

## **Evaluation of Drag Reduction by Cationic Surfactant in Crude Oil**

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### **Abstract**

**In our quest in finding drag reduction chemicals we are continuing to synthesize the cationic surfactants. In this project not only we are going to prepare a cationic surfactant  $RCH_2(CH_3)_3X$  which X could be chloride or bromide ion then we are going to study its drag reducing properties in a pipeline which is building by our research group now. The effect of concentration of surfactant in drag reduction will also be studied.**

### **1. Introduction**

In petroleum industry, oil transportation from well to refineries, production units ... is very important. There are different methods for transportation which one of them is transportation by pipeline.

There are some factors which should be considered in pipeline:

1. length of pipeline
2. pressure drop in pipeline
3. oil pumping energy

These three factors are related to each other directly so that for a longer the pipeline, higher pressure drop in pipeline and also more pumping energy is needed, since by decreasing pressure drop pumping energy in pipeline, will reduce. Different methods for reducing extra pressure drop were developed. One of them is adding one type of additives to reduce drag force. These additives are called surfactants (DRA) which are studied in this project.

### **2. Drag Reducing Agent (DRA)**

DRA for oil pipelines have played an important role in recent years, enabling efficient use of the capacity of pipeline systems. One area where it has proved to be very important is in allowing new discoveries to be transported via existing pipeline systems, making it possible to economically produce marginal fields. However, the use of DRA in the transportation of crude from new fields requires an understanding of the effect of the performance of the DRA on transported oil in pipeline.

Drag Reducing Agents ("DRA") or Drag Reducers ("DR") are chemical agents used to reduce or minimize the frictional pressure loss caused by turbulence in the pipeline.

To qualify as a drag reducer candidate for crude oil pipelines a polymer must:

- (1) Be effective at low concentrations
- (2) Be relatively shear stable during the flow
- (3) Cause no downstream refining problems.

Commonly, some of the surfactants are employed as drag reducing agents. Surfactants are classified as anionic surfactant, cationic, nonionic or amphoteric ones.

### 3. Type of surfactants

#### Anionic Surfactants

Are dissociated in water in an amphiphilic anion, and a cation, which is in general an alkaline metal (Na<sup>+</sup>, K<sup>+</sup>) or a quaternary ammonium. They are the most commonly used surfactants. They include alkylbenzene sulfonates (detergents), (fatty acid) soaps, lauryl sulfate (foaming agent), di-alkyl sulfosuccinate (wetting agent), lignosulfonates (dispersants) etc... Anionic surfactants account for about 50 % of the world production.

#### Nonionic Surfactants

Come as a close second with about 45% of the overall industrial production. They do not ionize in aqueous solution, because their hydrophilic group is of a nondissociable type, such as alcohol, phenol, ether, ester, or amide. A large proportion of these nonionic surfactants are made hydrophilic by the presence of a polyethylene glycol chain, obtained by the polycondensation of ethylene oxide. They are called polyethoxylated nonionics.

In the past decade glucoside (sugar based) head groups, have been introduced in the market, because of their low toxicity. As far as the lipophilic group is concerned, it is often of the alkyl or alkylbenzene type, the former coming from fatty acids of natural origin. The polycondensation of propylene oxide produce a polyether which (in opposition to polyethylene oxide) is slightly hydrophobic. This polyether chain is used as the lipophilic group in the so-called polyEOpolyPO block copolymers, which are most often included in a different class, e.g. polymeric surfactants, to be dealt with later.

#### Cationic Surfactants

Are dissociated in water into an amphiphilic cation and an anion, most often of the halogen type. A very large proportion of this class corresponds to nitrogen compounds such as fatty amine salts and quaternary ammoniums, with one or several long chain of the alkyl type, often coming from natural fatty acids. These surfactants are in general more expensive than anionics, because of a high pressure hydrogenation reaction to be carried out during their synthesis. As a consequence, they are only used in two cases in which there is no cheaper substitute, i.e. (1) as bactericide, (2) as positively charged substance which is able to adsorb on negatively charged substrates to produce antistatic and hydrophobant effect, often of great commercial importance such as in corrosion inhibition.

