تعزيز اداء البوليمر PEO في تقليل المقاومــة الهيـدروليكية في نظــام الجريــان المضــطرب بإضافة خافض التوتر السطحي SDBS ألايوني

سرمد ك فخرالدين*.**.* و حيدر أ.عبد الباري*

*كلية الهندسة الكيميائية وهندسة الموارد الطبيعية، جامعة ماليزيا باهانج، جامبانج 26300، كوانتان، باهانج، ماليزيا،

**قسم هندسة البترول، كلية الهندسة، جامعة كركوك، 36001 كركوك، كركوك، العراق

الخـــلاصـــة

البولي ايثيلين أوكسيد (PEO) هو بوليمر غير ايوني، واستخدم على نطاق واسع كعامل في تقليل المقاومة الهيدروليكية. ومع ذلك، فأن قدرتها على كبح المقاومة الهيدروليكية لجدار نظام الجريان المضطرب تعد محدودة. ولذلك في هذا البحث ، تم إضافة خافض التوتر السطحي ألايونيسلفونات الصوديوم دوديسيل البنزين (SDBS) الى محلول البوليمر لتحسين كفائتةفي تقليل المقاومة الهيدروليكية للجدار. في هذا البحث تم استخدم تركيزاتمختلفة من البوليمر تتراوح على النحو الاتي(10 و 20 و 40 و 60 جزء من المليون) وكذلك من خافض التوتر السطحي(100 و 200 و 400 و 500 جزء من المليون). خلال التجارب تم قياس الخصائص الفيزيائية كاللزوجة، والتوصيل الكهربائي للمحاليل لتقييم مقدار التجاذب بين المواد في المحلول. وقد أكدت القياسات الحاصله من تجارب التوصيل الكهربائية أن التجاذببين محلول البوليمر و خافض التوتر السطحي يحدث بين نقاطتي ال CAC-PSP. وكذالك أجريت قياسات نسبه التقليل من المقاومة الهيدروليكية للجدارعند اضافة محلول البوليمر وعند اضافةالمحلول المركب من البوليمر و خافض التوتر السطحياستخدام جهاز القرص الدوار.وقد أظهرت نتائجالجهازفرق كبير في المقاومة الهيدروليكية بين المحلول المركب من خافض التوتر السطحي الايوني والبوليمر مقارنة مع محلول البوليمر النقي. هذا التحسن في خفض المقاومةالهيدروليكية عند اسنخدام المحلول المركب يعزى الى الانجذاب بين البوليمر و خافض التوتر السطحي والذي بدوره يودي الى تغير شكل سلسلة البوليمر من الشكل اللولبي الى الشكل المستقيم والذي عزز قدرة البوليمر لتقليل المقاومة الهيدروليكية للجدار. أظهر المحلول المركب من البوليمر وخافض التوتر السطحيأعلى نسبةفي تقليلالمقاومة الهيدروليكية والتي تقدر ب 50 ٪ عند استحدام تركيزات خليط 60 جزء من المليون من البوليمر مع 200 جزء في المليون من خافض التوتر السطحي . وبالرغم من ذلك، فانه لوحظ عند استخدام تركيزات أعلى من خافض التوتر السطحي، ان المقاومة الهيدروليكية قد ازدادت وذلك يرجع إلى زيادة اللزوجة النسبية للمحلول المركب والتي بدورها تزيد من المقاومة الهدروليكيه للجدارعند تدفق السائل.

