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# Long-Term High Temperature Stability of Functionalized Graphene Oxide Nanoplatelets in Arab-D and API Brine

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36 KEYWORDS Graphene oxide, brine stability, high salinity, reservoir imaging, grafting-to,  
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38 diazonium salts, imidazolium

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41  
42 ABSTRACT. Partially reduced graphene oxide (prGO) was covalently functionalized with an  
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44 diazonium containing, imidazolium based, polyzwitterionic polymer to afford a composite  
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46 material with excellent dispersibility and long-term stability in high salinity brines including  
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48 standard API and Arab-D found in deep oil reservoirs. When heated at 90 °C, the dispersions  
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50 remained stable in excess of 140 days. These results suggest the utility of imidazolium-based  
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52 polymers for brine stabilization as well as the use of diazonium containing polymers for a  
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54 ‘grafting-to’ approach to nanocarbon functionalization.  
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## Introduction

The stabilization of nano-sized materials in aqueous environments with high salinities (high ionic strength) has become an important area of research due to the relevance of these materials for the petroleum industry. The delivery of nanoscale materials deep into oil reservoirs are of particular interest, as these materials can act as imaging enhancers and/or act reporter probes, providing useful information on the state of the reservoir, which is essential to the improvement of recovery yields. Designing effective reservoir imaging materials is challenging as a result of the fact that the internal environment of oil reservoirs contains high salinity and high temperature brines, which can readily destabilize nano-materials injected into them.

In an attempt to address the above issues and successfully stabilize materials in high ionic strength reservoir environments, work by Johnston *et al* in 2013.<sup>1</sup> showed that iron oxide nanoparticles wrapped with sulfonic salt containing polyacrylate/acrylamide-type polymers could effectively stabilize the nanoparticles in American Petroleum Institute (API) brine (aqueous 8 wt% sodium chloride and 2 wt% calcium chloride) at 90 °C for up to one month. The ionic nature of the polymer successfully imparted electrosteric stabilization and repulsion required to stabilize the nanoparticles against agglomeration in the brine.

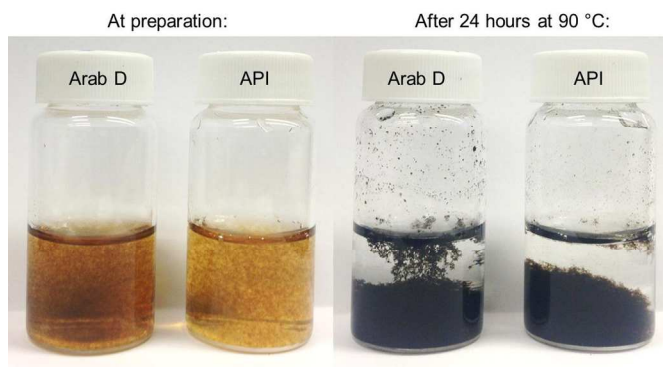
Another example, also using an ionic polymer, was shown to stabilize carbon nanoparticles in API brine as reported by Tour *et al* in 2012.<sup>2</sup> Polyvinyl alcohol was grafted onto the surface of the nanoparticles and could be sulfonated with a chlorosulfonic acid treatment. It was shown that the lightly sulfonated nanoparticles could be stably dispersed in API brine at 100 °C. The unsulfonated nanoparticles were not dispersible in the brine. The highly sulfonated nanoparticles were not as stable as the lightly sulfonated variant, and formed a suspension of small particulates

