The Use of Polymers in the Treatment of Produced Oily Waters

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Abstract: In this work, a new flocculant agent was developed based on a non-ionic and water-soluble polymer, poly-(vinyl alcohol) (PVA), in order to treat oily waters from peteroleum production. Changes on its HLB were made to generate hydrophobic zones that work like flocculant agents, based on "hydrophobic bridges mechanism." Incorporation of 12 to 18 carbon atoms and carbamate groups in several concentrations were carried out. Little insertions of hydrophobic groups reduce the brine solubility, due to the inter- and intramolecular interactions; however, certain content of carbamate groups increases the resistance in a brine environment. The influence of molecular weight and the hydrolysis grade of PVA were verified as the flocculation efficiency. Their performance was verified in synthetic oily emulsion by flocculation tests. The flakes generated are different from those generated when using commercial products. High amount of additive decreases the flocculation efficiency. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1473–1479, 2004

Key words: poly(vinyl alcohol); chemical modification; flocculation; oily water

INTRODUCTION

Oil production is normally accompanied by a concomitant production of large amounts of water. The separation of produced water and its purification prior to discarding represent an important technological challenge for the oil production industry. For instance, a well producing 20,000 m^3/day of oil with a (Basal Sediments and Water) BSW of 50% and a (Total Oil and Grease) TOG of 300 mg/L would produce 3 tons of oil and grease per day. In order to minimize environmental impacts, these residues must be reduced to acceptable levels; this is particularly important in offshore operations where the most obvious destination of the produced waters are the oceans.[1,2]

The oil contained in produced oily waters often is in the form of very stable emulsions. For these systems oil/water separation by the usual physical procedures is difficult, in particular in offshore operations, where space, production facilities, and residence times are limited.[2] The use of chemicals as flocculants or flotation agents is common practice in these cases.[3] The products generally recommended are cationic polyelectrolytes[4]; however, the field use of these polymers is limited due to the possibility of solid residues formation that in the form of oily sludge accumulate in the treatment plant facilities reducing, after some time,

the efficiency of the equipment. In this study, other polymers, like poly(ethylene oxide) (PEO) or poly(vinyl alcohol) (PVA), that present a good performance as flocculating agents[5] for other systems, and functionalized PVA containing hydrophobic alkyl chains and/or carbamate groups are assayed for oil/water separation. Furthermore, some studies to identify the causes of sludge formation are also presented.

EXPERIMENTAL

Materials

The nonionic polymers used in this work were commercial samples kindly supplied by the manufacturers and were used without further purification. PVA1 is a poly(vinyl alcohol) (PVA) presenting a molecular weight of around 72,000 (Vetec, Quimica Fina Ltd. Rio de Janeiro, Brazil). PVA2 and PVA3 are products manufactured by Air Products and Chemicals, Inc. (Allentown, PA), commercialized as Airvol 165 and 540, respectively. Both polymers present molecular weights between 140,000 and 180,000 but PVA2 is 100% hydrolyzed and PVA3 has a hydrolysis degree between 87 and 89%. Ucarfloc 302, 304, and 309 are water-soluble poly(ethylene oxide) (PEO), presenting molecular weights of 5, 7, and 8 × 10^6, respectively, produced by Union Carbide (Union Carbide Corporation, Denbury, CT), here called PEO 1, 2, and 3.

Commercial polyelectrolytes used to assist the oil separation at the platform (Petrobras, Rio de Janeiro,
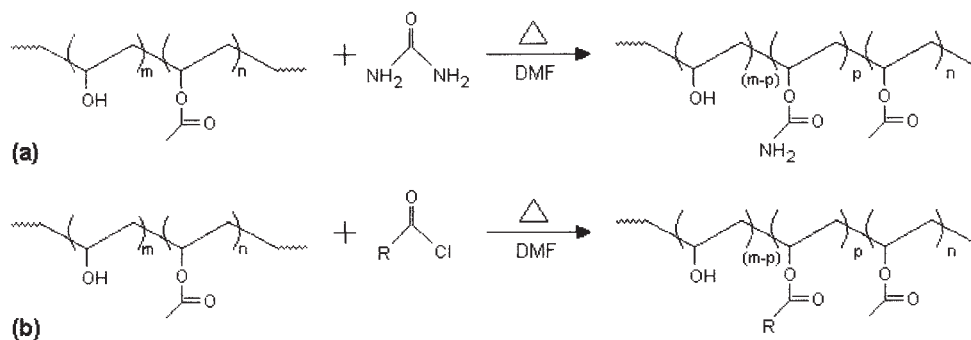
Figure 1 Reaction scheme of PVA: (a) carbamatation, and (b) esterification.