#### Amphoteric or Zwitterionic Surfactants

When a single surfactant molecule exhibit both anionic and cationic dissociations it is called *amphoteric* or *zwitterionic*. This is the case of synthetic products like betaines or sulfobetaines and natural substances such as aminoacids and phospholipids.

### 4. Drag Reduction Calculation

The relative performance of a drag reducer may be expressed in terms of drag reduction percent. At a constant flow rate, drag reduction percent is defined as:

$$DR \% = \frac{\Delta P - \Delta P^{\circ}}{\Delta P} \times 100 \quad (1)$$

Where

$\Delta P$  is the pressure drop of the untreated fluid

$\Delta P^o$  is the pressure drop of the fluid containing the drag reducer

But, At a constant pressure drop, drag reduction percent is defined as:

$$DR \% = \frac{Q - Q^o}{Q} \times 100 \quad (2)$$

Where

$Q$  is the flow rate of the untreated fluid

$Q^o$  is the flow rate of the fluid containing the drag reducer

## 5. Drag Reducing Mechanism

A drag reducer does not work in laminar flow regimes. This is because drag reduction occurs by an interaction of the polymer molecules of the drag reducer with the turbulence formation of the flowing fluid or hydrocarbon. In a hydrocarbon stream, the DRA lowers the frictional pressure loss caused by turbulence in the pipeline. In order to understand how turbulence is created and why the turbulence could cause a frictional pressure drop in a fluid flow, and also how drag reducers could reduce the turbulence and thus the frictional pressure loss, it is necessary to describe the structure of turbulent flow.

In turbulent flow regimes, there are three different zones or layers. Nearest the pipeline wall is a zone called laminar sub layer. In this zone, the fluid follows the pipeline flow in a typical laminar flow regime. The increase in point velocity as the point moves away from the wall, is linear function of the distance from the wall, and directly parallel to the wall in the direction of pipe flow. There are no cross flows in this zone.

In the very center of the pipe is the turbulent core zone. This zone is the largest region and includes most of the fluid in the pipe. This is the zone of the eddy currents and random motion of turbulent flow. The turbulent core carries all of the flow where variations in point velocity are random and dependent of this distance. Between the laminar sub layer and turbulent core zones lies the buffer zone. In the buffer zone, variation of point velocity with point position is not established. This zone is important because it is here that the turbulence first forms.

Now we will discuss how turbulence is created and why the turbulence could cause a frictional pressure loss in a fluid flow and also how a DRA could reduce the frictional pressure loss caused by the turbulence. A portion of the laminar sub layer called "streak" will occasionally move up to the buffer zone. Once the streak enters the buffer zone, it will begin to vortex and oscillate, moving faster as it gets closer to the turbulence core. Finally, the streak becomes unstable and breaks up as it throws fluid into the core of the flow. This ejection of fluid in the core is called "turbulent burst". The burst creates the turbulence in the core. Energy is wasted in different directions causing the drag and pressure loss.

Drag reduction occurs by an interaction of the polymer molecules of the drag reducer with the turbulence of the flowing fluid. Drag reducer polymers interfere with the bursting process or inhibit the formation of turbulent burst and prevent the turbulence from being formed, or at least reduce the degree of turbulence, and in turn, reduce the drag or pressure loss. The drag reducer polymers somehow stretch in the flow, absorb the energy in the streak and thereby prevent the turbulent burst. As such, drag reducer polymers are most active in the buffer zone.

In general terms, the higher the degree of turbulence of the fluid in the pipeline, the higher the drag reducing performance. Therefore, the drag reducing performance is

increased as the fluid velocity and flow rate increase and as the fluid viscosity and the pipeline diameter decrease or following the Reynolds number formula. The higher the Reynolds number, the higher the drag reducing performance. Reynolds number is a dimensionless number which is used to determine the type of flow (laminar, critical or turbulent) in a pipeline and expressed in a formula as below:

$$R_e = \frac{\rho V D}{\mu} \quad (4)$$

A fluid flow with a Reynolds number less than 2000 is a laminar flow. A turbulent flow has a Reynolds number more than 5000. Between laminar and turbulent flow, there is a critical flow regime with Reynolds number more than 2000, but less than 5000. Reynolds number is the first indication to determine whether drag reducer could work or not in a fluid flow in a pipeline system. As explained before, drag reducer could work only in turbulent flow regime, so it must have a Reynolds number of more than 5000.

