Chemically Induced Destabilization of Water-in-Crude Oil Emulsions

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The effect of systematic changes in the structure of chemicals commonly used in demulsification operations (alkyphenol polyalkoxylated resins and polyurethanes) on the stability and properties of brine-in-crude oil emulsions was assessed experimentally. The relative rates of water separation were characterized via bottle tests and rheometry. Equilibrium interfacial tensions were also measured. Transient changes in drop size distributions were quantified using nuclear magnetic resonance. The phenolic resins promoted coalescence of droplets. Optimum performance was obtained with resins exhibiting intermediate hydrophilicity in a manner consistent with the condition of least emulsion stability for conventional oil–water–surfactant systems. In contrast, polyurethanes promoted flocculation but only slow coalescence. The performance of polyurethanes improved with increase of molecular weight. Phenolic resins and polyurethanes acted synergistically when added simultaneously, rendering water separation rates significantly higher than those observed when they were used individually. Polyurethanes aided sedimentation of water at moderate concentrations (ca. 200 ppm) by “bridging” nearby droplets, but they retarded coalescence when added at significantly higher concentrations, even when phenolic resins were present. Plausible mechanisms for demulsification that are consistent with these findings are proposed and discussed.

1. Introduction

It is a pleasure for us to contribute to this issue honoring Darsh Wasan, whom the senior authors have known for many years. Our paper deals with emulsion stability, an area of great interest to Darsh and to which he has made numerous contributions.

Water is normally present in crude oil reservoirs or is injected as steam to stimulate oil production. Water and oil can mix while rising through the well and when passing through valves and pumps to form in most cases relatively stable dispersions of water droplets in crude oil (w/o), which are usually referred to as oilfield emulsions. Indigenous materials of the crude oil, such as asphaltenes, resins, and naphthenates, adsorb at the water–oil interfaces and form interfacial films that confer stability against phase separation.1–3 The presence of water in crude oil is undesirable because it undermines the commercial value of the crude and the operation of refining equipment. Also, emulsions usually exhibit viscosities significantly higher than those of the crude oil, thus increasing the energy input required for transport in pipelines. For these reasons, the prevention and remediation of oilfield emulsions is a problem of technological importance for the petroleum industry.

Methods to induce phase separation in water-in-crude oil emulsions can be classified in three main categories: mechanical, electrical, and chemical.4 Chemical demulsification consists of the addition of minute amounts of chemical compounds (usually 10–1000 ppm) to enhance phase separation rates. It is the most economical and commonly used method of dehydration of crude oils.5 A combination of chemical and mechanical or chemical and electrical is often the best choice for practical applications.

Each component plays a specific role in the performance of a modern demulsifying formulation. Amphiphilic molecules with moderate-to-high molecular weight (typically above 3000 Da), such as polyalkoxy-lated alkyphenolformaldehyde resins and complex block copolymers, are usually responsible for the separation of a large fraction of the dispersed aqueous phase. For that reason, they are often termed water droppers. Several studies suggest that these molecules act by modifying the compressibility6–8 and rheological properties9–11 of the water–oil interfacial films that stabilize the emulsion in a way that favors the drainage of the thin films between approaching drops and therefore coalescence and phase separation.

Molecules with very high molecular weight (usually above 10 000 Da) such as ethoxylated–propoxylated amine polyols act as flocculants by adsorbing at the water–oil interfaces and interacting with like molecules also adsorbed at the interfaces of nearby drops. These molecules act more slowly due to their lower diffusivities, and are effective in removing remaining small water drops and tight, fine emulsions once most of the dispersed phase has been removed by the water droppers.12

Low molecular weight compounds (typically below 3000 Da), such as common surfactants, exhibit high interfacial activity and diffuse faster than other components with higher molecular weight.9 Therefore, they can suppress more effectively the interfacial tension gradients that occur in deforming interfaces of approaching drops, which otherwise would retard drainage of the corresponding thin films that precede film rupture and coalescence.7

Solvents are used as carriers of the active molecules, and they can play a critical role in the performance of...
a demulsifying formula. Aromatic hydrocarbons such as toluene and xylene and water-miscible hydroxy compounds such as 1-butanol, 2-propanol, and monoethyle-
ene glycols are often used as solvents in the formulation of commercial demulsifiers.6 The solvent must be chosen to minimize the size of the aggregates that these active molecules may form in solution, so they can be dispersed readily once dosed to the emulsion. A poor selection of solvent may result in a delay in the rate of phase separation, and therefore in an increase in the concentra-
tion of demulsifier needed to resolve the emulsion in a practical time frame.

Few studies are found in the literature reporting the effect of systematic changes in the chemistry of demul-
sifiers on their performance, probably because such information is often left unpublished for commercial reasons or is patent-protected.

Abdel-Azim et al.13 reported the effect of changes in the degree of ethoxylation, number of amino groups, and the degree of substitutions in aromatic rings of poly-
alkoxylated amines used to induce phase separation in synthetic water-in-benzene emulsions stabilized by asphaltenes. These authors found that (a) removal of water was favored by an increase in the degree of ethoxylation (i.e., by an increase in the hydrophilic–
liphilic balance (HLB) of the demulsifier from 6 to 14); (b) polyalkoxylated p-diaminobenzenes were more efficient as emulsion breakers than polyalkoxylated monoaminobenzenes with the same HLB; (c) binuclear aromatic amines (polyalkoxylated 1-naphthylamine) were more efficient than mononuclear aromatic amines (polyalkoxyalted aniline) with the same HLB. Therefore, demulsification was favored by an increase in the number of polar groups and in aromaticity. The authors claimed that such changes in the structure of the demulsifiers favor their adsorption at the water–oil interfaces and therefore the displacement/solubilization of asphaltenes clustered in this region.

