

# Environmentally Acceptable Drag-Reducing Surfactants for District Heating and Cooling

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**ABSTRACT:** The aim of this work was to find drag-reducing surfactants for both district heating and cooling that are environmentally more acceptable than the organic salts of quaternary ammonium compounds that so far have dominated this application. Vortex inhibition of test solutions in glass beakers has been used to screen a large number of surfactant mixtures, various electrolytes, and temperatures. For the most interesting products, the pressure drop in a test loop was measured at various flow rates and temperatures. *N*-cetyl sarcosinate and *N*-stearyl betaine, the latter together with Na-dodecylbenzene sulfonate, give good drag reduction (DR) properties at 65–100 and 45–85°C, respectively. The sarcosinate is sensitive to pH changes, whereas the betaine-sulfonate complex is more robust. Ethoxylates of oleic acid monoethanolamide show good DR properties at 0–25°C. At an increased salt concentration, a mixture of this surfactant with an ethoxylated oleyl alcohol worked well. At a still higher salt concentration, e.g., sea water, a combination of *N*-cetyl betaine and alkylbenzene sulfonate showed DR.

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**KEY WORDS:** Cooling, drag reduction, ethoxylated amide, heating, *N*-alkyl betaine, *N*-alkyl sarcosinate, salt effect.

Reduction in pump work when using drag-reduction (DR) additives was shown to be 70% in a full-scale test (1) which may lead to substantial cost savings when electric power is expensive. Use of a DR additive often makes it possible to expand the distribution net without changing the main transfer lines. Drag reduction by surfactants is usually explained by the surfactant's ability to form long, cylindrical micelles, which are often called wormlike or threadlike micelles. A necessary condition for DR is also an ordering of these micelles by the flowing medium. The goal of this work was to find environmentally better alternatives to the organic salts of quaternary ammonium compounds, which have been dominant as DR additives for district heating and cooling (1–6).

The work comprised organic syntheses, screening tests for DR, and finally DR tests on interesting products in a test loop. Only the last two parts of this work will be treated here.

DR will be particularly useful in district cooling because the power input to the circulation pumps leads to an equiva-

lent heating effect on the cooling medium. DR performance has been previously reported for both anionic (7,8) and non-ionic surfactants (9–11). The major part of laboratory-scale DR tests (12–16) and all full-scale tests for both cooling (4,5) and heating (1–3) have, however, been carried out with cationic surfactants and an organic counterion.

The rather high toxicity of quaternary ammonium compounds on marine organisms and the slow biodegradation of organic counterions of the hydroxynaphthoate type may have contributed to the fact that DR additives have not come into commercial use so far.

## EXPERIMENTAL PROCEDURES

**Materials.** *N*-2-hydroxycetyl, *N*-methylglycinate (C<sub>16</sub>-sarcosinate) has the structure: CH<sub>3</sub>(CH<sub>2</sub>)<sub>13</sub>-CH(OH)CH<sub>2</sub>-N<sup>+</sup>H(CH<sub>3</sub>)CH<sub>2</sub>COO<sup>-</sup>. *N*-2-hydroxystearyl, *N*-methylglycinate (C<sub>18</sub>-sarcosinate) has the corresponding structure with 18 carbon atoms in the hydrophobic part. *N*-cetyl betaine (C<sub>16</sub>-betaine) has the structure: CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>COO<sup>-</sup>, and *N*-stearyl betaine (C<sub>18</sub>-betaine) has a similar structure.

The following surfactants used in this investigation are commercial products. Na-dodecylbenzene sulfonate (Na-LAS) has the structure C<sub>12</sub>H<sub>25</sub>-C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub><sup>-</sup>Na<sup>+</sup> and is a mixture of isomers with the phenyl group attached to the 2, 3, 4, 5, and 6 positions of the linear (unbranched) dodecyl chain. Oleyl hexaethylene glycol ether (OLA-6) has the structure CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>CH=CH(CH<sub>2</sub>)<sub>8</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>6</sub>OH, where the polyglycol chains are distributed according to the Weibull-Nycander theory (17). Oleic acid ethanolamide tri/tetra/pentaethyleneglycol ether (OMA-3/4/5) has the structure: CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>CH=CH(CH<sub>2</sub>)<sub>7</sub>CONHCH<sub>2</sub>CH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>3/4/5</sub>OH, where the polyglycol chains are distributed in the same way as for OLA-6. The oleic acid used for the production of OMA-3, OMA-4, and OMA-5 emanated from rapeseed oil and had the following composition: oleic acid 60%, linoleic acid 20%, linolenic acid 9%, palmitic acid 4%, gadoleic acid 2%, erucic acid 2%, and 3% of various saturated acids. All surfactants, with the exception of Na-LAS, were synthesized by Akzo Nobel Surface Chemistry AB (Stenungsund, Sweden).

The water used was deionized unless stated otherwise. As a model for sea water, the following amounts of technical-grade

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salts were added per liter of deionized water: 38 g NaCl, 5 g  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , and 5 g  $\text{MgSO}_4$ . The NaOH, HCl, and  $\text{H}_2\text{SO}_4$  solutions for pH adjustments were made from analytical-grade chemicals. The hard water, containing  $\text{NaNO}_2$ , which was used in one of the cooling applications, had the following composition (expressed as g/L deionized water):  $\text{NaNO}_2$  1.12,  $\text{NaNO}_3$  0.26,  $\text{NaBO}_2 \cdot 4$  aqueous 0.26,  $\text{Ca}(\text{NO}_3)_2 \cdot 4$  aqueous 0.52,  $\text{MgSO}_4$  0.17.