**Note:**

High molecular weight DRA are shear sensitive, and drag reducing performance could be affected when passing high shear force region in pipeline system, such as T's, bends, partly open valves, and specially pumps. The general rule of drag reducer injection is always to inject drag reducer on the discharge side of the pump. And if drag reduction is required along a pipeline system with N pump station, the drag reducer must be injected at N points or at every pump station, unless the pump station is by-passed.

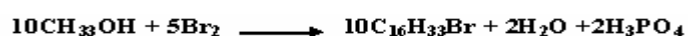
## 6. Experimental Set up and Procedure

### 6.1 Preparation of Surfactant (C<sub>16</sub>TAB & C<sub>16</sub>TAC)

In order to synthesize the desired cationic surfactant, basic material such as alcohol is used. At first alkyl halides was made by reacting hexadecanol with bromide or tional chloride, then the product reacted with trimethyl amine to obtain the desired surfactant. Procedure of synthesize is as follows:

#### 6.1.1 Method of Synthesizing Bromohexadecane

In order to synthesize bromohexadecane from hexadecanol we used hexadecanol, phosphor, bromine, de ethyl ether and dehydrated calcium chloride. For this reason 121 gr hexadecanol and 34 gr phosphor was reacted in the flat butt balloon and it was stirred with magnetic mixer, then 44gr bromine was added, by refluxation process. After 15 min refluxation, the balloon was cooled in room temperature and after that sufficient amount of de ethyl ether was added. Balloon contents were removed by filtering solid materials (residual phosphor). The product was poured in the separating funnel and it was washed again with 10% sodium bicarbonate solution. The removed product was heated to vaporize ether then it was dried by dehydrated calcium chloride. (Sodiumtiosulfite can be used for removing additional bromine).



#### 6.1.2 Synthesize of C<sub>16</sub>TAB from Bromohexadecane

In order to synthesize hexadecyltrimethylammoniumbromide we used astonitril, bromohexadecane and trimethyl amine as ingredient. 100 ml astonitril with 15 ml bromohexadecane and 33 ml trimethyl amine were poured in to the 250 ml flat butt balloon and were heated in the reflux situation for 24 hours. After that the balloon

content was poured in to a beaker and it was cooled gently. The related setup is shown in Figure 1. The products deposited in the white crystalline form. After that the obtained deposits were dried in the room temperature. These white crystals are observable as shown in Figure 2.



Figure 1. Heating acetonitril, bromohexadecane and trimethyl amine mixture under vacuum air condition.



Figure 2. The synthesized white crystals of hexadecyltrimethylammoniumbromide ( $C_{16}H_{33}N(CH_3)_3Br$ )

### 6.1.3 Method of Synthesizing Chlorohexadecane

In order to synthesize chlorohexadecane from hexadecanol we used hexadecanol, thionyl chloride, sodium bicarbonate and dehydrated calcium chloride. For this reason 60.5 gr hexadecanol is poured in a flat butt balloon and it was stirred with magnetic mixer, simultaneously 119 gr thionyl chloride is poured slowly. After 10 hours refluxation, the balloon was cooled in room temperature and then it was washed with water and 10% sodium bicarbonate solution and it was washed again with water. The removed product was dried by dehydrated calcium chloride.



### 6.1.4 Synthesize of $C_{16}TAC$ from Chlorohexadecane

In order to synthesize hexadecyltrimethylammoniumchloride we used acetonitril, chlorohexadecane and trimethyl amine as ingredient. 100 ml acetonitril with 26 ml chlorohexadecane and 7 ml trimethyl amine were poured in to the 250 ml flat butt balloon and were heated in the reflux situation for 24 hours. After that the balloon content was poured into a beaker and it was cooled gently. Then product was deposited as white crystal. After filtration of product it was washed with solvent and at the end it was dried in air.



## 7. Pipeline Test

### 7.1 Apparatus

crude oil pump, surfactant, pipeline (1/2" & 24 meter), pipe fitting, injection pump and transducer. (Figure 3.)

