the viscosity.

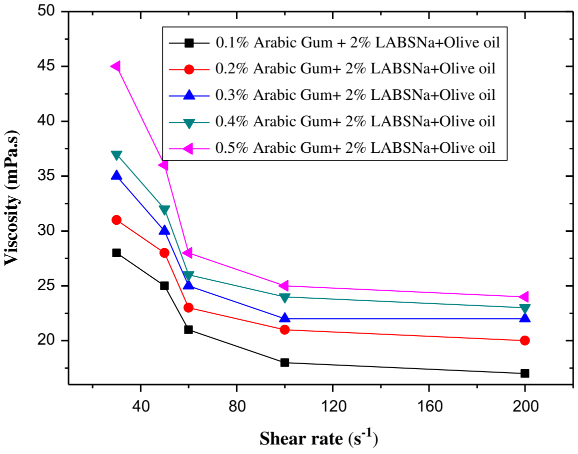

Fig. 6. Effect of Arabic gum concentration on the viscosity.

Arabic gum, LABSNa, and oil. These curves show, in this case also, that the viscosity decreases with increasing shear rates, it is noted that the viscosity decreases rapidly to a velocity of 50 rpm s^{-1} and that from 100^{-1} rpm s^{-1} viscosities remain unchanged.

4. Conclusions

This work is a contribution to the comprehension to the phenomena of interaction between the main formulation parameters of microemulsion: oil and surfactant and some additives: polymers, to improve the characteristics of a formulation such as stability, for use in various practical situations. To this end, we used two techniques of measurements: the conductometric and viscosimetric methods. These methods can provide information on the evolution of selected systems. Then, we focused to study the effects that may exist in a system containing water-soluble charged polymers: starch, Arabic gum, and cetomacrogol, and an anionic surfactant: the LABSNa and the effect of these combinations on physicochemical and rheological properties of such systems. Based on the results of the conductivity, it can be concluded: the existence of a linear curve representing the conductivity as a function of surfactant concentration and the curves show two breakpoints at the CMC (and CAC) in the presence of polymers and the PSP. The study of the viscosity was used to determine the behavior of the tested systems. Thus, examination of the results of viscosity vs. shear rate, exhibits the same behavior for each polymer used in the presence of oil. Finally, this study showed that the combination of polymer and surfactant show the existence of interactions between the systems.

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