Egyptian Journal of Petroleum (2015) **24**, 363–374

HOSTED BY

Egyptian Petroleum Research Institute

Egyptian Journal of Petroleum

www.elsevier.com/locate/egyjp
www.sciencedirect.com

FULL LENGTH ARTICLE

Resolution of water in crude oil emulsion by some novel aromatic amine polyesters

A.M. Al-Sabagh, N.M. Nasser, E.A. Khamis *, M. Abd-El-Raouf

Egyptian Petroleum Research Institute (EPRI), Nasr City, Cairo, Egypt

Received 18 June 2014; accepted 17 August 2014

KEYWORDS

Demulsification;
HLB;
Aromatic polymeric surfactants;
Ethoxylated aromatic amines;
Polyesterification

Abstract In this work, three aromatic amines (p-toluidine, p-nitroaniline and p-chloroaniline) were chosen as bases for the repatriation of some nonionic polyesters. These amines were ethoxylated with different total number of ethylene oxide units 6, 12, 18. The prepared ethoxylated amine diols were polyesterified with maleic anhydride and polypropylene oxide polyethylene oxide block copolymers in polyesterification reaction. The demulsification efficiency of these demulsifiers was investigated using the bottle test. The effects of the molecular weight, concentration, asphaltene content, water content, Hydrophile Lipophile Balance (HLB) and temperature on the demulsification efficiency were investigated. The surface active properties were correlated with their demulsification efficiency. It was found that, $NAE_{18}D$ gave the best result in the demulsification process. The demulsification efficiency was discussed on the light of surface active properties, interfacial tension and the factors affecting the demulsification. The surface-active properties of the prepared demulsifiers were measured at 60 °C.

1. Introduction

Water-in-oil emulsions were stabilized by a wide range of materials that appear naturally in the heavy crude oil, such as asphaltenes (natural surfactants) and clays [1]. To resolve water from the emulsion to meet the pipeline and shipping specifications, the destabilization of emulsion is essential. Demulsification can be achieved by three means: mechanical, electrical, and chemical. The addition of chemicals in terms of demulsifiers was the most widely used method [2].

An effective demulsifier was a surface-active compound that can adsorb onto the water/oil interface and change its properties such that water droplets aggregate and coalescence [3–11]. A great number of demulsifiers have been developed during the past decades. Since the 1930s, the nonionic surfactants have been introduced and have found wide application as demulsifiers. It is well-known that a nonionic surfactant contains two different groups: hydrophilic and hydrophobic. The hydrophilic part commonly includes oxyethylene, hydroxyl, carboxyl, or amine groups, while the hydrophobic part includes mainly groups of the alkyls, alkylphenols, or oxypropylenes. The efficiency of a demulsifier was determined by the nature of the emulsion and the characteristics of the used demulsifier. Currently, in the oil industry, the selection of a demulsifier was still based mainly on trial and error after

* Corresponding author. Tel.: +20 2 22747917.
E-mail address: emyali81@gmail.com (E.A. Khamis).
Peer review under responsibility of Egyptian Petroleum Research Institute.

http://dx.doi.org/10.1016/j.ejpe.2015.07.015

some preliminary screening such as the bottle test using the Sany glass. However, attempts have been made to correlate the efficiency of demulsifiers with their surface, interfacial, and chemical properties [12].

The first object of the present work focuses on the preparation of a new family of nonionic polyesters to use them in the resolution of water in crude oil emulsion. The novel polyesters are based on new diols. These diols are ethoxylated (p-toluidine, p-nitroaniline and p-chloroaniline) at three different ethylene oxide units. The polyesters were characterized and performed as demulsifiers at different water and asphaltene contents of emulsion. The second object of this work was to investigate the surface and interfacial properties of these polyesters, to correlate them with their demulsification efficiency. The work was extended to study the factors affecting the demulsification efficiency.

2. Experimental

2.1. Materials used

2.1.1. Chemicals used

Aromatic amines; p-toluidine, p-nitroaniline and p-chloroaniline were supplied from Aldrich chemical company whereas maleic anhydride was obtained from Merck chemical company. Polyethylene oxide polypropylene oxide block copolymer 5000 was supplied from Stepan chemical company. The other chemicals were of technical grade and were used as received without further purification.