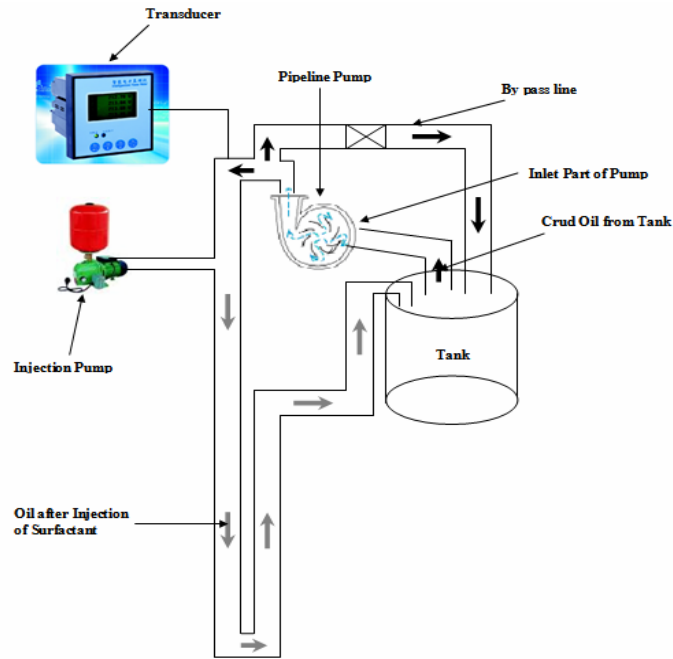


Figure 3. Apparatus of pipeline test

### 7.2 How to calculate the injection flow rate of injection pump?

Fore example for 100 ppm concentration of oil in pipeline and 204 cc/sec flow rate we have:

$$100 \text{ ppm} = 100 \times 10^{-6} \text{ gr/cc}$$

$$\begin{array}{r} 100 \times 10^{-6} \text{ gr} \\ \text{X gr/sec} \end{array} \qquad \begin{array}{r} 1 \text{ cc} \\ 204 \text{ cc/sec} \end{array}$$

Therefore  $x = 0.0204 \text{ gr/sec}$  (grams of surfactant should be injected)

$$\begin{array}{r} 32000 \times 10^{-6} \text{ gr} \\ 0.0204 \text{ gr/sec} \end{array} \qquad \begin{array}{r} 1 \text{ cc} \\ \text{X cc/sec} \end{array}$$

Therefore  $x = 0.64 \text{ cc/sec}$  (rate of injection of surfactant).

So other injection flow rates are calculated in similar way.

Before injection of surfactant the injection pump should be calibrated. Because injection flow rate change with concentration of surfactant it should be calibrated by initial solution of surfactant (32000 ppm). Before injection of any surfactant (0 ppm) seven different flow rates and corresponding pressures, pressures are recorded by transducer, are measured then the injection of surfactant at different concentration was started. In each step of experiment it should be wait to stable the flow rate of pipeline and complete effect of surfactant.

### 8. Result

Physical property of crude oil used in experiments are tabled in table 1.

Table1. Physical property of crude oil used in experiment		
Temperature (°C)	Kinematics viscosity (cs)	Specific gravity
25	12.5	0.8535
40	6.6	0.852
50	5.1	0.8511

