

CRITICAL MICELLE CONCENTRATION AND THE EFFECT OF SOLUTION AGE ON DRAG REDUCTION PERFORMANCE OF ANIONIC SURFACTANTS

*Hayder A Abdul Bari, Emma Suali and Zulkafli Hassan

Faculty of Chemical and Natural Resources Engineering, University Malaysia Pahang, Malaysia

ABSTRACT

In the present study, Ammonium lauryl sulfate was introduced as new drag reducing agent in aqueous media flowing through pipelines. A built up rig with ratio of pipe length to diameter (L/D) is equal to 59 was used to achieve the purpose of this work which to test the critical micelle concentration and the effect of using different ages of solution for 300ppm (wt) of anionic surfactants. The drag reduction performance of the surfactant under investigation was also analyzed for different concentrations and flow rate of anionic surfactants, which 200ppm, 300ppm, 400ppm, 500ppm and 600ppm, respectively. It was found that the starting point of critical micelle concentration of ammonium sulfate lauryl was detected within range 140 to 200 ppm. The highest drag reduction was achieved is 50% at Re equal to 11235 for 600ppm of solution and the fresh solution gave better drag reduction compared to other ages of solution. The drag reduction decreases as the age of solution increases. After 4 days, the ammonium lauryl sulfate increases the drag in pipes.

Keywords: Drag reduction, critical micelles concentration, turbulent flow, anionic surfactants.

INTRODUCTION

Power saving is the main concern for all research regarding on drag reduction. One of the well known drag reducing agents are surfactants. Surfactants were acknowledged as drag reducing agent since 1949. The drag reduction phenomenon is interesting from a practical point of view because fluids are mostly transported through pipes and a drag reduction occurred by adding a small amount of drag reducing agent. The phenomena behind the drag reduction are quite complicated to understand. Among the parameter that has been identified as sources that lead to understanding of mechanism in drag reduction is the concentration of solution, the flow Reynolds number, the type of materials, the age of solution, the CMC, flow pattern and so on. (Myska and Mik, 2003; Cho *et al.*, 2007). For the past few years, the formation of micelle in surfactants solution identified as the key to understand the mechanism behind the drag reductions. The CMC determination of surfactants is important not only to understand the drag reduction phenomena but also to understand the colloid and surface behavior of surfactant solute, which in turn determine its industrial usefulness and biological activity. An additive of surfactants changes the surface tension and the specific conductance of the carrying fluid and the pressure drop per unit length in pipes and channels. Hence, the CMC of surfactant can be analyzes through the values of surface tension and specific conductance of surfactants solution (Wiseman *et al.*, 1998). The CMC was obtained in a change of slope of specific conductance against solution

concentration and the slope of surface tension against the log concentration of surfactants (Saux *et al.*, 2004). These CMC values are easily affected by addition of other chemical in solution as explained in Sukzamrancit and Sirivat (2007) work. They found that the values of CAC and CMC from conductivity and surface tension measurements indicate that salt stabilizes micelle formation in HTAC solutions while conducting an investigation using couette cell (Sukzamrancit and Sirivat, 2007).

Most of surfactants are not suited for industrial systems because of their degradation and environmental impact. Based on this concern, Rozenblit *et al.* (2006) investigated the pressure drag reduction and the flow pattern of surfactant that having negligible environmental impact. They found that the flow pattern of solution also influence the drag reduction. Hence, there are a lot of parameters need to investigated in order to optimize the application of drag reducing agent specially surfactants. In this present study, the effect of age of solution and the CMC of ammonium lauryl sulfate was investigated in 0.0254 m internal diameter of pipe.

MATERIALS AND METHODS

Ammonium Lauryl Sulfate

Ammonium lauryl sulfate also known as ammonium dodecyl sulfate, which is product of Sigma-Aldrich Sdn.Bhd was used as investigated material in this experiment. This material is well known as anionic surfactant with molecular weight (Mw) 283.43 and the density is 1.02g/cm³. This anionic surfactant are very

*Corresponding author email: hayder@ump.edu.my

high-foam surfactants that disrupt the surface tension of water by forming micelles around the polar water molecules and readily biodegradable.

Experimental system

Figure 1 shows the experimental rig uses for the purpose of this experimental study. As shown in figure 1, this experimental rig consist of 0.0127m, 0.0254m and 0.0381m inside diameter and the length of 2 m made from transparent PVC pipe. Each pipe divided into vertical and horizontal part in which the testing sections were installed in horizontal part with a distance equal to 0.5 m. The first testing point located about 50 times the internal diameter (50.D) to ensure the turbulent flow is fully developed before the testing section.