Brazil), here called polyelectrolyte A, B, and C, were also tested for comparison.

Three samples of crude oil from the Brazil basin, here called Crude Oil 1, 2, and 3, were used to prepare synthetic emulsions.

Stearoyl and lauroyl chloride (Sigma Aldrich Quimica Brasil, Ltd., São Paulo, Brazil; 99% of purity) and urea were used for the chemical modification reactions of PVA.

Chemical modification of polymers

Two PVA samples presenting molecular weights of 72,000 (PVA1) and 140,000 (PVA2) were chemically modified by functionalization with carbamate groups and hydrophobic alkyl chains. The incorporation of carbamate groups (urethanes) in the structure of PVA was made by reaction of urea with PVA in the ratio of 1 : 1, using dimethylformamide as solvent.[6] The reaction temperature was fixed at 145°C, and the time varied from 30 to 180 min. The esterification was carried out subsequently, following the Schotten–Baumann reaction[7] using acyl chlorides with hydrocarbon chain length varying from 12 to 18 carbon atoms. The temperature was fixed at 145°C, and the reaction time was 2 h. The solvent was also dimethylformamide for this reaction. The reaction schemes are presented in Figure 1.

Polymer characterization

Polymer samples were characterized by H^1-NMR, using DMSO-d_6 as solvent, at 300 MHz, in a Varian Inova-300 equipment. The hydrolysis degrees (DH %) of the non-modified PVAs were determined by the ratio between the peak areas relative to the hydroxyl and the sum of the peak area relative to the hydroxyl and to the methyl groups of the acetate. The molar content of the carbamate groups (Carb %) incorporated to the PVA was done by the ratio between the peak area of the NH_2 group (relative to the carbamate group) and the sum of the peak areas relative to

methyl, acetate, hydroxyl, carbamate, and the end methyl group of the hydrophobic segment. The molar content of the hydrophobic group (Hydrof %) incorporated to the PVA was done by the ratio between the peak area relative to the end methyl group of the hydrophobic segment and the sum of the peak areas relative to acetate, hydroxyl, carbamate, and the end methyl group of the hydrophobic segment. DMSO-d_6 was used as reference for the chemical shifts.[8]

Synthetic emulsions

1 L of brine containing 50,000 ppm of sodium chloride (NaCl) and 5,000 ppm of calcium chloride (CaCl$_2$) was prepared in a 2 L flask using a high-speed stirrer (Turrax PT 3100, Polytron). After complete dissolution of the salts, 1 mL of oil was slowly added and the agitation was increased to 15,000 rpm. After 15 min, the emulsion was diluted by mixing with 1.5 L of brine and maintained under agitation at 5,000 rpm for a further period of 15 min. The adjustment of pH, when necessary, was completed during this period.

Total oil and grease (TOG) measurements

The total oil and grease content present in the solutions, before and after the flocculation tests, was measured using two alternative procedures: (1) Infrared absorption at 810 nm using Horiba OCMA-350 oil content analyzer, that measures the axial deformation of the C—H bonds of the compounds present in the oil; or (2) fluorimetry using a TD-360 FastHex apparatus (Turner Designs, CA), that measures mainly the polyaromatic fraction present. Carbon tetrachloride and hexane were respectively used for oil extraction in these two methods. As the two experimental procedures measure different parameters, the absolute values of TOG obtained with each technique are not necessarily identical. However, comparisons are valid when dealing with relative values representing only removal efficiency and product performance.

