Available online at www.sciencedirect.com
ScienceDirect
Journal of Petroleum Science and Engineering 56 (2007) 296–302
JOURNAL OF PETROLEUM SCIENCE & ENGINEERING
www.elsevier.com/locate/petrol

Hexa-triethanolamine oleate esters as pour point depressant for waxy crude oils

A.A. Hafiz *, T.T. Khidr

Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt

Received 11 January 2006; received in revised form 6 October 2006; accepted 9 October 2006

Abstract

New crystal modifier surfactants were developed by esterification of hexa-triethanolamine with oleic acid to prepare mono, di, and tri-esters. The synthesized esters were confirmed by IR spectroscopy and the molecular weight of the major compound in the reaction mixture was determined by MS analysis. Surface properties of the synthesized modifiers, including critical micelle concentration (CMC), effectiveness (π_{cmc}), maximum surface excess (Γ_{max}) and minimum surface area (A_{min}) were determined at 30 °C. The synthesized esters were evaluated as flow improver (FI) and pour point depressant (PPD). Hexa-triethanolamine mono-oleate was most efficient for crude oil (I), and hexa-triethanolamine tri−oleate was most efficient for crude oil (II).

Keywords: Hexa-triethanolamine oleate esters; Flow improver; Pour point depressant

1. Introduction

The presence of paraffin waxes in crude oil represents serious problems to the production, transportation, and refiner. Many of these problems can be effectively resolved by the appropriate application of crystal modifier chemicals. However, when the chemical is a surfactant and combined with hot water or solvents, the procedures are quite effective (Barrow, 1966). Change in physico-chemical equilibrium condition due to decreases in temperature below melting point, causes crystallization and losses in component solubility which may start accumulation (Misra et al., 1995). Paraffin deposits have caused formation plugging during stimulation treatment and interfered in low temperature oil pumping (Zhang et al., 2003a; Wang et al., 2003). Pour point depressants (PPDs)/flow improvers (FIs) are used as chemical additives when transporting crude oils at temperatures below their wax appearance temperatures (WAT). There are many kinds of polymers that are used as PPDs to influence the behavior of the paraffin crystallites formation (Bunger and W, 1981; Carcia, 2000; Al-sabagh et al., 2002; Pedersen, 2003; Song et al., 2005). Wax is not the only component in a crude oil. Other constituents in the crude oil i.e. asphaltenes, resins, lighter distillates, polar aromatics etc., should also be considered as important factors while ascertaining the behavior of a crude oil. Asphaltenes are very large heterogeneous molecules with condensed aromatic nuclei, which may associate to form colloidal sized particles that strongly influenced the viscosity of the oil medium and affect the crystallization of the wax (Brood et al., 1971; El-Gamal et al., 1997; Frohlich and Rice, 2005). In order to improve the efficiency of the additives, theoretical analyses explain the interactive mechanism, co-crystallization, nucleation, or improved wax solubility (Zhang et al., 2003b).

Triethanolamine is condensed in the presence of different catalysts, and the structure and degree of

* Corresponding author.
E-mail address: ynamal2002@yahoo.com (A.A. Hafiz).

0920-4105/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.petrol.2006.10.003

polymerization were determined via mass spectroscopy as a molecular weight of the major component that results during the synthesis process (Hfiz, 1997; Hafiz and El-Din, 2005). Dimer and trimer form of ethanolamine were esterified with oleic acid to prepare the corresponding monoester (Hafiz and Abdou, 2003).

In this paper, the prepared surfactants were evaluated as pour point depressant/flow improver for waxy crude oils with different wax and asphaltene content.

2. Experimental

2.1. Materials

- Triethanolamine and oleic acid from Aldrich Chemicals.
- Two Egyptian waxy crude oils [umbarkca 20 (I) and umbarkca 14 (II)] were used for evaluating the performance of the synthesized polymeric additives.

Their physico-chemical characteristics are given in Table 1.

Table 1
Physical characteristics of crude oils

Properties	Methods	Crude oils	
		I	II
Pour points (°C)	IP 15/67 (86)	24	15
Density at 70 °C	ASTM, D 1217-93	0.8886	0.7891
Kinematic viscosity	IP 71		
Cst, 40 °C		19.33	10.73
Cst, 100 °C		6.73	2.50
Wax content (wt.%)	WPOP 46–64	11.2	10.2
Asphaltene content (wt.%)	IP 143	2.1	0.22
Distillation (°C)	IP 24/84		
IBP.		108	95
20		220	110
40		250	130
60		300	150
80		350	200
90		370	250
FBP		380	290

2.2. Synthesis of hexa-triethanolamine

Triethanolamine (1 mol, 149 g) was charged in a three-necked flask and solid NaOH (0.04 mol, 1.6 g) was added while stirring. The reaction mixture was then heated to 220–260 °C until the theoretical amount of water (54 ml) was collected in the Dean–Stark tube (Katzman and Epstein, 1941; Bellos and Lovett, 1985; Fikentscher et al., 1995; Kane and El shall, 1996; Hafiz and Abdou, 2003). The product was purified by washing with a solution of 5% acetic acid and then dissolved in petroleum ether (b.p. 40–60 °C). The organic layer was separated and the solvent was distilled off to give the pale yellow viscous liquid of hexa-triethanolamine (T_6).

2.3. Esterification of hexa-triethanolamine (T_6): General procedure

T_6 (1 mol) was added to oleic acid (1 or 2 or 3 mol) in a three-necked flask in the presence of *p*-toluene sulfonic acid (0.005 mol, 0.086 g) as a catalyst. The reaction mixture was heated at 150 °C with continuous stirring until the theoretical amount of water was collected. The product was purified by washing with a hot solution of 5% sodium carbonate and then dissolved in petroleum ether (b.p. 40–60 °C). The organic layer was separated and the solvent was distilled off (Hafiz and Abdou, 2003). The products obtained were hexa-triethanolamine mono-oleate (E_1T_6) after collecting 18 g of water, hexa-triethanolamine di-oleate (E_2T_6) after collecting 36 g of water and hexa-triethanolamine tri-oleate (E_3T_6) after collecting 54 g of water.

Infrared spectra for T_6, (E_1T_6), (E_2T_6) and (E_3T_6) were recorded using a Fourier transform infrared (IR) spectrophotometer (ATI Mattson, Genesis Series™). An HP model MS 5988 mass spectrometer was used to determine molecular weight.

2.4. Surface tension measurements

Surface tension measurements were obtained using De-Nouy Tensiometer (Kruss-K_6 type) applying a platinum ring technique. Freshly prepared aqueous solution of the product (E_1T_6, E_2T_6 and E_3T_6) in deionized water was prepared with a concentration range of 0.01–0.001 mmol/L at 30 °C. The ring was washed twice after each reading first by ethanol then distilled water (Findly, 1963).

The apparent surface tension was measured 5 times for each sample within 2 min interval between each reading (Hafiz et al., 2005).

Critical micelle concentration (CMC) was determined from the relation between different concentrations and surface tension at this concentration, the point at the curve breakdown is CMC.

2.5. Evaluation tests

The three prepared oligomers were tested for their effectiveness as flow improvers for the Egyptian waxy crude oils through the pour point test according to the ASTM-97 (Annual Book of ASTM Standards, 1991) procedure and kinematic viscosity to the IP 71 (The Institute of Petroleum, London, 1993a).