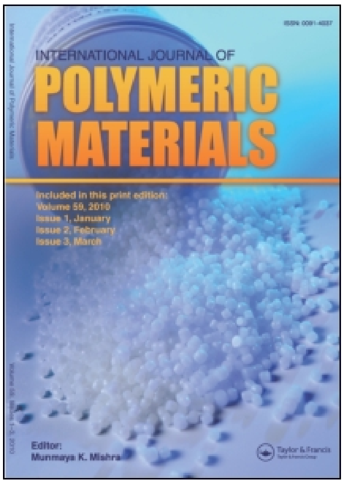

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NONIONIC SURFACTANTS FROM POLY(ETHYLENE TEREPHTHALATE) WASTE: II. EFFECT OF TEMPERATURE, SALINITY, pH-VALUE, AND SOLVENTS ON THE DEMULSIFICATION EFFICIENCY

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The effect of temperature, NaCl concentration (salinity), pH-value, and solvents on the demulsification efficiency of the demulsifiers synthesized from poly(ethylene terephthalate) waste [polyoxyethylenated glycolized product of PET (POGP)] in breaking synthetic water-in-benzene emulsions stabilized by petroleum asphaltenes have been investigated. The demulsification efficiency of the studied polymeric surfactants was found to increase as the temperature was raised and the salinity of the aqueous phase decreased. Neutral pH-value of the aqueous phase of the emulsion was found to be the optimum value causing maximum demulsification efficiency. Water and 1,2 propylene glycol were found to be the best solvents for the prepared demulsifiers offering maximum demulsification efficacy.

Keywords: Demulsifiers; Temperature; pH-value; Salinity

INTRODUCTION

Recent development in oil-contaminated soil remediation by using a surfactant solution flooding approach [1–7] requires an efficient emulsion-breaking technique, since a large amount of oil-in-water emulsions must be demulsified for oil separation. In the surfactant-enhanced remediation of oil-contaminated soils, the excellent solubilization and emulsification properties of surfactants are applied to allow fluids to remove oils efficiently from the

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soils, resulting in wastewater effluent containing large amounts of oil-in-water emulsions. One would expect that the high efficiency of surfactants to recover oils would produce stability of emulsions in the wastewater effluent and prevent the oils from being easily separated from the effluent in the latter treatment.

It is well known that emulsions are generally stabilized by repulsive charges on the surface of the dispersed phase and by adsorbed layers that act as an interfacial barrier to prevent the close contact or coalescence of the dispersed droplets. Demulsification is usually achieved by physical and/or chemical methods. Physical methods, such as the use of heat [8, 9] or electrical field [10–12], are to increase the contact frequency of dispersed droplets. Chemical methods, such as the use of demulsifiers [13–18] or acid/base [19, 20], are to affect the interfacial properties of the adsorbed layers on the droplet surfaces and increase the coalescence rate of dispersed droplets. Among the methods, the pH adjustment by using acid/bases in destroying the emulsion stability has certain advantages over other methods since it is usually cheaper and easier to be applied in a process.

Strassner [19], studied the effect of pH on the stability of Venezuelan crude oil–water emulsions. He observed that a pH-value of 10.5 produced the least stable emulsions, he found that a basic pH produced oil-in-water (O/W) emulsions, while, an acidic pH produced 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 optimum for treating most oilfield emulsions.

On the other hand, it has been shown that any change in temperature causes changes in the interfacial tension between the two phases (oil and water) [21], in the nature and viscosity of the interfacial film [22], in the relative solubility of the emulsifying agent in the two phases [23], and in the thermal agitation of the dispersed droplets [24]. Therefore, temperature changes usually cause considerable changes in the stability of emulsions; they may invert the emulsion or cause it to break [25].

The effect of salinity of the aqueous phase on the stability of oil-in-water type emulsions has been extensively studied by several authors [26–28]. However, for water-in-oil type of emulsions, they received very little attention and still need a great deal of research.

Graham *et al.* [29] compared the activity of demulsifiers when they are added with dissolution *versus* when they are added without dissolution in a solvent before addition to the emulsion. 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 first article in this series [30], we have introduced the influence of molecular weight and hydrophilic–lipophilic balance (HLB) of a series of polyoxyethylenated glycolyzed product of PET (POGP) on their demulsification efficiency. Synthetic water-in-benzene emulsions stabilized by petroleum asphaltenes has been utilized to simulate water-in-crude oil natural emulsions.