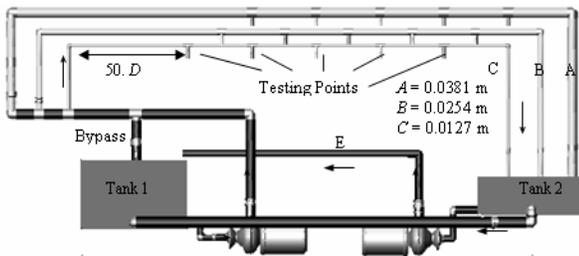


Fig. 1. The experimental rig.

The Ultraflux Flowmeter Minisonic P was used to measure the flow rate of fluid in pipelines. The purpose of using this exterior portable ultrasonic measurement is to avoid any disturbance might happen in the flow pattern. Baumer Differential Pressure Gauges were used to detect the pressure drop in pipelines with maximum differential pressure readings up to 0.16 bars. Cole Parmer Viscometer analyzer is used to analyze the viscosity of each solution. In order to analyze the critical micelle concentration, the surface tensions of each solution were analyzed using SEO DST60 tensiometer and the specific conductances were analyzed using Cyberscan Con 410 conductivity meter. All samples were taken and analyze in room temperature.

Experimental procedure

The experimental work was carried out in 0.0254 internal diameter pipes and the ratio of pipe length to pipe diameter (L/D) is equal to 59. The data of pressure drop in pipe for water before the addition of anionic surfactants are initially used in the calculations of drag reduction in which the drag reduction in pipes is defined as:

$$\text{Reduction (\%)} = \left(1 - \frac{\Delta P_a}{\Delta P_b} \right) 100 \quad (1)$$

Where; ΔP_b is pressure drop before and ΔP_a is after the addition of surfactant solution. First, the tap water is circulated through the experimental rig from tank 1 to

tank 2. From tank 2, it then pumped to tank 1. This procedure is repeated to obtain the constant value of pressure drop for water alone. The bypass pipe uses to control the fluid flow rate. In order to verify the appropriateness of this procedure, the friction factor of water were plotted against the Reynolds number as shown in figure 2. Second, the first solution which is the fresh anionic surfactants with 300ppm (wt) concentration was added into tank 1 and pumped through the testing pipe. The flow rates are controlled using valve in each pipe. The whole experimental system was clean up after each experiments. The next solution is prepared in tank based on age of solution, which the ages of solution excluding the fresh solution are 1day, 2 days, 4 days, 6 days and 8 days, respectively. The last experiment involved experimental rig is investigation on drag reduction for fresh solution with different concentrations namely 200ppm, 300ppm, 400ppm, 500ppm and 600ppm, respectively. The drag reductions for each solution are calculated using equation (1) as specified above. In order to obtain the accurate results each experiment are repeated about 3 times.

Finally, the surface tension of ammonium lauryl sulfate was investigated using Du Nuoy Ring method. The samples with different concentration (ppm), which are 50, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650 and 700, respectively was prepared in 1000ml volumetric flask before the analysis. The specific conductance was investigated for the same samples as specified for surface tension investigation. All the measurement as described was done in room temperature.

RESULTS AND DISCUSSION

Figure 2 shows the relationship of friction factor of water with the Reynolds number of the fluid flow rate. The figure included both the laminar flow and Virk maximum drag reduction flow asymptotes. It is clearly shown that the values of the water flow in pipes used in the present experiment lies near the Blasius asymptote, which proved the appropriateness of the experimental method and shown a good starting point towards more accurate readings. The friction factors are calculated based on equation as specified below:

$$f = \frac{2\tau_w}{\rho V^2} \quad (2)$$

$$\tau_w = \frac{D\Delta P}{4L}$$

The Blasius equation is defined as (Yunus and Cimbalá, 2006):

$$f = 0.0791Re^{-0.25} \quad (3)$$

and Virk's asymptote is defined as (Virk *et al.*, 1970) :

$$f = 0.59Re^{-0.58} \quad (4)$$

Whereas the Reynolds number in pipe is defined as:

$$Re = \frac{\rho VD}{\mu} \tag{5}$$

Moreover, the friction factors in pipes based on laminar flow are defined as:

$$f = \frac{16}{Re} \tag{6}$$

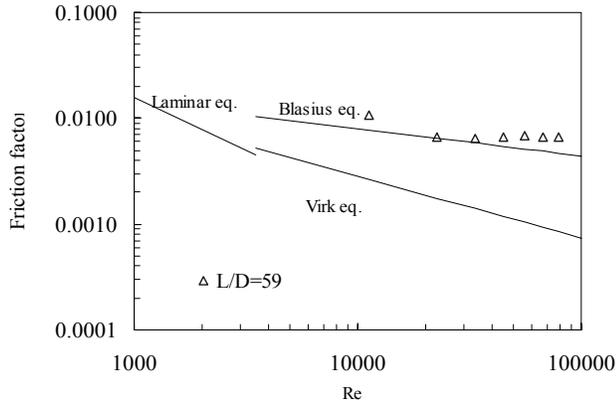


Fig. 2. Relationship between friction factor and Re of water in PVC pipe.

