Pressure drops during the flow of solutions of cocamidopropyl betaine and cocamide DEA mixtures with the addition of ethylene glycol

Rózańska Sylwia, Rózański Jacek, Wagner Patrycja, Warmbier Ewelina

1 Poznan University of Technology, Institute of Chemical Technology and Engineering, Department of Chemical Engineering and Equipment, 60-965, Poznan, Poland
2 Corresponding author: e-mail: jacek.rozanski@put.poznan.pl

The paper presents the results of experimental studies on pressure drops during the flow of cocamidopropyl betaine (CAPB) and DEA cocamide solutions with the addition of ethylene glycol. The degree of drag reduction during the flow of the CAPB/DEA aqueous solution and with the 10% addition of ethylene glycol was similar. A significant reduction in pressure drops was also observed at the 20% concentration of ethylene glycol. However, the increase in the concentration of ethylene glycol resulted in the reduction of flow resistance at higher temperatures. The resistance of the micellar microstructure of CAPB/DEA solutions to mechanical degradation depends strongly on the pH level. Significant changes in flow properties were observed when the initial pH was alkaline.

The solution with initial pH close to neutral was stable over time, though reduced resistance to degradation with time was also observed.

Keywords: drug reduction, pressure drop, rheology, surfactants solutions.

INTRODUCTION

One of the properties of surfactants is their ability to decrease turbulent pressure drops during the flow of surfactant solutions in ducts. The phenomenon of drag reduction is induced by surfactants, which are capable of forming long micelles, referred to as thread-like or worm-like micelles, in the solution. Based on the resistance of surfactant solutions to permanent mechanical degradation, they have found applications in central heating systems.

In recent years, there has also been a rise in the popularity of central cooling systems. Surfactants may also find applications in these systems as additives reducing pressure drops. Central cooling systems use low-temperature water (chilled water), hence the need to develop surfactants that can lead to reducing pressure drops under such conditions. In addition, the refrigerant contains a certain amount of anti-freeze additives, typically ethylene glycol or propylene glycol.

In the literature, there is only scarce information on the reduction of drag at low temperatures. Under such conditions, oleylmethylbis(hydroxyethyl) ammonium chloride (Ethoquad O/12), also with the addition of ethylene glycol, has proven itself to be an effective option. Wei et al. used oleyl trimethylaminimide (a zwitterionic surfactant) dissolved in a 20% solution of ethylene glycol as a drag-reducing additive. The surfactant was found to be hydraulically active in the temperature range from −5 °C to 25 °C. At low temperatures, significantly lower pressure drops were also observed during the flow of solutions of a surfactant belonging to the group of amine oxides (oleyldimethylamineoxide). The addition of this surfactant to aqueous solutions of propylene glycol (PG) and ethylene glycol (EG) causes a decrease in turbulent drag at temperatures as low as −20 °C. In the temperature range from 3 °C to 40 °C, a mixture of cocamidopropyl betaine (CAPB) and cocamide DEA can be used in central air conditioning systems. CAPB and DEA are corrosion inhibitors.

The study carried out by Cho and Kasza shows that at low temperatures the process of permanent mechanical degradation of drag-reducing polymers slows down. According to these authors, polyacrylamide solutions can be used in district cooling systems if the chilled water temperature is around 7 °C.

As can be concluded from the literature review outlined above, the surfactant solutions proposed for use in central cooling systems contain a certain amount of anti-freeze additives, usually ethylene glycol or propylene glycol. Since the presence of glycols in the solution can affect the process of micellar association, pressure drops observed during the flow of surfactant solutions in pure water and with the addition of glycols may differ. The aim of the study reported in this paper was to determine the effects of ethylene glycol on the reduction of drag induced by a mixture of cocamidopropyl betaine and cocamide DEA.

EXPERIMENTAL PART

Experimental set-up

Model tests were carried out using two experimental stands adapted to work in the temperature range from −5 °C to 70 °C (stand 1) and from 15 °C to 20 °C (stand 2). The diagrams and detailed descriptions of the experimental stands are presented in an earlier paper. The flow of the fluid in the stand 1 was generated by a Grundfos UPE 25-60B centrifugal pump. The temperature of the fluid was preset using a PolyScience thermostat equipped with a 1000W cooling unit. The stand was equipped with a single measuring tube section with the internal diameter \( d_w = 11.1 \text{ mm} \) (length of the inlet section: 0.9 m, length of the measuring section \( L = 2.6 \text{ m} \)). The flow rate was measured by means of a rotameter working in the range of \( 2.78 \cdot 10^{-5} \text{ to } 2.78 \cdot 10^{-4} \text{ m}^3/\text{s} \) (SED Flow Control GmbH, Germany).