Importantly, it was shown in the same study that in all cases there is an optimum dosage for demulsification. Optimum dosages ranged between 50 ppm for the binuclear aromatic amines and 300 ppm for the poly-
alkoxylated ethylenediamines. Addition of demulsifiers beyond their optimum resulted in an increase in the stability of the emulsion, probably due to the formation of a new stabilizing film in which the excess of demul-
sifier would play a significant role.

Amaravathi and Pandey14 presented a survey of patent literature for the synthesis and chemistry of ethylene oxide (EO) + propylene oxide (PO) polymeric demulsifiers and their performance on resolving water-
in-crude oil emulsions. The description includes EO + PO copolymers of alkoxylated alkylphenolformaldehyde resins, bisphenol A bis[glycidyl ether] EO + PO copoly-
mers, EO + PO copolymers of amino compounds, esters of poly(propylene glycol)s and poly(ethylene glycol)s, and EO + PO copolymers of sulfur compounds. In contrast to the former study, these authors noted that in some cases an increase in EO content could reduce the effectiveness of the demulsifier.

Breen12 showed that the efficiency of a given demul-
sifying formula depends heavily on the H/C ratio of the oil phase. In general, demulsifiers are more effective when the oil phase exhibits high aromaticity, i.e., low H/C ratio. The stability of untreated emulsions also diminished with an increase in the aromaticity of the oil, probably due to enhanced solubilization of the asphaltenes in the crude. In agreement with this view, Masliyah et al.15 performed studies on emulsions of water in Athabasca bitumen and showed that asphalt-
enes with lower H/C ratio (1.1) (i.e., higher aromaticity) and higher O/C (0.03) (i.e., more polar characteristics) adsorb preferentially at the water–oil interfaces, whereas those with higher H/C ratio (1.2–1.3) and lower O/C ratio (0.01–0.02) are solubilized in the oil phase. It was observed that emulsion stability was conferred mainly by the fraction of asphaltenes that is less soluble in the crude oil, i.e., by those asphaltenes exhibiting low H/C and high O/C ratios. Stable emulsions can be formed using only this less-soluble fraction of asphaltenes when it is dispersed in a “good” (aromatic) solvent or when it is present with resins at a moderate to high resin–
asphaltene ratio.16

This paper provides further insight on the destabili-
zation of oilfield emulsions by chemical means. Experimental results on the effect of systematic changes in the structure of chemicals commonly used in demulsi-
fication operations (alkylphenol polyalkoxyalted resins and polyurethanes) are reported and discussed, and plausible mechanisms that are consistent with the experimental findings are proposed.

### Table 1. Crude Oil Analyses

<table>
<thead>
<tr>
<th>property/component</th>
<th>units</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>API</em></td>
<td></td>
<td>28.7</td>
</tr>
<tr>
<td>shear viscositya</td>
<td>mPa·s</td>
<td>23</td>
</tr>
<tr>
<td>relaxation time (T&lt;sub&gt;2,bulk&lt;/sub&gt;)</td>
<td>ms</td>
<td>57</td>
</tr>
<tr>
<td>hydrogen index</td>
<td></td>
<td>0.928</td>
</tr>
<tr>
<td>self-diffusion coefficientsb</td>
<td>D&lt;sub&gt;LM&lt;/sub&gt;</td>
<td>m&lt;sup&gt;2&lt;/sup&gt;/s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>σ&lt;sub&gt;0&lt;/sub&gt;</td>
</tr>
<tr>
<td>SARA analysisc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>saturates wt %</td>
<td></td>
<td>32.48</td>
</tr>
<tr>
<td>aromatics wt %</td>
<td></td>
<td>50.90</td>
</tr>
<tr>
<td>resins wt %</td>
<td></td>
<td>14.28 (9.19)</td>
</tr>
<tr>
<td>asphaltenes wt %</td>
<td></td>
<td>2.34 (1.50)</td>
</tr>
<tr>
<td>loss in evaporation wt %</td>
<td></td>
<td>35.7</td>
</tr>
</tbody>
</table>

a Shear viscosity measured at 30 °C and shear rate of 66 s<sup>−1</sup>

b Assuming log-normal distribution of diffusion coefficients with logarithmic mean D<sub>LM</sub> and geometric standard deviation σ<sub>0</sub>

c Composition of oil topped at 60 °C with N<sub>2</sub> stream. Numbers in parentheses stand for composition of oil as received (before topping). Tests performed by Baseline DGSI–Analytical Laboratories.

### 2. Materials and Methods

Water-in-crude oil emulsions were prepared by dis-
persing brine (5 wt% NaCl) in crude oil. Relevant properties and results from chemical analyses of this crude oil are listed in Table 1. Asphaltenes and resins originally present in the crude oil sufficed to stabilize the emulsions.