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3 upon heating. The long-term stability of the stable dispersion over time was not examined;  
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5 however, the nanoparticles were shown to act effectively as carriers for a reporter molecule when  
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7 injected into a simulated reservoir environment. Other relevant work in this area by Vansco and  
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9 coworkers has shown that a polyimidazole betaine was dispersible in 22.6 wt% NaCl solutions.<sup>3</sup>  
10  
11 Long-term stability was not reported.  
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16 To meet the demanding conditions for solubility and stability in brine at elevated temperatures,  
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18 we have focused on the functionalization of nano-sized graphene sheets (<1 μm). An advantage  
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20 of this approach is the large surface area and chemical reactivity of the graphene oxide basal  
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22 plane,<sup>4-6</sup> which facilitated functionalization as well as the potential ability to transport adsorbed  
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24 nanomaterials deemed of interest.<sup>7-10</sup> As a result, success with this system could find utility for  
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26 stabilizing and transporting different payloads (molecules or nanoparticles).  
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31 Highly oxidized graphene oxide (made with a 5:1 permanganate ratio versus the typical 3:1)  
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33 forms stable dispersions in aqueous concentrated sodium chloride solutions up to 5 wt%, as  
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35 reported by Johnston and coworkers.<sup>11</sup> The stability of the GO sheets in the brine was ascribed to  
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37 the presence of a large number of negatively charged groups on the sheet edges that provide  
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39 sufficient electrostatic repulsion even in a high ionic strength environment. This GO could be  
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41 used to stabilize oil/water emulsions, but was not examined under harsher conditions including  
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43 higher ionic strength brine and/or elevated temperatures.  
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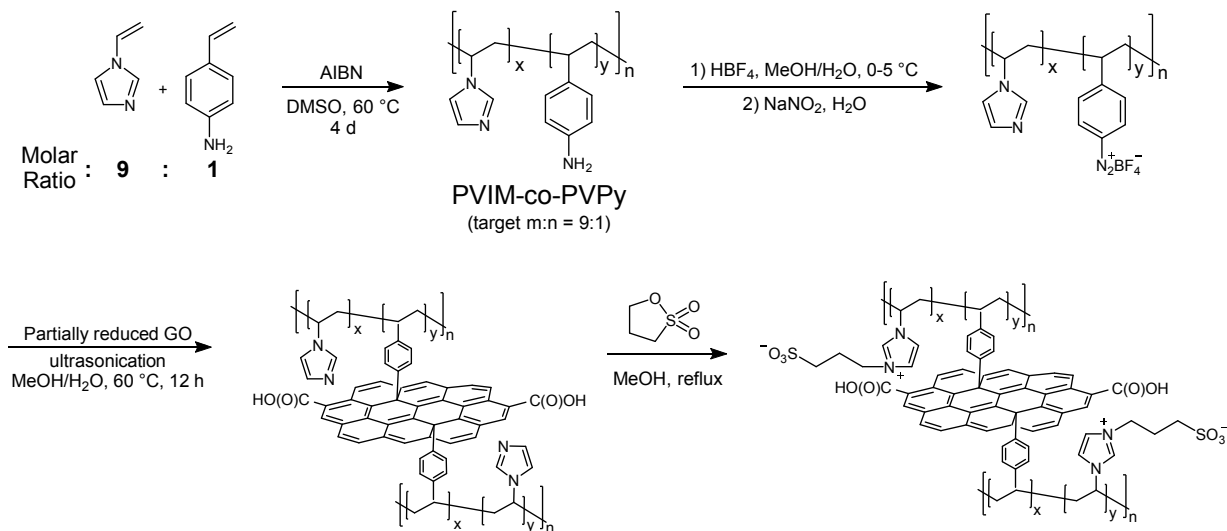
49 In our experiments graphene oxide is not stably dispersed at room temperature or above in the  
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51 target brines tested all of which contained divalent ions, including the standard API (Figure 1).  
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53 This was attributed to electrostatic crosslinking and destabilization of the negatively charged  
54  
55 groups present on the GO sheets, particularly by the divalent calcium ions.  
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**Figure 1.** Unstable mixtures of GO in Arab D and API brines at initial preparation and after 24 h at 90 °C.

We were able to successfully stabilize submicron sized GO sheets (*ca.* 300 nm) by covalently attaching poly(vinylimidazole)-*co*-poly(aminostyrene) copolymer (PVIM-*co*-PYPy)<sup>12</sup> onto the sheets through diazonium chemistry. The attached polymer was then be subjected to a post-functionalization reaction with 1,3-propane sultone to yield a zwitterionic-type polymer (Scheme 1). In addition to <sup>1</sup>H NMR, the structure of this polymer was examined through an HSQC NMR experiment, the results of which suggest a random copolymer with a ratio of 10:1 imidazole:aniline units (Figure S6).