2.1.2. Formation water used

The sample of formation water was obtained from the Petro Gulf Company, Suez Gulf, Egypt and its physicochemical characterization is shown in Table 1.

2.1.3. Crude oil used

Two types of asphaltenic crude oils were submitted by the Suez Oil Company (SUOCO), East Desert, Egypt and one waxy crude oil was submitted by the Qarun Petroleum Company, West Desert, Egypt and their general physicochemical properties are shown in Table 2.

2.2. Preparation of the demulsifiers

2.2.1. Ethoxylation of aromatic amines

p-Toluidine, p-nitroaniline and p-chloroaniline were charged into a closed reaction vessel individually with 0.5 g Na–metal as a catalyst and heated to between 150 and 180 °C with continuous stirring while passing a stream of nitrogen gas through the system for 2 min. The nitrogen stream was, then, replaced by ethylene oxide gas at a rate, which was regulated by monitoring the Hg level of the manometer. The reaction was carried out for different interval times after which the apparatus was filled with nitrogen, cooled and the reaction vessel was weighed. The difference in weight indicated the amount of ethylene oxide consumed in the reaction. The number of moles of ethylene oxide can be calculated on the basis of the number of amine moles. [10,13]. The total number, n, of ethylene oxide units were 6, 12 and 18. The product was then dissolved in isopropanol and then salted out with supersaturated NaCl solution. The organic layer was then separated and isopropanol was distilled off. The ethoxylated product obtained showed a brown viscous liquid appearance.

Table 1 General characterization of formation water.

Total dissolved solids	44,372 mg/L
Resistivity	0.01915 Ohm m at 19 °C
Conductivity	52.2 mS/M at 19 °C
Density	1.0322022 g/ml
pH	7.74 at 19 °C
Salinity	39,996 mg/L
Specific density	1.03304

Table 2 Physicochemical properties of the used untreated crude oils.

Specification	Method	Asphaltenic crude oil		Waxy crude oil
		Type I	Type II	Type III
Specific gravity (60/60 °F)	IP 160	0.973	0.874	0.8156
API gravity at 60 °F	IP 160	26.29	40.955	43
Kinematic viscosity at 60 °F (c. St)	IP 71	294.972	222.87	2.5
Asphaltene content (wt.%)	IP1 43	8.7	7.2	1.6
Wax content (wt.%)	UOP 46	2.5	2.9	15.4
Water content (vol.%)	ASTM, D – 4006	0.5	0.5	0.5

2.2.2. Polyesterification of the ethoxylated aromatic amines

The ethoxylated aromatic amines (0.55 mol) were charged individually into the reaction vessel with (0.55 mol) block copolymer, the reaction mixture was heated to 80 °C in N_2 atmosphere then 1 mol of maleic anhydride was added, and the temperature was raised to 190–200 °C for 4 h. The extent of the reaction was followed-up by monitoring the acid value. The reaction product was permitted to cool at room temperature and was stored in a dark reagent bottle [8]. The molecular weight and the polydispersity were determined by GPC and the nitrogen content was determined by the quartz method. Table 3 shows the chemical designations and some physical properties for the prepared polyesters. The general formula for the prepared aromatic polyester surfactants are shown in Fig. 1.

IR spectra are recorded in a Fourier transform infrared spectrophotometer (FT-IR 1615, Perkin Elmer, USA) with KBr pellets.

2.3. Preparation of water in crude oil emulsions

In a 250 ml beaker, the crude-oil was stirred at 25 °C (200 rpm) while the formation water was added gradually to the crude oil until the two phases became completely homogenized [14]. The emulsions were produced at different ratios of crude oil to water, namely 90:10, 70:30 and 50:50, respectively.

2.4. Hydrophile Lipophile Balance (HLB)

The HLB of the prepared demulsifiers were calculated according to the most commonly used formula for the nonionic surfactant; $HLB = 20 \times M_H/(M_H + M_L)$