Induced air flotation and jar tests

These two tests were used to assess the efficiency of the additives assayed for the separation of oil-in-water emulsions.

For the flotation tests, 2.5 L of synthetic emulsion were dribbled into the cell of a Wenco induced air flotation unit. A small aliquot of emulsion was collected for TOG analysis. Subsequently, agitation was set at 9,000 rpm and the additive solution added. After 1 min, flotation was accomplished allowing the passage of air at a flow rate of 110 L/h for 1 min. After this period, a small aliquot was collected for the determination of the final TOG. A blank test under similar conditions but without the addition of polymer was carried out in all cases to calculate the efficiency of the product.

The jar tests were carried out in a conventional apparatus (Lactea Laboortecnica Ltd. São Paulo, Brazil), in which five samples are simultaneously tested under identical conditions. 500 mL of a stock synthetic emulsion or produced water were poured into each of five 1,000 mL beakers. The agitation speed was set at 300 rpm, and the volume of polymer solution required to attain the final concentration was added to each beaker. Thereafter agitation was reduced to about 60 rpm and maintained at this speed for 15 min. After this period elapsed, the dispersions were left at rest to permit the separation of the oil phase, and aliquots were collected for TOG analysis.

Tests using produced water

The efficiency of various flocculants for the separation of produced oily water was assessed using the jar test unit. The samples were collected from an offshore platform in which the treatment of the produced emulsions presents some difficulties. The production facilities are a set of hydrocyclones followed by dissolved gas flotation vessels. Commercial polyelectrolytes are added after the hydrocyclones. The water samples were collected at the discharge of the hydrocyclones prior to the flotation process and the polyelectrolyte addition point.

RESULTS AND DISCUSSION

Chemical modification of PVA

Hydrocarbon chains of different molecular weights were introduced to the PVA molecule by esterification in order to obtain new molecules containing hydrophobic segments in a hydrophilic backbone. It is expected that such molecules can act, by van der Waals forces, as flocculant for the drops of oil in water microemulsions. This study intends to evaluate the influence of the length and of the content of the hydro-
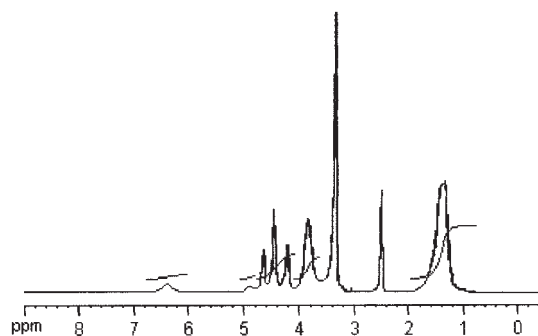

Figure 2 H[1]-NMR spectrum of PVA2–C18-U(60).

carbon chains introduced to the PVA on the flocculation process of synthetic oily water.

The products obtained from the PVA esterification reactions exhibited dramatic changes in their properties in solution, even though a very little amount of hydrocarbon chains was introduced in the PVA structure.[9] Such modified molecules become insoluble in water and in other solvents such as N,N-dimethylformamide. Since this study intends to obtain water-soluble polymers presenting different hydrophobicity degrees, the first step was to carry out a reaction to introduce carbamate groups in the PVA structure in order to increase de hydrophilicity of the molecules. After that, the modified molecules were submitted to the esterification reaction in order to obtain molecules presenting different hydrophilic-hydrophobic balance.

The chemical reactions to modify the PVA molecule were carried out in solution as follows: (1) reactions to introduce the carbamate groups at several times (from 30 to 180 minutes); (2) esterification reaction using the suitable acid chloride (depending on the desirable hydrocarbonic length). The names given to the products can identify: (1) the PVA used; (2) the length of the hydrocarbon chain introduced by the esterification reaction; and (3) the reaction time (in minutes) to introduce the carbamate group; for example, PVA2-C12-U(60).

Polymer characterization

The results obtained for the PVA1 and PVA2 hydrolysis degree were 88.5 and 100 mol %, respectively.