In the stand 2, the flow of the fluid in the system was induced by a Grundfos CH4-30 centrifugal pump. The fluid flow rate was adjusted as required via a system of control valves and rotameters. A tube with the internal diameter \( d_w = 10 \text{ mm} \) was used in the tests (length of the inlet section 1.4 m and the length of the measuring...
section \( L = 2.295 \text{ m} \)). Stand no. 2 was used in research on the stability of CAPB/DEA solutions.

In both experimental stands, the temperature of the fluid was measured upstream of the inlet to the measuring tube section and downstream of the outlet, with the aid of PT100 sensors connected to an HD32.7 RTD Dataloger (Delta OHM). The temperature was measured to an accuracy of \( \pm 0.1 \text{ K} \). For each surfactant solution at a given temperature, rotometer scaling was performed by weight method. The rotameters used for the fluid flow rate measurements were calibrated for each surfactant solution at a given temperature. The accuracy of the volumetric flow rate measurement after scaling the flow meters was less than 1% of the actual value. Pressure probes were built into the walls of the test tubes and connected by flexible hoses to a digital differential pressure gage. Two differential digital manometers with the following measuring ranges were used in the tests: from 0 Pa to 3.5 \( \times 10^4 \text{ Pa} \) (IMT Manoprot model 3922, accuracy class 0.2%) and from 0 Pa to 3.5 \( \times 10^5 \text{ Pa} \) (IMT Tecsis Digicomb model 1901, accuracy class 0.25%).

Based on the measurement of the pressure drops \( \Delta P \) and the volumetric flow rate, the value of the friction coefficient was calculated from the Darcy-Weisbach equation:

\[
\lambda = \frac{2 \cdot \Delta P \cdot d_n}{\omega^2 \cdot \rho \cdot L}
\]  

(1)

where: \( \omega \) – mean flow velocity, \( \rho \) – fluid density.

DR parameters characterizing the degree of drug reduction were calculated using the equation:

\[
DR = \frac{\lambda_f - \lambda_t}{\lambda_f} \cdot 100\%
\]

(2)

\( \lambda_f \) is the flow drag coefficient for the surfactant solution, \( \lambda_t \) is the flow drag coefficient calculated from the equation for the turbulent flow range of Newtonian fluids. The values of \( \lambda_t \) were calculated with the same Reynolds number as \( \lambda_f \) from the Prandtl-Kármán equation.

**COMPOUNDS USED IN THE STUDY**

Two surfactants with the trade names Rokamina K30 and Rokamid KAD produced by PCC Exol SA were used in the study. Rokamina K30 is an aqueous solution of the amphoteric alkylamidopropyl betaine surfactant obtained based on coconut oil acids (cocamidopropyl betaine, CAPB). Rokamid KAD contains the non-ionic surfactant of coconut oil diethanolamide (DEA). Ethylene glycol (EG) was purchased from Donauchem (Poland, Rokietnica/Poznań) with a purity of 99.94 wt %.

The surfactant concentrations were determined based on the results of pressure drop measurements during the flow of aqueous CAPB/DEA solutions presented in the paper\(^2\). In the solutions containing ethylene glycol, the concentration of CAPB was 0.12%, while the concentrations of DEA were 0.1%, 0.12%, and 0.14%.

**RESEARCH RESULTS AND DISCUSSION**

**Rheological measurements**

Figure 1 shows viscosity curves obtained at 5 °C for CAPB/DEA solutions containing EG. CAPB/DEA solutions are non-Newtonian fluids. In the viscosity curves obtained for the solutions containing 10% EG (0.12% and 0.14% DEA), a shear-thickening range can be distinguished. The occurrence of a shear-thickening range has been observed during the flow of many other surfactant solutions. It is known to be associated with the formation of shear-induced structures (SIS). The complex behaviour of viscosity \( \eta \) as a function of shear rate poses a problem for the calculation of the Reynolds number. Applying the generalized Re number proposed by Metzner and Reed\(^3\) in this case requires the plotting of the viscosity curve at high shear rates, which is impossible due to the formation of Taylor vortices. For these reasons, the Reynolds number was calculated from the equation valid for Newtonian fluids, using the viscosities of the EG solutions.

**Pressure drops**

Figure 2 shows the effect of cocamide DEA concentration on the dependence of the degree of reduction DR on the Re number for solutions containing 10% EG and 0.12% CAPB. At the Re values >7,000, the DR values are similar for all the solutions assessed in the study. At lower Reynolds numbers, higher DR values were obtained only for the solution containing 0.14% cocamide DEA. The results shown in Figure 2 apply to the fluids at the temperature of 10 °C. At higher temperatures, the solution containing 0.14% cocamide DEA was found to be unstable during the flow, which was manifested by significant changes in pressure drop over time at a set average flow rate. In addition, the DR parameter assumed lower values. Consequently, the solutions containing 0.1% and 0.12% cocamide DEA were selected for further tests.
The DR value is affected not only by the concentration of surfactants but also by the concentration of ethylene glycol. Pressure drop measurements showed that increasing the ethylene glycol concentration to 20% caused a sharp increase in pressure drop during the flow of a CAPB/DEA solution at the concentration of 0.12%/0.1%.