Enhancement of PEO performance in reducing turbulent flow drag with the addition of SDBS anionic surfactant

Sarmad K. Fakhrulddin*˒** and Hayder A. Abdulbari*

*Faculty of Chemical and Natural Resources Engineering, Universiti University Malaysia Pahang,
Gambang 26300, Kuantan, Pahang, Malaysia,

**Petroleum Engineering, Department, University of Kirkuk, Kirkuk 36001, Iraq

Corresponding Author: Sarmad KamalFakhrulddinemail: sarmadfakhrulddin@gmail.com

ABSTRACT

Polyethylene Oxide (PEO) is a non-ionic polymer, which has been used widely as a drag reduction (DR) agent. Nevertheless, its ability to reduce drag in turbulent flow is yet limited. Thus, in this paper, a study to improve the ability of PEO to reduce drag in a turbulent flow through addition of an anionic surfactant (sodium dodecyl benzene sulfonate (SDBS)) is presented. The Various concentration ranges of PEO (10, 20, 40, and 60 ppm) and SDBS (100, 200, 400, and 500 ppm) were studied. The physical properties, viscosity, and electrical conductivity were measured to evaluate the interaction in a complex solution. The electrical conductivity measurements confirmed that the interaction between the polymer-surfactant solutions takes place between the CAC-PSP points. The drag reduction measurements were done using a rotating disk apparatus (RDA). The RDA results showed substantial findings when the anionic surfactant-polymer solution was compared to the pure polymer solution. The interaction between the polymer and the surfactant results in transforming the polymer from coil to straight-like body, which enhanced the polymer drag reduction ability. The PEO-SDBS solution showed the highest DR of 50 %, at a mixture concentration of 60 ppm of PEO with 200 ppm of SDBS. Nonetheless, at higher concentrations, the DR value dropped due to the increase in the relative viscosity of the solution, which enhanced the resistance to the flow.

Keywords: Drag Reduction; Friction Factor; PEO; RDA; SDBS.

INTRODUCTION

The frictional drag of a turbulent flow can be energetically reduced by the addition of tiny amounts of additives, such as polymeric chain particles (Li et al., 2006; Yusuf et al., 2012) and surfactants micelles (Li et al., 2008). Application of drag reduction (DR) phenomenon is established in several regions such as closed-circuit pumping (Wei et al., 2009), oil well fracturing operations (Le Brun et al., 2016), transportation of crude oil in pipelines (Burger et al., 1982; Karami and Mowla, 2012), hydraulic transferral of solid particle suspensions (Ravelet et al., 2013), irrigation system and water supply (Khalil et al., 2002), sewage systems to prevent overflow during heavy rain (Brostow et al., 2009), and increasing the output of water jet during firefighting (Figueredo and Sabadini, 2003).

The polymer additives have been widely used as drag reduction agents due to their harmlessness and because of being inexpensive and easy in removing features. The polymer additive choice is

affected by various parameters such as polymer molecular concentration, molecular weight and charge on the chain, viscosity, degradation temperature, solvents, linearity, and flexibility (White et al., 2004). However, the general selection of a polymer as an additive is subject to the type of solvent. For instance, in the case of water as the solvent, non-ionic polymer polyethylene oxide (PEO) and ionic polymer polyacrylamide (PAM) have been utilized as the drag reducing agents (Al-Yaari et al., 2009; Zhang et al., 2011a), whereas, in hydrocarbon fluid systems, cyclohexane, chlorobenzene, toluene, and benzene have been reportedly used as non-polar drag reducers, including commercial polysaccharides such as polystyrene (PS) and polyisobutylene (PIB) (Lee et al., 2010).

