Monatshefte für Chemie 127, 621–629 (1996)

Monatshefte für Chemie
Chemical Monthly

Propylene Oxide-Ethylene Oxide Block Copolymers as Demulsifiers for Water-in-Oil Emulsions, I. Effect of Molecular Weight and Hydrophilic-Lipophylic Balance on the Demulsification Efficiency

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Summary. A series of propylene oxide (*PO*)-ethylene oxide (*EO*) block copolymers with different *EO*/*PO* ratios and molecular weights have been prepared and tested for their demulsification potency in breaking synthetic water-in-benzene emulsions stabilized by asphaltenes. Their partition coefficients between benzene and water were determined by means of UV absorption. NMR spectroscopic analysis was used for determining the actual *PO*/*EO* ratios of these block copolymers. The effects of hydrophilic-lipophilic balance (HLB) and molecular weight of the prepared surfactants on their demulsification efficiency were investigated. It was found that the demulsification efficiency is directly proportional to both HLB and molecular weight.

Keywords. Block copolymer; Demulsifiers; Water-in-Oil emulsion; Ethylene oxide; Propylene oxide.

Propylenoxid-Ethylenoxid-Blockcopolymere als Emulsionsbrecher für Wasser-in-Öl-Emulsionen, 1. Mitt. Effekt des Molekulargewichts und des Hydrophilie-Lipophilie-Gleichgewichts auf die Effizienz der Emulsionsbrechung

Zusammenfassung. Eine Reihe von Propylenoxid (*PO*)-Ethylenoxid (*EO*) Blockcopolymeren mit verschiedenen *EO*/*PO*-Verhältnissen und Molekulargewichten wurden hergestellt und auf ihre Effizienz bezüglich des Brechens von durch Asphalt stabilisierten synthetischen Wasser/Benzol-Emulsionen untersucht. Ihre Verteilungskoeffizienten zwischen Benzol und Wasser wurden mittels UV-Spektroskopie ermittelt. Das *PO*/*EO*-Verhältnis wurde NMR-spektroskopisch bestimmt. Die Effekte von Hydrophilie-Lipophilie-Gleichgewicht (HLB) und Molekulargewicht auf die Effizienz der Wirkung wurden untersucht. Das Emulsionsbrechungsvermögen ist direkt proportional zu HLB und indirekt proportional zum Molekulargewicht.

Introduction

There is an increasing number of crude oil fields that are producing both crude oil and water, both onshore and offshore [1]. The water produced with the crude oil may be a discrete phase as it flows up the well riser, but it is mixed with the crude oil at the well head chokes and valves where significant mixing, turbulence, and pressure drop occur. The produced water-in-crude oil emulsion is then stabilized by various surface active agents naturally occurring in the crude oil [2–4]. These emulsions attain their stability from the presence of asphaltenes which are composed of condensed aromatic rings containing saturated carbon chains, naphthenic rings, and metals. Asphaltenes are adsorbed at the water-oil interface forming an interfacial film of remarkable strength and elasticity which prevents the dispersed water droplets from coalescence [5].

The coproduction of water with crude oil gives rise to a variety of problems. These include: the expense of pumping or transporting the water *via* pipeline or tanker; the corrosion of pipe work, pumps, production equipment, and downstream overhead distillation columns; the additional production equipment required to give export quality crude oil; the poisoning of downstream refinery catalysts; and the problems associated with increased oil viscosity as a consequence of finely dispersed water within the crude oil. Thus, there are a number of commercial and operating reasons for removing the emulsified water from the crude oil. Consequently, those factors which either enhance or reduce oil emulsion stability are of considerable importance to the oil industry.

Polymeric surfactants are most commonly used to break water-in-crude oil emulsions. For testing the efficiency of these surfactants as demulsifiers, several authors [6–8] have utilized synthetic water-in-oil emulsions to simulate water-in-crude oil natural emulsions. The main reasons for utilizing these synthetic emulsions are:

(1) Crude oil/water natural emulsions contain many variables that influence emulsion stability [9] such as the percentage of asphaltenes, percentage of water or brine, percentage of salt, their chemical constitution, and the thermal history [10]. All these variables can't be controlled since they change drastically from one batch to another and cause a great confusion for the proper scientific study [11].

