

Propylene Oxide-Ethylene Oxide Block Copolymers as Demulsifiers for Water-in-Oil Emulsions, II [1]. Effects of Temperature, Salinity, *pH*-Value, and Solvents on the Demulsification Efficiency

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Summary. The effects of temperature, NaCl concentration (salinity), *pH* value, and solvents on the demulsification efficiency of propylene oxide (*PO*)-ethylene oxide (*EO*) block copolymers in the breaking of synthetic water-in-benzene emulsions stabilized by petroleum asphaltene have been thoroughly investigated. The demulsification efficiency of the studied polymeric surfactants was found to increase with increasing temperature and decreasing salinity of the aqueous phase. A neutral *pH* value of the aqueous phase of the emulsion was found to be optimal for efficient demulsification. Water and water compatible solvents were found to be the best solvents for the prepared demulsifiers with respect to demulsification properties.

Keywords. Demulsifiers; Temperature; *pH* Value; Salinity; Solvents.

Propylenoxid-Ethylenoxid-Blockcopolymeren als Emulsionsbrecher für Wasser-in-Öl-Emulsionen, 2. Mitt. [1]: Einflüsse von Temperatur, Salzgehalt, *pH*-Wert und Lösungsmitteln auf die Demulsifikationsfähigkeit

Zusammenfassung. Die Einflüsse von Temperatur, NaCl-Konzentration, *pH*-Wert und Lösungsmitteln auf die Fähigkeit von Propylenoxid-Ethylenoxid-Blockcopolymeren (*PO-EO*), durch Asphalte stabilisierte Wasser-in-Benzol-Emulsionen zu brechen, wurden eingehend studiert. Die Wirksamkeit der untersuchten polymeren oberflächenaktiven Substanzen steigt mit steigender Temperatur und sinkendem Salzgehalt der wässrigen Phase. Am besten verläuft die Demulsifikation bei neutralem *pH*-Wert. Wasser und vergleichbare Lösungsmittel eignen sich am besten zur Erzielung einer hohen Wirksamkeit der verwendeten Emulsionsbrecher.

Introduction

It has been shown that in emulsions any change in temperature causes changes in the interfacial tension between the two phases (oil and water) [2], in the nature and viscosity of the interfacial film [3], in the relative solubility of the emulsifying agent in the two phases [4], and in the thermal agitation of the dispersed droplets [5].

Therefore, temperature changes usually cause considerable changes in the stability of emulsions; they may invert the emulsion or cause it to break [6].

The effect of salinity of the aqueous phase on the stability of oil-in-water type emulsions has been extensively studied by several authors [7–9]. However, the water-in-oil type has received little attention and still needs a great deal of research.

Strassner [10] studied the effect of the *pH* value on the stability of Venezuelan crude oil-water emulsions. He observed that a *pH* value of 10.5 produced the least stable emulsions and that a basic *pH* produced oil-in-water (*O/W*) emulsions, whereas an acidic *pH* gave rise to water-in-oil (*W/O*) emulsions. Crude oil/brine systems showed preferred but frequently different optimum *pH* ranges for demulsification. *Strassner* suggests that a *pH* range of 5–12 appears most suitable for treating most oilfield emulsions.

Graham et al. [11] compared the activity of demulsifiers with respect to their state before addition to the emulsion (dissolved or neat). The study revealed that a demulsifier which is dissolved in a solvent gives a better separation of the phases than does an undiluted demulsifier. In the present paper, we investigate the effect of the solvent used to dissolve *PO-EO* block copolymers with respect to their ability to break water-in-benzene emulsion stabilized by petroleum asphaltenes.

In our previous article [1], we have introduced the influence of molecular weight and hydrophilic-lipophilic balance (HLB) of a series of propylene oxide ethylene oxide (*PO-EO*) block copolymers on their demulsification efficiency. Synthetic water-in-benzene emulsions stabilized by petroleum asphaltenes have been utilized to simulate natural water-in-crude oil emulsions.

The present work focuses on studying the effect of temperature, *pH* value, NaCl concentration in the aqueous phase (salinity), and different types of solvents used to dissolve the demulsifiers on the demulsification efficiency of *PO-EO* block copolymers in the breaking water-in-benzene emulsions stabilized by asphaltenes.

Results and Discussion

In our previous publication [1], we concluded that the most efficient *PO-EO* block copolymeric demulsifiers in breaking synthetic water-in-benzene emulsions stabilized by asphaltenes are **A4** and **B4** whose specifications are summarized in Table 1. Therefore, **A4** and **B4** have been chosen as the objects of interest for the present investigation.