The interaction between polymers and different types of surfactants is not uncommon in a variety of applications including cosmetics industries, oil recovery, and drug delivery (Bai et al., 2010; Stoll et al., 2011; Abdulbari et al., 2015). The binding of non-ionic polymers with surfactants occurs according to the surfactant micelles charge. For instance, an anionic charge of surfactants micelles is considered more active when connecting with non-ionic polymer chains than other types of surfactant as reported by Zhang et al. (2011b) and Nagarajan (1989). These studies supported the theory that the size of the head group and hydrophobicity of anionic micelles are the primary reasons that give a significant effect on total interaction. It is supposed that the non-ionic polymer chains do not combine with the cationic and non-ionic surfactant micelles in a wide-range of conditions. However, in the existence of some types of ion such as sodium (Na) and magnesium (Mg), the interaction between non-ionic polymers with a cationic surfactant may be enhanced. The addition of anionic surfactant to the polymer can result in either extending or deforming the polymer chain. The self-assembly monomers occurs at certain concentration called critical micelles concentration (CMC). The interaction between polymers and surfactants usually occurs at a certain polymer-surfactant concentration known as the critical aggregation concentration (CAC) and continues up to a point where the polymer is already saturated with the surfactant (polymer saturation point (PSP)). When the surfactant is added in-between the CAC and PSP points, an expansion of the polymer would occur but on the other hand if the addition is in the region beyond the PSP point, the deformation of the polymer chain will occur. Many studies have reported the use of polymer surfactants as drag reduction agents. Matras and Kopiczak published a study on the effect of a complex mixture of non-ionic polymer PEO and cationic surfactants cetyltrimethylammonium bromide (CTAB) with sodium salt as counter-ion on drag reduction efficiency in a straight circular pipe (Matras and Kopiczak, 2014; Matras and Kopiczak, 2015). Based on their findings, the presence of micelle surfactants in the polymer solution shows that the flow became linear in the first zone of turbulent flow, resulting in an expansion of the stable transitional area. In another study by Mohsenipour et al., the drag reduction efficiency was investigated by using a complex consisting of non-ionic polymer (PEO) with two types of surfactant an anionic surfactant (sodium dodecyl sulphate sulfate (SDS)), and a cationic surfactant (octadecyl trimethyl ammonium chloride (OTAC)) in a pipeline flow loop (Mohsenipour and Pal, 2013a). In their study, three different concentrations of anionic polymer (PAM) (100, 250, and 500 ppm) and non-ionic polymer PEO (500, 1000, and 2000 ppm) were studied. It was concluded that the polymer-surfactant complex has a strong effect on the fluid flow (lower friction wall) as a drag reducer when compared with systems that were powered by either polymer or surfactant. The polymer-surfactant interaction

demonstrated a considerable effect at low combination concentration ratios. All types of surfactant micelles, when added to a non-ionic polymer solution, may cause an extension in the molecules chains, and therefore, this could infer that the expansion of the polymer chains makes them less prone to decay under high shear stress. However, when the concentration or the selected range of the polymer is too large, it may result in an increase in the viscosity of the solution and could be economically unreasonable (Mohsenipour and Pal, 2013b).

This study for the first time presents a method for the enhancement of PEO drag reduction ability at a very low concentration of PEO through the addition of SDBS cationic surfactant. The addition of SDBS to the polymer was investigated in terms of physical properties of interaction between the polymer and the surfactant and its effect on the drag reduction even at very low polymer concentrations.

MATERIAL AND METHOD

Materials and solution preparation

The non-ionic polymer PEO and the anionic surfactant SDBS were purchased from IRO Group Inc., China, and China Dexin Co., LTD, China, respectively. Both PEO (MW: 8×10^6 g/mol) and SDBS (MW: 348.5 g/mol ; purity: 95 %) were added to a desired amount of deionized (DI) water for the preparation of various concentration ranges of PEO (10, 20, 40, and 60 ppm) and SDBS (100, 200, 400, and 500 ppm). In order to ensure that the mixtures are completely distributed, a magnetic stirrer plate was used to blend the polymer in the distilled water at relatively low speed to avoid the breakdown of the polymer molecules as the mixtures continued to stir for 24 h.

Physical properties assessment

The physical properties, viscosity, and electrical conductivity of the mixture were measured using a Cannon-Fenske viscometer tube (size 50) and the Eutech Instruments (Model PCD 650), respectively. The conductivity, measured in mS, was performed at a temperature of about 25 ± 0.3 °C. Similarly, the relative viscosity at low shear was estimated using the relation described in Eq.1, which shows the relationship between the flow times of a solution (tp) with the flow time of the solvent (ts). This was carried out at room temperature (25 ± 0.3 °C).

$$\eta_r = \frac{t_p}{t_w},$$
(1)