(2) Reconstituted water/crude oil emulsions give ambiguous results because the crude oil may contain traces of the demulsifiers which have been used for separating water from the crude oil during its production [12].

(3) The crude oil contains a very complicated mixture of hydrocarbons; it is therefore very difficult to describe with precision the nature of the hydrocarbon phase present in the crude oil [13].

The present study aims at synthesizing *PO-EO* block copolymers to be used as water-in-oil emulsion breakers. The influence of the structural variations in the molecular architecture of the prepared demulsifiers such as HLB and molecular weight on their demulsification efficiency is the main objective of this investigation. The use of synthetic water-in-benzene emulsions stabilized by asphaltenes for testing the demulsification efficiency is based on the previously mentioned advantages of using synthetic emulsions.

Results and Discussion

Two types of polyethylene glycols (*PEG*) with different molecular weights (4000 and 6000 g/mol) were propoxylated. The amount of *PO* was varied to obtain polymeric

Table 1. Specifications of the synthesized *EO-PO* block copolymers

	MW of *PEG*	No. of moles of *PEG*	No. of moles of *PO*	Theoretical MW
A1	4000	0.2	13.790	8000
A2	4000	0.2	9.196	6667
A3	4000	0.2	5.900	5714
A4	4000	0.2	3.440	5000
B1	6000	0.2	20.700	12000
B2	6000	0.2	13.790	10000
B3	6000	0.2	8.860	8571
B4	6000	0.2	5.172	7500

surfactants with different hydrophilic lipophilic balance (HLB). The characteristics of the synthesized *PO-EO* block copolymers are summarized in Table 1.

Nuclear Magnetic Resonance Analysis of PO/EO Ratios

In some recent published articles [14–16], ^{1}H NMR spectroscopic analysis has been used for determining the *PO/EO* ratio for *EO/PO* block copolymers. In these articles, the authors' considerations were focused on two signals. The first is located at 0.9–1.3 ppm (assigned to the CH_3 group protons of the oxypropylene unit), the second at 3.4–3.8 ppm (assigned to the CH_2 protons of the oxyethylene unit plus the CH protons of the oxypropylene unit). The ratio of the integrals of these two signals was utilized successfully by these authors for determining the *PO/EO* ratio. Accordingly, the same procedure was applied throughout this work for determining the *PO/EO* ratios of the synthesized block copolymers.

The ^{1}H NMR spectra of the synthesized block copolymers allow clear detection of the above mentioned two signals. The integral values derived from these spectra and the corresponding theoretical ones are listed in Table 2. The theoretical integral

Table 2. HLB, *PC*, and ^{1}H NMR integral values for the synthesized block copolymers

	HLB	*PC*	Theoretical integral		Experimental integral	
			0.9–1.3	3.4–3.8	0.9–1.3	3.4–3.8
A1	10	1.33	3	8.3	3	7.8
A2	12	1.90	3	10.9	3	9.0
A3	14	2.03	3	15.0	3	13.8
A4	16	3.00	3	24.1	3	23.2
B1	10	2.45	3	8.2	3	6.7
B2	12	2.57	3	11.0	3	9.6
B3	14	2.57	3	15.0	3	14.1
B4	16	2.93	3	23.0	3	21.23

values were calculated from the ratio of *PO*:*EO* and the number of protons responsible for each signal. Table 2 reveals that there is a good agreement between the theoretical and the measured integral values. This leads to the speculation that the propoxylation reactions were completed as designed. Accordingly, the calculated HLB and molecular weights of the prepared copolymers could be confirmed.

Preparation of Synthesized Water-in-Benzene Emulsions Stabilized by Asphaltenes

Asphaltenes are polynuclear aromatic compounds substituted with aliphatic chains and naphthenic hydrocarbons and occur naturally in the crude oil as surface active species that have the ability to be adsorbed at the crude oil/water interface and form a rigid film around the dispersed water droplets preventing their coalescence [17]. The interfacial film formed by the asphaltenes is characterized by a great mechanical strength, therefore causing a great stability of the emulsions [18]. Accordingly, asphaltenes were selected to stabilize the synthetic emulsions.