**Methods.** To facilitate testing of a large number of surfactant mixtures, electrolyte concentrations, and temperatures, a simple screening test was designed, based on the vortex inhibition results of Gordon and Balakrishnan (18). The test solution (40 mL) was placed in a 50-mL glass beaker and placed on a magnetic stirrer, which was kept at a speed of 900 rpm. When the vortex had a depth of less than 2 mm, it was considered as DR conditions. For measuring relaxation time, a 150-mL glass beaker with a height of 90 mm was used to contain 100 mL of test solution, a Teflon-covered magnetic bar,  $6 \times 20$  mm, and also a turbine-type mixer (Ultra Turrax; Jahnke & Kunkel, Staufen, Germany). The beaker was placed on a combined magnetic stirrer and heating plate, and the stirrer was run continuously at 700 rpm. Under DR conditions, i.e., when no vortex was formed, the turbine mixer was started and run for 60 s at 9500 rpm and then stopped. In most cases, a deep vortex could then be seen, and the time was recorded when this vortex had disappeared again. This time was taken as the relaxation time for micelles.

When an interesting system was identified, it was tested in a test loop, which is schematically shown in Figure 1. The total volume of liquid in the apparatus could be varied between 7 and 20 L. The temperature in the open tank could be controlled within the range of 4–100°C. The apparatus was well-insulated to minimize temperature differences in the system. The pump was a stainless-steel centrifugal pump (Grundfos CRN 2-150 C9021; Grundfos, Bjerringbro, Denmark). The flow was controlled by valves and by varying the pump motor speed (speed control Telemecanique Altivar 16). The maximum flow was around 35 L/min. Two different flow meters were used, one for high flows (Brooks 10-1307; Brooks, Huddersfield, United Kingdom) and one for low flows (Brooks 8-1307). The pressure loss was measured with a differential manometer (DRUCK LTD. ptx 120/wl, 0–350

mBar; DRUCK, Barendrecht, Holland). The pressure drop test section for DR measurement consisted of two stainless-steel tubes. The first was a 3.6-m straight section of stainless-steel pipe with an inner diameter of 10 mm. The pressure difference was measured between four pressure taps, of which the first was located 1 m from the entrance of the tube. After a 180° turn, there was a 3-m stainless-steel pipe with an inner diameter of 8 mm, also with four pressure taps, the first more than 0.8 m from the entrance of the tube.

To study the DR effect, the pressure loss  $\Delta P$  was measured over the section  $L$  as a function of the mean flow rate  $v$ . The dimensionless Moody's friction factor,  $\lambda$ , was plotted vs. the Reynold's number, based on the viscosity of water.

$$\lambda = \frac{2D\Delta P}{\rho L v^2} \quad [1]$$

$$Re = \frac{v D \rho}{\mu} \quad [2]$$

where  $L$  = section length,  $D$  = pipe diameter,  $\rho$  = density of the fluid,  $\Delta P$  = pressure loss,  $v$  = mean flow rate, and  $\mu$  = dynamic viscosity.

Fanning's friction factor ( $f$ ) as a function of  $Re$  for water in hydrodynamically smooth pipes in turbulent flow are described by the so-called Prandtl-Karman equation:

$$\frac{1}{\sqrt{f}} = 4 \text{Log} (Re \sqrt{f}) - 0.396 \quad [3]$$

Virk (19) found empirically a maximum DR asymptote for high polymers, which is independent of the additive properties. This asymptote follows the equation:

$$1\sqrt{f} = 19 \text{Log} (Re \sqrt{f}) - 32.4 \quad [4]$$

Moody's and Fanning's friction factors are related as follows:

$$\lambda = 4f \quad [5]$$

All measurements were performed at constant temperature. The  $\lambda$  values for each of the two sections (8 and 10 mm) were calculated as the average of the  $\lambda$  values measured for the three section lengths. The average  $\lambda$  value was plotted against the Reynold's number. The wall shear stress  $\tau_w$  is calculated as follows:  $\tau_w = \Delta P D / 4L$ ,  $\tau_w = \lambda Re \cdot v \cdot \mu / 8D$ . The  $\tau_w$  values were calculated from the average values of  $\lambda$  and are given as a function of the flow rate. The critical wall shear stress is the value of  $\tau_w$  where it starts to increase rapidly, indicating that the DR-forming structures are beginning to disrupt.

## RESULTS AND DISCUSSION

The results from the screening tests are summarized in Tables 1 and 2. Table 1 gives an overview of the useful temperature ranges for the three various groups of surfactants studied. Table 2 is a study of the effects of some electrolytes on the working range and cloud point (CP) of a particular fatty acid amide ethoxylate solution. The results of the relaxation time vs. temperature for  $C_{16}$ -betaine + Na-LAS 6:1 with

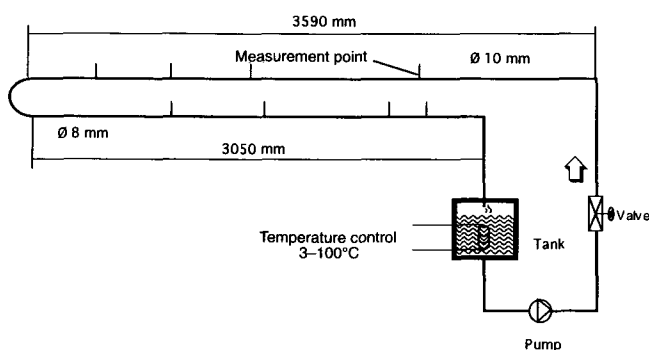


FIG. 1. Schematic picture of the drag-reducing test apparatus.

**TABLE 1**  
Temperature Intervals for DR Function<sup>a</sup>

Surfactant	Conc. active matter (g/L)	Water composition	Temp. interval for DR
OMA-5 + OMA-3 4:1	2.0	Deionized	None
OMA-5 + OMA-3 4:1	4.0	Deionized	20–40
OMA-5 + OMA-3 4:1	2.0	2 mmol/L NaHCO <sub>3</sub>	0–40
C <sub>16</sub> -sarcosinate	0.2	Deionized	30–90
C <sub>18</sub> -sarcosinate	0.1	Deionized	70–100 <sup>b</sup>
C <sub>16</sub> -betaine + Na-LAS 6:1	1.0	Deionized	7–50
C <sub>16</sub> -betaine + Na-LAS 6:1	1.0	2 mmol/L NaHCO <sub>3</sub>	3–50
C <sub>18</sub> -betaine + Na-LAS 8:1	0.5	Deionized	50–85
C <sub>18</sub> -betaine + Na-LAS 8:1	0.5	2 mmol/L NaHCO <sub>3</sub>	60–85

<sup>a</sup>According to the screening test method; DR, drag reduction; OMA-3/4/5, tri/tetra/pentaethyleneglycol ether; Na-LAS, Na-dodecylbenzene sulfonate. The solution pH was adjusted to 9.5 in all tests.

