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## Dewatering of petroleum crude oil emulsions using modified Schiff base polymeric surfactants

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## ABSTRACT

The new discoveries of increasingly heavy oil represent a major challenge for the oil industry because of its undesirable properties, such as its tendency to form stable emulsions and high viscosity and acidity. Dependent upon the production scheme, very stable water-in-oil emulsions can be formed from these oils, for which the complete separation of oil and water phases using conventional processes requires excessive heating, chemical addition, and high residence time. In the present work, the improvement of existing technologies and the development of new additives to decrease the temperature of the treatment processes of these emulsions are very important to ensure the processing of these oils in view of productivity gains. In this respect, the rate of demulsification of different types of crude oil emulsions using series of Schiff base polyethoxylates as demulsifiers was evaluated. The chemical structure of the prepared surfactants was determined by FTIR and <sup>1</sup>H NMR analyses. Characterization of the surface activity of the prepared surfactants is performed to investigate the relation between the structure of surfactants and their performances. The interfacial properties of the prepared demulsifiers at the oil–water interfaces were investigated by means of the interfacial tension relaxation method. The results showed that the slow relaxation processes at low concentration because of stronger adsorption ability of the prepared demulsifiers. This was attributed mainly to rearrangement in the conformation of the molecules appeared with increasing demulsifier concentration. The demulsification efficiency of the prepared demulsifiers for the synthetic crude oil emulsions was determined at different temperatures using bottle test. The demulsification rate increased with surfactant concentration up to the onset of surfactant aggregation in the oil, water phase and a third, surfactant-rich phase.

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## 1. Introduction

Most of the oil fields around the globe are producing oil that is often accompanied by significant amounts of water. Many types of emulsions are created in the same produced fluids during production. These emulsions may be oil-in-water (O/W), water-in-oil (W/O), or complex emulsions such as oil-in-water-in-oil (O/W/O) or water-in-oil in-water (W/O/W), depending on the water, the oil, energy in the flow, and oil-to-water ratios (Dodd, 1960; Mohammed et al., 1993; Acevedo et al., 1993; McLean et al., 1998; Ese et al., 1998). Petroleum dewatering has been a challenge in conventional crude oil industry for several decades (McLean et al., 1998). Most of the studies on stability mechanisms of water in-crude oil emulsions can be divided into two categories: interfacial tension and interfacial rheology studies, (Dodd, 1960; Mohammed

et al., 1993; Acevedo et al., 1993; Ese et al., 1998). Comparative studies on emulsion stability using modeling of components and solvents (McLean and Kilpatrick, 1997), indicated that the properties of interfacial material are responsible for emulsions stability (Hunter, 1986; McLean and Kilpatrick, 1997; Layrisse et al., 1984; Acevedo et al., 1992). The majority of the studies showed that water-in-crude oil emulsions are stabilized by a rigid film or “skin” at the oil–water interface (Dodd, 1960; Taylor, 1992; Acevedo et al., 1993). A typical dehydration plant operation usually comprises the following six major steps: separation by gravity settling, chemical injection, and heating, addition of fresh (less salty) water, mixing, and electrical coalescing. The treatment involves allowing time for water drops to settle out and be drained off. Settling time and draining are accomplished in wash tanks, separators, and desalting vessels. Settling and draining can be speeded up using one or more of the following actions: injecting chemicals (demulsifier), applying heat, adding diluents (freshwater), and applying electricity (Al-Otaibi, 2004). Therefore, it is expected that the most important

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parameters affecting performance of the dehydration are settling time, mixing time, chemical dosage, crude temperature, and wash water flow rate ratio.

In heavy oil production, the efficiency of extracting clean dry oil from the produced fluids depends on the process conditions as well as the choice of chemical additives used to destabilize the emulsions. The effectiveness of the measurements used to destabilize these emulsions depends on the properties of the surfactants such as the hydrophile–lyophile balance (HLB) as well as on properties of the oil and water phase. The complication arises from the treatment and production of the fluids was attributed to the presence of solids in the fluid (Angle, 2004). Demulsification of crude oil emulsions has been attracted great attention and many published work was recently reviewed, (Angle, 2004; Sjoblom et al., 2001) and gained an importance discussion to specific cases (Bailes and Kuipa, 2001; Xia et al., 2004; Stark and Asomaning, 2005; Zhang et al., 2005). The majority of the studies focused on simple model systems, and few studies focused on complex field emulsions, which are often more difficult to obtain. The demulsifier combinations often used for emulsion treatments become ineffective as more complex emulsions are produced. Commercial demulsifiers are polymeric surfactants, such as copolymers of polyoxyethylene (PE) and polyoxypropylene (PO) or alkylphenol–formaldehyde resins, dodecylbenzenesulphonic acid, or blends of different surface-active compounds (Kokal, 2005). In the previous works (Atta et al., 2008a, 2008b) new surfactant blends were prepared by etherification of Schiff base surfactants. There are two challenges faced us in this work to separate water from the crude emulsions which are emulsion stability and demulsification at temperature below 60 °C. In our quest for new polymeric demulsifiers, we have focused on Schiff bases, condensed organic derivatives containing azomethine groups C=N–. In this work we have synthesized a new class of soluble such Schiff bases and evaluated them as demulsifiers for crude petroleum at temperatures not exceeding 60 °C. The correlation between the surface activity of the prepared Schiff base surfactants and their performance as demulsifiers is another goal of the present work. The proposed work aims also to examine the interfacial behaviors to determine and improve the poor performance of the demulsifiers.

