

DRAG REDUCTION IN PIPELINES BY CATIONIC SURFACTANT ADDITIVES

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تقليل الفواقد في خطوط الأنابيب باستخدام إضافات من المركبات ذات النشاط السطحي الكتيونية

ملخص البحث :

يتناول هذا البحث تقليل الفواقد عند سريان محاليل المركبات الكتيونية ذات النشاط السطحي (أملاح الأمونيوم الرباعية - ملح سلسلات الصوديوم) في أنابيب ذات أقطار ٦٤٧ مم و ٢٤٦٩ مم وسريان ذات أرقام رينولدز تتراوح بين ١٠٠٠٠ و ١٠٠٠٠٠ عند درجات حرارة تتراوح بين ٣٠°م و ١٢٠°م. كما يتناول البحث تأثير تغيير تركيب وتركيز تلك المركبات وكذا تأثير درجة الحرارة والقص الميكانيكي على تقليل الفواقد. وقد أثبتت أملاح ثلاث ميثيل الأمونيوم فعالية كبيرة في تقليل الفواقد عند سريان الماء في خطوط الأنابيب بينما لم يثبت أملاح ثنائي ميثيل الأمونيوم تلك الفعالية. وقد بينت التجارب أن أقصى درجة حرارة يمكن عندها تقليل الفواقد تعتمد على طول مجموعة الألكيل في المركبات الكتيونية ذات النشاط السطحي وثقل تلك الدرجة بوجود كمية كبيرة من السلاسل الهيدروكربونية القصيرة نسبياً. كما وجد أن التركيز المؤثر لتقليل الفواقد هو ١٥٠٠ جزء في المليون من أملاح الأمونيوم الرباعية مضافاً إليها ١٥٠٠ جزء في المليون من ملح سلسلات الصوديوم كما وجد أن هذه المركبات تعطي تقنياً أكبر للفواقد.

ABSTRACT

This work is concerned with the drag reduction using cationic surfactants, (quaternary ammonium amino-sodium salicylate), dissolved in water. Drag reduction measurements were carried out in 6.17 and 2.69 mm diameter tubes, for Reynolds numbers from 10^4 to 10^6 and for temperature range of 30° to 120° C. The influence of surfactant composition, temperature, mechanical shear, concentration and sodium salicylate concentration on the drag reduction were investigated. Trimethyl ammonium amine salts are most effective drag reducing agents, while alkyl dimethyl ammonium amine salts are not effective. Length of alkyl group has a major effect on the upper temperature limit for drag reduction. Appreciable amount of shorter chain reduces the maximum temperature. Concentrations of 1500 ppm of quaternary ammonium amine and 1500 ppm of sodium salicylate are needed for effective drag reduction for C₁₂ amines. Cationic surfactants of this type was found to produce higher drag reduction values in the larger tube than that for non-ionic surfactants or for high polymer solutions.

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NOHENCLATURE

Δp pressure drop in the pipe, Pa.
 D pipe diameter, m.
 L pipe length, m.
 D_r drag reduction, (%),
 t temperature, °C,
 λ measured friction loss coefficient,
 λ_s solvent friction loss coefficient,
 Re solvent Reynolds number,
 ρ mass density, kg/m³,
 μ dynamic viscosity, kg/m.s,
 τ shear stress, N/m².

Abbreviations

CTAS Cetyl Trimethyl Ammonium Salicylate, (Arquad 16-50),
 TTAS Tallow Trimethyl Ammonium Salicylate, (Arquad 18-50)
 ETAS Erucyl Trimethyl Ammonium Salicylate, (Kemamine Q-2983C),
 CPySal Cetyl Pyridinium Salicylate .
 NaSal Sodium Salicylate,
 RTASAlkyl Trimethyl Ammonium Salicylate,
 RPySal Alkyl Pyridinium Salicylate .
 CMCII Concentration at. which the surfactant monomers form rodlike micelles.

-1- INTRODUCTION

The problem of efficient energy utilization has become an important topic of energy policy. The reduction of flow pressure losses in pipelines represents a main application for drag reducing additives. While high polymer drag reducing additives have been extensively investigated, the use of low molecular weight cationic surfactant complexes, which form large micelles in aqueous solutions, has received much less attention.