<sup>b</sup>Temperatures above 100°C have not been tested.

surfactant concentration of 1.16 g/L and water Ca(NO<sub>3</sub>)<sub>2</sub> 2 mmol/L, pH 6.6, are temperature (°C) and relaxation time (min), respectively: 10 (7.0), 13 (3.0), 16 (1.5), 18 (1.3), 20 (1.0), and 26 (0.5).

All results from the loop tests are presented as plots of the average  $\lambda$  value as a function of the solvent Reynold's number. Together with the experimental results, lines for the Prandtl-Karman equation for turbulent flow and the Virk asymptote for maximum DR are drawn. All concentrations refer to the active material. The results and discussion are divided into two parts, one for high- and one for low-temperature systems.

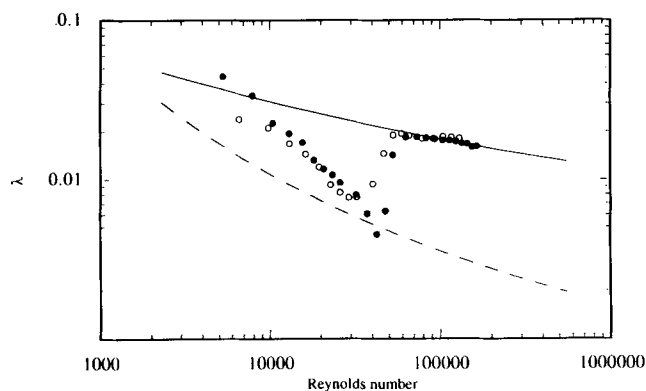
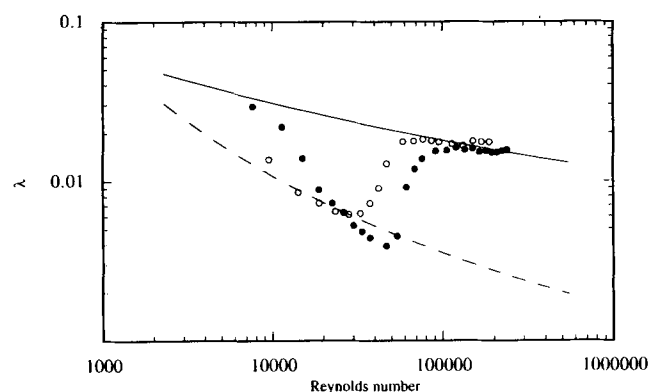
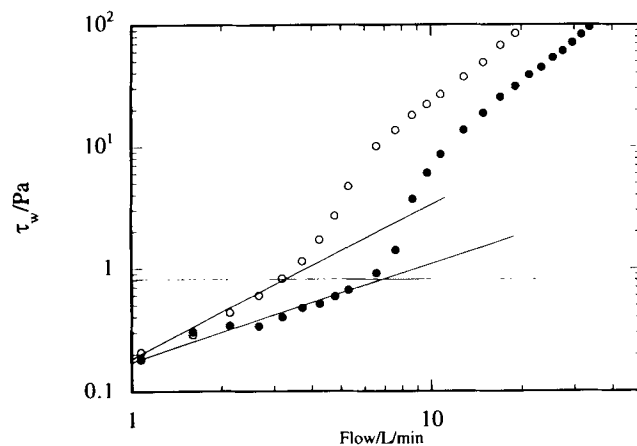
**High temperature systems: sarcosinates.** Table 1 shows that sarcosinates are working at low concentrations and high temperatures. Figure 2 shows the result with 0.5 g/L of a rather pure C<sub>16</sub>-sarcosinate at 66°C and pH 8.45. This temperature is at the lower end of the surfactant's working range, and the DR properties seem to be rather satisfactory. This is also true for the same surfactant at 98°C and pH 8.2 (Fig. 3). Figure 4 gives the wall shear stress  $\tau_w$  as a function of the flow. The critical wall shear stress is apparently about 0.8 Pa for both the 8-mm and the 10-mm tubes. The DR-effect turned out to

**TABLE 2**  
Temperature Intervals for DR of Fatty Acid Amide Ethoxylate Solutions<sup>a</sup>

Conc. of added electrolyte (mmol/L)	NaHCO <sub>3</sub>		Na <sub>2</sub> SO <sub>4</sub>		MgSO <sub>4</sub>	
	Temp. interval for DR	Cloud point	Temp. interval for DR	Cloud point	Temp. interval for DR	Cloud point
0.5	18–39	35 <sup>b</sup>	17–38	33	0–28	18
1	14–38	40 <sup>b</sup>	8–39	26	0–18	10
2	0–40	25	0–35	16	0–12	5
4	0–30	16	0–18	6	0–12	—
6	0–20	10	0–13	4	0–8	—
8	0–15	8	0–10	—	0–8	—

<sup>a</sup>The temperature intervals were determined according to the screening method. Surfactant: OMA-5 + OMA-3 4:1; concentration: 2.0 g/L; solution pH: 9.5. See Table 1 for abbreviations.

<sup>b</sup>Only slight haze was formed—uncertain values.