**Scheme 1.** Synthesis of polymer PVIM-co-PVPy and functionalization of partially reduced graphene oxide.



It has been shown repeatedly that zwitterionic groups (i.e. species containing linked cationic and anionic groups with an overall neutral charge) have excellent brine solubility and stability due to what is referred to as the antipolyelectrolyte effect.<sup>13</sup> This effect causes the chain to expand upon addition of electrolytes which help to stabilize it against agglomeration/destabilization through steric effects (electrosteric stabilization).<sup>14</sup> Such materials have been used in applications as seawater antifouling coatings<sup>15</sup> but have also been suggested for potential use in enhanced oil recovery.<sup>16</sup> The zwitterionic polymer-partially reduced GO (prGO) composite material discussed in this report was shown to be stable in both standard API brine, as well as a higher ionic strength brine known as Arab-D, with excellent long-term stability upon standing at 90 °C (140 days to-date). The dispersion stability was monitored both visually and spectroscopically. Dynamic light scattering (DLS) was used to monitor changes in average particle size over time.

## Experimental

*General Materials and Methods:* All chemicals were purchased from Sigma-Aldrich and used as received unless stated otherwise. X-ray photoelectron spectroscopy (XPS) analyses were performed on a Versaprobe II X-ray photoelectron spectrometer from Physical Electronics with a monochromated Al K $\alpha$  X-ray source (1486.6 eV) and operated at a base pressure of  $1 \times 10^{-9}$  Torr with 45.7 Watts of power, a 200  $\mu\text{m}$  spot beam size and a take-off angle of 45°. The XPS spectra were analyzed and atomic peaks were integrated using the CasaXPS software to determine the relative atomic percentages of the element species present in the samples. Thermogravimetric analyses were performed on a TA Instruments Discovery TGA in the range of 50 – 800 °C at a constant ramp rate of 20 °C min<sup>-1</sup> under nitrogen atmosphere. Percent transmittance (%T) spectra of composite in brine samples were taken on a Varian Cary 6000i instrument using a zero/background correction in quartz cuvettes. Dynamic light scattering (DLS; Brookhaven Instruments BI-200SM) of the brine dispersed composites was performed by adding a small amount of the tested dispersions into filtered brine. The data was collected in triplicate at a 90° scattering angle for 3 min at room temperature and fitted using the CONTIN algorithm.

*Graphite Oxide Preparation Procedure:* 10 g graphite (natural flake, Alfa Aesar, 2-15  $\mu\text{m}$ ) was ball-milled at 30 Hz for 30 min, then dispersed in 200 mL conc. H<sub>2</sub>SO<sub>4</sub> and stirred at 0 °C. 30 g KMnO<sub>4</sub> was added portionwise over a 2 h period so not to allow the temperature to exceed 20 °C. The mixture was allowed to return to room temperature and stirred overnight, then 500 mL of ice-water was added slowly. Following this, 20 mL of 30% H<sub>2</sub>O<sub>2</sub> was added. 500 mL ice-water was then poured into the reaction and stirred for 3 h. The resulting solids were then collected via ultracentrifugation and redispersed in 10% aq. HCl, and subsequently washed with