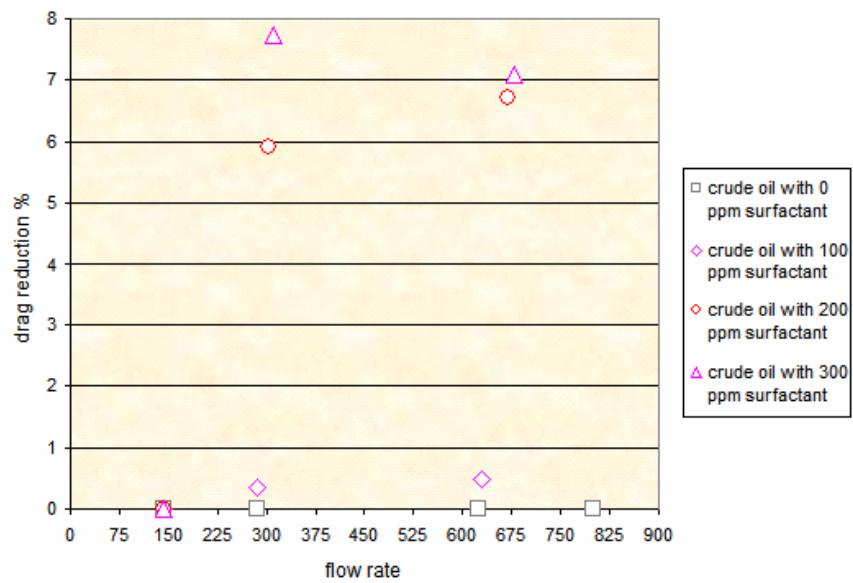


Fig.4 Drag reduction vs. pipeline flow rate (C<sub>16</sub>TAC)

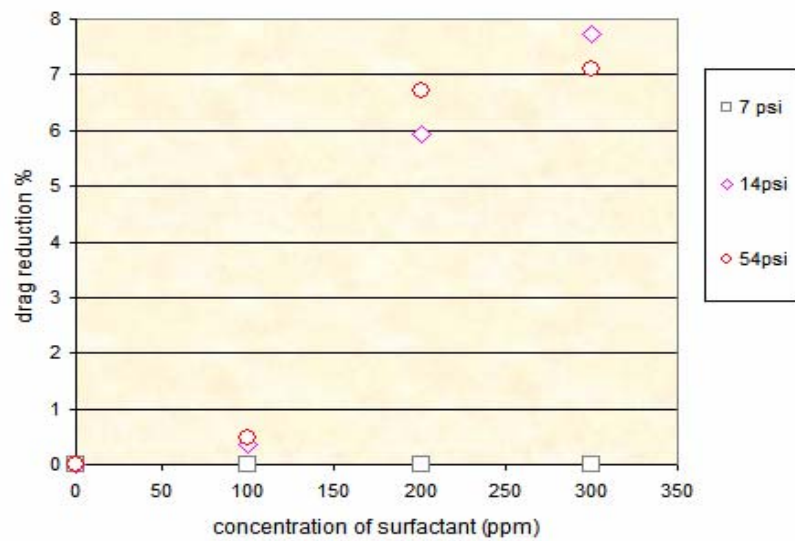


Fig.5 Drag reduction vs. concentration of surfactant (C<sub>16</sub>TAC)

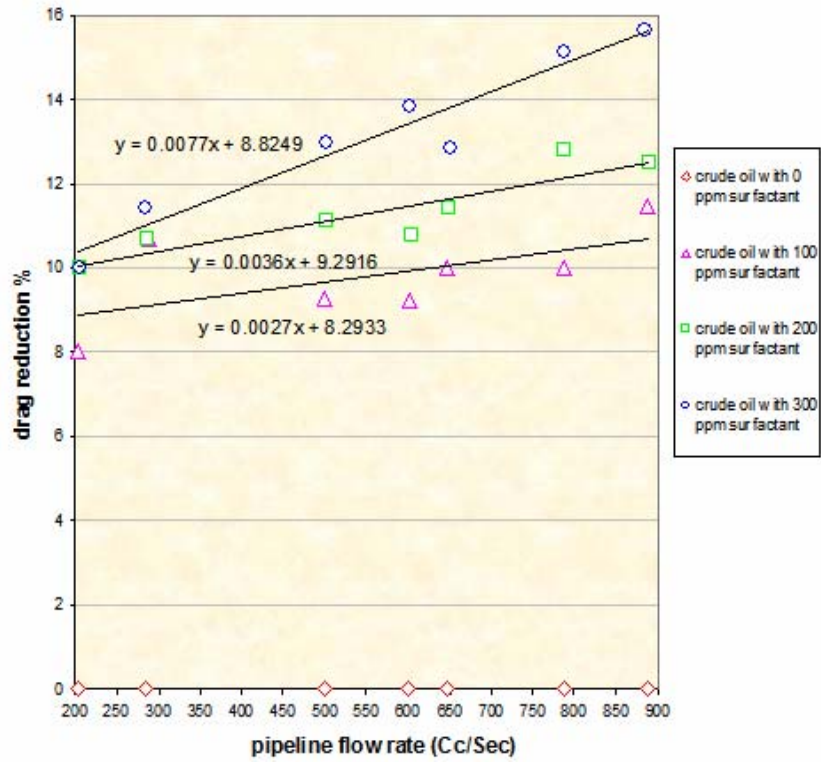


Fig.6 Drag reduction vs. pipeline flow rate at constant concentration (C<sub>16</sub>TAB)