The PVA modified samples were also characterized by H[1]-NMR. Figure 2 shows the spectrum of the sample PVA2-C18-U(60), and Table I shows the composition of all obtained products. For PVA1, it can be observed that 2 hours are enough to introduce about 12 mol % of carbamate group in the PVA structure. As expected, the content of the hydroxyl groups is reduced due to the incorporation of carbamate and ester groups. It is also observed that the content of the

TABLE I
Characterization of the Chemically Modified Polymers

	Molar % of monomer units			
Product	Acetate	OH	Carbamate	Ester
PVA1	14.5	88.5	0	0
PVA1-C18-U(120)	12.2	75.0	12.0	0.8
PVA2	0	100.0	0	0
PVA2-C12-U(30)	0	96.1	3.5	0.4
PVA2-C12-U(60)	0	94.4	5.1	0.5
PVA2-C12-U(120)	0	89.0	10.4	0.6
PVA2-C12-U(180)	0	87.8	11.6	0.6
PVA2-C18-U(60)	0	93.6	5.6	0.9
PVA2-C18-U(120)	0	88.7	9.7	1.6
PVA2-C18-U(180)	0	88.1	11.0	0.9

TABLE II
Separation of Synthetic Emulsions Prepared Using Crude from the Crude Oil 1 Field Using Nonionic Polymers at 10 ppm

Product	Final TOG (ppm)	TOG removal (%)
Branco	84	58.8
PVA3	51	75.3
PEO1	102	35.4
PEO2	110	32.0
PEO3	68	61.1

acetate groups is reduced, probably due to the partial hydrolysis induced during the reactions. PVA1 is a sample partially hydrolyzed, so that its chemical modification produces molecules containing 4 different kinds of groups: carbamate (hydrophilic part introduced), long chain ester (hydrophobic part introduced), hydroxyl, and acetate (from the partial hydrolysis); this can become more difficult to establish the correlation structure × properties × performance. So we also used PVA2, which is a 100% hydrolyzed sample and will produce molecules that do not contain acetate group. It is observed (Table 1) that by reacting PVA and urea during 30, 60, 120, and 180 minutes, we obtained PVA molecules containing about 3, 5, 10, and 11 mol % of carbamate groups, respectively. It means that the incorporation of carbamate groups increases with time at a rate of ~ 0.06 mol %/min. As observed for PVA1, the hydroxyl groups content was reduced due to the incorporation of carbamate and ester groups.

We obtained two series of PVA 2 containing carbamate and long chain ester: one series using hydrocarbon chain containing 12 carbons and the other containing 18 carbons. In both series the ester content was kept approximately constant, but the carbamate content was changed; this produced samples presenting different hydrophilic-hydrophobic balance.

The PEO series, instead, seems to be less efficient. This seems rather peculiar considering that PEO is extensively used as flocculating agents for dispersions containing mineral particles like silica, clays, or iron oxides, as well as for other systems.[10]

In order to verify the influence of the origin of the oil on the flotation efficiency, complementary studies were carried out using emulsions prepared using samples of Crude Oil 2 and Crude Oil 3. A preliminary survey showed that the emulsions prepared with oil from the Crude Oil 2 field presented higher stability. However, the percentages of removal using Airvol 540 or other polymers were similar for all three samples, indicating that within the experimental conditions prevailing in the flotation cell, no detectable differences could be identified in laboratory tests.

The separation of synthetic emulsions by modified flocculation agents was carried out using a jar test unit. In this type of device, shear-induced emulsion separation is lower as the agitation is less intense than in the induced air flotation. The phase separation, however, may be less efficient since, in most cases, the flotation step is omitted. The studies were carried out for various samples prepared by modification of PVA1 and PVA2, at various concentrations and at pH 3, 5, and 7.

Three functionalized polymers were selected for this work. These were identified as PVA1-C18-U(120), PVA2-C12-U(30), and PVA2-C18-U(60), where the

Separation of synthetic emulsions by various flocculation agents

Tables II and III present the efficiency of various polymers in the separation of synthetic emulsions using induced air flotation tests. The emulsions were prepared using Crude Oil 1; and the results show that, although the final TOG values attained are relatively high, some of the polymers present an acceptable performance in terms of percentage of removal. Airvol 540, a PVA with a molecular weight of 124,000, for instance, presented removals above 80%.