**FIG. 2.** Moody's friction factor  $\lambda$  as a function of Reynold's number for a 0.5 g/L solution of C<sub>16</sub>-sarcosinate at 66°C and pH 8.45: ○, 8-mm pipe; ●, 10-mm pipe; —, Virk asymptote; —, Prandtl-Karman.**FIG. 3.** Moody's friction factor  $\lambda$  as a function of Reynold's number for a 0.5 g/L solution C<sub>16</sub>-sarcosinate at 98°C and pH 8.2. See Figure 2 for key.**FIG. 4.** Wall shear stress  $\tau_w$ /Pa as a function of the flow rate in L/min for a 0.5 g/L solution of C<sub>16</sub>-sarcosinate at 98°C and pH 8.2. See Figure 2 for key.

be rather sensitive to the solution pH, which is illustrated in Figures 5 and 6, both at 80°C. The good DR effect at pH 9.34 is practically lost at pH 9.65. The chemical stability of the sarcosinates is good, but in some instances, the surfactant crys-

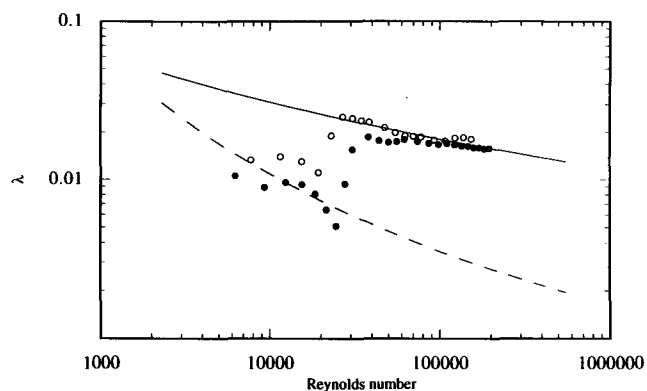


FIG. 5. Moody's friction factor  $\lambda$  as a function of Reynold's number for a 0.5 g/L solution  $C_{16}$ -sarcosinate at 80°C and pH 9.34. See Figure 2 for key.

tallized when the temperature was lowered, usually the day after an experiment was run.

*N,N*-diethylglycine has a  $pK_1$  of 10.47 (20), and the *N*-alkyl-sarcosinate used in this study can be assumed to have a similar  $pK_1$  value. If this is true, then a small change of pH in the region around pH 10 will make a substantial change in the proportion of sarcosinate in anionic form, and this in turn will change the micelle size and shape.

The *N*-alkylsarcosinates are effective at low concentrations and rather high temperatures, when the alkyl group has 16 or 18 carbon atoms. They are easily biodegradable and exhibit normal toxicity on marine organisms, but their tendency to crystallize at lower temperatures and their sensitivity to changes of pH reduces their application potential. However, a mixture of sarcosinates with different alkyl groups will lower the crystallization temperature significantly.

**Betaines + Na-LAS.** Mixtures of zwitterionic and anionic surfactants may give viscoelastic solutions (21,22). As zwitterionic surfactants of the betaine type and most of the anionic surfactants in use are known to be rapidly biodegradable, a number of these combinations were screened to see if they also have good DR properties. The rapid degradation is of

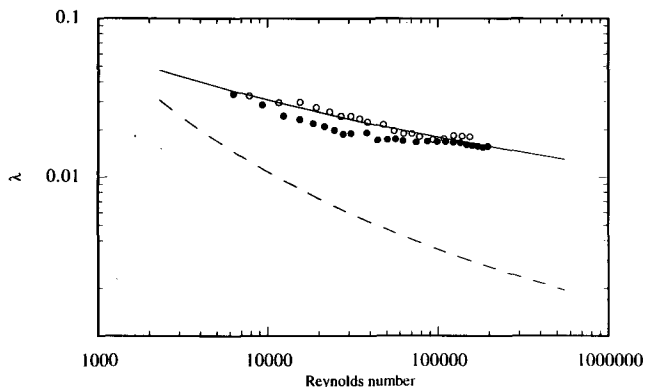


FIG. 6. Moody's friction factor  $\lambda$  as a function of Reynold's number for a 0.5 g/L solution  $C_{16}$ -sarcosinate at 80°C and pH 9.65. See Figure 2 for key.

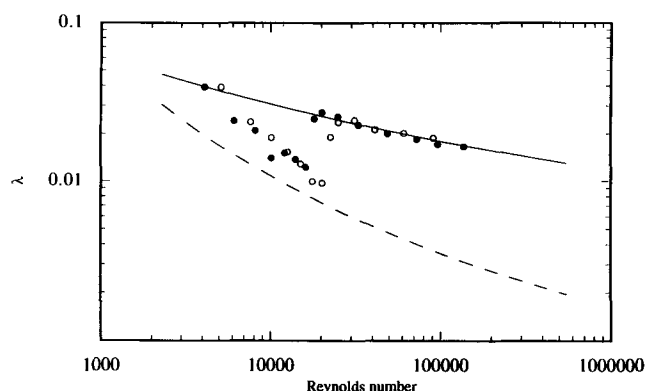


FIG. 7. Moody's friction factor  $\lambda$  as a function of Reynold's number for a 2 g/L mixture of  $C_{18}$ -betaine and Na-dodecylbenzene sulfonate in weight proportion 87:13 at 50°C. See Figure 2 for key.

particular value if the circulating water eventually would leak directly to a river or a lake. Table 1 shows that suitable combinations of *N*-alkylbetaines and Na-LAS can give a good DR effect at medium to high temperatures. This work resulted in a promising mixture of 1 mol Na-dodecylbenzene sulfonate (Na-LAS) and 6.56 moles of *N*-stearylbetaine ( $C_{18}$ -betaine) which showed good DR properties in the temperature range of 50–85°C when tested at a concentration of 2.0 g/L at 50°C and 0.25 g/L at 85°C (Figs. 7 and 8).

