DURABILITY OF A DRAG REDUCING SOLUTION

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ABSTRACT:
Effectiveness of drag reduction by small addition of a surfactant in the turbulent flow of water depends on the structure and concentration of the additive, temperature of the solution and turbulence intensity, possible flow disturbance by a mechanical obstacle and the content of ions in water, but also on the age of the surfactant solution. We show how important aging effects are in connection with total surfactant concentration, in particular how rheological parameters of the drag reducing solution change with time.

ZUSAMMENFASSUNG:
Der Strömungswiderstand in Fernwärmeleitungen hängt bei der Zugabe geringer Mengen von Tensiden in die turbulenten Strömungen nicht nur von der Additivzusammensetzung, Additivkonzentration, Temperatur, Turbulenzintensität, mechanische Strömungsstörung ab, sondern auch von der Ionenstärke und dem Alter der Lösung. In diesem Beitrag wurde daher der Einfluss der Konzentration als Funktion des Lösungsalterung untersucht. Die rheologische Eigenschaften der Lösungen zeigten sich als zeitabhängig.

RÉSUMÉ:
L'efficacité de la réduction de la résistance de la traînée dans l'écoulement turbulent de l'eau par l'ajout d'un surfactant dépend de la structure et de la concentration de l'additif, de la température de la solution, de l'ampleur de la turbulence et la perturbation éventuelle de l'écoulement par la présence d'un obstacle, de la quantité d'ions présents dans l'eau mais également de l'âge de la solution micellaire. On souligne l'importance de ces effets de vieillissement en rapport avec la concentration totale en tensio-actifs en montrant en particulier comment les caractéristiques rhéologiques de la solution changent en fonction du temps.

KEY WORDS: drag reduction, surfactants, viscoelasticity, degradation of additives

1 INTRODUCTION

It is believed that long thread-like micelles are responsible for surfactant turbulent drag reduction. Such a micelle microstructure ensues by mixing a cationic surfactant with a counter ion compound after a certain concentration is reached. The advantage of surfactant additives is their good resistance against mechanical degradation. Even though high shear will break up the micelle microstructure, the microstructure reassembles again after the shear is decreased and after some additional regeneration time the drag reduction is recovered [1]. However, age degradation is different: Surfactant solution loses gradually its drag reducing ability with time. Mechanical degradation of surfactants is a transient process in comparison to permanent mechanical degradation of polymeric additives [2 - 4] while age dependent degradation of surfactants is permanent.

The influence of age on mass ratio of the cationic Hexadecyltrimethyl ammonium bromide (CTAB) to Sodium salicylate (NaSal) was investigated earlier [5]. It was found that suitable mixture for turbulent drag reduction is made by equal mass of both components and that some excess of NaSal improves the durability in the range of low pressure drops while there is a negative influence of high pressure drops. Approximate limit is a critical wall shear stress about 6 Pa. The stability of drag reduction with age depends also on total concentration of both components which is the matter of investigation presented in this paper.

Surfactant CTAB was supplied by Sigma Aldrich Chemie GmbH as 96% powder and NaSal was purchased from Fisher Scientific with 99.5% purity. Maximum total concentration investigated was 3.82 g/l, the ratio CTAB to NaSal was kept constant 1:1.1. Experiments were done with tap water.

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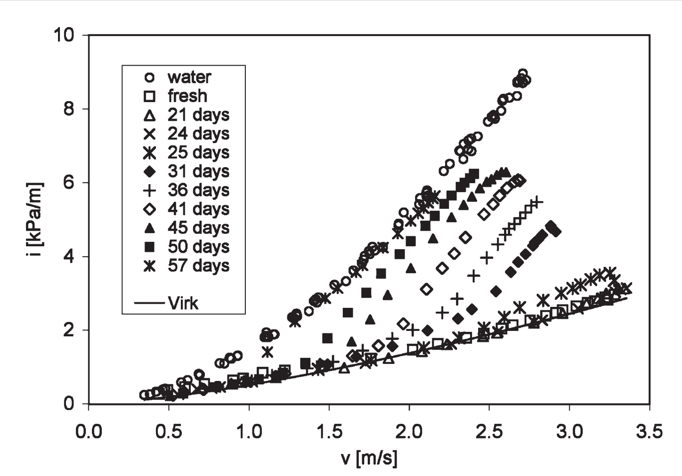