Furthermore, these polymeric drag reducing additives can undergo mechanical degradation by shearing action of the pumps and other parts of the flow circuits. Rose et al., [1], studied aqueous alkyl trimethyl ammonium salicylate solutions by using the following alkyls; Cetyl-(C₁₆ or CTAS), Tallow-(C₁₈ or TTAS) and Erucyl-(C₂₂ or ETAS). These alkyls are formed from the corresponding chlorides combined with sodium salicylate; Na Sal. At a critical temperature for a given surfactant system and concentration, the drag reduction began to decrease rapidly.

Drag reduction was regained upon cooling. Reversible shear degradation occurred at higher Reynolds numbers by increasing the tube diameter. Rose et al., (1), proposed that the use of these surfactant solutions could provide flow energy saving.

Hoffmann et al., [2], studied the behavior of solutions that containing CPy Sal, and various amounts of excess NaSal rodlike micelles grew rapidly as the excess NaSal concentration increased

to 0.5 mM in 1 mM C Py Sal. Ohelendorf et al., [3], correlated the micellar behavior with drag reduction in RTA Sal and RPy Sal solutions. They verified the effects proved by previous workers as :

- pipe diameter effects: as the diameter increased, the maximum drag reduction was extended to higher Reynolds numbers, although degradation occurred reversibly at a fixed wall shear stress for each solution.
- increasing temperature eventually caused a loss of drag reduction.

Ohelendorf et al., [4], reported that drag reduction, in these cationic surfactant solutions, occurred at concentrations above the CMCII. (i.e. when the rodlike micelles were present).

2- EXPERIMENTAL INVESTIGATION

Experimental investigation has been carried out according to the following scheme, [5] :

- 1) Preparation of different concentrations of cationic surfactant ammonium salt and adding different quantities of sodium salicylate solution for measurements of drag reduction measurements.
- 2) Measurements of pressure drop and flow rate for different diameters tube at different solution concentrations and temperatures.
- 3) Heating the prepared solutions to 90 ° for about 12 hours, before carrying out the actual measurements to ensure that the solutions are in thermodynamic equilibrium.

Different cationic surfactant are tested as; Arquad 16-50, Arquad 18-50, Arquad 5-50, Arquad 7-50, Kemamine Q-2983 C, Kemamine Q-2803 C, DDAB, Ethoquad O/12, Ethoquad R 12/75, and Dico. Their chemical structures, as given by the producing companies, are shown in Tab.(1).

The experimental technique and procedure have been explained in details in [5]. The procedure may be summarized as follows :

- 1- measurements of pressure drop and flow rate for water in a pipe of 6.17 mm diameter, at different temperature level as a base for comparison.
- 2- preparation of solutions of different concentrations of cationic surfactant ammonium salt, with addition of sodium salicylate solution.
- 3- heating of the previously prepared solution to approximately 90 °C, for about 12 hours, before carrying out the actual tests, to ensure that the solution is in thermodynamic equilibrium.
- 4- carrying out the drag reduction measurements for surfactant solutions at different temperatures, in tubes of 6.17 and 2.69 mm diameters.

Tab.(1). Composition, Effective Temperature Ranges of Drag Reduction and Maximum Wall Shear Stress of the Tested Cationic Surfactants

Trade Name Composition	ARQUAD 16-50	ARQUAD 18-50	ARQUAD 5-50	ARQUAD 7-50	ETHIO- QUAD 18/77	ETHIO- QUAD 0/17	ETHIO- QUAD R12 /75	KEIMAR- III 02983C	KEIMA- HIII 02883C
CH ₃ ⊙	3	3	3	3	3	1	3	3	3
CH ₂ CH ₂ OH⊙	0	0	0	0	7	7	2	0	0
C ₁₄	12	1	1	3		2			
C ₁₄ **									
C ₁₆	73	5	16	27	19	4			
C ₁₆ '			1	3		4			
C ₁₈	11	90	12	18	89	14		1	1
C ₁₈ '		1	55	42	2	75	20		
C ₁₈ **			14	4			30		
C ₂₀ '		1							6
C ₂₀							10	6	
C ₂₂									90
C ₂₂ '							40	92	
C ₂₄									
(T _{min} -T _{max}) 'C	10-60	10-90	10-80	10-70	10-80	10-80	10-90	60-110	40-120
τ_w (max), N/m ²	300,0	210,0	180,0	220,0	150,0	190,0	200,0	150,0	120,0

(*) Means one double bond in the hydrocarbon chain.
 (**) Means two double bonds in the hydrocarbon chain.