## 2. Experimental

### 2.1. Materials

Octadecyl amine (ODA), dodecyl amine (DDA), and *p*-hydroxybenzaldehyde (HBA) were obtained from Aldrich Chemical Co., and used without purification. All solvents were purchased from Aldrich Chemical Co. (Germany).

Table 1 shows details of the Land Balayium crude oil (produced from Petrobel Co., Egypt) and its origin. On the other hand, the formation water was obtained from production wells (produced from Petrobel Co., Egypt).

**Table 1**  
Physicochemical properties of the tested land balayim crude oil.

Test	Method	Results
API gravity	Calculated	25
Specific gravity 60/60 (°F)	IP 160/87	0.896
Wax content (wt%)	UOP 46/64	5
Asphaltene content (wt%)	IP 143/84	13
Pour point (°C)	IP 15/67(86)	18

### 2.2. Preparation of Schiff base surfactants

#### 2.2.1. Synthesis of Schiff base monomers

The reactions were completed in three-necked flask (0.5 L capacity) equipped with a condenser, magnetic stirrer, thermometer, dropping funnel and nitrogen atmosphere inlet. The flask was charged with ODA or DDA (0.25 mol) and 200 ml absolute ethanol. HBA (0.25 mol) were dissolved in 200 ml absolute ethanol and the solution was added into flask within 1 h with stirring in the presence of nitrogen gas. The temperature of reaction was gradually increased up to reflux for 3 h. The reaction was cooled to filtrate the solution.

The products of condensation of HBA with ODA and DDA were designated as ODS and DDS, respectively.

#### 2.2.2. Ethoxylation of Schiff-base monomers

A high pressure stainless steel autoclave (Parr model 4530, USA) of 1 L capacity, 400 psi maximum pressure and 180 °C maximum temperature was used for ethoxylation reaction. The autoclave is equipped with a magnetic drive stirrer, an electric heating mantle with a thermocouple inserted in the reactor body, a cooling coil, a pressure gauge and a drain valve. The prepared ODS, DDS and their polymers were charged into the reaction vessel with Na metal as a catalyst (0.3 wt%), the reaction mixture was heated to 180 °C with continuous stirring while passing a stream of nitrogen gas through the system for 10 min to flush out air. The nitrogen stream was then replaced by ethylene oxide. The ethylene oxide was introduced through the inlet gas valve until the desired amount of ethylene oxide was reacted. Generally, as a result of the introduction of ethylene oxide, the pressure was substantially increased as indicated by the pressure gauge, until it reached a maximum value. The pressure drop indicates ethylene oxide consumption. The reaction completion was established when the pressure reached its minimum value. At this stage, heating was stopped and the content was cooled gradually to ambient temperature by means of the cooling coil connected to the reactor carrying cold water. After cooling, the product obtained was discharged, weighed and neutralized with HCl. The ethoxylated products of ODS and DDS at different ethoxylation times can be designated as EODS, EDDS-1 and EDDS-2, respectively.

### 2.3. Measurements

The resin and asphaltene contents of crude oil were determined according to standard procedure ASTM D2000 methods (ASTM-2007D, 2000).

The relative solubility number (RSN) values of the surfactants were measured by the newly developed method using ethylene glycol dimethyl ether and toluene as titration solvents. In this method, 1 g of surfactant was dissolved in 30 mL of solvent consisting of toluene and ethylene glycol dimethyl ether and the resultant solution was titrated with deionized water until the solution became persistently turbid. The volume of water in mL was recorded as the RSN number.

The solubility tests were performed in different solvent media for EODS, EDDS-1 and EDDS-2, at a concentration of 40% (w/v), at room temperature, with xylene, ethanol, and xylene/ethanol (75:25).

The nitrogen content was measured with a Tecator Kjeltch auto analyzer. A Tecator 1007 digester was used for the initial digestion of the samples.

Infrared spectra were determined with a Perkin-Elmer model 1720 FTIR (KBR). While, <sup>1</sup>H NMR spectra of the prepared Schiff base monomers and polymers were recorded on a 400 MHz Bruker Avance DRX-400 spectrometer.

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