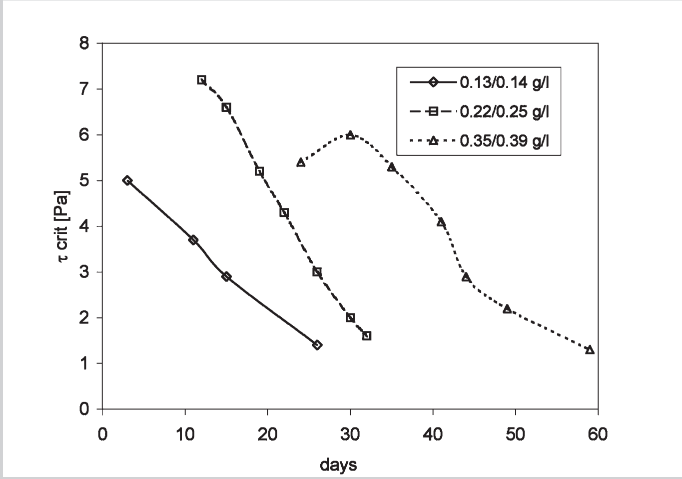

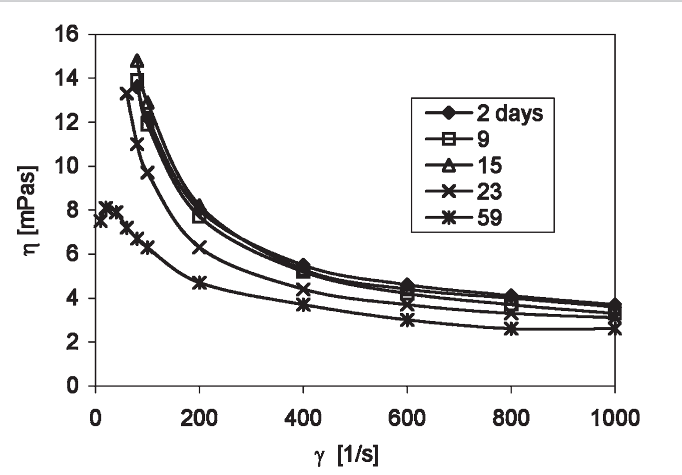

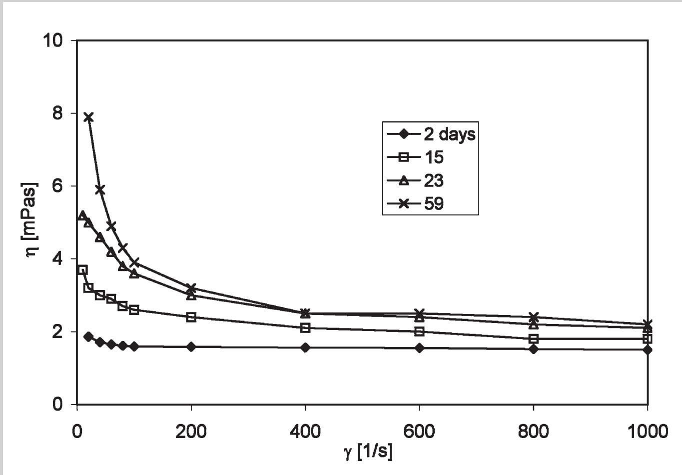

Figure 7 (left above): Degradation of the solution with shown concentration by age. Full curve is the Virk asymptote.

Figure 8 (right above): Dependence of critical wall shear stress on age of the solution.

Figure 9 (left below): Time change of apparent viscosity η, in a high concentrated solution which showed relatively time independent drag reduction.

Figure 10 (right below): Time change of apparent viscosity of the diluted solution.

Decrease of critical wall shear stress, $\tau_{w,\,crit}$, with time is shown in Figure 8 for three low concentrated solutions. Values of the shear stress can however be determined only approximately. We see that CTAB solutions degrade with age; degradation depends on total concentration and is permanent. From Figures 4, 6, and 7 approximate values of Re_{crit} can be assembled. The dependence of Re_{crit} goes in-line with degradation. The results presented so far allows us now to summarize drag reduction capability of the cationic surfactant CTAB. The viscoelastic surfactant (as well as similar CTAC - Cetyltrimethyl ammonium chloride) is not such a good drag reducer as the cationic non-viscoelastic Arquad SV50 [8] which shows more reliability and durability in the concentration spectrum up to 2.0/2.85 g/l [7].

It is generally presumed that the shape of rod-like micelles is the main cause for drag reduction effect. We can speculate that the bounds responsible for formation of this shape are weakening with time when the micelles are strained [9 - 10].