Rotating disk apparatus experiment

The rotating disc methods are one of the simplest alternatives for replicating drag reduction properties in the piping system (Holm et al., 2004). Thus, the rotating disk apparatus (RDA) was used in this study to investigate the drag reduction efficiency of PEO and SDBS. The RDA design, as shown in Figure 1, consists of a frame, a fluid container, a rotating disk, a disk holding shift, a torque sensor, an electric motor, a thermocouple, a controller interface, and a PC.
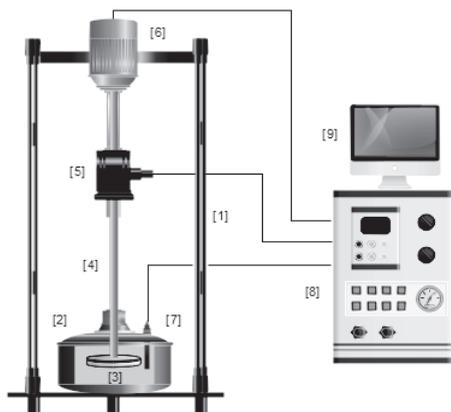
Figure 1. Schematic diagram of the rotating disk apparatus for drag reduction measurement: (1) outside frame, (2) fluid container, (3) rotating disk, (4) disk holding shift, (5) torque sensor, (6) electric motor, (7) thermocouple, (8) controller interface, and (9) PC.

Technically, in RDA, the discs are rotated in a tank of water, at high velocities to create a shear force, which can be measured by reading the torque value in the system. As drag reduction occurs only in turbulence flow, all experiments were conducted at a disk rotation speed of at least 600 rpm to ensure that turbulence has been generated. The occurrence of the turbulence was confirmed by the Reynolds numbers (N_{Re}) value, which exceeded 3 x 10^5 (Choi and Jhon, 1996). The N_{Re} was determined using the relation in Eq. 2:

$$N_{Re} = \frac{\rho \, r^2 \omega}{\mu} \tag{2}$$

where, ω is the disk rotational speed ((2*π*$r$pm)/60), r is the radius of the disk, μ is the fluid viscosity, and ρ is the fluid density. The torque (mN.M) for the pure solvent (distilled water in this case) and the solution (all concentrations) at a speed of 1800 rpm was measured. The estimated percentage drag reduction (% DR) was calculated using Eq. 3:

$$\%DR = \left(\frac{T_D - T_S}{T_D}\right) * 100 \tag{3}$$

where, T_d is the torque in the distilled water and T_s is the torque in the solution. All experiments were carried out at room temperature (25 ± 0.3 ºC).

RESULTS AND DISCUSSION

Sets of experiments were carried out to study the properties of polymer additives and their mixtures with surfactant at different concentrations on drag reduction. Apart from that, the influence of adding surfactant micelles into a polymer solution with respect to drag reduction was also investigated. Figure 2 showed the assessment of the viscosities of the PEO-SDBS solutions and from the plot, the relative viscosity of PEO/SDBS mixtures at different concentrations was shown and the trend of the outcome was similar to earlier findings as reported by Müller et al. In their study, they added sodium dodecyl sulfate (SDS), which is an anionic surfactant, to a PEO solution at lower concentration and discovered that the relative viscosity of the resulting solution did not show any significant change until a point when the CAC of the polymer solution was reached (Müller et al., 2003). From the CAC point onwards,