The drag-reducing properties of the abovementioned solution are rapidly lost when the temperature is raised above 85°C. The large difference in concentration between 50 and 85°C should not be taken as an indication of a difference in effect between these temperatures. The surfactant mixture will most probably be effective with 0.25 g/L at 50°C also. Variation of pH between 7 and 10.5 had no influence on the DR properties in the screening tests, a result that should be expected considering the strong acid character of the two components. Both components are also easily biodegradable, and their effect on marine organisms is normal for surfactants with the same critical micellar concentration (22). While the crystallization temperature (Krafft point) for the  $C_{18}$ -betaine

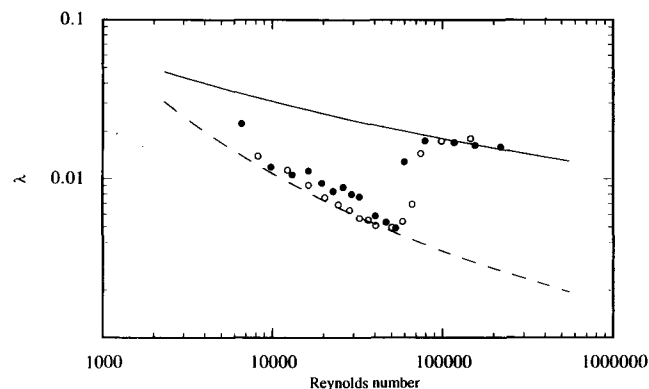
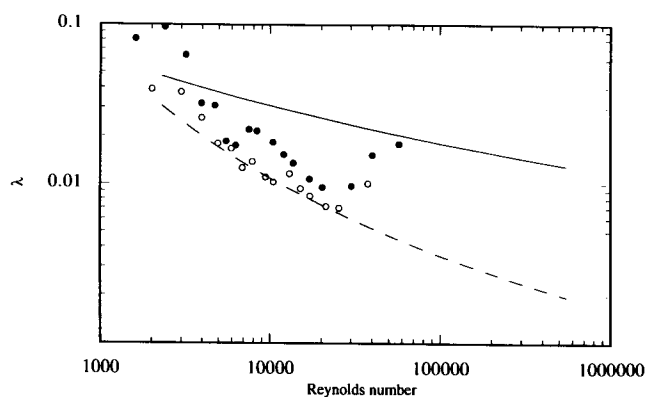


FIG. 8. Moody's friction factor  $\lambda$  as a function of Reynold's number for a 0.25 g/L mixture of  $C_{18}$ -betaine and Na-dodecylbenzene sulfonate in weight proportion 87:13 at 85°C. See Figure 2 for key.

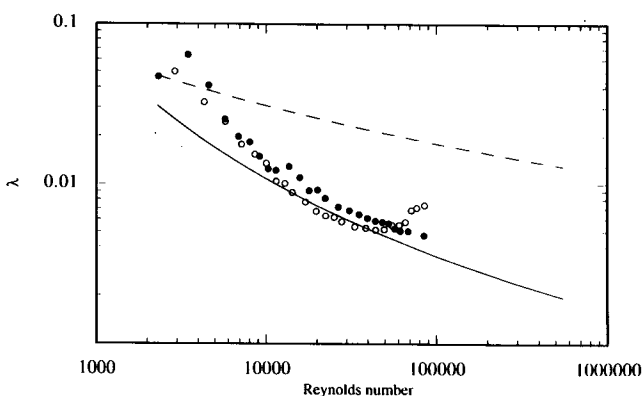
is 30°C, the corresponding temperature for the mixture of betaine and Na-LAS is 22°C. A lowering of the Krafft point in mixtures of anionic and zwitterionic surfactants also has been found by Tsujii *et al.* (23).

**Low temperature systems.** Ethoxylated fatty acid monoethanolamides have previously been shown to give good DR properties (11), and the first system tested at a low temperature was a mixture of OMA-5 (3.2 g/L) and OMA-3 (0.8 g/L) in a solution containing 0.125 g/L of  $MgSO_4$  at pH = 8.2 (Fig. 9). Without this rather small addition of salt, no DR effect was exhibited by the mixture at temperatures below 20°C. Figure 10 gives the result at 7°C and Figure 11 at 21°C. The system gives excellent results in the temperature range 7–21°C where the DR effect increases with temperature. At 21°C, pump capacity was not great enough to produce a flow, causing DR breakdown. At approximately 12°C, some cloudiness appeared, which increased to rather cloudy at 21°C. The solution also apparently lost its viscoelastic behavior at around 12°C.

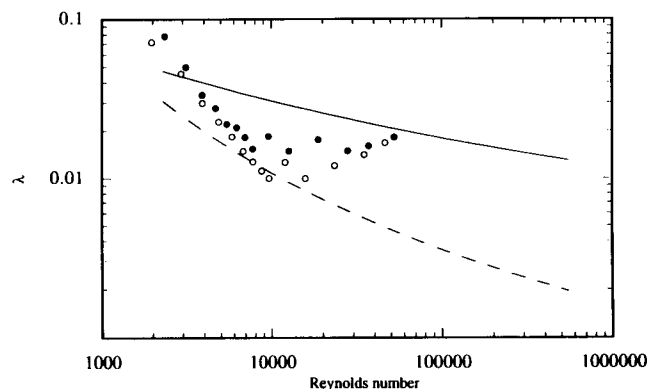
The strong influence of  $MgSO_4$  on the DR properties is most probably due to the presence of 3 mol% of fatty acid



**FIG. 9.** Moody's friction factor  $\lambda$  as a function of Reynold's number for a mixture of pentaethyleneglycol ether (3.2 g/L), triethyleneglycol ether (0.8 g/L), and  $MgSO_4$  (0.125 g/L) at 7°C and pH = 8.2. See Figure 2 for key.



**FIG. 10.** Moody's friction factor  $\lambda$  as a function of Reynold's number for a mixture of pentaethyleneglycol ether (3.2 g/L), triethyleneglycol ether (0.8 g/L), and  $MgSO_4$  (0.125 g/L) at 21°C and pH = 8.2. See Figure 2 for key.