Maximum emulsion stability of asphaltenes stabilized emulsions often occurs when asphaltenes are added in a concentration that causes incipient precipitation [19]. At this particular concentration, asphaltenes constitute a monolayer film between water droplets and the continuous organic phase. In the present study, different concentrations of asphaltenes were added to a water/benzene mixture containing 20% water in order to select the highest concentration of asphaltenes (critical concentration of asphaltenes, *CCA* above which precipitation takes place. The *CCA* was found to be 0.25 g asphaltenes/100 ml water/benzene mixture. However, it was also found that the percentage of asphaltenes depends on the water content in the emulsion. In this respect, the *CCA* decreases upon decreasing the water content below 20%.

The water/benzene volume ratio that causes maximum emulsion stability was investigated. The data for the influence of changing the water/benzene phase volume ratio on the emulsion stability of the synthesized emulsions stabilized by 0.25% asphaltenes indicated that the emulsions containing 20–30% water in benzene possess the maximum stability. As the percentage of water in the emulsion was decreased below 20%, a precipitation of the asphaltenes was noticed. When the percentage of water exceeded 30%, an instantaneous water separation occurred at 50 °C. This may be attributed to the increased probability of the dispersed water droplets to come into contact and to coalesce. This conclusion is in accordance with previous findings and explanations published by *Dodds* [20] and *Lissant* [21]. Since the demulsifiers are used as aqueous solution, the lowest possible quantity of water required to synthesize the stable emulsion (20%) was used. This situation permits the possibility of adding an extra amount of water as an aqueous solution of the demulsifier without reducing the stability of the emulsion.

From the previous discussion, the conditions responsible for preparing the most stable emulsions were selected. This synthetic emulsion is used in the following to simulate water/crude oil natural emulsions and also to evaluate the newly prepared surfactants as demulsifiers.

Table 3. Demulsification efficiency of demulsifiers after 24 h at different concentrations of demulsifiers

	% coalescence					
	50 ppm	100 ppm	200 ppm	300 ppm	400 ppm	500 ppm
A1	6.7	11.8	28.3	36.2	50.0	–
A2	6.7	13.6	29.2	38.5	50.0	–
A3	7.0	15.5	29.2	46.2	53.6	–
A4	19.0	59.1	70.8	76.9	53.6	50.0
B1	8.6	17.3	33.3	42.3	46.4	–
B2	7.6	18.2	29.2	42.3	57.1	–
B3	12.4	16.4	33.3	42.3	50.0	–
B4	11.4	17.3	80.8	92.3	75.0	70.0

Before studying the effect of the structural variables on the demulsification efficiency, a screening test was undertaken in order to find out the optimum concentration at which the best performance is obtained for each demulsifier.

As indicated before, the demulsification efficiency of the *PO-EO* block copolymers (series **A** and **B**) was measured at different times at 50 °C. This temperature was selected to match the actual situation encountered at the oil field production facilities used for separating the water from the crude oil. The time span of the tests was 24 hours, and the concentration of the demulsifiers was varied from 50 ppm to 500 ppm with respect to the total volume of the emulsion. The demulsifiers were dissolved in water to form solutions of a concentration of 100 ppm per ml of the solution. The final demulsification efficiency (after 24 hours) expressed as % coalescence, based on the initial volume of water in the synthetic emulsion plus 1 ml H_2O/each 100 ppm demulsifiers used in the test, are summarized in Table 3 as a function of demulsifier concentration.

The data quoted in Table 3 reveal that the demulsification efficiency increases as the concentration of the demulsifier increases up to a certain value. At this concentration, the demulsifier molecules perform a complete coverage of the benzene/water interface. Further increase of the demulsifier's concentration results in a subsequent dissolution of the demulsifier in either benzene or water depending on its relative solubility, partition coefficient, and HLB. This leads to an enhanced stability of the emulsion due to the repulsion forces generated by the layers of surfactant molecules adsorbed on the droplets' surface.

Influence of the Structural Variations of the Demulsifiers on their Demulsification Efficiency

The selection of a demulsifier in a commercial application is based on the process of trial and error. However, it is an important target to answer the very important question upon structural variables influencing the demulsification efficiency of the demulsifier. An attempt to answer this question is presented below, based on studying the demulsification efficiency of a series of demulsifiers of systematic variation in molecular weight and HLB.