The present work deals with the effect of temperature, pH-value, salinity (NaCl concentration in the aqueous phase), and different types of solvents used to dissolve the POGP demulsifiers on their demulsification efficiency in breaking water-in-benzene emulsion stabilized by asphaltenes.

EXPERIMENTAL

The complete method of the synthesis and structure verification of the POGP demulsifiers together with the preparation of the water-in-benzene stabilized by asphaltenes emulsion have been described in the first article in this series [30]. However, in the present paper, the salinity or NaCl concentration and pH-value of the emulsion's aqueous phase was altered. Analytical reagent grade chemicals were utilized for accomplishing this work. The studied NaCl concentrations were 0 (distilled water), 0.1, 0.3, 0.5, 0.7 and 1 M. 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 while addition of the acid or base aqueous solutions dropwise with constant stirring using a magnetic stirrer.

Bottle Testing for Determining the Demulsification Capability of the Prepared POGP

The bottle test was used to estimate the capability of the investigated demulsifiers (D1 – D3) in breaking synthetic water-in-benzene emulsions. The demulsifiers were dissolved in either one of the following AR grade solvents: water, benzene (B), toluene (T), xylene (X), isopropanol (iP), ethylene glycol (EG), diethylene glycol (DG), triethylene glycol (TG), 1,2-propylene glycol (PG), 1,4-butylene glycol (BtG), and glycerol (G). The desired volume from the solution (the volume containing 300 ppm with respect to total volume of the emulsion) was added to the emulsion in 100 ml graduated cone shaped tubes covered with Teflon lids. The emulsion/demulsifier mixture was homogenized by sonication with an ultrasonic processor (model VCX 600, Sonics and Materials Inc., USA) for 30 seconds at room temperature. The emulsions were placed in a thermostated water bath adjusted at 35°C, 50°C or 70°C. The amount of separated water was detected and registered for each condition (pH, type of solvent and degree of salinity after 24 hr, and at different times for each temperature). In all experiments, a blank was utilized for comparing the separated water in absence of the demulsifier.

RESULTS AND DISCUSSION

The specifications of the demulsifiers D1 – D3, as reported in the first article in this series [30], are summarized in Table (1). The present investigation deals with studying the effect of temperature, pH-value, degree of salinity, and the effect of solvents on the efficiency of the previously synthesized demulsifiers in breaking water-in-benzene emulsion stabilized by asphaltenes.

Effect of Temperature

The effect of temperature on the demulsification efficiency of the demulsifiers has been investigated. Three different temperatures (35°C, 50°C and 70°C) were selected for the achievement of this study because they match the actual processing temperatures present at the oil fields production facilities. Table (2) demonstrates clearly this effect at different times using

TABLE 1 Specifications of D1 – D3 demulsifiers

	Max. demulsification efficiency after 24 hr		*% Coalescence for*		
	Concentration (ppm)	*% Coalescence at 35°C*	*300 (ppm) at 35°C after 24 hr*	*Molecular weight*	*HLB*
D1	500	57.9	46.0	1922	12.50
D2	400	74.2	63.9	2722	14.70
D3	300	99.0	99.0	8722	18.39

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

	Percentage coalescence upon using 300 ppm of								
Time	*D1 at*			*D2 at*			*D3 at*		
(hr)	35°C	50°C	70°C	35°C	50°C	70°C	35°C	50°C	70°C
0.25	33.3	35.8	38.0	36.2	37.1	39.2	47.0	49.5	52.1
0.50	34.2	36.5	39.4	37.5	38.2	40.5	47.8	50.1	53.0
0.75	34.7	37.0	40.1	40.5	41.1	42.9	51.1	53.5	55.6
1.00	35.1	39.2	43.1	45.8	47.2	49.6	58.5	61.5	64.5
2.00	38.2	41.2	44.9	47.9	49.3	52.0	65.5	68.2	71.6
3.00	39.7	42.2	45.6	50.1	51.4	53.5	65.9	69.4	73.1
4.00	39.7	44.2	46.9	50.2	54.0	56.1	85.9	88.3	91.1
5.00	41.5	45.5	48.6	57.9	58.7	62.2	86.6	91.1	95.7
6.00	41.5	47.1	50.5	58.1	63.4	68.7	90.0	92.9	96.1
24.0	46.0	51.9	55.3	63.9	67.7	72.4	99.0	99.5	100