Effect of temperature

The effect of increasing the demulsification temperature on the demulsification efficiency of the demulsifiers **A4** and **B4** has been investigated. Two different

Table 1. Specifications of **A4** and **B4** *PO-EO* block copolymeric demulsifiers [1]

	Conc. at which max. demulsification occurs (ppm)	% max coalescence at 50 °C after 24 h	Molecular Weight	HLB
A4	300	76.9	5000	16
B4	300	92.3	7500	16

Table 2. Percentage coalescence at different times and temperatures using optimum concentrations of demulsifiers

Time (h)	Percentage coalescence for			
	A4 (300 ppm) 50°C	70°C	B4 (300 ppm) 50°C	70°C
0.25	30.8	38.5	30.8	38.5
0.50	61.5	65.4	38.5	45.4
0.75	69.2	73.1	38.5	53.8
1.00	69.2	73.1	53.8	61.5
2.00	69.2	76.9	61.5	69.2
3.00	69.2	76.9	69.2	69.2
4.00	69.2	76.9	69.2	80.7
5.00	73.1	84.6	76.9	84.6
6.00	73.1	88.5	76.9	92.1
24.0	76.9	92.3	92.3	100

temperatures (50°C and 70°C) have been selected for this study because they match the actual processing temperatures present at oilfield production facilities. Table 2 demonstrates this effect at different times using conditions at which maximum demulsification occurs (20% v/v water-in-benzene containing 0.25% w/v asphaltenes). It is obvious from Table 2 that the demulsification efficiency of the investigated *PO-EO* block copolymers increases substantially by raising the temperature from 50°C to 70°C. This effect is attributed to the influence of the elevated temperature on the interfacial film composed of adsorbed asphaltenes. Asphaltenes are considered to be the prime motivator for the stability of the studied water-in-benzene emulsion. This stability is caused by the formation of a stable viscoelastic film of a great mechanical strength [12] which sterically hinders the close approach of two coalescing water droplets. Increasing the temperature results in a decrease of the interfacial shear viscosity [13] which in turn will result in an increase of the rate of film drainage [14]. The increase in temperature also increases the number of effective collisions occurring between two dispersed water droplets prior to their coalescence. Finally, increasing the temperature will result into an increased density difference between the dispersed phase (water) and the dispersion medium (benzene) resulting in enhanced emulsion breakdown [15].

Effect of NaCl concentration of the aqueous phase

It is very important to highlight the effect of salinity (NaCl concentration) on the demulsification ability of the investigated demulsifiers since the actual oilfield emulsions are often encountered with brine. Fig. 1 illustrates the dependence of the demulsification efficiency of the tested demulsifiers on the degree of salinity of the aqueous phase. Concentrations ranging between 0 and 1 M were used to represent different salinities of the aqueous phase. It is obvious from this figure that the demulsification efficiency decreases by increasing the degree of salinity. This is

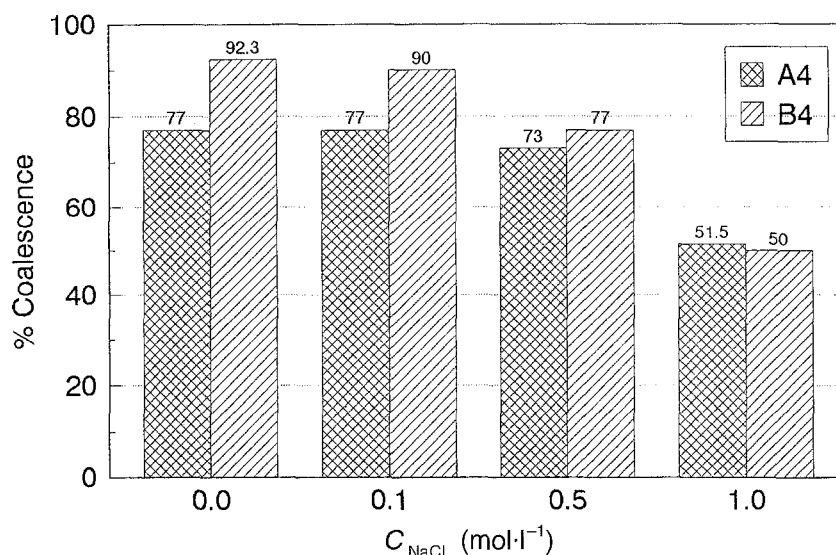
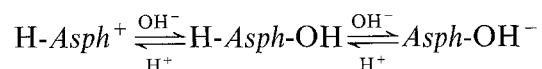


Fig. 1. Dependence of the demulsification efficiency of demulsifiers **A4** and **B4** on the degree of NaCl concentration of the aqueous phase

attributed mainly to the decreased solubility of the demulsifiers in the aqueous phase as a result of increasing its salinity. Consequently, the apparent HLB values of the demulsifiers will decrease, thus decreasing their demulsification ability [1].

