Steady Shear and Dynamic Properties of Drag Reducing Surfactant Solutions

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Abstract:
The rheological behavior of oilfield surfactants (Aromox® APA-T and APA-TW) at various concentrations was studied using steady shear and dynamic testing. The results showed that the solutions exhibit non-Newtonian behavior at all concentrations, with their rheological character influenced by the temperature and ionic content of the base fluid. Temperature was observed to have a significant effect on viscosity and dynamic data. The apparent viscosity at different temperatures could be reduced to a single master curve using horizontal and vertical shift factors. However, satisfactory scaling could not be attained for the dynamic or viscoelastic data. Molecular scaling using characteristic time for data at different concentrations proved unsuccessful due to the strong non-Newtonian character of surfactant solutions. Scaling relations between rheological parameters and concentration indicated the presence of long micelles in APA-T solutions. APA-TW solutions, on the other hand, contained branched micelles.

Key words:
surfactants, non-Newtonian behavior, rheology, viscoelasticity, concentration, temperature

1 INTRODUCTION

The application of surfactants in the petroleum industry is varied and diverse. Surfactants are used in a myriad of roles within the oil and gas industry. In drilling operations, surfactants can act as thinners, lubricants, and emulsifiers. Examples of some surfactants are lignosulfonates and sulfonated asphalt, which function as thinners and emulsifiers, respectively [1]. For cementing operations, surfactants are used as spacer fluids that condition the wellbore in preparation for pumping cement. They act as viscosifiers when added to completion brines. For enhanced oil recovery operations, surfactants are used for interfacial tension reduction. Other applications include the following: matrix diversion, filter cake removal, and wellbore cleanouts [2]. More recently, surfactants have been developed for hydraulic fracturing operations. Exploration and exploitation of less permeable reservoirs encouraged research into formulations of viscous fluids for stimulation. Polymer fluids, introduced in the 1960s, were observed to cause formation damage and thereby hinder production [3]. This is because the relatively large size of polymer molecules has a greater tendency to plug pore throats. Thus, it became important for researchers and the industry to develop fluids that not only are sufficiently viscous to initiate and propagate fractures but also are non-damaging to the formation. This led to the development of polymer-free viscoelastic surfactant (VES) fluids.

Viscoelastic surfactants contain molecules that are smaller (5,000 times smaller) than guar molecules [2]. Moreover, they satisfy other criteria for their widespread use. These criteria are low pressure drop in pipes, ability to transport and place proppants, and flow back with little or no formation damage [2]. The role of surfactants has been expanded to operations in low and high temperature reservoirs as well as to unconventional plays such as coalbed methane reservoirs [3]. For coalbed methane applications, VESs have proved effective at minimizing formation damage, which ultimately results in greater production. Shear degradation with surfactants is temporary when compared to permanent degradation with polymers. They are non-damaging to hydrocarbon formations because they leave no residue in pore spaces. A drawback of surfactants is loss of functionality at elevated temperatures.

Many industrial applications, especially in the chemical and petroleum industries, involve solids transport by
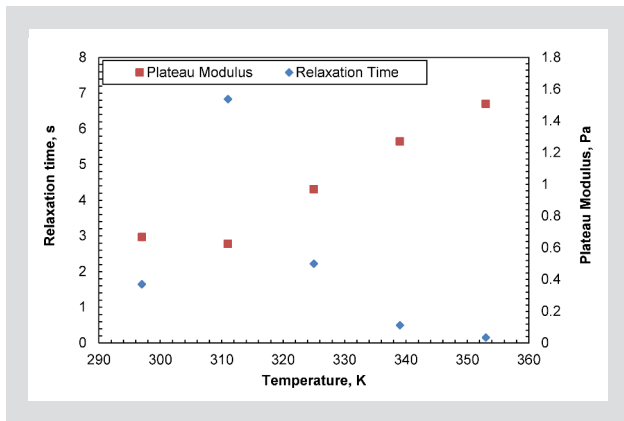
Figure 9: Maxwell parameters versus temperature for 4 % APA-T.