Figure 3 shows a comparison of different concentrations of anionic surfactant on drag reduction against Reynolds number. From the figure it can be noticed that, as the concentration of surfactant increases, the drag reduction also increases. The maximum percentage drag reduction achieved was 50% at 11235 Re for 600 ppm of solution and the lowest value of drag reduction was achieved is 0.75% at 78645 Re for 200ppm. The results show also that the percentage drag reduction decreases after passing the maximum performance point in each curve. This is because of the break up of the micelles structure in very high shear regions, which occurred in high degree of turbulent flow. The formation of micelle in ammonium lauryl sulfate solution was proved and shown in figure 4 and 5.

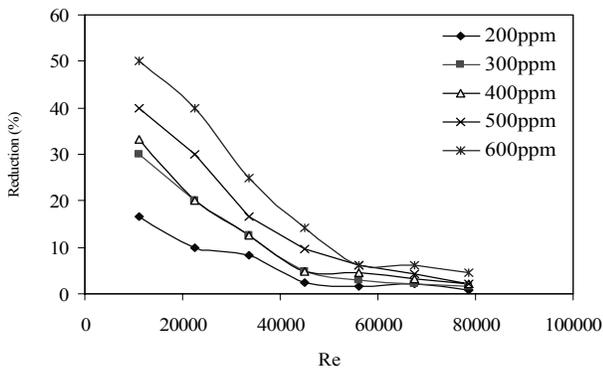


Fig. 3. The comparison of drag reduction for different concentrations.

As shown in figure 4, there is a break in the curve occurred in 0.00050M of ammonium sulfate lauryl solution. This break in the curve, with its sharp reduction in the conductivity of the solution, indicating a sharp increase in the mass per unit charge of the material in solution, is interpreted as evidence of the formation at that point of micelles from the unassociated molecules of surfactant, with part of the charge of the micelle neutralized by associated counterions (Rosen and Milton, 2004). In figure 5, the surface tension was measured using the Du Nouy Ring method as specified below:

$$\gamma = \frac{F}{L} + cF \tag{7}$$

$$cF = 0.7250 + \sqrt{\frac{1.452\gamma^*}{C^2(D-d)} + 0.04534} - \frac{1.679}{R/r} \tag{8}$$

From experimental work, the surface tension decreases as the concentration of solution increases but after reaching the value of 0.00075M, the surface tension is constant even though the concentration increases. These measurements confirm the transition from the surfactant monomer form to monomer micelle equilibrium over this range of concentration. The values of molarity of solution which is 0.00051M equal to 142 ppm and 0.00075M is equal to 208ppm was obtained from calculation as specified below:

$$M \text{ (mol/L)} = C \text{ (ppm)} \times \frac{1}{MW \text{ (g/mol)}} \times \rho \text{ (kg/L)} \tag{9}$$

These values are quite similar even though obtained using different methods. From this result it can be concluded that the critical micelle concentration occurred around 140 to 200ppm concentration of solution.

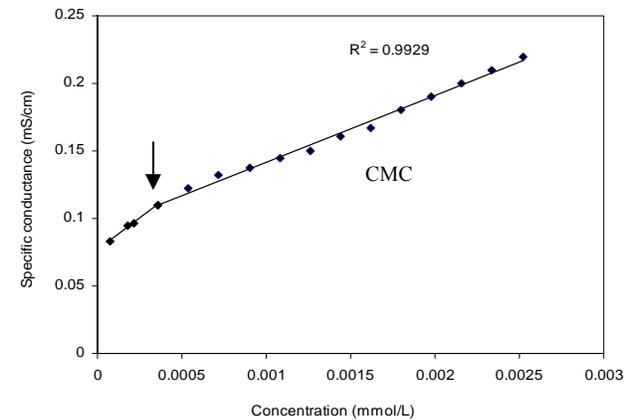


Fig. 4. Specific conductance versus concentrations of ammonium lauryl sulfate

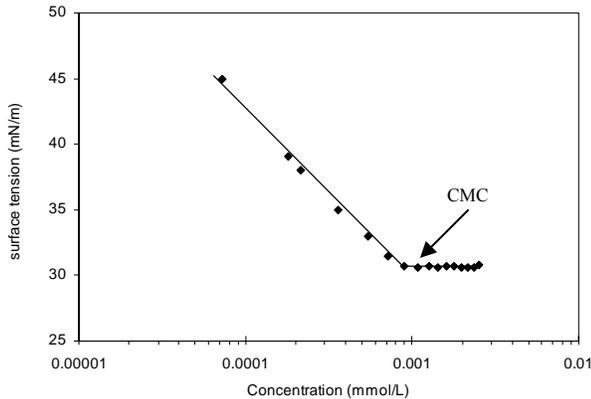


Fig. 5. Surface tension against concentration of ammonium lauryl sulfate solution.