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3 copious amounts of DI water. The solids were then dialyzed against DI water until the water  
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5 reached a pH of approximately 4.  
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9 *Synthesis of poly(vinylimidazole)-co-poly(aminostyrene) (Polymer I):* 1-vinylimidazole, 4-  
10 aminostyrene and DMSO were distilled prior to use. 1-vinylimidazole (2.51 g, 26.7 mmol), 4-  
11 aminostyrene (0.32 g, 2.7 mmol), azobisisobutyronitrile (AIBN, 0.48 g, 0.29 mmol) and DMSO  
12 (5mL) were combined in a Schlenk tube with a stir bar (feed ratio imidazole:aniline::10:1). The  
13 mixture was degassed by freeze-pump-thaw (3 ×) and sealed under static inert atmosphere and  
14 stirred at 60 °C for four days. The resulting lightly yellow viscous solution was cooled and  
15 diluted by the addition of methanol. The mixture was precipitated into acetone (2 ×) and then  
16 dried overnight to produce a clear hard yellow solid. Polymer I was characterized by <sup>1</sup>H NMR  
17 (MeOD-d4) as shown in SI Figure S4.  
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31 *Synthesis of Covalently Functionalized Polymer I – partially reduced graphene oxide (prGO)*  
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33 *Composite:* First, 15 mL of graphene oxide dispersed in deionized water (1 mg mL<sup>-1</sup>) was diluted  
34 up to a total volume of 30 mL with deionized water. *l*-Ascorbic acid (15.1 mg) was added and  
35 the mixture was stirred at 60 °C for one hour and then rapidly chilled to <5 °C and set aside for  
36 immediate use. Separately, polymer I (150.5 mg) was dissolved in methanol (50 mL) under mild  
37 sonication (5 min) and stirring. 48% aq. tetrafluoroboric acid (25.8 mg) was dissolved in  
38 deionized water (10 mL) and added to the methanol mixture. The solution was subsequently  
39 chilled to <5 °C. In separate vial, sodium nitrite (9.8 mg) was dissolved in deionized water (2  
40 mL) and likewise chilled. The sodium nitrite solution was added to the solution of polymer I  
41 with stirring and after 15 min the chilled partially reduced graphene oxide (prGO) dispersion was  
42 added slowly and stirred for 30 min. Afterward, the mixture was sonicated for 30 min and then  
43 stirred at 60 °C overnight. The cooled solution was concentrated *in vacuo* and then sufficient  
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3 acetone was added to induce flocculation and the solids were collected by centrifugation (5k  
4 rpm; 15 min). The solids were air dried and used directly in the next step.  
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9 *Synthesis of Zwitterionic Polymer I – prGO Composite Dispersion:* The above composite  
10 solids were sonically dispersed in methanol (100 mL) and then 1,3-propane sultone (350.2  
11 mg) was added. The mixture was refluxed under inert atmosphere overnight and then 30 mL of  
12 deionized water was added. Afterward the cooled solution was centrifuged (2.5k rpm, 15 min)  
13 and the supernatant was decanted. The remaining solids were washed with methanol and  
14 deionized water and after centrifugation the supernatant was combined with the previously  
15 collected solution. The methanol was removed from the supernatant in vacuo to afford the  
16 zwitterionic *Polymer I – prGO* composite as a dispersion in water (~45 mL) and stored in a  
17 sealed container. The remaining solids isolated from centrifugation were lyophilized.  
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31 *Preparation of Low Salinity Arab-D Brine:* Sodium chloride (37.3 g), calcium chloride  
32 dihydrate (24.9 g), magnesium chloride hexahydrate (6.6 g), barium chloride (5 mg), sodium  
33 sulfate (0.3 g) and sodium bicarbonate (0.26 g) were dissolved to a total volume of 500 mL in  
34 high purity distilled water.  
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42 *Preparation of American Petroleum Institute (API) Brine:* Sodium chloride (20.0 g) and  
43 calcium chloride dihydrate (5.0 g) were dissolved in high purity distilled water (225 mL).  
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48 **Table 1.** Relative Weight  
49 Percentages of Salts in Brine  
50 Solutions

| Salt Species                         | Arab D | API  |
|--------------------------------------|--------|------|
| NaCl                                 | 7.5%   | 8.0% |
| CaCl <sub>2</sub> ·2H <sub>2</sub> O | 5.0%   | 2.0% |
| MgCl <sub>2</sub> ·6H <sub>2</sub> O | 1.3%   | -    |
| BaCl <sub>2</sub>                    | 0.001% | -    |
| Na <sub>2</sub> SO <sub>4</sub>      | 0.006% | -    |
| NaHCO <sub>3</sub>                   | 0.005% | -    |

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3 *Brine Stability Testing of Zwitterionic Polymer I – prGO Composite at 90 °C:* To two separate  
4 capped bottles with seals labeled Arab-D and API brine were added 90 mL of each respective  
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6 brine solution. Then 10 mL of the composite in water were added to each to afford a 9:1 volume  
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8 ratio. The bottles were sonicated for 5 min and then allowed to stand undisturbed in an oven set  
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10 at 90 °C. Aliquots (3 mL) for characterization were taken immediately after preparation (before  
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12 heating), after 24 hours (day 1) and again on days 10, 20, 30, and 140. Pictures were taken on  
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14 those days in smaller scintillation vials and those solutions were promptly returned to the larger  
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16 bottles (Figure 2).  
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## 22 **Results and Discussion**