TABLE III
Separation of Synthetic Emulsions Prepared Using Crude from the Crude Oil 1 Field Using Nonionic Polymers at Various Concentrations

Product	Conc. (ppm)	Final TOG (ppm)	TOG removal (%)
PVA3	2	38	80.2
	5	24	85.8
	10	39	75.3
	20	27	85.2
PEO2	2	40	76.9
	5	76	62.0
	10	135	31.5

TABLE IV
Separation Efficiency for PVA and PVA Modified Copolymers

Product Concentration (ppm)	Carb.[a]	Ester[a]	TOG removal (%) pH = 5		
			pH = 5		
			5	30	120
PVA1	0	0	7.07	−4.47	—
PVA1-C18-U(120)	12.0	0.8	56.89	31.43	—
PVA2	0	0	−14.07	12.185	26.98
PVA2-C12-U(30)	3.5	0.4	26.96	30.73	−10.55
PVA2-C12-U(60)	5.1	0.5	14.20	4.94	1.14
PVA2-C12-U(120)	10.4	0.6	10.50	10.38	3.28
PVA2-C12-U(180)	11.6	0.6	−17.73	−26.01	−36.34
PVA2-C18-U(60)	5.6	0.90	24.07	19.66	3.57
PVA2-C18-U(120)	9.7	1.6	—	1.32	−4.84
PVA2-C18-U(180)	11.0	0.9	15.97	3.58	−4.78

[a] Molar % of monomer units.

first group of characters represent the PVA used; the second, the hydrocarbon moiety chain length; and the third, the urea-polymer reaction time.

Table IV presents the results obtained for these various functionalized polymers at pH = 5, for three concentrations. The best results were obtained for the polymer presenting a molecular weight of 70,000, functionalized with an 18-C alkyl chain and an uretanization time of 180 min, at a concentration of 5 ppm. For PVA2 a more comprehensive study was intended.

Although the increase in the separation efficiency was low, some speculative conclusions may be withdrawn from the preliminary results presented in Table IV.

The efficiency seems to be reduced as the degree of uretanization is increased. This effect may be the result of a higher solubility of the polymer induced by the polar carbamate groups. On the other hand, efficiency is higher for all the polymers at 5 ppm. For 30 and 120 ppm, the emulsions seem to have their stability increased in the presence of the functionalized polymer. For the bridging flocculation of dispersions containing sub-micron solid particles, this behavior is ascribed to an increased stabilization due to the appearance of steric repulsion forces at high surface coverage.[11]

Separation of produced water by various flocculation agents

As shown in Table V, neither the nonionic flocculants nor the chemically modified samples presented a good performance for the separation of oily waters. Low separation efficiencies were also obtained at higher concentrations as well for the other additives considered in this study. These data contrast with those described in the previous section for synthetic emulsions in which at least some polymers achieved intermediate separation efficiencies. The results illustrate

an important difference between emulsions prepared using synthetic brines and produced oily waters. In general, the latter systems represent dispersions presenting higher stability for which the oil/water separation is a considerably more difficult process.

At the platform from which the produced water samples were collected, cationic polyelectrolytes are used to assist the oil separation and removal. Table VI shows some results obtained for three commercial samples of polyelectrolytes using the Jar Test. Sample A presented very good removals independently of the initial oil and grease concentrations. The TOG values obtained after the jar tests were, in all cases, below 20 ppm.

Similar values were obtained at different periods of the day and for samples collected at other locations of the water treatment facilities of the platform. Sample B also presented good removals, but it is less efficient than polyelectrolyte A, as values above 20 ppm were often obtained. Finally, sample C was the least efficient polyelectrolyte, presenting low removals and high TOG values even for relatively high concentrations.

It is interesting to note that the removal efficiency was observed to be dependent on the aging of the samples prior to being submitted to the separation test (i.e. treatment with polyelectrolyte and Jar Test).