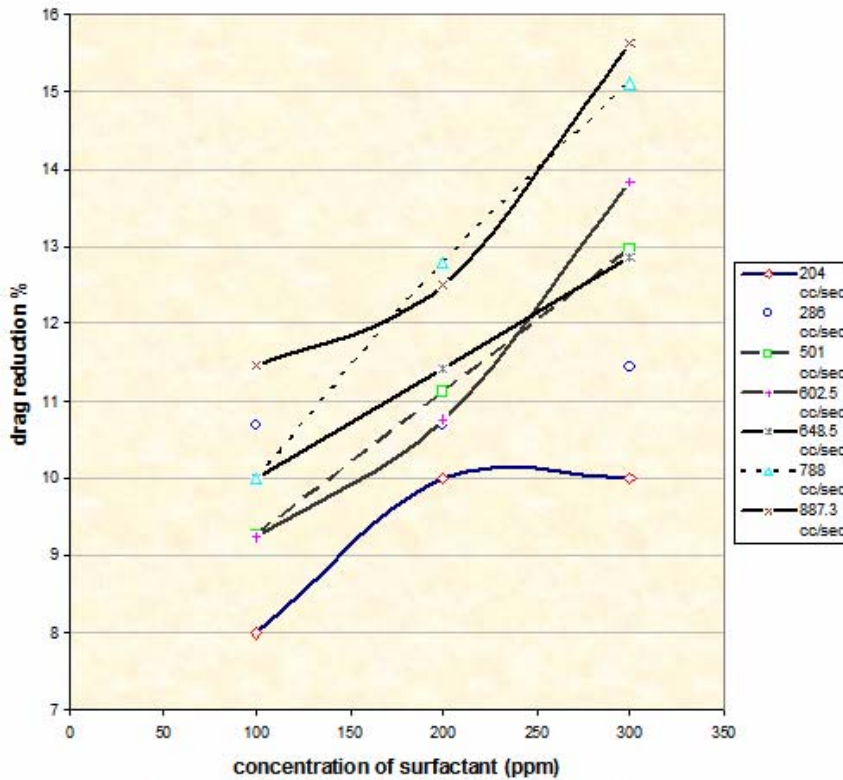


Fig.7 Drag reduction vs. concentration of surfactant at constant flow rate (C<sub>16</sub>TAB)