the relative viscosity of the solution continued to increase until PSP point was reached. In this study, there was no increase in the viscosity of the solution at low PEO concentration of 10 ppm even when the concentration of SDBS was increased to 310 ppm. But as the SDBS concentration was increased to 500 ppm, which was the PSP point, there was a decline in the relative viscosity of the solution. Normally, the shape of the pure polymer is in the form of coils, but once the surfactant was added to it, the coils started to stretch. However, in this case, the high concentration of SDBS in the solution led to the deformation of the polymer molecules, which caused a reversal of the shape back to the coil shape. This is due to the electrostatic repulsion that existed between the free micelles and the micelles that were attached to the polymer, which resulted in the reduction of the length of the polymer chains with eventual increment in the viscosity of the solution. Similarly, when the concentrations of PEO and SDBS were increased to 20 and 250 ppm, respectively, the relative viscosity of the solution didn't experience much change. The viscosity of the solution remained the same until the concentration of SDBS was more than 250 ppm. At this higher SDBS concentration (> 250 ppm), the viscosity of the solution started to increase proportionally with the increase in the SDBS concentration until the PSP point was reached. From the studies, it was observed that, at the PEO concentrations of 40 ppm and 60 ppm, similar trends of changes in viscosity were noticed at a given concentration of SDBS. It was also noticed that the concentration of the SDBS in a given solution significantly determined the level of change in the viscosity of the solution and how it declined at the PSP point. The CAC points of a solution containing 40 ppm of PEO and 60 ppm of PEO were at 200 ppm and 150 ppm, respectively. Hence, it could be presumed as previously noted by Torres et al. that the CAC point of a PEO-SDBS solution can be reached earlier with an increase in the concentration of PEO in the solution. The higher the concentration of PEO in a given PEO-SDBS solution, the earlier it will take to reach the CAC point of the medium (Torres et al., 2008).
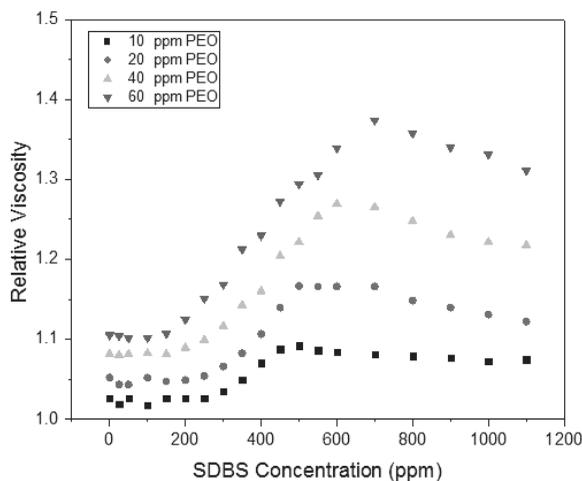
Figure 2. Relative viscosity for different PEO/SDBS combinations vs. SDBS concentration.

The CAC, PSP, and critical micelles concentrations (CMC) of the solution at 25 $^{\circ}$C were determined through the measurement of the electrical conductivity of the SDBS and PEO/SDBS solutions. The results of the measurements are shown in Table 1. From Table 1, it was observed that, at a PEO concentration of 10 ppm, the CAC and PSP were at 282 ppm and 415 ppm, respectively, which were

quite different from the data obtained during the viscosity measurements. On the contrary, when the PEO was at a higher concentration of 20, 40, and 60 ppm, the CAC and PSP points obtained from the electrical conductivity measurements showed a slight deviation from the data obtained during viscosity measurement. However, it can be summarized that, at a higher PEO concentration, the CAC and PSP points obtained from the electrical conductivity and viscosities assessment could be similar and stable. The CMC in the SDBS aqueous solution, where the formation of micelles occurred, was 391 ppm, which was close to previous reports (Hou et al., 1999).

Table 1. Conductivity data for quiescent aqueous PEO/SDBS solutions at 25 °C.

	CMC	CAC	PSP
SDBS	391	-	-
PEO/SDBS in 10 ppm PEO	-	282	415
PEO/SDBS in 20 ppm PEO	-	254	492
PEO/SDBS in 40 ppm PEO	-	190	586
PEO/SDBS at 60 ppm PEO	-	165	708