TABLE V
Produced Water Separation by PVA and PVA Modified Copolymers

Product	TOG (ppm)	TOG removal (%)
Original sample	69.7	—
PVA1-C18-U(120)	63.4	9.2
PVA2	63.6	8.6
PVA2-C12-U(30)	65.5	6.0
PVA2-C18-U(60)	42.6	38.8

TABLE VI
Produced Water Separation by Three Different Commercial Polyelectrolytes

Product	Concentration (ppm)	Original TOG (ppm)	Final TOG (ppm)	TOG removal (%)
	20	418	19	95
	30	585	17	97
	60	463	19	96
	60	585	11	98
Polyelectrolyte A	60	1283	11	99
	60	456	15	97
Polyelectrolyte B	200	451	29	94
	60	463	142	69
Polyelectrolyte C	100	456	41	91

When the water was treated within a period of less than two hours after collection, the removals obtained using polyelectrolyte A at concentrations from 10 to 60 ppm were above 97% in all the cases. When the treatment was carried out 24 hours after the sample collection, the removal was between 90 and 94% for the same concentration range. For samples stored and delivered to the ground facilities for analysis and treatment, the removal was below 50% for 40 ppm, attaining values close to 95% only for polyelectrolyte concentrations above 100 ppm.

Sludge formation and flocculation efficiency

A disadvantage inherent to the use of polyelectrolyte for the treatment and separation of produced oily waters is the formation of solid residues. This material accumulates in the water treatment facilities of the platform, forming deposits generically denominated as "sludge."

The formation of sludge causes operational problems in production platforms because it reduces the efficiency of the water treatment process and generates large amounts of undesirable solids that must be periodically removed and discarded. These difficulties were, in fact, the reasons that justified the present study.

In contrast to other additives such as nonionic polymers or anionic polyelectrolytes that remain soluble, the separation of solid particles is a distinctive characteristic of the interaction of polyelectrolytes with some types of produced waters. For the water from the Crude Oil 2 field, the three polyelectrolytes studied in the previous section formed solids. This precipitation occurred with samples collected in any of the various stages of the treatment, and even with water presenting fairly low TOG levels. The formation of solid residues seems to be directly connected to the polyelectrolyte efficiency in the oil/water separation process. Chemicals that do not form solids (as the
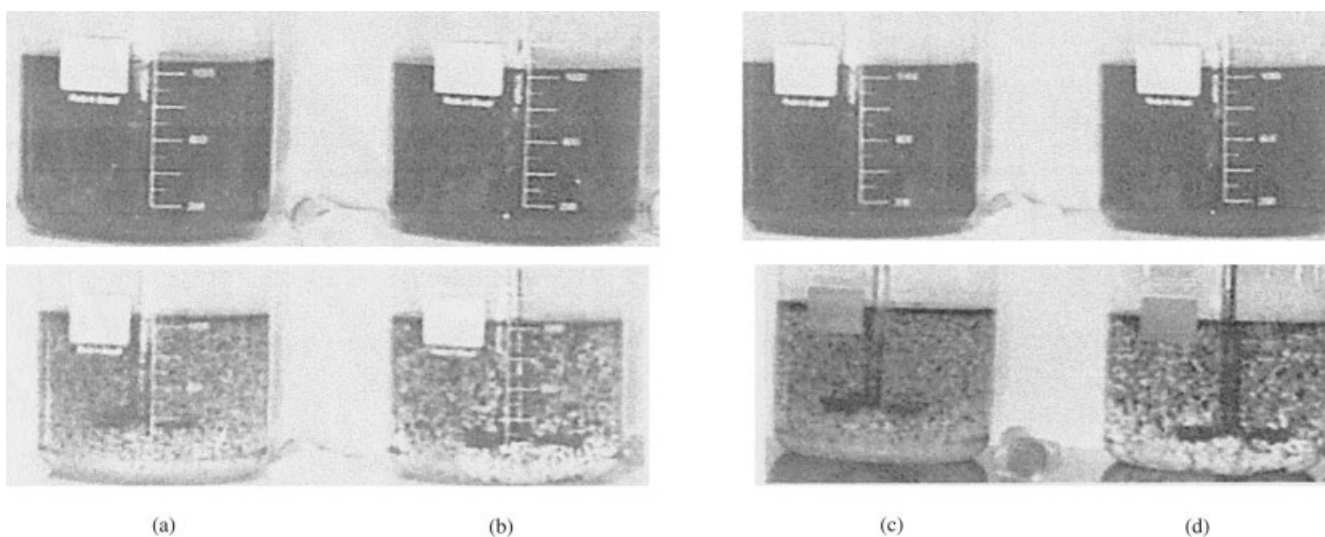