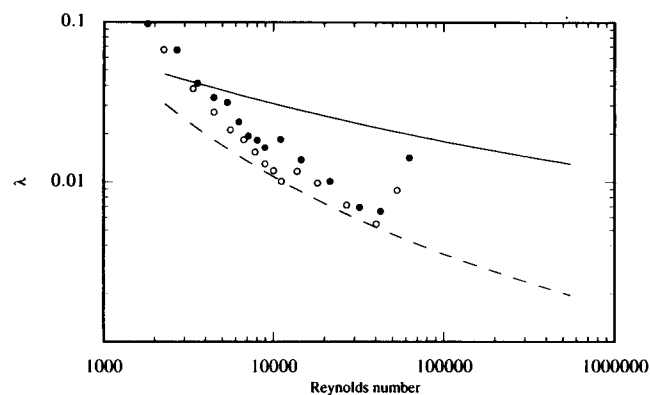


**FIG. 11.** Moody's friction factor  $\lambda$  as a function of Reynold's number for a mixture of 6 moles of ethylene oxide (3 g/L), pentaethyleneglycol ether (3 g/L), and 6.6 g/L of a salt mixture similar to an anticorrosion additive (see Materials section) at 6.4°C and pH around 9.5. See Figure 2 for key.

soap in the OMA-5 and OMA-3 products. The magnesium ions will screen the negative charges of the carboxylate groups and thus decrease their effective size. This in turn leads to a closer packing of the head groups at the micelle surface, and this will influence the size and shape of the micelles. The CP of this surfactant mixture also will be lowered by the addition of magnesium sulfate.

To elucidate the effect of various electrolytes on the DR working range and CP of this particular type of nonionic surfactants, a series of screening tests were made, and the results are given in Table 2. It is evident that divalent magnesium ions have a much stronger influence than sodium ions, but also that sulfate ions are more effective than monovalent hydrogen carbonate ions (at pH 9.5, 85% of the carbonate ions are in monovalent form).

Another way of compensating for the soap present in the ethoxylated ethanolamides should be to add a suitable cationic surfactant. A number of such mixtures were tested with the screening method. Oleyl amine and OMA-5 in a molar proportion of 1:20 gave good results in the screening



**FIG. 12.** Moody's friction factor  $\lambda$  as a function of Reynold's number for a mixture of 6 moles of ethylene oxide (3 g/L), pentaethyleneglycol ether (3 g/L), and 6.6 g/L of a salt mixture similar to an anticorrosion additive (see Materials section) at 11.2°C and pH around 9.5. See Figure 2 for key.

test, and measurements in the test loop were made with this combination at pH 9.7, both at 6.6°C and 4.1 g/L and at 12°C and 2.05 g/L. The results are shown in Figures 11 and 12. Some data for the 8-mm tube are below the Virk maximum drag-reducing asymptote. The fatty acid soaps in the OMA-5 amounted to 3% on a molar basis, but it was necessary to add 5 molar % of oleyl amine to achieve good drag-reducing properties, i.e., the mixture was slightly cationic. The discrepancy may be explained by a part protonation of the amine at pH 9.7, but also by our observation that a small amount of a charged surfactant, either anionic or cationic, is needed for a good DR effect with these ethoxylated amides.

In the two examples above, the solutions were made up with deionized water, but 1 mmol  $\text{MgSO}_4/\text{L}$  was added in the first case. Water with a higher electrolyte content, such as sea water or hard tap water, with  $\text{NaNO}_2$  added as an anticorrosion agent, did not exhibit DR properties with any of the abovementioned combinations. From the work of Zakin and Chang (9), it is known that ethoxylated fatty alcohols can give good DR properties at increased ionic strength. However, it is necessary to use a rather high concentration of the ethoxylated alcohols for a sufficient DR effect in the type of hard water, with added  $\text{NaNO}_2$ , as described in the Materials section (Fig. 13).

Numerous screening tests with various combinations of nonionic surfactants in the abovementioned hard water with  $\text{NaNO}_2$  indicated that a combination of 60% oleyl alcohol + 6 moles ethylene oxide (OLA-6) and 40% ethoxylated ethanol amide (OMA-5) had a good DR performance at 3 g/L and 6–21°C (Figs. 14, 15, and 16). The solution was clear at low temperatures but began to get cloudy at 11°C, and at the same temperature, the apparent viscoelastic properties started to disappear. In contrast to this, the DR properties improved at higher temperatures, up to 25°C. This high DR effect above the CP may be explained either by a DR effect of the surfactant-rich phase itself or by a sufficient amount of wormlike micelles in equilibrium with the surfactant-rich phase. As the water phase, in equilibrium with the surfactant-rich phase,

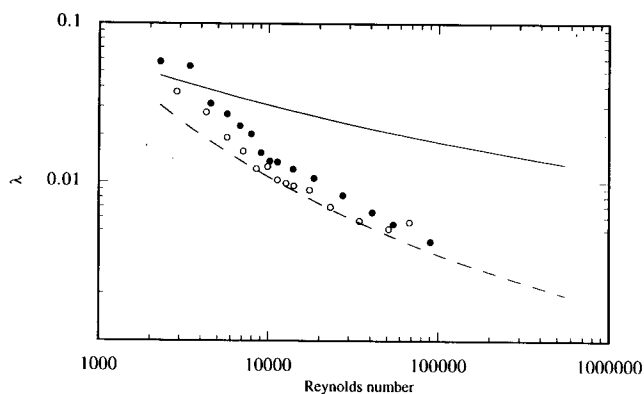


FIG. 13. Moody's friction factor  $\lambda$  as a function of Reynold's number for a mixture of 6 moles ethylene oxide (3 g/L), pentaethyleneglycol ether (3 g/L), and 6.6 g/L of a salt mixture similar to an anticorrosion additive (see Materials section) at 20.5°C and pH around 9.5. See Figure 2 for key.