Effect of HLB of the Demulsifiers on their Demulsification Efficiency

The HLB concept, first introduced by *Griffin* [22], is normally used as an important parameter to predict the action of emulsifiers on a certain water-oil emulsion [23]. However, this concept has not been used extensively by scientists working in the field of demulsifiers. In the present study, the HLB value of the block copolymers was varied by altering the degree of propoxylation of *PEG* of a certain molecular weight.

The HLB values were calculated by *Griffin*'s equation as follows:

$$\mathrm{HLB} = \%\ \mathrm{ethoxylation}/5$$

The calculated values of HLB and the measured *PC* (partition coefficient) values for the block copolymers under investigation are collected in Table 2. It can be seen that the HLB of the surfactants increases with increasing ratio of ethylene oxide relative to propylene oxide units. The same dependence is applicable on the *PC* values. Accordingly, it is obvious that both HLB and *PC* depend primarily on the degree of propoxylation.

The data reveal that the amount of water separated after 24 hours, expressed as percentage coalescence, is in accordance with the increase in HLB and *PC*. This finding may be explained by the following speculations:

(1) The increase in the HLB value increases the solubility of the surfactant in the aqueous phase (dispersed phase). When the demulsifier is initially introduced to the water-in-oil emulsion, it will be more thermodynamically stable at the interface of the water droplets. Accordingly, the concentration of the surfactants in the interface increases by increasing their HLB value. As the concentration of the surfactant increases at the interface, a continuous hydrophilic pathway is formed between the dispersed water droplets. This leads to a rupture of the interfacial oil film surrounding the water droplets.

(2) Another point of view regarding the enhanced demulsification efficiency of the more hydrophilic surfactants is based on the study performed by *Eley et al.* [24] and *Laurence* and *Killner* [25] on water/oil containing asphaltene emulsions. They stated that the destabilization of water-in-oil emulsions can be achieved by the addition of surface active agents which promote oil-in-water emulsions. It is well known that water soluble surfactants are more capable of stabilizing oil-in-water emulsions and *vice versa* [26]. The present work deals with a water-in-oil emulsion, and hence it is clear that the higher the HLB and *PC*, the higher the demulsification efficiency.

Cooper et al. [27] have found that demulsifiers with an HLB ranging between 15 and 20 are considered most effective in breaking water-in-oil emulsions. The present results confirm *Cooper*'s finding where the most effective demulsifiers are those having HLB equal 16 (*i.e.*, **A4** and **B4**).

Effect of Molecular Weight on the Demulsification Efficiency

The molecular weights of group **A** and **B** demulsifiers and their HLB are listed in Tables 1 and 2. It can be seen from these tables that the molecular weights decrease in the order **A1** > **A2** > **A3** > **A4**. Similarly, the values of the molecular weights of group **B** compounds are arranged according to the same sequence, *i.e.*

B1 > **B2** > **B3** > **B4**. This decrease in molecular weight within each group is due to the decreasing number of the incorporated propylene oxide units. This reduction in molecular weight is certainly accompanied with an increase in the HLB. Since the efficiency is associated with the HLB value, it is inversely proportional to molecular weight within each group. Upon comparing the demulsifiers that possess the same HLB from group **A** and group **B**, *i.e.* **A1**/**B1**, **A2**/**B2**, **A3**/**B3** and **A4**/**B4**, Table 3 shows that the maximum demulsification efficiency is assigned to the demulsifier of highest molecular weight. This finding is in accordance with the work published by *Berger et al.* [28].

Different explanations of the effect of molecular weight on the demulsification efficiency are based on the excluded volume and the dimensions of the polymeric molecule. According to various articles published by *Abdel-Azim* and collaborators [29–34], the excluded volume of the polymeric molecule (the volume occupied by the molecule) increases with increasing molecular weight due to the expansion of its hydrodynamic radius. This increase leads to an increase in the number of the asphaltenes molecules excluded from the interface. Consequently, the required film thinning for the asphaltene layer is enhanced which results in an increase in the demulsifier's efficiency.