Effect of the pH value of the aqueous phase

The influence of the *pH* value of the emulsion's aqueous phase has been studied in relation to the demulsification efficiency of the *PO-EO* block copolymers. As can be seen from Fig. 2 (dependence of the demulsification efficiency of demulsifiers **A4** and **B4** vs. *pH* value of the emulsion), the maximum demulsification efficiency is attained at a neutral *pH* whereas it decreases in both directions. This may be explained by the following speculation: asphaltenes adsorbed at the benzene/water interface are considered amphoteric [16], and the water droplets will acquire a negative charge in basic medium and a positive charge in acidic medium due to the ionization equilibrium of asphaltenes as given below.



It is a well known fact that surface charges on the dispersed water droplets interface cause electrostatic repulsion. Therefore, acidic or basic *pH* values result in enhanced emulsion stability by offering an electrostatic barrier to coalescence [17] in addition to the already existing steric barrier. Our present findings confirm the work of *Strassner* [10] who suggested that a *pH* range of 5–12 represents the optimum for treating most oil-field emulsions.

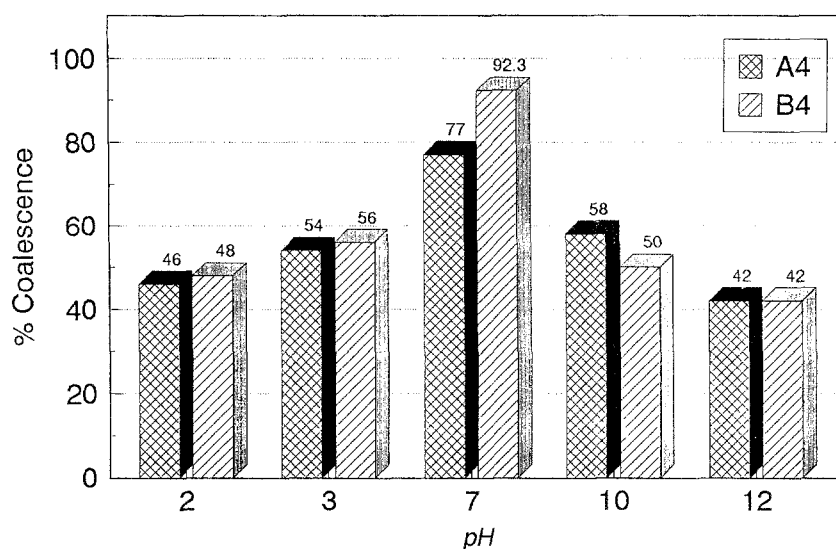


Fig. 2. Dependence of the demulsification efficiency of demulsifiers A4 and B4 on the pH value of the aqueous phase

Effect of Solvents

Solid or viscous demulsifiers have to be dissolved before application. In addition of prompting the rapid solubility of the demulsifier in the oil, solvents also aid in depressing the pour point of the demulsifiers facilitating their use at low temperatures. The three main classes of solvents studied in this context are: 1) water, 2) water miscible hydroxy compounds, and 3) aromatic hydrocarbons. Examples of group 2 are *n*-butanol, isopropanol, and monoethylene glycol; hydrocarbons used for this purpose are benzene, toluene, and xylene.

The role of solvents in the effectiveness of surfactants is of primary importance and has been briefly discussed by Canevari [18]. The forthcoming discussion deals with testing the influence of the water (*W*), isopropanol (*IP*), ethylene glycol (*EG*), 1,4-butylene glycol (*BG*), glycerol (*G*), diethylene glycol (*DG*), triethylene glycol (*TG*), 1,2-propylene glycol (*PG*), benzene (*B*), toluene (*T*), and xylene (*X*) on the demulsification efficiency of the investigated *PO-EO* block copolymers. Fig. 3 shows the influence of the type of solvent used to dissolve the demulsifier on its demulsification efficiency for A4 and B4. It is clear from this figure that both water and 1,4-butylene glycol are the most efficient solvents causing the highest demulsification efficiency compared to the others.