Figure 6 shows the results of drag reduction on different age of solution for 300ppm of anionic surfactants. This result shows that, the drag reduction decreases as the ages of solution increases. The highest drag reduction obtained was 30% for fresh solution. The negative values of drag reduction after 4 days show that ammonium lauryl sulfate has a poor ability to acts as self repairable. Basically, this result shows a disagreement with the literature for different type of surfactants, hence in the future it is recommended to study the influence of age of solution as well as the concentrations effect. From literature, most of surfactants has a good stability with time, which they have the ability to restore the broken micelles in turbulent flow during several hours and left in contact with air. In Myska and Mik works, they found that after 66 days the surfactants solution still shows the ability to reduce drag. In their investigation, they found that the large recovery time enables better reformation of micelles (Myska and Mik, 2004).

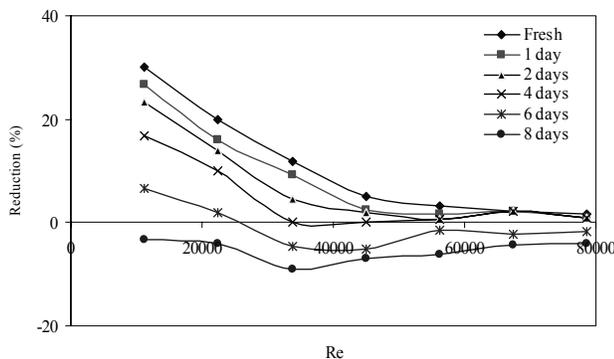


Fig. 6. The comparison of drag reduction for different age of solution.

CONCLUSION

This present work lead to the conclusion that, the age of solution influence the effectiveness of drag reduction, which interpreted due to structure of micelle are weakening with time. From analysis for CMC, it was found that the first appearance of ammonium lauryl sulfate micelle was within the range of 140 to 200ppm. Ammonium Lauryl sulfate can be categorized as poor drag reducing agent due to its negative drag reduction values after 4 days. Future works should be done in order to verify whether the higher concentration of solution have the same performance as drag reducer with age of solution as achieved in experiments for 300ppm of solutions.

Notation

ρ	solvent density
μ	absolute viscosity of solvent
D	internal diameter of pipe
L	pipe length
V	means velocity of solvent
M	molarity
C	concentration
R	Radius of ring
D	Density of water
F	force
Re	Reynolds number
L/D	pipe ratio
ΔP	pressure drop in pipe
f	friction factors
τ_w	wall shear stress
MW	molecular weight
γ^*	Surface tension of water
r	radius of wire of ring
d	density of sample
L	length

ACKNOWLEDGMENTS

The authors would like to thanks University Malaysia Pahang for providing the grant to support this research.

REFERENCES

- Cho, SH., Tae, CS. and Zaheeruddin, M. 2007. Effect of fluid velocity, temperature, and concentration of non-ionic surfactants on drag reduction. *Energy Conversion and Management*. 48:913-918.
- Myska, J. and Mik, V. 2004. Degradation of surfactant solutions by age and by a flow singularity. *Chemical Engineering and Processing*. 43:1495-1501.
- Saux, TL., Varenne, A. and Gareil, P. 2004. Determination of aggregation thresholds of UV absorbing anionic surfactants by frontal analysis continuous capillary

electrophoresis. *Journal of Chromatography A*. 1038: 275-282.

Suksamranchit, S. and Sirivat, A. 2007. Influence of ionic strength on complex formation between poly (ethylene oxide) and cationic surfactant and turbulent wall shear stress in aqueous solution. *Chemical Engineering Journal*. 128:11-20.

Wiseman, P., Kennedy, CA., Marangoni, DG. and Palepu, R. 1998. A Viscometric and Conductometric Investigation of the Micellar and Solution Properties of Two Headed Surfactant Systems, the Disodium 4-Alkyl- 3-sulfonatosuccinates. *Journal of Solution Chemistry*. 27 (3). Doi: 0095-9782/98/0300-0217.

Rozenblit, R., Gurevich, M., Lengel.Y. and Hetsroni, G. 2006. Flow patterns and heat transfer in vertical upward air–water flow with surfactant. *International Journal of Multiphase Flow*. 32:889-901.

Rosen. and Milton, J. 2004. *Surfactants and Interfacial Phenomena*. Hoboken, NJ, USA. John Wiley & Sons, Inc. pp.105.