(a)   (b)   (c)   (d)

Figure 3 Photographs showing the formation of solid particles as the result of interaction between produced water and polyelectrolytes.
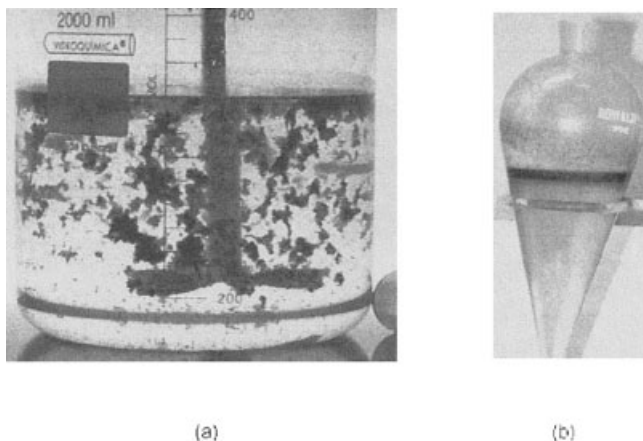
Figure 4 Photographs showing aggregates and oil contaminates solid particles.

nonionic) do not present oil removal, whereas those forming precipitates separate the oil rather efficiently.

The sequence of photographs presented in Figure 3 illustrates some of the issues of this precipitation. Photograph A shows the initial situation observed after the addition of polyelectrolyte to the water sample. Subsequently, solids particles are formed (B). The particles grow and become impregnated with oil (C) and, eventually, migrate toward the liquid surface (D). When the sample is decanted for a relatively long time, the oil and the particles concentrate at the surface (Fig. 4a). At this stage, the aqueous phase presents low levels of oil and grease. However, if the sample is agitated, the oil is reincorporated to the water and the TOG increases. As shown in Figure 4b, the addition of kerosene prevents the re-dispersion as the oil is extracted to the organic phase, but solid particles covered with oil accumulate at the interface. It seems consistent to infer that the formation of sludge is related to the formation and persistence of these particles.

It is difficult to identify the causes of the precipitation considering only the analytical data for the produced water. As in most of the cases, Na^+, Ca^{++}, K^+, Ba^{++}, and Sr^{++} are the dominant cation and Cl^- and HCO_3^-, the dominant anions. The presence in the solid residues of large amounts of calcite may suggest a possible mechanism in which the polyelectrolyte may flocculate these particles and subsequently, the

aggregates could be covered by the oil, serving as a base for the formation of the oily sludge. The process, however, must be confirmed by additional experimental work.

CONCLUSION

A series of modified poly(vinyl alcohol) presenting different hydrophilic-hydrophobic balance were obtained in this work. Some of these modified nonionic polymers presented good efficiency for the oil/water separation in the case of synthetic emulsion. However, their performance was not enough to justify the use of these products in field operations.

Important differences were observed between synthetic emulsions and produced oily water in relation to the performance of the chemicals for the oil/water separation. This fact, together with the effect of aging observed for the efficiency of the polyelectrolytes, indicates that the simulation of the separation of oily water in laboratory work presents serious limitations.

The formation of solid residues seems to be directly connected to the polyelectrolyte efficiency in the oil/water separation process. Chemicals that do not form solids (as the nonionic) do not present oil removal, whereas those forming precipitates separate the oil rather efficiently.

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