Two homologous series of chemicals were provided by Nalco Energy Services to perform demulsification tests: (a) six polyoxyethylene (EO) + polyoxyp propane (PO) alkylphenolformaldehyde resins (further referred to as PR<sub>X</sub>), with molecular weights around 3500 Da and varying amounts of EO + PO groups in their structure (Table 2) at a constant EO/PO ratio (3:1); (b) five cross-
linked polyurethanes (PU<sub>Y</sub>) obtained from the polymer-
erization of poly(propylene glycol) with toluene diiso-
cyanate. The polyurethanes were synthesized to differ in molecular weight (Table 3) by controlling the extent of cross-linking. Figure 1 shows plausible chemical structures for these compounds.17,18 A blend of xylenes (Fisher Scientific) was used to disperse the chemical
Figure 1. Plausible structures of the chemicals used in demul-
sification experiments. (a) EO + PO alkylphenolformaldehyde
resins (PRx); (b) cross-linked polyurethanes PU y, showing the basic
groups for linear (1) and crossed (2) linking (after refs 17 and 18).

Table 2. EO + PO Content of the Phenolic Resins PRx
Used in This Investigation

<table>
<thead>
<tr>
<th>Phenolic resin</th>
<th>PR1</th>
<th>PR2</th>
<th>PR3</th>
<th>PR4</th>
<th>PR5</th>
<th>PR6</th>
</tr>
</thead>
<tbody>
<tr>
<td>EO + PO in molecules (wt %)</td>
<td>25</td>
<td>33</td>
<td>41</td>
<td>46</td>
<td>54</td>
<td>66</td>
</tr>
</tbody>
</table>

Table 3. Weight-Average Molecular Weight of the
Polyurethanes PU y Used in This Investigation

<table>
<thead>
<tr>
<th>Polyurethane</th>
<th>PU1</th>
<th>PU2</th>
<th>PU3</th>
<th>PU4</th>
<th>PU5</th>
</tr>
</thead>
<tbody>
<tr>
<td>mol wt (Da)</td>
<td>12 125</td>
<td>14 200</td>
<td>16 243</td>
<td>18 878</td>
<td>20 455</td>
</tr>
</tbody>
</table>

(chemical:xylene ratio = 1.5:1 (w/w) in all cases) before they were used in tests.

The ability of these chemicals to destabilize w/o
emulsions was evaluated with the so-called “bottle test”,
which consists of determining by inspection the amount of
water that separates from a quiescent emulsion
sample with time. For each bottle test, a 200-mL batch
of emulsion was prepared by mixing brine (30 vol %)
and crude oil (70 vol %) in a standard 250-mL glass
vial, capped and shaken by hand for 1 min and further placed
in a jacket through which fluid from the thermo-
static bath was circulated. The spindle was set to rotate
at 50 rpm (shear rate = 66 s⁻¹). The viscometer was
programmed to read and store in memory viscosities at
times previously specified. Viscosity measurements were
performed at T = 30.0 ± 0.1 °C. The emulsification
protocols described above were designed to minimize
vortex formation and intake of air bubbles. Air bubbles
are undesirable because they create air—liquid inter-
facial area within the dispersion and increase the
viscosity of the emulsion.

Drop size distributions were measured at 30 ± 1 °C
via nuclear magnetic resonance (NMR) using a MARAN
II spectrometer (2.2 MHz, Resonance Inc.). For these
experiments, emulsion samples were prepared as indi-
cated for the viscosity tests, and then they were stirred
with a high-speed device (nonaerating stirrer, Glas-col
Apparatus Co.) at 10 000 rpm for 10 min to further
reduce the initial drop sizes and improve the resolution
of the NMR measurements. The technique developed by
Peña and Hirasaki19 was used to determine the
surface relaxation rate of magnetization ρ for this
system in the absence of demulsifier, which was found
to be ρ = 0.85 μs/μm². This value was further used to
interpret results from NMR—CPMG experiments per-
formed on emulsions at preestablished time intervals
once the demulsifier was added as discussed later.

Finally, the equilibrium interfacial tensions of brine
and crude oil after phase separation were measured at
30 ± 1 °C using a spinning drop tensiometer (Non
Linear Systems, model 300). Aliquots of oil and water
were withdrawn with a 5-mL syringe equipped with a
2-in. needle. The tip of the needle was placed
approximately 2 mm above or 2 mm below the water—oil
interface to withdraw samples of oil and water, respec-
tively.

3. Results and Discussion

3.1. Performance of Polyalkoxylated Alkyl-
phenolformaldehyde Resins. Figure 2 shows (filled
circles) results from a bottle test in a w/o
emulsion treated with 240 ppm (volume) of the phenolic resin PR₃
(the actual dosage was 400 ppm, which includes 160
ppm xylene). Pictures of the sample at the beginning
and end of the test are inserted in the plot. It is seen
that the phenolic resin promoted water separation, since
a clear layer of decanted water was collected at the
bottom of the container. Interestingly, it is also seen in
Figure 2 that most of the water (approximately 80%)
wetted by Goldszal and Bourrel.\textsuperscript{21} To explain this, treated resins with intermediate hydrophilicity was also separated within the first 2 h of the test, but it took nearly 4 days to separate the remaining 20\%. This trend indicates that the phenolic resin caused separation of most of the water in a relatively short time, but did not render complete separation of the water phase in a practical time scale. Figure 2 also indicates that no water separation was observed in the absence of demulsifier (squares).