Figure 3 showed the effect of adding different concentrations of PEO polymer on drag reduction in the RDA. The RDA was set up in the same pattern as other experimental setups previously discussed here. From Figure 3, it was observed that PEO at a maximum concentration of 60 ppm clearly enhanced the drag reduction efficiency, but beyond this concentration, the drag reduction efficiency started to decrease. There are two phases of the influence of polymer concentration on DR at a fixed rotational velocity: firstly, with the increase in polymer concentration, the DR percentage is improved due to an increase in the number of polymer molecules, which is distracting the turbulent in the solution; and secondly, at an increased concentration of the polymer in the solution, there is an increase in the viscosity of the solution, which will ultimately lead to a decrease in the efficiency of drag reduction. In this study, therefore, the maximum PEO concentration was maintained at 60 ppm.
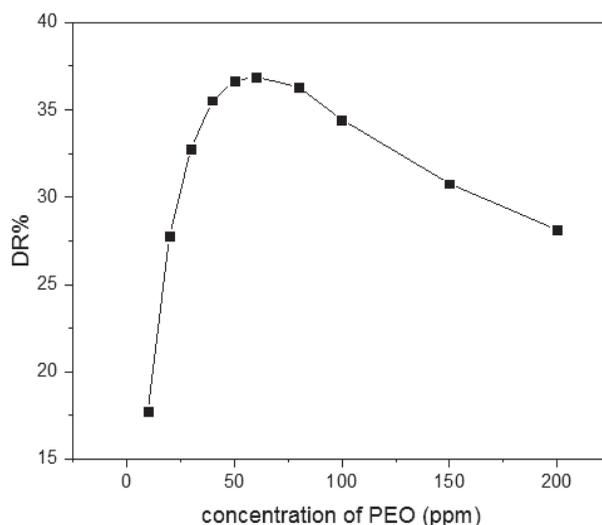
Figure 3. Drag reduction efficiency of PEO polymer at different concentrations.

The effect of adding various concentrations of the surfactant SDBS was studied. The studied concentrations of SDBS were 100, 200, 300, 400, and 500 ppm. These concentrations were added to the mixtures at a specified concentration of PEO. The results of each run are presented in separate figures. Generally, it was observed that the percentage of drag reduction (%DR) increased with the increase of the Reynolds number (Re). From Figure 4 it can be seen that even at a low concentration of SDBS (less than the CAC point (refer to Table 1)), there was a slight enhancement in the percentage of DR, which indicated the ability of the SDBS to enhance enhance DR without necessarily having any interaction with the polymer. Nonetheless, once the concentration of the SDBS was higher than the CAC value, the percentage of DR increased significantly (Figure 4). In fact, the highest percentage of DR was obtained at an SDBS concentration of 500 ppm, which was the highest SDBS concentration studied. The drag reduction was improved at SDBS concentrations of 400 ppm and 500 ppm due to the increase in the number of micelles, which are attached to the polymer coil and cause it to expand further. From the results of this study, drag reduction efficiency was up to 36 %, which was twice the value recorded with just pure polymer.
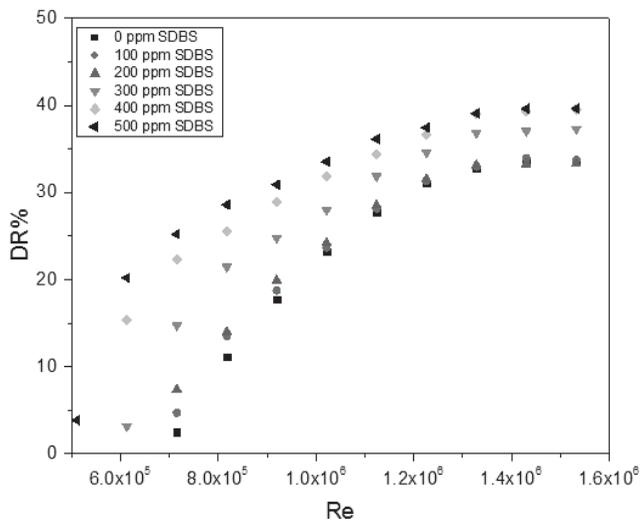
Figure 4. Effect of SDBS concentration vs. Reynolds number on %DR for PEO/SDBS mixtures for 10 ppm of PEO solution.