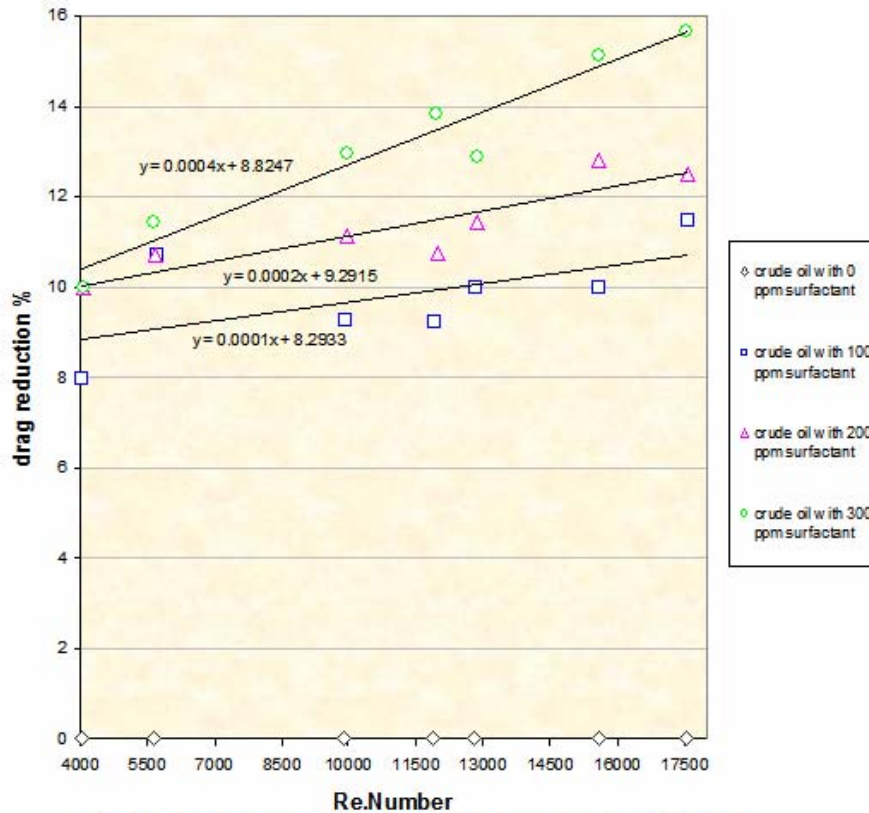


Fig.8 Drag reduction vs. Re. Number at constant concentration ( $C_{16}TAB$ )

## 9. Discussion

The tests were designed to answer to the following question:

How much drag reduction, if any, could be obtained at low concentrations of polymer in large crude oil pipelines?

1. According to Fig. 4, Fig. 6 drag reduction increases with increasing flow rate.
2. According to Fig.5, Fig.7 drag reduction increases with increasing concentration of surfactant.
3. The more concentration of surfactant in oil, the more drag reduction with increasing flow rate.
4. With a similar discussion about flow rate and Reynolds we found that, drag reduction increases with surfactant concentration and liquid flow rate.
5. Because the temperature at all experiments was approximately constant its effect on viscosity and other parameters was considered to be negligible.

## 10. Conclusion and Recommendation

By reducing pressure loss, we can optimize pipeline operation in several ways, such as increasing flow rate in the existing pipeline system whilst maintaining the operating pressure, reducing pipeline operating pressure whilst maintaining total throughput or flow rate, reducing energy and operating costs by lowering pumping energy along the pipeline system, and many other applications.

So major conclusions from this work are:

1. Drag reduction is an economic method for increasing pipeline throughput on both a temporary or long-term basis.
2. The drag reducer has been effective at low concentrations,
3. Although the drag reducer is relatively shear stable in pipeline flow, it is destroyed by pipeline booster pumps.

4. High performance at low concentration levels of the modified polymer is particularly attractive in offshore production operations where space and deck loading are critical factors.
5. We know that head due to pressure drop is as follow:

$$H = \frac{\Delta P}{\gamma}$$

Where

H is head

$\Delta P$  is pressure drop

$\gamma$  is specific weight

So we can conclude that decreasing in pressure drop as a result of surfactant decrease head. This result indicated that it could be possible to increase the pumping rate of a system with using surfactant at a constant head. (See fig. 9)

6. Because a suitable flow meter was not available the experimental data might have some percent of error.

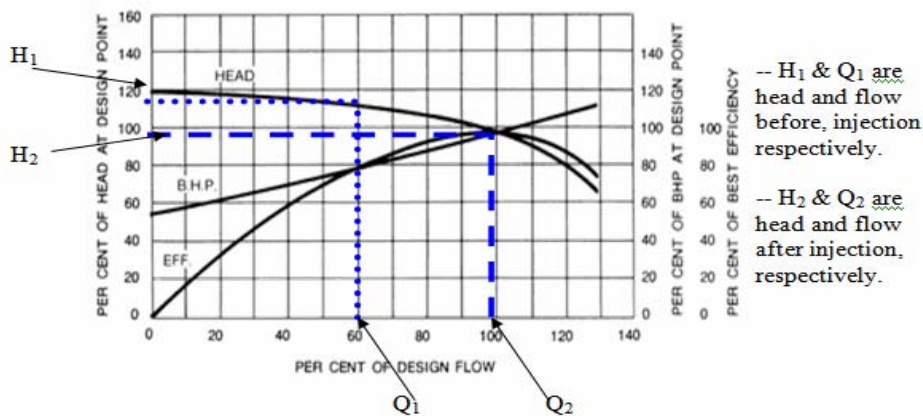


Fig. 9 Pump characteristic curve

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