However, a significant reduction in drag was observed at the cocamide DEA concentration of 0.12%. Figure 3 shows a comparison of the relationship DR = f(Re) for the aqueous solution of CAPB/DEA without and with the addition of ethylene glycol. An increase in EG concentration led to a greater reduction in drag.

Figure 3. Influence of the concentration of ethylene glycol on the degree of reduction DR for solutions containing CAPB and DEA cocamide (T = 10 °C)

During the flow in central cooling systems, the fluid temperature changes by a dozen degrees Celsius or so. Consequently, the surfactant additives used should lead to a decrease in pressure drop over the entire range of temperature variations occurring in the system at hand. Figures 4 and 5 show the effects of temperature on the DR = f(Re) relationship for the 10% and 20% ethylene glycol solutions with added CAPB/DEA. For the EG solution at the concentration of 10%, the degree of drag reduction expressed by the DR parameter was stable at around 70% over the entire temperature range (from 0 °C to 20 °C). The findings were slightly different for the 20% EG solution. In this case, similar DR values were achieved in the temperature range from –5 °C to 10 °C, while at 15 °C and 20 °C there was a significant decrease in the values of the DR parameter in the low Reynolds number range.

Figure 4. Influence of temperature on the value of the DR parameter during the flow of a 10% ethylene glycol solution with the addition of CAPB/DEA (0.12%/0.1%) (approximate pH value was 6.8)

Stability of CAPB/DEA solutions

Based on the studies available in the literature, a reduction in drag resulting from the addition of cationic and amphoteric surfactants decreases with time, and the micellar microstructure becomes more susceptible to mechanical degradation. Figure 6 shows an example of the relationship between the friction coefficient λ and the Re number for an aqueous solution of CAPB/DEA. Three characteristic ranges of λ variation can be distinguished. Up to the critical value of Re\(c_1\), the friction coefficients decreased with increasing Re values and are considerably smaller than the values calculated from the Prandtl-Kármán equation. Above the value of Re\(c_1\), drag begins to subside rapidly, which is manifested by increasing λ values, while above the value of Re\(c_2\), drag disappears completely. Based on the literature data, the values of Re\(c_1\) and Re\(c_2\) rise with increasing tube diameter, while the corresponding critical shear stress values τ\(w,c_1\) and τ\(w,c_2\) are independent of it. The occurrence of the critical Reynolds numbers Re\(c_1\) and Re\(c_2\) is evidence that the micellar microstructure responsible for inducing drag undergoes mechanical degradation. When the flow rate is decreased, the micelles are rebuilt and the phenomenon of drag reduction is observed again. The resistance of micellar associates to permanent mechanical degradation is attributed to the physical nature of interactions between surfactant molecules.

Figures 7 and 8 show the relationship between the DR parameter as a function of the Re number obtained from the pressure drops measured during the flow of CAPB/DEA solutions at various time intervals after the...
preparation of the solution. Two experiments were conducted, with the fluids differing in their initial pH. Figure 7 shows the results obtained for the test solution with an alkaline pH after preparation (following the addition of sodium hydroxide). In this case, there was an increase in the critical value of the Reynolds number $Re_{c1}$ with time, while after 50 hours of pumping there was also a decrease in the degree of drag reduction $DR$. Each series of pressure drop measurements was followed by pH measurements. The results are shown in Figure 7. What they show that the pH of the solution decreased with time, which might be explained by the progressive hydrolysis of cocamidopropyl betaine.

Different findings were observed for the solution with the initial pH of 6.7, where no changes were observed in the degree of drag reduction. However, the values of the critical Reynolds number $Re_{c1}$ decrease, though at a far slower rate than in the CTAC/NaSal solutions and the CPAB/DEA solution at an alkaline pH.

**CONCLUSIONS**

The pressure drop measurements showed drag reduction occurring during the flow of CPAB/DEA solutions with the addition of significant amounts (up to 20%) of ethylene glycol. For these reasons, CPAB/DEA solutions can be used at temperatures down to -5 °C. The pressure drop measurements performed in the study show that aqueous CPAB/DEA solutions undergo ageing, which is manifested primarily by changes in the critical Reynolds number ($Re_{c1}$) at which the phenomenon of drag begins to decline. The resistance of the micellar microstructure of CPAB/DEA solutions to mechanical degradation depends strongly on the pH level. Significant changes in flow properties were observed when the initial pH was alkaline. The solution with initial pH close to neutral was stable over time, though reduced resistance to degradation with time was also observed.

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**LITERATURE CITED**