It is of interest to highlight some important observations concerning the results shown in Fig. 3. The influence of the aromatic solvents on the efficiency of the demulsifiers is represented by benzene, toluene, and xylene. It can be seen that the efficiency of the demulsifier solution decreases with increasing number of methyl groups in the solvent molecule. This is attributed to the difference between the solubility parameters of benzene and that of toluene and xylene. Since the experiment was performed on a benzene-water emulsion, the demulsifier solutions in benzene possess the highest demulsification efficiency compared to the solutions of

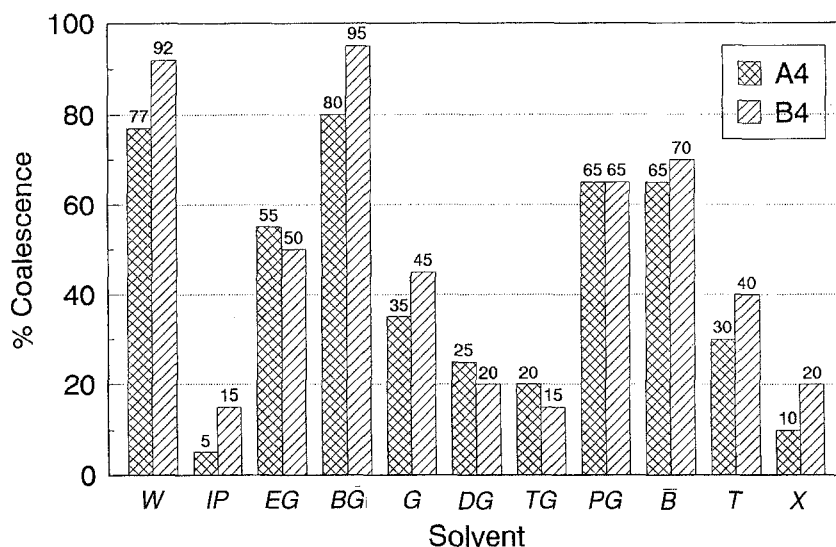


Fig. 3. Dependence of the demulsification efficiency of demulsifiers A4 and B4 on the solvent (for abbreviations of solvents, see text)

these demulsifiers in both toluene and xylene. Ethylene glycol, 1,2-propylene glycol, and 1,4-butylene glycol show an increasing order of efficiency as solvents for the demulsifiers under investigation. Finally, ethylene glycol, diethylene glycol, and triethylene glycol exhibit a decreasing order of demulsification efficiency as solvents for the investigated demulsifiers. This may be attributed to the difference in their solvation power. The general conclusions drawn from the previous results for the choice of an appropriate solvent for a given demulsifier may be summoned as follows: the solvent used for dissolution of an *EO-PO* block copolymeric demulsifier for breaking water-in-oil emulsions should be preferentially compatible with the dispersed phase (water) rather than with the continuous phase (benzene).

Conclusions

- Raising the temperature leads to an increase in the demulsification efficiency of the investigated *PO-EO* block copolymers.
- The demulsification efficiency decreases as the salinity of the emulsion's aqueous phase increases.
- The maximum demulsification efficiency is obtained when the *pH* value of the emulsion's aqueous phase equals 7.
- Water and water compatible solvents are considered to be the best solvents for the prepared demulsifiers. The solutions of the demulsifiers in these solvents afford the highest demulsification efficiency.

Materials and Methods

The complete methodology of synthesis and structure verification of *PO-EO* block copolymers together with the preparation of water-in-benzene emulsions stabilized by asphaltenes have been described

previously [1]. However, in the present paper, salinity (NaCl concentration) and *pH* value of the emulsion's aqueous phase have been altered. Analytical reagent grade chemicals were utilized for accomplishing this work. The studied NaCl concentrations were 0, 0.1, 0.5, and 1 *M* (distilled water). Dilute solutions of both hydrochloric acid and sodium hydroxide were utilized to adjust the *pH* value of the emulsion's aqueous phase to the desired value which was detected by a Schott Geratte digital *pH* meter supplied with a glass electrode and a reference electrode dipped in the aqueous phase during dropwise addition of aqueous acid or base solutions with constant stirring using a magnetic stirrer.

Bottle testing for demulsification efficiency determination

The bottle test was used to estimate the capability of the investigated demulsifiers (**A4** and **B4**) in breaking synthetic water-in-benzene emulsions. The demulsifiers were dissolved in either one of the following AR grade solvents: water, benzene, toluene, xylene, isopropanol, ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,4-butylene glycol, and glycerol. They were added at the recommended optimum concentration (300 ppm with respect to total volume of the emulsion) to the emulsion in 100 ml graduated cone shaped tubes stopped with teflon lids. The emulsion-demulsifier mixture was shaken 200 times by hand and placed in a thermostatted water bath adjusted at 50 °C or 70 °C. The amount of separated water was detected and registered for each condition (*pH*, type of solvent, degree of salinity, and degree of temperature) after 24 h. In all experiments, a blank was utilized for comparing the separated water in absence of the demulsifier.

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