Bottle tests were performed on emulsions treated with all the phenolic resins listed in Table 2. Figure 3 shows (filled circles) the percentage of water separated after 12 h at 30 °C as a function of the relative content of EO + PO groups in the phenolic resin. An increase in the length of the EO + PO headgroup confers hydrophilicity to the phenolic resins. For that reason, the affinity of the resin shifts from lipophilic to hydrophilic as the EO + PO content is increased. The results shown in Figure 3 for \( T = 30 \) °C clearly indicate that the performance of the phenolic resin is optimum for the resin PR\(_3\), which exhibits an intermediate EO + PO content.

In agreement with this result, Taylor\textsuperscript{20} showed that the minimum stability of emulsions of water in a Kuwaiti crude oil treated with commercial ethoxylated nonylphenol formaldehyde resins (Novolak and Resol series) is achieved with five ethylene oxide (EO) units per phenol group. Molecules with a lower or higher number of EO groups would be solubilized preferentially in the oil or water phase, respectively, and would exhibit lower efficiency in water removal. Molecules with the optimum degree of ethoxylation for demulsification would exhibit intermediate crude oil–water solubility.\textsuperscript{21–23}

Optimum demulsification performance of polyalkoxylated resins with intermediate hydrophilicity was also observed by Goldszal and Bourrel.\textsuperscript{21} To explain this behavior, these authors invoked the Winsor’s \( R \) parameter,\textsuperscript{24} which is often used to describe the phase behavior of water–oil–surfactant systems:\textsuperscript{25}

\[
R = A_{CO}/A_{CW}
\]  

where \( A_{CO} \) and \( A_{CW} \) stand for the net surfactant–oil and surfactant–water interaction energies per unit interfacial area, respectively. If the surfactant is lipophilic, \( A_{CO} > A_{CW} \), whence \( R > 1 \). Contrarily, \( R < 1 \) is representative of hydrophilic surfactants. Goldszal and Bourrel\textsuperscript{21} suggested that a maximum in demulsification performance corresponds to a physicochemical condition for which \( R = 1 \). At such a condition, emulsions made with conventional oil–water–surfactant systems exhibit minimum stability.\textsuperscript{26,27} Optimum demulsification performance of chemicals exhibiting intermediate hydrophilicity or balanced partitioning of the demulsifier between the liquid phases has been observed in other investigations.\textsuperscript{22,23}

Figure 3 also shows the amount of water separated after 12 h in bottle tests performed at 50 °C (open circles). The maximum water separation was observed in this case when using the resin PR\(_1\), and not the resin PR\(_2\) as before. Therefore, an increase in temperature required an increase in the fraction of EO + PO groups present in the phenolic resin to observe maximum water separation. This trend is consistent with the above-mentioned ideas, since an increase in temperature leads to a decrease in the interactions between the surfactant and the water phase (i.e., to a reduction in \( A_{CW} \)), due to temperature-driven dehydration of the polyalkoxylated surfactant headgroups. For that reason, a transition \( R \approx 1 \rightarrow R > 1 \) occurs for the resin PR\(_3\), whence emulsion stability increases. For the same reason, a transition \( R < 1 \rightarrow R \approx 1 \) takes place for the resin PR\(_4\), whence emulsion stability diminishes. Water separation for the test at 50 °C improved with respect to the tests performed at 30 °C when using phenolic resins with low (PR\(_1\) and PR\(_2\)) and high (PR\(_3\) and PR\(_4\)) EO + PO content, because an increase in temperature causes a reduction in the viscosity of the oil phase, and therefore leads to an increase in the sedimentation velocity of droplets.

Figure 4 shows a picture of the samples from the bottle test at 30 °C reported in Figure 3, 5 months after the beginning of the test. The acronym PR\(_5\) indicates the phenolic resin that was dosed in each case.
neither in this case nor when more hydrophilic resins were used (PR\textsubscript{4} through PR\textsubscript{6}). However, when a hydrophobic resin was used, some turbidity was observed in the decanted water layer. This fact is indicative of selective partitioning of the resins toward the aqueous phase. It was confirmed via microscopy that the observed turbidity is due to the presence of micron-sized particles, apparently oil droplets, which are unable to cream due to Brownian forces. Hydrophilic resins would favor the formation of oil-in-water (o/w) emulsions as mentioned above, and they probably stabilize the observed oil droplets against coalescence.