The present results reveal that:

- The condition required for preparing the most stable emulsion is 20% water-in-benzene containing 0.25% asphaltenes.
- The calculated HLB for the investigated *PO-EO* block copolymers is in accordance with the measured *PC* values, and hence the *PC* value may be used for predicting the HLB of the demulsifiers.
- The demulsification efficiency of the synthesized *PO-EO* block copolymers is directly proportional to their HLB within the same group of demulsifiers. On the other hand, for demulsifiers having the same HLB, the demulsification efficiency increases with increasing molecular weight.

Experimental

Synthesis of PO-EO Block Copolymers

A high pressure stainless steel autoclave model Parr 4530 of 1l capacity was utilized for the propoxylation reaction. The propoxylation of polyethylene glycol (*PEG*) was carried out according to the following technique: *PEG* (0.2 mol) and pelletized sodium metal (2 wt% of the *PEG*) as a catalyst for the reaction were charged in the autoclave. The system was flushed with nitrogen gas and then the temperature was gradually raised at a rate of 10°C/min to 165°C. The desired amount of *PO* (as pointed out in Table 1) was introduced through a pressure pipette by the aid of nitrogen gas. A stirring speed of 500 rpm was applied.

As a result of the introduction of *PO*, the pressure was substantially increased until it reached a maximum value. As *PO* was engaged in the polymerization reaction, the pressure decreased until it reached a minimum when all *PO* was consumed. At this stage, heating was stopped, and the contents were cooled to ambient temperature. The reactants were transferred to a suitable container for purification. The produced polymers were purified using the purification procedure described by *Marian et al.* [35]. The produced block copolymers are designated as **A1**–**A4** and **B1**–**B4** based on the molecular weight of *PEG* and the calculated HLB values (cf. Table 1).

Determination of the Partition Coefficient (*PC*)

The partition coefficient is the ratio of the solubility of a surfactant in the aqueous phase to its solubility in the oil phase. The procedure was carried out by dissolving 0.25 g of the surfactant sample in 25 ml benzene which represents the oil phase; 25 ml of distilled water were added, and the mixture was shaken by an automatic flask shaker for 0.5 h. The flask was tightly stoppered and left in a water bath at 25 °C to separate into two layers. The upper layer (benzene) was taken off, and its UV absorbance was determined. The concentration of the dissolved surfactant in the benzene was then estimated from a calibration curve representing the intensity of the absorbance as a function of concentration. By knowing the concentration of the surfactant in the benzene phase, the concentration of the surfactant in the aqueous phase was computed from the initial concentration. Accordingly, Partition Coefficient = Solubility in an aqueous phase/Solubility in an oil phase.

A calibration curve was obtained for each surfactant by measuring the UV absorbance of a series of concentrations of the surfactant dissolved in benzene. The following concentrations were prepared: 1, 0.8, 0.6, 0.4, 0.2, and 0.1%. The absorbance was measured by a Shimadzu U.V. spectrophotometer, model 120.02, adjusted at 355 nm representing maximum absorbance.

Proton Magnetic Resonance Analysis of *PO-EO* Block Copolymers

The *PO-EO* block copolymers were dissolved in $CDCl_3$ and analyzed using a Jeol NMR spectrometer operating at 280 MHz. The integrals of the signals at 0.9–1.3 ppm and 3.4–3.8 ppm were compared. The former signal is assigned to the methyl protons of the oxypropylene unit, the latter one to the CH_2 protons of the oxyethylene unit and to the CH_2 and CH protons of the oxypropylene unit.

Preparation of Water-in-Benzene Emulsions Stabilized by Asphaltenes

Asphaltenes were separated from Land Belayim crude oil (containing 8% asphaltenes) according to the IP 143/84 standard test method for the precipitation of asphaltenes by *n*-heptane. The stabilized water-in-benzene synthetic emulsions were prepared by dissolving the asphaltenes in benzene to form a solution containing 0.25 wt.% of asphaltenes. The prepared solution was mixed with water to form an emulsion containing 20% water (v/v). The mixture was shaken by means of a flask shaker for 0.5 h.