Figure 10: Reduced moduli parameters for 4 % APA-T solution at various temperatures: (a) Reduced loss modulus amd (b) reduced storage modulus.

ciple is used. The time-temperature superposition (TTS) is primarily used to examine the equivalency between frequency and temperature. This principle simply assumes equal temperature dependence on relaxation mechanisms [37] and assesses the similarity of responses at several temperatures [17]. Three approaches were tested for reducing the 4 % solution to a single master curve for $G'(\omega)$. The first approach uses the method of reduced variables with the horizontal shift factor from Equation 11a. The second approach involves scaling the angular frequency with the relaxation time, which has been successfully applied to surfactant solutions [37]. The third approach (Figure 10) scales the moduli axis with the plateau modulus and the frequency axis with the relaxation time [39]. The results of the TTS show an inability to reduce the data to a single curve irrespective of the scaling technique. As a result, it may be stated that there are possible structural changes within the sample that are not solely due to temperature. Fluids displaying this sort of behavior are called "thermorheologically" complex fluids.

With these findings, it obvious that structural changes in WLMs occur with increasing temperature. The largest value of τ_R at 311 K suggests the presence of long micelles as stress relaxation is reduced. At higher temperatures (> 311 K), the presence of shorter micelle length is unlikely because the mesh and entanglement network density increases with temperature. This is confirmed by an increase in G_o with temperature. An explanation for this observation can be attributed to branching or formation of joints in micellar network. These joints slide along the micelle length, resulting in faster stress relaxation [24].

6 CONCLUSIONS

The rheological behavior of Aromox® APA-T and APA-T solutions at different concentrations was investigated using steady shear and dynamic oscillatory testing. The influence of concentration and temperature on rheological properties was reported. The zero-shear rate viscosity increased with concentration, as expected. An in-
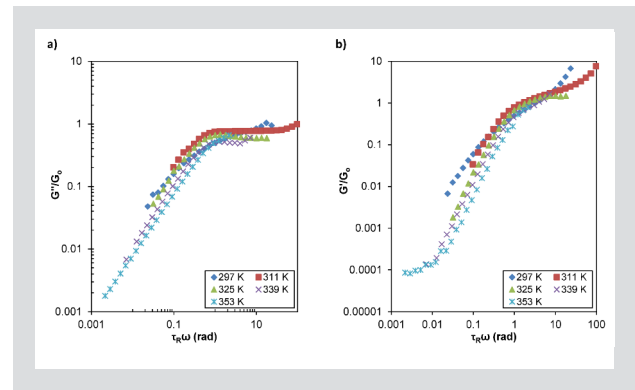
crease in concentration promotes formation and growth of rod-like micelles. Temperature had a significant effect on the rheological character of test solutions. The zero-shear rate viscosity increased with temperatures between 297 K and 311 K. Correspondingly, the relaxation time increased with temperature within the same range. This observation can be attributed to the growth and entangling of worm-like micelles. At higher temperatures, the zero-shear rate viscosity and relaxation time decreased with temperature. The plateau modulus increased with temperature.

Scaling relationships with concentration were compared to theoretical values. For APA-T solutions, the higher exponents for zero-shear rate and relaxation time with concentration indicated the presence of long micelles. These longer micelles were responsible for higher zero-shear rate viscosity and greater viscoelastic response. APA-TW solutions, on the other hand, contained branched micelles because scaling exponents were lower than theoretical values. Further studies involving the use of visualization techniques is recommended to complement and confirm rheological observations.

Master curves were generated for 4 % APA-T and 5 % APA-TW steady shear data at different temperatures. However, all attempts to generate master curves for viscoelastic data failed due to the thermorheologically complex nature of these fluids. Molecular scaling using the characteristic time for data at different concentrations proved unsuccessful because the non-Newtonian character of surfactant solutions prevented the collapse of data to a single curve.

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