⊙ Number of groups

An example of the obtained results, for 2000 ppm kemamine Q-2983 C- 2000 ppm NaSal solution, at different temperatures and tube diameters are shown in Fig.(1). These results are based on the raw data of pressure drop and flow rate and by using the following relations for calculation of the flow velocity u , pressure drop Δp , Reynolds' number Re and the drag reduction D_r . [5] :

$$u = Q / (\rho D^2/4) \quad (1)$$

$$\Delta p = \lambda L/D \left(\rho v^3 / 2 \right) \quad (2)$$

$$Re = \rho D v / \mu \quad (3)$$

$$D_r = \left(1 - \lambda / \lambda_0 \right) \quad (4)$$

3-1 RESULTS AND DISCUSSIONS

The effects of surfactant structure, temperature, mechanical shear, concentration and additive concentration on the turbulent

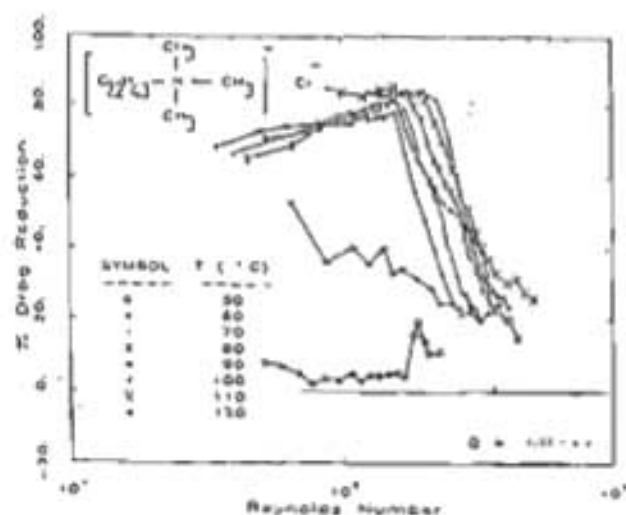


Fig.(1), Drag Reduction as Function of Re at Different Temperatures for Solutions Q-2983 + NaSal (2000/2000 ppm)

flow behavior of different cationic surfactant. (ammonium salt), solutions were studied. All runs are for 2.69 and 6.17 mm diameter tubes.

3-1 Effect of Cationic-Structure

Figures (2) and (3) show the effect of cationic structure on the drag reduction for DDAB solution at concentration of 2000 ppm and of 2000 ppm DDAB + 500 ppm sodium salicylate at different temperature. For this compound, which contains relatively small hydrocarbons chain ($C_{10}H_{21}$), the results show that no drag reduction is obtained in the temperature range of 40° to 70° C, and a very little drag reduction at 90° C. This may be attributed to the disability of the molecules to pack together to form rodlike micelles under such conditions of operation. [4].

When the cationic surfactant compound, containing longer hydrocarbon chain (C₁₈ H₃₅), was tested for drag reduction as shown in figure (4), the results showed that the Arquad 16-50 is an effective drag reducer in the temperature range from 30° to 60 °C, with maximum drag reduction of 75 %. This drag reduction may be due to the existence of rodlike micelles. These additives were found to loose their effectiveness, for drag reduction, at temperatures above 60°C. This may be attributed to the exceeding of the transition concentration for the formation of rodlike micelles into spherical micelles for dilute surfactant solutions of concentrations less than 2500 ppm. [3].

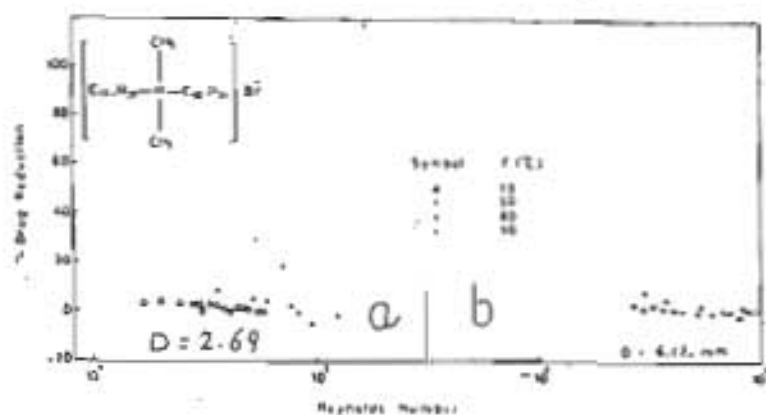


Fig.(2), Drag Reduction as Function of Re , at Different Temperatures for Solution containing 2000 ppm N, N-Dimethyl Didecyl Ammonium Bromide.