Bottle Testing for the Determination of the Demulsification Efficiency

The bottle test was used to estimate the capability of demulsifiers in breaking water-in-oil emulsions utilizing the above mentioned simulated synthetic emulsion. The demulsifiers were added at different concentrations (ranging from 50 ppm to 500 ppm) to the emulsion in 100 ml graduated cone shaped tubes stoppered with teflon lids. The emulsion-demulsifier mixture was shaken 200 times by hand and placed in a thermostatted water bath adjusted at 50 °C. The amount of separated water was detected and registered for each concentration at specific time intervals (0.25, 0.5, 0.75, 1, 2, 3, 4, 5, 6, and 24 h). In all experiments, a blank was utilized for comparing the separated water in absence of the demulsifier due to the influence of temperature.

References

[1] Graham DE (1988) Spec Pub R Soc of Chem **67**: 55
[2] Thompson DG, Taylor AS, Graham DE (1985) Colloids Surf **15**: 175
[3] Ivanov IB, Jain RK, Somasundaran P, Traykov TT (1974) J Colloid Interface Sci **51**: 1819
[4] Bridie AL, Wanders TH, Zegveld W, Vander Heijde HB (1980) Marine Pollut Bull **11**(12): 343
[5] Marsden SS, Ishimoto K, Chen L (1988) Colloids Surf **29**: 133

[6] Sjoeblom J, Mingyuan L, Chirsty AA, Tiren G (1992) Colloids Surf **66**: 55

[7] Sjoeblom J, Urdahl O, Hoeiland H, Christy AA, Johansen EJ (1990) Prog Colloid Polym Sci **82**: 131

[8] McMahon AJ (1992) NATO AST, ser, ser c (Emulsion: Fundam Pract Approach) **363**: 135

[9] Bhardwaj A, Hartland S (1994) Ind Eng Chem Res **33**(5): 1271

[10] Schramm LL (1992) Emulsions Fundamentals and Applications in the Petroleum Industry. ACS, Washington, DC, p 313

[11] Madea JR, Fruth SM, Miller CA, Burbower AB (1976) Env Sci Technol **10**: 1044

[12] Staiss F, Boehm R, Rainer K (1991) SPE Prod Eng **6**(3): 334

[13] Hockenberry HR, Lisser JE (1977) J Soc Lub Eng **33**: 247

[14] Adal M, Flodin P, Gottberg E, Holmberg K (1994) Tenside Surf Det **31**(1): 9

[15] Schmitt TM (1992) Analysis of Surfactants. Marcel Dekker, New York, p 310

[16] Naylar CG (1986) J Am Oil Chem Soc **63**: 1201

[17] Liem AJS, Woods DR (1974) Rev of Coalescence Phenomena, AlChE Symp Ser **70**: 8

[18] Little R (1974) Fuel **53**(4): 246

[19] Vander Waarden M (1958) Kolloid Z **156**: 116

[20] Dodds JA (1980) J Colloid Interface Sci **77**: 317

[21] Lissant KJ (1980) Emulsion and Emulsion Technology. Marcel Dekker, New York, p 122

[22] Griffin WC (1949) J Soc Cosmet Chem **1**: 311

[23] Becher P (1985) Encycl Emulsion Technol **2**: 425

[24] Eley DD, Hey MJ, Symonds JD (1988) Colloids Surf **32**: 87

[25] Laurence ASC, Killner KW (1948) J Inst Petrol **34**: 28

[27] Cooper DG, Zajic JE, Cannel EJ, Wood JW (1980) Cand J Chem Eng **58**: 576

[28] Berger PD, Hsu C, Arendell JP (1988) SPE Production Engineering, November, 522

[29] Abdel-Azim AA, Huglin MB (1982) Eur Polym J **18**: 735

[30] Abdel-Azim AA, Huglin MB (1983) Polymer **24**: 1308

[31] Abdel-Azim AA (1993) Polym Bull **30**: 579

[32] Abdel-Azim AA (1994) Macromol Chem Phys **195**: 159

[33] Abdel-Azim AA (1993) Macromol Chem Rapid Commun **14**: 339

[34] Abdel-Azim AA, Tenhu H, Merta J, Sundholm F (1993) Polym J **25**(7): 671

[35] Marian M, Petri S (1989) Academia Medyczna Pol **138**: 484

Received August 10, 1995. Accepted (revised) February 1, 1996