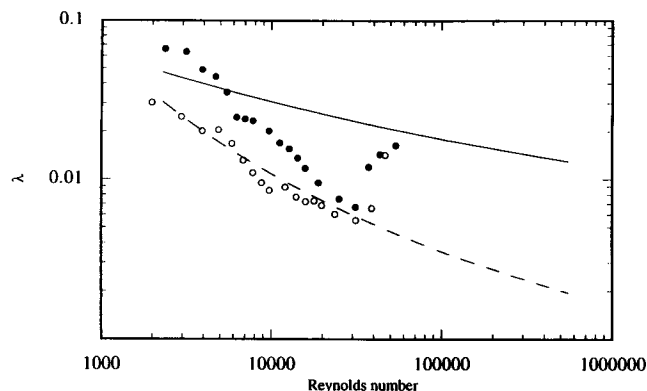


FIG. 14. Moody's friction factor  $\lambda$  as a function of Reynold's number for a mixture of pentaethyleneglycol ether (4 g/L) and oleylamine 0.1 g/L at 6.6°C and pH = 9.7. See Figure 2 for key.

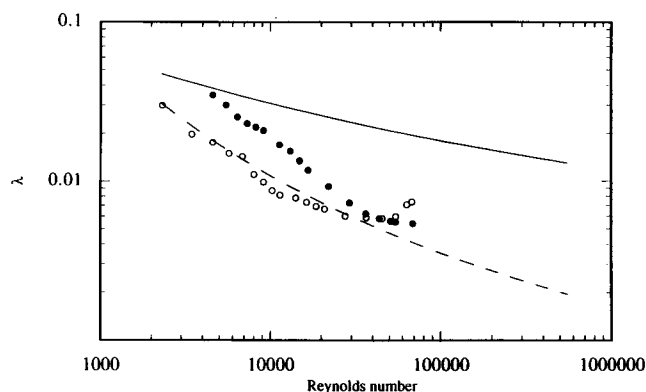


FIG. 15. Moody's friction factor  $\lambda$  as a function of Reynold's number for a mixture of pentaethyleneglycol ether (2 g/L) and oleylamine 0.05 g/L at 12°C and pH = 9.7. See Figure 2 for key.

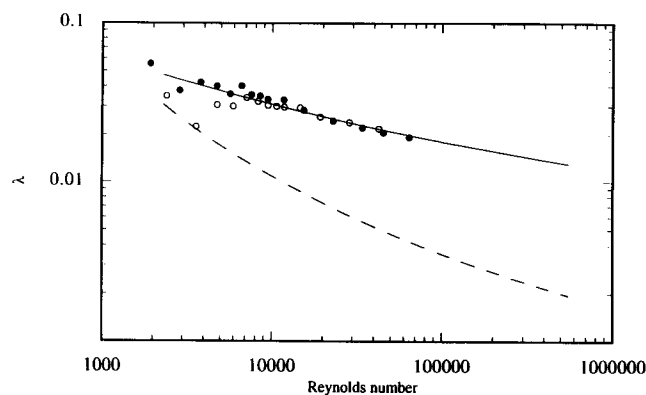


FIG. 16. Moody's friction factor  $\lambda$  as a function of Reynold's number for a mixture of  $\text{C}_{16}$ -betaine 1.1 g/L and Na-dodecylbenzene sulfonate 0.1 g/L in a salt water solution (see Materials section) at 13°C and pH 5.8. See Figure 2 for key.

does not show any apparent viscoelasticity, we assume that elongated structures in the latter phase are mainly responsible for the DR properties. Screening tests with water similar to that from the North Sea indicated that good DR properties

could not be achieved with surfactants based on polyglycol ethers, but a combination of  $C_{16}$ -betaine and Na-LAS looked promising at low temperatures. Na-LAS and  $C_{16}$ -betaine in a molar ratio of 1:12 in sea water was thus DR-tested at 13 and 24°C and a total concentration of 0.56 g/L (Figs. 16 and 17).

The DR effect seems to be limited to low Reynold's numbers, but this is most probably dependent on a rather long induction time for the structures giving the DR properties. It is assumed here that these structures consist of more or less parallelized cylindrical micelles, and that the induction time is the time for the micelles to change from a random to a parallel order by the influence of liquid flow. It can be postulated that these structures would be destroyed in the pump and the regulating valve that follows. The micelles may also be, at least partly, disrupted in the pump.

A good indication that the induction is slow is found in the fact that the DR effect in the 10-mm tube, which is entered first by the flow, is significantly less than in the 8-mm tube. The time for the water passage from the regulating valve back to the tank is rather short in this circuit, about 20 s at  $Re = 10^4$ . If the induction time is assumed to be in the same order of magnitude, it would explain both the difference between the 10-mm and the 8-mm tube and the limited overall DR effect. The screening method for the relaxation time was applied on a solution of  $C_{16}$ -betaine + Na-LAS in hard water at 10–26°C, and the results are shown earlier. The strong temperature dependence can be explained by a significant disruption of the micelles by the turbine mixer. The restructuring to threadlike micelles is most probably a much slower process than the parallelization of these micelles after a minor disturbance caused by a valve or a sharp bend of the tube.

*N*-alkyl sarcosinates have good DR properties for district heating, but they also have rather high crystallization temperatures. *N*-alkyl betaines in combination with anionic surfactants have good DR properties, both at low and high temperatures, depending on alkyl chainlength. Drag-reducing agents for district cooling can be based on fatty acid amide ethoxylates and adapted to various salt contents of the water by

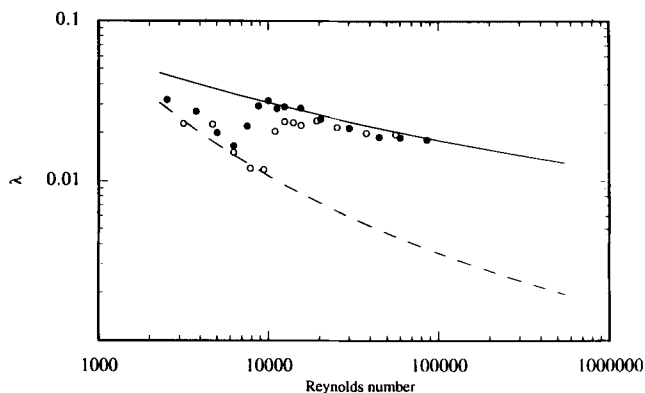
changing the degree of ethoxylation or by adding an alcohol ethoxylate.