The loss of drag reducing effectiveness above a critical wall shear stress is very important. An example of the critical wall shear stress are listed in Tab. (2). For the considered solution the critical shear stress was found to be almost constant in the temperature range of 30° to 60° C. It was found also that it is reversible such that the drag reduction could be recovered if the wall shear stress, or the temperature, are reduced. For Arquad 16-50, it is clear from Fig. (5), that this additive mixture is effective drag reducing agent in the temperature range of 30° to 90° C. Higher upper effective temperature range may be due to the longer alkyl chain length which results in larger and more stable micelles at high temperature.

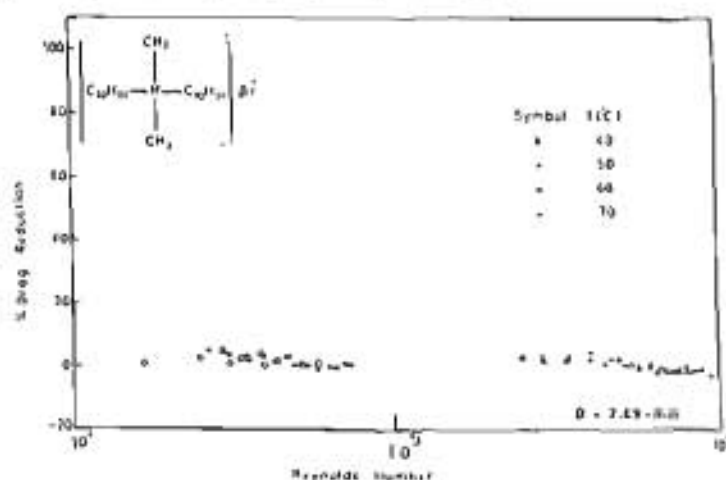


Fig.(3), Drag Reduction as Function of Re for Solutions containing 2000 ppm N, N-Dimethyl Didecyl Ammonium Bromide - 500 ppm NaSal.

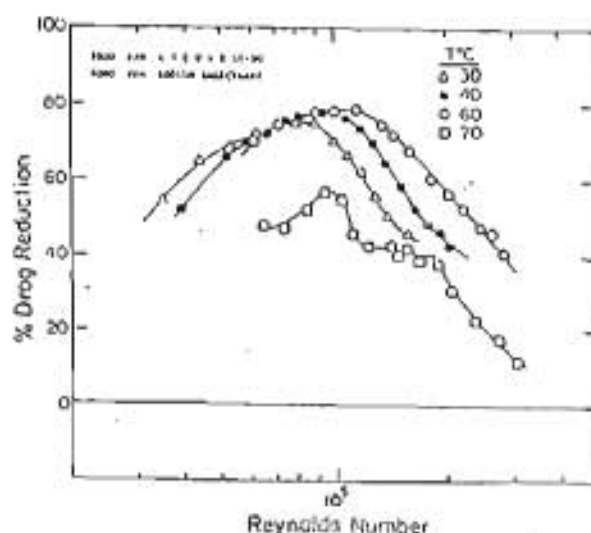


Fig.(4), Drag reduction as function of Re for Solutions Containing 2000 ppm Hexadecyl Trimethyl Ammonium Chloride-2000 ppm NaSal

Generally, it was found that the longer the alkyl chain in the surfactant structure, the higher the upper temperature limit for drag reduction. This may be due to the increase in the size of micelles which form more stable rodlike aggregates even at high temperatures. This result gives a useful criterion in choosing the suitable surfactant for the convenient application. Table (1) shows that, as the chain length increases the temperature range will increase. The table shows also that the maximum wall shear stress is reduced by increasing the chain length.