Figure 5 shows (filled circles) results from equilibrium interfacial tension measurements on the samples depicted in Figure 4 at 30 ± 1 °C, 5 months after performing the test. Such a long separation time was permitted, aiming to collect enough decanted water from the samples that separated more slowly so the interfacial tension measurement could be performed, without applying centrifugation. It is observed that a minimum in interfacial tension was measured for the sample treated with the phenolic resin PR\textsubscript{3}. The interfacial tension recorded for this sample (0.15 mN/m) was approximately 2 orders of magnitude smaller that those measured from samples treated with the minimum and maximum EO + PO content (10.22 mN/m for PR\textsubscript{1} and 5.40 mN/m for PR\textsubscript{6}, respectively). The interfacial tension of water and crude oil in the absence of demulsifier was 23 mN/m. Results from bottle tests are also included in this figure (triangles), expressed here as the time required to separate 50% of the water phase (t\textsubscript{50\%}). The agreement between these trends is qualitative; i.e., the fastest separation was observed for the system that exhibited minimal equilibrium interfacial tension. This finding is consistent with the interpretation of the optimum demulsification efficiency as the result of balanced physicochemical affinity of the demulsifier (either by itself or associated with indigenous materials of the oil—asphaltenes and resins) for both phases. Finally, the interfacial tension that was measured at the optimum EO + PO content (0.15 mN/m) is higher than the values typically found for microemulsion—water interfaces (0.01−0.0001 mN/m).\textsuperscript{25} A middle (microemulsion) layer was not observed in this test, probably because of the low concentration of demulsifier used in these experiments (240 ppm).

The performance of phenolic resins was also studied via transient viscosity measurements. While the bottle tests measure the amount of water that can be detected visually at the bottom of the container, the viscosity test provides an indication of the amount of water that remains dispersed in the oil phase. Reporting the performance of a demulsifier in terms of its ability to reduce \( \eta \) can be appealing in practice, particularly when the demulsifier is advertised as a viscosity reducer, i.e., when it is expected to avoid or suppress the onset of high viscosities that are often associated with emulsion formation in oil extraction and transport operations.

Figure 6 shows transient shear viscosities of an untreated emulsion with \( \phi = 0.30 \) (open circles), and also of an emulsion treated with 240 ppm phenolic resin PR\textsubscript{3} (filled circles). The dashed line indicates the shear viscosity of the crude oil (23 mPa s). The viscosity \( \eta \) of an emulsion diminishes when the volume fraction of the dispersed phase \( \phi \) is reduced, and it matches the viscosity of the continuous phase \( \eta_C \) in the limit \( \phi \rightarrow 0 \).\textsuperscript{28,29} For that reason, the apparent viscosity of an emulsion diminishes as phase separation takes place. This plot indicates that some sedimentation of water droplets occurred for the untreated emulsion. The addition of the phenolic resin significantly enhanced the water separation rate. The fact that \( \eta \) did not reach \( \eta_C \) after 3 h indicates that some water still remained dispersed in the oil phase.

Figure 7 shows viscosity measurements for emulsions treated with the phenolic resins PR\textsubscript{1} through PR\textsubscript{6} as a function of their EO + PO content at three different times and at \( T = 30 ^\circ C \). It is seen that the decay in shear viscosity was more pronounced for the emulsion treated with the resin PR\textsubscript{3}. This result is consistent with the bottle tests, and also with the fact that emulsion stability is minimal at the optimum formulation for demulsification.

\subsection*{3.2. Performance of Cross-Linked Polyurethanes}

Bottle tests were performed at \( T = 30 ^\circ C \) by adding 240 ppm cross-linked polyurethanes PU\textsubscript{3} to a set of emulsion
samples. In this case, a clear layer of decanted water did not form after 5 months, thus indicating that cross-linked polyurethanes were not as effective as alkyl-phenol formaldehyde resins in promoting coalescence of droplets. Instead, the bottom of the samples exhibited a brownish coloration, which is indicative of a higher concentration of water droplets in that region. This colored layer was evident a few hours after the beginning of the test.

Figure 8 reports viscosity measurements for emulsion samples treated with the cross-linked polyurethanes at \( T = 30 \, ^\circ\text{C} \) and at three different times, as a function of the molecular weight of the cross-linked polymer. It is seen that these chemicals promote flocculation and settling, since the emulsion viscosity diminished with time in all cases. Furthermore, the decay in viscosity was significantly faster for the polymer exhibiting the highest molecular weight ( PU5). These data show that viscosity measurements can be used to characterize the performance of demulsifiers when bottle tests do not render clear-cut information.

Bottle tests in which 200 ppm polymer PUy were added together with 40 ppm phenolic resin PR3 at \( T = 30 \, ^\circ\text{C} \) were also performed. Results from such tests are summarized in Figure 9. In all cases, complete water separation was achieved in 2 h or less, and after only 12 min when the polyurethane with highest molecular weight (PU5) was used. The time needed to separate 50\% of the water phase decreased monotonically from 26 to 9 min as the molecular weight of the polyurethane was increased. These results confirm that the effectiveness of the cross-linked polymer increases with its molecular weight. This finding is consistent with a mechanism postulating that these molecules act as flocculants and promote group sedimentation, because as the molecular weight is increased, so does the number of polar groups present in the polymer molecule through which it can “anchor” at the water—oil interfaces. These results also demonstrate that the two chemistries (phenolic resins in combination with cross-linked polyurethanes) act synergistically, because the time required for complete separation was significantly shorter than those that would be observed for the individual components.

Equilibrium interfacial tension measurements were performed 1 week after the beginning of the bottle tests reported in Figure 9. Interfacial tensions changed monotonically between 0.43 and 0.15 mN/m with increase of polymer molecular weight, and they were comparable to the minimum in interfacial tension that was obtained when the resin PR3 was tested in the absence of cross-linked polyurethanes (Figure 5). These results indicate that the polyurethanes did not alter significantly the balance of interaction energies at the water—oil interfaces that determine the optimum condition for demulsification and phase separation. As observed for the samples treated with phenolic resins only (Figure 5), a qualitative agreement was obtained in the trends for interfacial tension and \( \gamma_{50\%} \).