3 RHEOLOGICAL RESULTS

Viscoelastic properties of the CTAB/NaSal samples in tap water were investigated in rotational rheometer RS300 (ThermoHaake) with double gap cylinder system for both viscosity measurements and oscillation measurements. Stationary flow curves (CR modus) were obtained at 20°C in the range of shear rates 0.1 to 1000 s^{-1}. Oscillation measurements were performed in frequency sweeps (CS modus) with a frequency range from 0.01 to 10 Hz at constant stress 1 Pa. Stress sweeps (CS modus) were performed in the stress range 1 – 200 Pa at frequency 1 Hz. The aging of the samples were studied for two months from their preparation. Complex time dependent rheological material properties make it difficult if not impossible to predict the proper viscosity of these solutions [11].

Viscosity curves of two CTAB/NaSal solutions, i.e. the dependence of apparent viscosity, η, on shear rate, $\dot{\gamma}$, are in Figures 9 and 10. Apparent viscosity of 1.21/1.33 g/l and 0.46/0.5 g/l solutions shows a distinct increase of viscosity with time. The constitutive Ostwald-de Waele equation was fitted to the obtained data. The solutions with 1.21/1.3 g/l, 0.62/0.68 g/l, 0.46/0.5 g/l and 0.24/0.27 g/l concentration showed the flow index is approaching or equal to 1 from the very start of experimenting, which means quasi-Newtonian behavior.

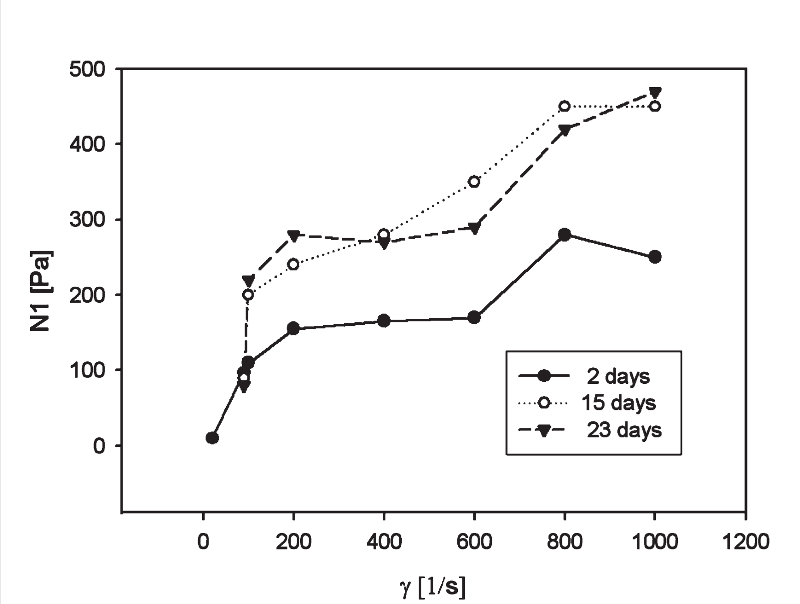

Figure 11: Measurement of viscoelastic properties shows a great scatter of data in low concentrated solutions like in this plot of first normal stress difference, N_1 [Pa], in dependence of shear rate.

Fresh solutions show loss modulus, *G''*, greater than storage modulus, *G'*, in the sweep of frequencies 0.1 to 10 Hz, which means that viscous properties prevail over elastic ones. This state remained throughout the aging of the samples. There was no influence of age on *G'*. Values of both moduli are very low, they were found to be below 0.05 Pa.

Surprisingly, viscoelastic character of CTAB/NaSal solution was confirmed by positive values of first normal stress difference, N_1 (Figure 11). Normal stress investigation was carried out in the cone and plate system. However, the very low concentrated solutions showed a considerable scatter of measured results.

4 CONCLUSIONS

The *i* - *v* curve, which shows the effectiveness of CTAB solutions, is stable in time until the critical wall shear stress is reached. At the flow above critical wall shear stress the solution loses quickly drag reduction effectiveness, at the flow with lower wall shear stress than the critical one the drag reduction remains stable. Nevertheless, the critical wall shear stress depends both on concentration and on age of the solution. The lower concentration the earlier starts the degradation. High concentration of CTAB/NaSal shows higher friction loss than water alone in the regime of low mean velocity. In the *i* - *v* curve an inflection point then appears. Apparent viscosity of the solutions changes not only with concentration but also with age. Elastic properties characterized by the storage modulus are much less time dependent.

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