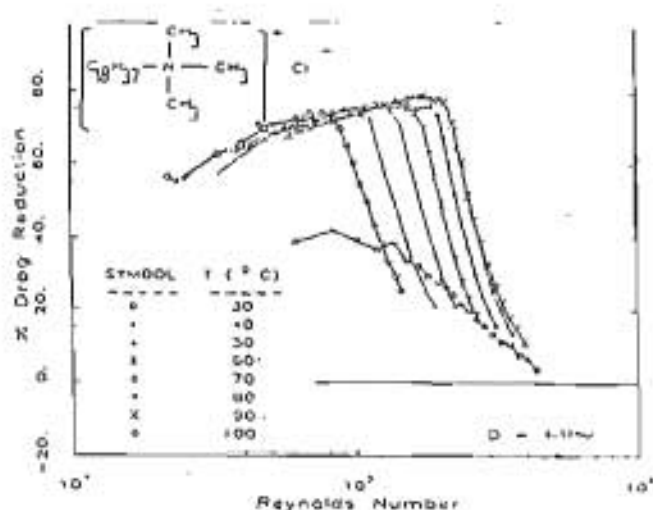


Fig.(5), Drag Reduction as Function of Re for Solution containing 2000 ppm Octadecyl Trimethyl Ammonium Chloride-2000 ppm NaSal

Based on the the previous results, the quaternary ammonium sodium salicylate mixtures are promising drag reducing additives for district heating systems. Mechanical degradation under high shear stresses is reversible. The maximum temperature may reach 110°C for trimethyl ammonium amine salts. The loss of drag reduction at critical temperature, is regained upon cooling.

3-2 Effect of Tube Diameter

Diameter effects on drag reduction was found to be different from those observed either in solutions of high polymer or non-ionic surfactant solutions. For the same working conditions, and for tubes of 2.69 and 6.17 mm diameter, Fig. (6) and (7) show that the drag reduction was higher in the larger tube. This may be due the greater wall shear stress in the smaller tube. Consequently, the effective micellar structure might be reduced; leading to smaller drag reducing activity. The maximum drag reduction extended to higher Reynolds numbers, by increasing the tube diameter. The mechanical degradation was found to occur at approximately a fixed critical wall shear stress.

3-3 Effect of Concentration of Cationic Surfactant

Figure (8) indicates that, by increasing the additive concentration from 1000 to 2500 wppm, (1 : 1 weight ratio), of Q2983 C : sodium salicylate, the drag reduction activity is improved and the critical wall shear stress is shifted to higher values. By increasing the surfactant concentration, the rod lengths increased and may result in formation of large stable rodlike micelles which improve the drag reduction performance.

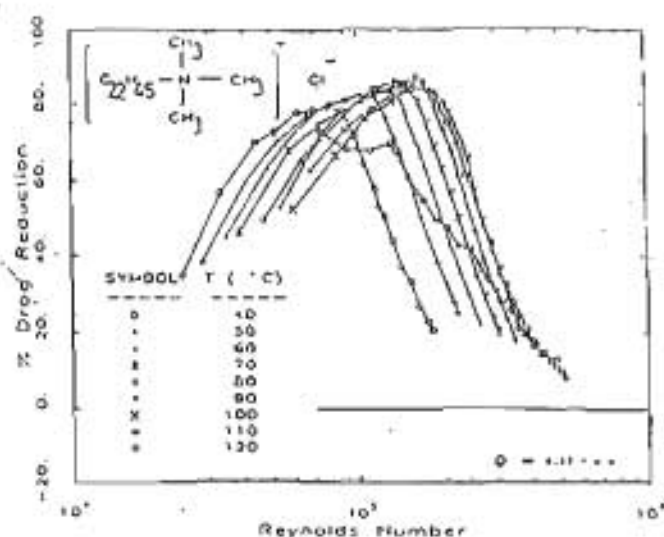


Fig.(6), Drag Reduction as Function of Re for Solutions containing Q-2803C NaSal (2000/2000 ppm) and $D = 6.17$ mm

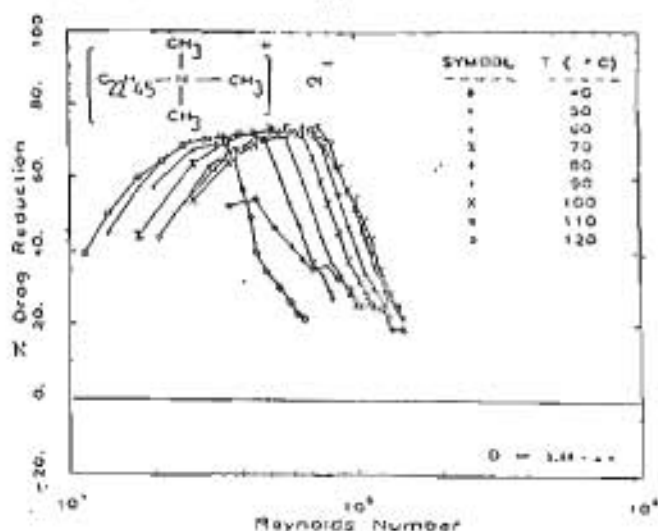


Fig.(7), Drag Reduction as Function of Re for Solutions containing Q-2803C NaSal (2000/2000 ppm) and $D = 2.69$ mm