3.3. Overdosage Effects. Figure 10 shows results from bottle tests designed to evaluate the effect of overdosage on the performance of these chemicals. The reference system is an emulsion sample treated with 40 ppm phenolic resin PR3 and 200 ppm polyurethane PU3. Two additional samples, one containing 3 times the former concentration of PR3 (120 ppm) and an equal concentration of PU3 (200 ppm), and another treated with the same concentration of PR3 (40 ppm) but thrice the reference concentration of PU3 (600 ppm), were also tested. Results indicate that an increase in the concentration of PR3 led to an increase in the rate of water separation, since the time needed to achieve complete separation was reduced from 24 to 18 min. In contrast, separation of water was not observed for the sample treated with 600 ppm PU3 within 24 h. This result demonstrates that an excess of cross-linked polyurethane inhibits the occurrence of coalescence in the system. Similar trends were obtained in bottle tests using PU3 in combination with other phenolic resins.

3.4. NMR Characterization of Emulsions Undergoing Phase Separation. A novel contribution of this work is the implementation of NMR to measure rapid changes in the drop size distribution of unstable emulsions via the so-called Carr-Purcell-Meiboom-Gill (CPMG) experiment. This test allows collecting a much larger data set per time unit than other NMR methods previously used for emulsions, thus enabling resolution...
of the drop size distribution in a shorter time frame.\textsuperscript{19} The method is noninvasive, whence repeated tests can be performed on the same sample. Widespread techniques to measure particle sizes in dispersed systems, such as light scattering, turbidimetry, and videomicroscopy, are not practical in this case because oilfield emulsions are opaque and dilution of the samples would be required.

The application of the NMR–CPMG experiment to w/o emulsions can be briefly explained as follows:\textsuperscript{19} A 90° radio frequency (rf) magnetic pulse followed by a train of 180° rf magnetic pulses is applied to an emulsion sample placed under a permanent magnetic field $B$ to shift the direction of its magnetization vector $M$ from parallel to perpendicular to $B$. As $M$ relaxes back toward the direction of $B$ upon cessation of the 90° rf pulse, the magnitude of its transverse component $M_{xy}$ is measured. Hence, a distribution of relaxation times $T_{2,i}$ that are descriptive of the transient behavior of $M_{xy}$ is calculated. For a signal measured from a fraction $f_i$ of $^{1}H$ nuclei confined in spheres with diameter $d_i$ (i.e., from protons in the water droplets), $T_{2,i}$ can be related to $d_i$ by the expression:\textsuperscript{31}

$$\frac{1}{T_{2,i}} = \frac{1}{T_{2,\text{bulk}}} + \frac{6\rho}{d_i}$$

Thus

$$d_i = 6\rho\left(\frac{1}{T_{2,i}} - \frac{1}{T_{2,\text{bulk}}}%\right)^{-1}$$

whence the drop size distribution is calculated. Here, $\rho$ is the surface relaxivity at the water–oil interface and $T_{2,\text{bulk}}$ is the characteristic relaxation time of the unconfined (bulk) water phase. Equations 2 and 3 are valid in the so-called fast diffusion regime, i.e., when $pd/D \ll 1$ with $D$ being the self-diffusion coefficient of water.

Figure 11 reports the transient drop size distributions of an emulsion treated with PR\textsubscript{3}. Drop diameters that could be resolved for the set of conditions used in these NMR–CPMG experiments ranged between 30 nm and 250 $\mu$m. It is seen in this figure that the phenolic resin PR\textsubscript{3} promoted rapid and monotonic growth of the mean and polydispersity of droplet sizes. The marked widening of the drop size distribution is indicative of a separation process in which droplets coalesce against large droplets and/or against a layer of bulk fluid. The sedimentation rate is proportional to the square of the drop diameter.\textsuperscript{32} Therefore, large drops travel faster throughout the bulk and collide with a larger number of droplets, thus increasing the number of successful collisions leading to coalescence.

The decanted water layer was separated from the oil phase 1 week after the beginning of the test, and the phases were also analyzed individually via NMR–CPMG. Figure 12 shows the distributions of relaxation times $T_2$ for the oil and water phases that were obtained from such analyses. For this particular water–crude oil system, it can be stated that signals for relaxation times above $\sim 700$ ms are characteristic of water molecules, while $T_2$ values below such a threshold are characteristic of components present in the oil phase. The transverse relaxation of the bulk water phase could be described with a single relaxation time $T_2\text{bulk}$ of 2.0 s, which is moderately smaller than the one that is obtained for the brine before emulsification (2.7 s). The $T_2$ distribution of the crude oil (solid curve) indicates that some water still remained dispersed after 1 week. The water signal that was detected is highlighted with a circle in Figure 12, and the corresponding drop size distribution is shown in the inserted plot. The relative areas of the oil and water peaks in the $T_2$ distribution can be used to estimate the volume fraction of each of the phases.\textsuperscript{19,30} By doing so, it was found that the amount of water remaining in the oil (grind out) is 0.7% of the total volume of the initial emulsion, while the decanted water account for 28.7%. The total water content is therefore 29.4 vol %, which is very close to the actual value (30%). This indicates that the phenolic resin is able to separate most, but not all, of the water present in the emulsion, as was noted earlier via viscosity measurements (Figure 6).