300 ppm of each demulsifier for comparison. The composition of the emulsions was 20% v/v water-in-benzene containing 0.25% w/v asphaltenes. This table reveals that the demulsification efficiency of the investigated demulsifiers increases by raising the temperature from 35°C to 70°C. This effect is attributed to the influence of raising the temperature on the interfacial film composed of adsorbed asphaltenes [8, 9]. Asphaltenes are considered 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 great mechanical strength [31] which hinders the close approach of two coalescing water droplets. Increasing the temperature results in a decrease of the interfacial shear viscosity [32] which in turn will result in an increase of the rate of film drainage [33]. 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 in an increased density difference between the dispersed phase (water) and the dispersion medium (benzene) resulting in enhanced emulsion breakdown [34].

Effect of Salinity of Aqueous Phase on the Demulsification Potency

Since the actual oil field emulsions are often encountered with brine, it is very important to highlight the effect of salinity (NaCl concentration) on the demulsification capability of the investigated demulsifiers. Figure 1

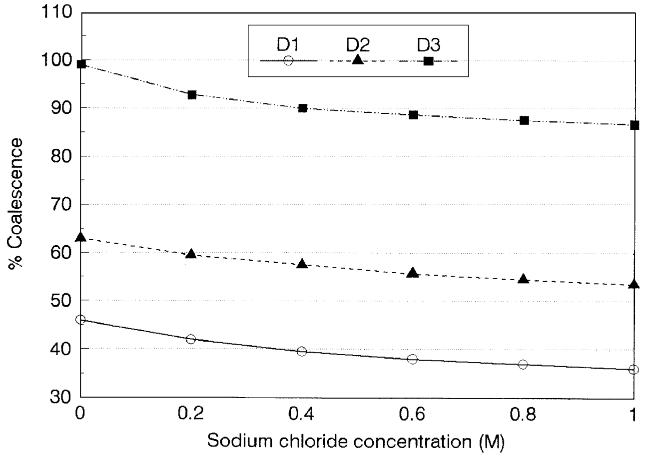

FIGURE 1 Effect of degree of salinity on the demulsification of the demulsifiers D1–D3 at 35°C.

illustrates the dependence of the demulsification efficiency of 300 ppm of the synthesized demulsifiers on the extent of salinity of the aqueous phase. Six concentrations of NaCl ranging between 0.0 and 1.0 M were used to demonstrate the effect of salinity concentration on the demulsification efficiency of the tested demulsifiers. This figure shows that the demulsification efficiency (expressed as % of coalescence) decreases regularly with increasing concentration of NaCl in the aqueous phase. This may be attributed to the decreased solubility of the demulsifiers in the aqueous phase as a result of increasing its salinity. This leads to a reduction in the apparent HLB values of the demulsifiers and hence a reduction of their demulsification ability [16].

Effect of pH of Aqueous Phase on the Demulsification Efficiency

As the emulsions were dispersed at room temperature the desired pH values were attained by using 37 wt% HCl solution or 10% NaOH solution. The pH values of the systems were detected by a pH meter (model SP-701, Suntex). The prepared emulsions at different pH values were immediately placed into graduated cone shaped tubes (100 ml capacity fitted with teflon lid) to measure the separated water in each case at 35°C. The amounts of separated water ware registered after 24 hr and the percentage of coalescence in each case was calculated. The variations of percentage of coalescence as a function of pH of the aqueous phase, for all demulsifiers, are presented in Figure 2. This figure reveals that the maximum demulsification efficiency is attained at a neutral pH whereas it decreases with increasing the acidity or alkalinity. This may be explained by the following consideration: asphaltenes adsorbed at the benzene/water interface are considered amphoteric [35], and the water droplets will acquire a negative charge in basic medium and a positive charge in acidic medium due to ionization equilibrium of asphaltenes according to the following equation [16]:

$$\mathrm{H-Asph^{+}} \underset{\mathrm{H^{+}}}{\overset{\mathrm{OH^{-}}}{\Longleftrightarrow}} \mathrm{H-Asph-OH} \underset{\mathrm{H^{+}}}{\overset{\mathrm{OH^{-}}}{\Longleftrightarrow}} \mathrm{Asph-OH^{-}}$$

It is well known that surface charges on the dispersed water droplets interface cause electrostatic repulsion. Therefore, acidic or alkaline medium result in enhanced emulsion stability by offering an electrostatic barrier to coalescence [36] in addition to the already existing steric barrier. Our present finding confirms the work of Strassner [19] who suggested that a pH of 5 – 12 appears optimum for treating most oil-field emulsions.