3-4 Effect of Additives Concentration

The addition of sodium salicylate to the cationic surfactant affect widely its behavior. Salicylate anions act as counter-ions to the oppositely charged cationic head-groups and assist spheres to rods transition of the micelles. Plots of the percentage drag reduction for 1500 ppm erucyl trimethyl ammonium chloride with varying amounts of sodium salicylate, at different temperature are shown in Fig. (9). By increasing the concentration of sodium

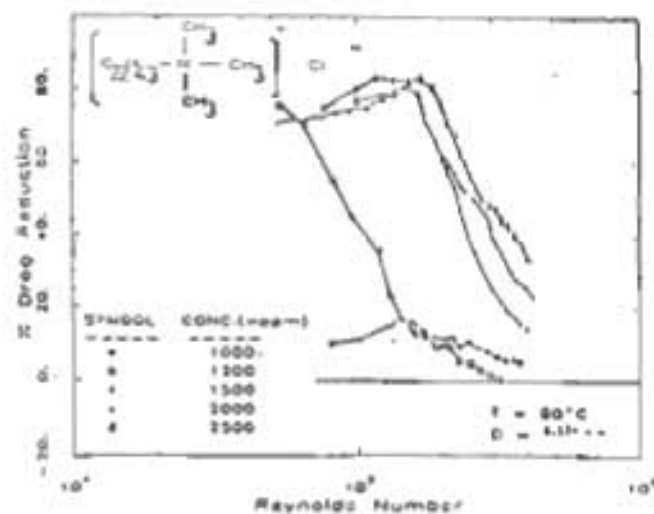


Fig.(8). Drag Reduction for Q - 2003C + NaSal at equal Concentration

salicylate to 1500 ppm and more. the system showed drag reducing activity. This may be due to the rapid growing of the rodlike micelles. Reversible shear degradation was observed at higher Reynolds number.

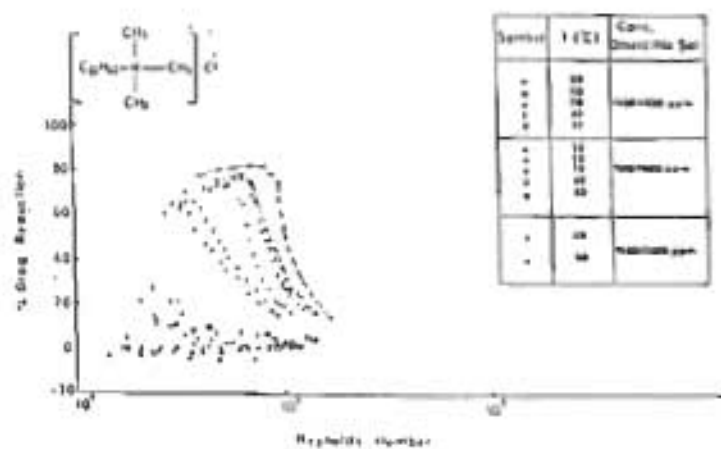


Fig.(9). Effect of NaSal Concentration on Drag Drag Reduction 1500 ppm Q 2'03 C.

4- CONCLUSION

Different structures of cationic surfactants, (quaternary ammonium salts), have been tested experimentally, for drag reduction. The following results may be concluded :

- The mechanical degradation under shear stress was found to be reversible with maximum working temperature of 110°C.
- The length of alkyl group has a major effect on the upper temperature limit of drag reduction. Appreciable amount of relatively shorter chain reduces the maximum temperature.
- Increasing the concentration of additive mixtures, erucyl trimethyl ammonium chloride / sodium salicylate, from (2000 / 2000) ppm to (2500 / 2500) ppm was found to raise the lower temperature limit for the drag reduction.
- The drag reducing ability and mechanical stability of additive mixture containing (erucyl trimethyl ammonium chloride-sodium salicylate by (1 : 1) weight ratio increased with concentration increase from 1000 to 2500 ppm. Excess sodium salicylate at different temperatures improved the drag reduction performance.
- The drag reduction increases as the tube diameter increases.
- The upper and lower temperature limits for drag reduction change with using different structures.

5- REFERENCES

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