The NMR–CPMG technique was also applied to an emulsion treated with 240 ppm polyurethane PU\textsubscript{3}. Results for the transient drop size distribution are plotted in Figure 13. A slow but steady growth of the large droplets is observed along with an increase in the polydispersity of drop sizes. It becomes clear from the data reported in Figure 13 that the growth in mean size and polydispersity is much slower in this case when compared with the corresponding trends that were obtained for the emulsion treated with the phenolic resin (Figure 11).

Since a water layer was not collected at the bottom of the container when the emulsion was treated only with cross-linked polyurethanes, NMR–CPMG experiments were performed in the presence of a magnetic field gradient in order to resolve the water–oil composi-
tion in different regions of the sample. When a gradient of strength $g$ is imposed, the steady magnetic field is not uniform in space and the Larmor frequency depends on the position of the nuclei $\omega(\mathbf{r}) = \gamma B(\mathbf{r})$. Two spins at positions $\mathbf{r}_1$ and $\mathbf{r}_2$, such that $B(\mathbf{r}_1) \neq B(\mathbf{r}_2)$, precess at different Larmor frequencies. The coil (“antenna”) of the spectrometer is tuned to measure the response of the region where spins precess at a specific Larmor frequency $\omega_0$. Therefore, only those spins are sensed by the spectrometer. This principle allows characterizing “slices” of the sample of interest. In this case, an additional contribution to the relaxation time $T_2$ is caused by the diffusion of the spins in the field gradient:

$$\frac{1}{T_{2,\nu}} = \frac{1}{T_{2,\text{bulk}}} + \frac{6\rho}{d_1} + \frac{(\gamma g t)^2D}{12} \quad (4)$$

where $t_E = 2t$ is the time between consecutive 180° rf pulses. The gyromagnetic ratio $\gamma$ is a characteristic constant of the nuclei that are being probed ($\gamma = 2.67 \times 10^8 \text{ rad T}^{-1} \text{s}^{-1}$ for $^1\text{H}$).

Figure 14 shows the $T_2$ distributions that were obtained after applying the above-mentioned technique on three regions (top, middle, and bottom) of the sample treated with the polyurethane PU3 1 week after the beginning of the test. The $T_2$ distributions of the crude oil (dashed line) and of the brine (dotted line) are also shown as reference. The relaxation of the brine was well described with a single relaxation time $T_2 = 2.2 \text{ s}$. This value agrees well with the $T_2$ that is calculated from eq 4 in the limit $d \to \infty$ ($T_2 = 2.3 \text{ s}$). The experiments were performed using $t_E = 400 \mu\text{s}$ and $g = 0.132 \text{ T/m}$. Sixteen stacks were accumulated in all cases and an average noise level of 2.3% was obtained. The “slices” that were characterized out of a sample of 38 mm in height had a thickness of 4.8 mm.

Figure 14 indicates that only oil was present in the top and middle regions of the sample, while the water phase was collected at the bottom. This assessment agrees with previous observations in bottle and viscosity tests, which indicated that the cross-linked polyurethane promotes sedimentation of water droplets even though a clear layer of decanted water is not observed at the bottom of the container. The absence of water droplets in most of the sample (Figure 14) indicates that this polyurethane can be used to remove small drops that otherwise would be “left behind”.

Finally, an NMR experiment with samples treated with a mixture of a phenolic resin (PR3, 40 ppm) and a cross-linked polyurethane (PU3, 200 ppm) was also performed. When both components were added, drop sizes grew beyond the resolution limit of the technique ($d_{\text{MAX}} = 250 \mu\text{m}$) within the time required to complete a CPMG test (4 min), and therefore meaningful data could not be collected. This result confirms that both components act synergistically as was mentioned in section 3.2 via bottle tests.

3.5. Mechanism of Chemical Demulsification. The results shown in preceding sections for emulsions treated with alkylphenolformaldehyde indicate that performance was optimum with a resin exhibiting an intermediate content of polar (polyoxyethylene—polyoxypropylene) groups. At such composition (1) the maximum water separation rate was observed, (2) the decay in shear viscosity was also more pronounced, (3) the equilibrium interfacial tension was minimal, (4) performance was affected by temperature in a manner consistent with conventional knowledge for the behavior of polyalkoxylated surfactants at the optimum formulation condition for microemulsion formation, and (5) NMR measurements indicated that the mean size and the polydispersity of drop sizes grew monotonically in time, on a relatively short time scale (minutes to a few hours). These results suggest that, at the optimum condition for phase separation, phenolic resins promoted fast coalescence.

In contrast, the cross-linked polyurethanes promoted flocculation and rapid settling of droplets. It was found...
that the performance of these chemicals improved as their molecular weight increased. NMR measurements indicated that the mean size grew monotonically in time, but at a significantly slower pace than the one observed for phenolic resins (hours to days). It was also demonstrated via NMR that these polymers removed droplets from the oil phase, but did not promote their coalescence once they were collected at the bottom of the sample. These results suggest that cross-linked polyurethanes lead to phase separation via fast flocculation and slow coalescence. Enhanced flocculation leads to group sedimentation rates and therefore to higher water decantation rates.