Similarly, Figure 5 showed the relationship between the percentage DR, and the Re. At PEO concentration of 20 ppm, the percentage of DR observed at SDBS concentrations of 100 and 200 ppm was minimal, and this could be attributed to the absence of any interaction within the mixture since the concentrations were still below the CAC value. Conversely, at increased SDBS concentrations of 300 and 400 ppm and PEO concentration of 20 ppm, the percentage of the drag reduction showed a significant improvement with maximum percentage reduction value of 45% recorded. This value was greater than the values achieved when the SDBS concentrations were the same but at a reduced PEO concentration of 10 ppm. This happened due to a large number of micelles that interacted and attached to the polymer coils. Noticeably, the %DR was reducing at SDBS concentration of 500 ppm, which negates the supposed phenomenon. The reduction in the percentage of DR was reduced at SDBS concentration of 500 ppm due to an excess number

of micelles in the solution, which weren't attached to the polymer coil. These free micelles in the solution promoted the repulsion charges between the free and attached micelles, which caused the reformation of the polymer coil. An interesting comparison can be made between the results of the %DR at SDBS concentration of 500 ppm with PEO concentration of 10 and those with PEO concentration of 20 ppm. Even though, at 10 ppm, the SDBS concentration was above the limit of the PSP, the %DR continued to increase, whereas, at PEO concentration of 20 ppm, the concentration of SDBS was within the limit of the CAC-PSP and yet the %DR keeps reducing. This certainly can be explained as the relative viscosity shifts from diluted solution to semi-diluted at a concentration of 20 ppm or in another way,; the viscosity at a PEO concentration of 20 ppm ought is higher than the viscosity at a PEO concentration of 10 ppm.
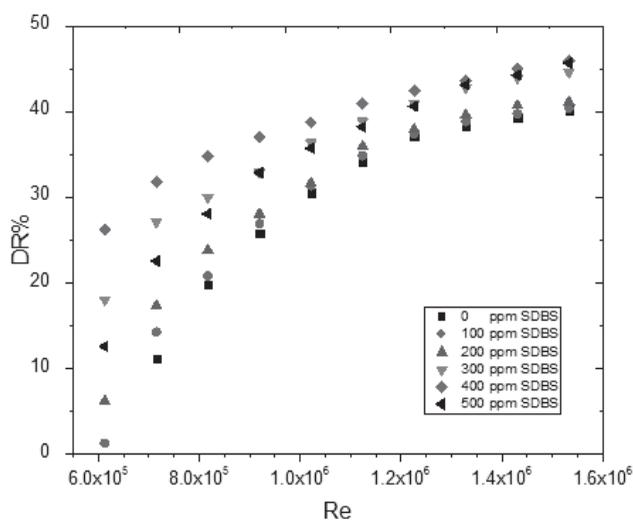
Figure 5. Effect of SDBS concentration vs. Reynolds number on %DR for PEO/SDBS mixtures for 20 ppm of PEO solution.

Comparatively, similar patterns of %DR were obtained with PEO concentration of 40 ppm and at varied SDBS concentrations (0 to 300 ppm) as shown in Figures 6. Though SDBS concentrations of 0, 100, and 200 ppm were below the CAC-PSP limits (195586- ppm), they surprisingly showed an increased %DR, which was even higher than those achieved at PEO concentration of 10 ppm. This result illustrated that the effect of the studied concentrations contributed more to the total viscosity of the solution than to the interaction and expansion of the polymer coil. Thus, an improvement was observed before the interaction point. In contrast, at SDBS concentrations of 400 and 500 ppm, the %DR significantly decreased even though the two concentrations were within the CAC-PSP values. This is due to the shift in the total viscosity of the solution, which ultimately affected the drag reduction.
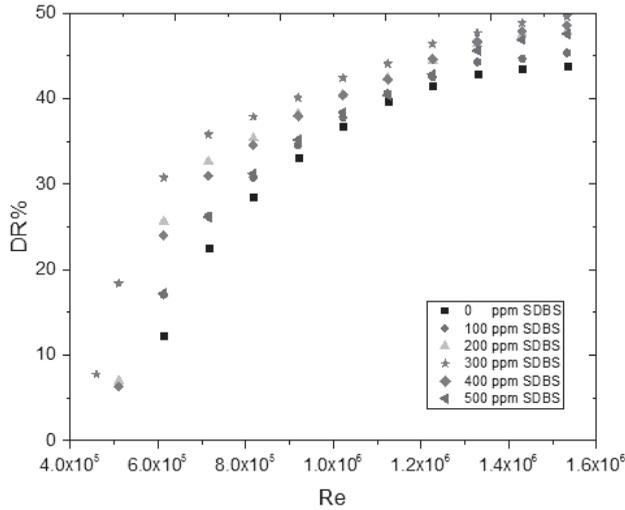
Figure 6. Effect of SDBS concentration vs. Reynolds number on %DR for PEO/SDBS mixtures for 40 ppm of PEO solution.