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## REFERENCES

1. Hammer, F., Demonstration of Smooth Water in the District Heating System of Herning, Denmark, in *International Symposium on Fluids for District Heating*, Technical University of Denmark, Copenhagen, 1991, pp. 139–150.
2. Steiff, A., W. Althaus, S. Groth, J. Helmig, H.-H. Kleuker, T. Wocadlo, and P.-M. Weinspach, Progress in the Application of Drag Reducing Additives in District Heating, in *Ibid.*, pp. 35–39.
3. Kleuker, H.-H., W. Althaus, A. Steiff, and P.-M. Weinspach, Results of the EC-Demonstration-Project in Völklingen (Germany), in *Ibid.*, pp. 123–137.
4. Cleary, C., S. Day, C. DeWolf, and J. Young, Advanced Fluids for District Cooling Systems: A Review and Progress Report, in *Ibid.*, pp. 3–33.
5. Young, J.C.O.C., Drag Reduction in the Chilled Water Distribution System of a 200-Ton Absorption Chiller, in *Official Proceedings of the 85th Annual Conference of the International District Heating and Cooling Association*, Vol. 85, JDHCA, Seattle, 1994, pp. 301–317.
6. Pollert, J., J. Zakin, J. Myška, and P. Kratochvíl, Use of Friction Reducing Additives in District Heating System Field Test at Kladno—Krocehlavy, Czech Republic, in *Ibid.*, pp. 141–156.
7. Greenhill-Hooper, M.J., T.P. O'Sullivan, and P.A. Wheeler, The Aggregation Behavior of Octadecylphenylalkoxysulfonates, *J. of Colloid and Interface Sci.* 124:77–87 (1988).
8. Savins, J.G., A Stress-Controlled Drag Reduction Phenomenon, *Rheologica Acta, Band 6, Heft 4*:323–330 (1967).
9. Zakin, J.L., and J.L. Chang, Polyoxethylene Alcohol Non-Ionic Surfactants as Drag Reducing Additives, in *International Conference on Drag Reduction*, BHRA Fluid, Cambridge, 1974, pp. 1–14.
10. Zakin, J.L., and H.-L. Lui, Variables Affecting Drag Reduction by Nonionic Surfactant Additives, *Chem. Eng. Commun.* 23:77–88 (1983).
11. Harwigsson, I., A. Khan, and M. Hellsten, Nonionic Surfactants as Drag Reducing Additives to Circulating Water System, *Tenside Surfactants, Deterg.* 30:174–178 (1993).
12. Shenoy, A.V., A Review on Drag Reduction with Special Reference to Micellar Systems, *Colloid Polym. Sci.* 262:319–337 (1984).
13. Ohlendorf, D., W. Interthal, and H. Hoffman, Surfactant Systems for Drag Reduction: Physicochemical Properties and Rheological Behavior, *Rheol. Acta* 25:468–486 (1986).
14. Bewersdorff, H.-W., and D. Ohlendorf, The Behavior of Drag-Reducing Cationic Surfactant Solutions, *Colloid Polym. Sci.* 266:941–953 (1988).
15. Bewersdorff, H.-W., B. Frings, P. Lindner, and R.C. Oberthür, The Conformation of Drag Reducing Micelles from Small-Angle-Neutron-Scattering Experiments, *Rheol. Acta* 25:642 (1986).
16. Chou, L.-C., and J.L. Zakin, Use of Mixed Cations and Mixed Counter-Ions to Extend the Effective Temperature Range for Drag Reducing Surfactant Additives, in *International Symposium on Fluids for District Heating*, Technical University of Denmark, Copenhagen, 1991, pp. 75–86.



**FIG. 17.** Moody's friction factor  $\lambda$  as a function of Reynold's number for a mixture of  $C_{16}$ -betaine 1.1 g/L and Na-dodecylbenzene sulfonate 0.1 g/L in a salt water solution (see Materials section) at 24°C and pH 5.8. See Figure 2 for key.

17. Weibull, B., and B. Nycander, The Distribution of Compounds Formed in the Reaction Between Ethylene Oxide and Water, Ethanol, Ethylene Glycol, or Ethylene Monoethyl Ether, *Acta Chem. Scand.* 8:847 (1954).
18. Gordon, R.J., and C. Balakrishnan, Vortex Inhibition: A New Viscoelastic Effect with Importance in Drag Reduction and Polymer Characterization, *Appl. Polymer Science* 16:1629–1639 (1972).
19. Virk, P.S., Drag Reduction Fundamentals, *AIChE J.* 21:625–656 (1975).
20. Basolo, F., and Y.T.J. Chen, Steric Effects and the Stability of Complex Compounds. III. The Chelating Tendencies of *N*-Alkylglycines and *N*-Dialkylglycines with Copper(II) and Nickel(II) Ions, *Am. Chem. Soc.* 76:953 (1954).
21. Saul, D., G.J.T. Tiddy, B.A. Wheeler, P.A. Wheeler, and E. Willis, Phase Structure Rheological Properties of a Mixed Zwitterionic/Anionic Surfactant System, *J. Chem. Soc. Faraday Trans. 1* 70:163–170 (1974).
22. Schöberl, P., K.J. Bock, and L. Huber, Ökologisch relevante Daten von Tensiden in Wasch- und Reinigungsmitteln, *Tenside Surfactants, Deterg.* 25:86–98 (1988).
23. Tsujii, K., K. Okahashi, and T. Takeuchi, Addition-Compound Formation Between Anionic and Zwitter-Ionic Surfactants in Water, *J. Phys. Chem.* 86:1437–1441 (1982).

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