When a phenolic resin and a cross-linked polyurethane were dosed concomitantly, water separation took place at a much faster rate (seconds to a few minutes). In this case, both types of molecules acted synergistically. The phenolic resins may have disrupted the rigid network of colloidal asphaltenes that otherwise would stabilize the drops against coalescence (Figure 15a.1,a.2). This would lead to the formation of “patches” of adsorbed asphaltenes surrounded by continuous regions depleted of these materials. Recent atomic force microscopy (AFM) images of single-layer Langmuir—Blodgett (LB) films of asphaltenes and mixtures of asphaltenes and a nonylphenol formaldehyde resin deposited on silicon wafers show the ability of phenolic resins to induce the formation of disconnected clusters of asphaltenes at the air—water interface.8 Kilpatrick36 has coined the term “islands of aromaticity” to refer to these isolated asphaltene domains. Depleted regions of two nearby droplets may come into contact after the film that separates them is drained. Following the ideas of Vrij,34 varicose capillary waves may develop in these regions and a hole can be formed when two waves at opposite interfaces touch each other (Figure 15a.3). The fact that the trends for water separation performance and interfacial tension were in qualitative agreement (Figure 5) supports the notion that hole formation dictates the onset of coalescence.

According to Kabalnov and Wennerström,35 coalescence will take place if the hole that is formed is able to overcome the energy penalty that is involved in reversing the interfacial curvature (as shown by $r_2$ in Figure 15b) and expanding against the film of adsorbed materials (Figure 15a.4). At the optimum formulation the spontaneous curvature of the interfacial films is zero and their interfacial tension and rigidity (bending modulus) are small. Hence, the energy penalty is relatively small for both o/w and w/o emulsions, and phase separation is rapid as seen here. As might be expected, coalescence was slow when w/o emulsions were treated with the more lipophilic resins. The energy penalty is large in this case because the spontaneous curvature of the film is opposite that of $r_2$ in Figure 15b, and hole formation is not favored.

A similar argument suggests that the onset of the reverse curvature $r_2$ should be favored for the more hydrophilic phenolic resins. However, the water separation rate diminished when the EO + PO content of the phenolic resins was increased beyond the optimum value (Figure 3). This result can be explained by

Figure 15. (a) Plausible conformation of indigenous materials (asphaltenes—asphaltene—resin aggregates), phenolic resin, and cross-linked polyurethane molecules at the water—oil interface when two water drops approach each other and the formation of a “hole” takes place. (b) Schematic representation of the hole, showing the region of near-zero interfacial curvature.
considering that as the resin became more hydrophilic, interfacial tension increased to values comparable to the tension in the absence of demulsifier (Figure 5). Therefore, disruption of the asphalteneic film became less efficient, which hints that the interfacial film was more rigid and resisted hole formation.

It is plausible to think that polyurethanes acted as “bridges” between drops, thus increasing the average time in which two nearby drops remain close to each other and therefore the probability for collisions leading to a successful coalescence event (Figure 15a.2). Coalescence events would also be favored by the fact that polyurethane molecules promoted group sedimentation, since both the rate of sedimentation and the cross-sectional area of the floc undergoing sedimentation increase.32

Finally, it was observed that when an excess of cross-linked polyurethane was added, coalescence was retarded. Since the polyurethanes are solubilized preferably in the oil phase, it can be expected that steric—entropic repulsion forces arise as the concentration of polymer increases. Stabilizing forces may originate not only from the interaction of adsorbed layers of polymer on approaching droplets as stated by the classic steric stabilization theory,36 but also from the energy penalty that would be associated with the distortion of the flocs. In light of these experimental findings, it can be concluded that when phenolic resins and polyurethanes are added concomitantly and at an appropriate dosage, fast flocculation (promoted mainly by a cross-linked polyurethane) and fast coalescence (aided by the presence of a phenolic resin) occur.

4. Conclusions

The effect of alkylphenol polyalkoxylated (EO + PO) resins and cross-linked polyurethanes of known structure and composition on the stability and properties of brine-in-crude oil emulsions was assessed experimentally via bottle tests, interfacial tension experiments, viscosity measurements, and nuclear magnetic resonance relaxometry. The phenolic resins promoted coalescence of droplets. The fastest rate for water separation was obtained when the emulsions were treated with resins exhibiting intermediate EO + PO content, in a fashion consistent with the optimum formulation for microemulsion formation in oil—water—surfactant systems. In contrast, cross-linked polyurethanes promoted flocculation and slow coalescence, and they were more effective with increase of molecular weight. When both types of molecules were added concomitantly, water separation rates were significantly higher than those observed when they were used individually. In this case, it seems that polyurethanes contributed to increase the water separation rate, but they retarded coalescence when added at high concentrations. These findings can be explained qualitatively in terms of a molecular mechanism that may involve the disruption of the asphalteneic film adsorbed at the water—oil interfaces by the phenolic resins, and the formation and expansion of holes between approaching droplets in regions depleted of asphaltenes. The action of the phenolic resins was supplemented by the cross-linked polyurethanes, which may act as “bridges” between droplets, thus increasing the probability for collisions leading to successful coalescence events.

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