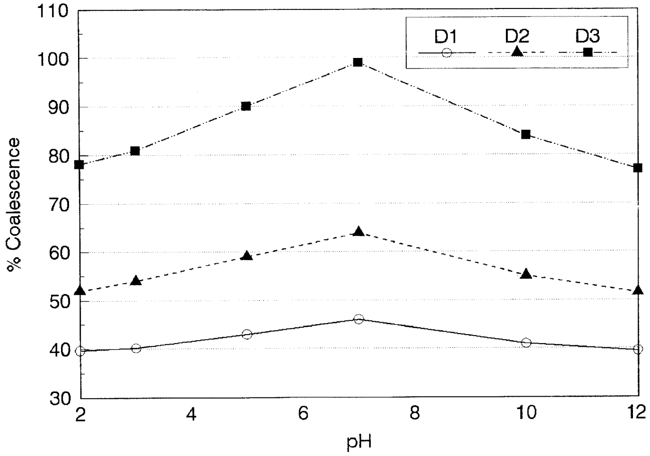

FIGURE 2 Effect of pH value on the demulsification of the demulsifiers D1 – D3 at 35°C.

Effect of Solvents

Solvents are used to dissolve solid or viscous demulsifiers and reduce their viscosity so that they can be uniformly mixed with the treated emulsion. In addition of prompting the rapid solubility of the demulsifier in the oil, solvents aid also in depressing the pour point of the demulsifiers facilitating their use at low temperatures.

The role of solvents in the effectiveness of surfactants is of primary importance and was briefly discussed by Canevari [37]. The following 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-GP block copolymers. Table (3) shows the influence of the type of solvent used to dissolve the demulsifier on its demulsification efficiency for D1 – D3 demulsifiers. It is clear from this table that both water and 1,2-propylene glycol are the most efficient solvents causing the highest demulsification efficiency (expressed as % coalescence) compared to the others.

It is of interest to highlight some important observation concerning the results shown in Table (3), firstly, the influence of the aromatic solvents on the efficiency of the demulsifiers is represented by the effect of benzene, toluene and xylene. It can be seen that the efficiency of the demulsifier solution reduces with the attendance of a methyl group in the solvent molecule, this reduction increases as the number of methyl groups increases. This is attributed to the difference between the solubility parameters of benzene and

TABLE 3 Effect of solvent type on the demulsification efficiency of demulsifiers D1–D3 at 35°C

	Percentage coalescence after 24 *hr upon using* 300 *ppm of*		
Solvent	*D*1	*D*2	*D*3
W	46.0	63.9	99.0
EG	43.0	59.0	94.6
DG	41.5	57.2	92.9
TG	40.8	56.0	90.2
PG	44.3	61.8	96.2
BG	42.5	59.1	92.9
IP	39.5	56.3	89.5
G	38.6	54.0	86.0
B	43.0	59.7	94.0
T	42.0	58.1	92.5
X	41.0	57.0	91.8

that of toluene and xylene. Since the preliminary experiment showed that the demulsifiers solutions in benzene possess the highest demulsification efficiency compared to the solutions of these demulsifiers in both toluene and xylene, the present study was performed on benzene–water emulsion. Secondly, ethylene glycol, 1,4-butylene glycol and 1,2-propylene glycol show an increased order of efficiency as solvents for the demulsifiers under investigation. Finally, ethylene glycol, diethylene glycol and triethylene glycol have a decreased order of efficiency as solvents for the investigated demulsifiers, this may be attributed to the difference in their solvation power.

CONCLUSIONS

The present results reveal that:

- Raising the temperature leads to an increase in the demulsification efficiency of the investigated PO-GP 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 1,2-propylene glycol were found to be the best solvents for the prepared demulsifiers. The solutions of the demulsifiers in these two solvents afford the highest demulsification efficiency.

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