Figure 7 showed the tendency of the %DR based on different SDBS concentrations at PEO concentration of 60 ppm. A significant increase in %DR was observed at SDBS concentrations of 100 and 200 ppm, which were almost close to the minimum CAC-PSP value. The highest %DR at PEO concentration of 60 ppm (50 %) was achieved at SDBS concentration of 200 ppm. It is precisely the same as the %DR achieved at PEO concentration of 40 ppm except that it was achieved with SDBS concentration of 100 ppm at PEO concentration of 60 ppm. However, at SDBS concentrations of 300, 400, and 500 ppm, the %DR tends to decline as a result of the contribution of the SDBS to the total viscosity of the solution.
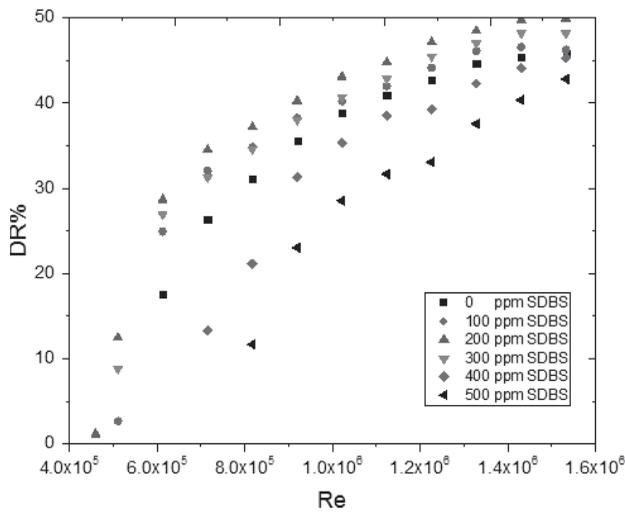
Figure 7. Effect of SDBS concentration vs. Reynolds number on %DR for PEO/SDBS mixtures for 60 ppm of PEO solution.

CONCLUSION

In this study, a new aspect of the polymer-surfactant complex was studied experimentally. Polyethylene Oxide (PEO) is a non-ionic polymer that was used together with a non-ionic SDBS surfactant to enhance the drag reduction efficiency in a turbulent flow. The relative viscosity for each concentration of PEO 10, 20, 40, and 60 ppm and SDBS 100, 200, 400, and 500 ppm was measured and discussed. The relative viscosities didn't change much at low concentrations of SDBS for each PEO concentration but started to increase significantly at certain SDBS concentrations, which indicated the CAC points. The point at which the decline started was known as the PSP. The electrical conductivity results showed a small difference in the CAC and PSP point values. Based on the experiments using RDA, the %DR at PEO concentrations of 10, 20, 40, and 60 ppm was 36%, 45%, 50%, and 50 %, respectively. The drag reduction using the polymer and surfactant reached about 50 % at a very low concentration (60 ppm of PEO and 200 ppm SDBS surfactant) of the polymer and surfactant. However, at PEO concentration of (60 ppm, a higher concentration of SDBS 300, 400, and 500 ppm) started to record a decrease in the drag reduction efficiency due to the increase in the total viscosity of the solution.

ACKNOWLEDGEMENT

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