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27 The ability to introduce addressable nano-materials into oil reservoirs presents an opportunity  
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29 for interrogating the internal state of oil wells with the goal of enhancing their output and  
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31 productivity. In our preliminary evaluation of materials of interest we chose to pursue stable sub-  
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33 micron sized graphene oxide nanosheets as a platform material based broadly on the relative ease  
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35 of modification of its basal plane through known chemistries and the potential to transport  
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37 materials of interest. In order to establish baseline dispersion and stability, two testing brines  
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39 were chosen: 1) low salinity Arab-D brine and 2) standard American Petroleum Institute (API)  
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41 brine. Arab-D brine can be found in the largest oil well in the world known as the Ghawar field  
42  
43 found in Saudi Arabia. Table 1 provides the relative weight percentages and salt compositions of  
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45 the high salinity brines. As compared to the standard API brine, the Arab-D brine possessed a  
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47 more complex salt mixture and a significantly higher content of divalent ion species like calcium  
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49 chloride and magnesium chloride.  
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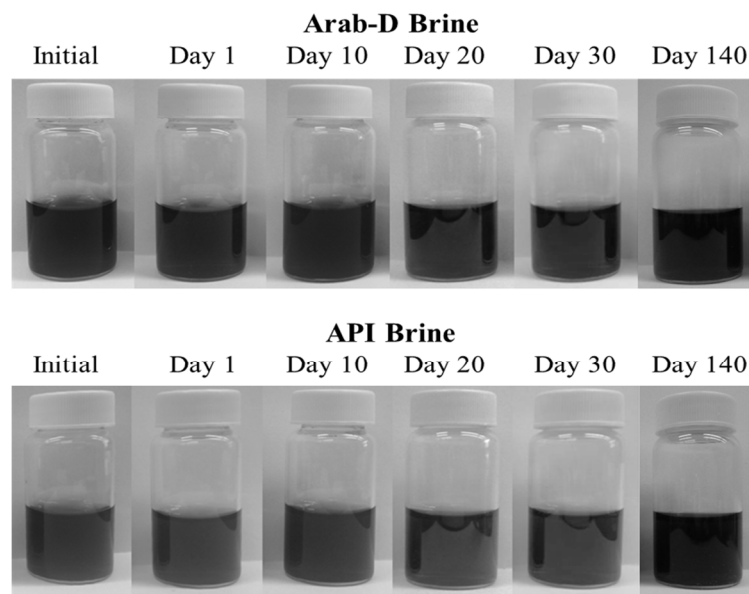
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3 Preliminary stability testing was performed on mixtures of water dispersed sub-micron sized  
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5 graphene oxide (GO; average DLS determined sheet diameter of  $338.2 \pm 27.9$  nm) with either  
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7 the Arab-D or API brines. These studies reveal that the GO was highly unstable in both brines  
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9 immediately upon mixing and after 24 h at 90 °C, as shown in figure 1.  
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12  
13 XPS of the black flocculated materials after thorough washing (see Supporting Information  
14  
15 Figure S2) revealed only the presence of calcium in addition to the rGO's carbon and oxygen  
16  
17 signals. This suggested that the primary cause of destabilization was probably the result of ionic  
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19 crosslinking of the negatively charged GO sheets by the divalent calcium cations.  
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24 As discussed in the introduction, it is known that zwitterionic species and polyzwitterions exhibit  
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26 the antipolyelectrolyte effect that can provide dispersion stability in high ionic strength  
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28 environments.<sup>9</sup> Therefore, an imidazole-based sulfobetaine zwitterionic copolymer was  
29  
30 developed containing aminostyrene groups. Specifically, a random copolymer of 1-  
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32 vinylimidazole and 4-aminostyrene with a molar feed ratio of 9:1 was prepared by radical  
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34 polymerization initiated by AIBN in DMSO and polymerized at 60 °C for four days (Scheme 1).  
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36 The aminostyrene groups permitted the use of diazonium chemistry<sup>17-20</sup> for producing covalent  
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38 attachments of the polymer chain directly to the graphene basal plane. Although the use of  
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40 diazonium species to covalently decorate the basal plane of graphene is well-established, we  
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42 believe that the use of a diazonium containing polymer in a 'grafting-to' approach is particularly  
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44 advantageous in covalently functionalizing graphene with a relatively high number of functional  
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46 groups.  
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53 Covalent functionalization of the graphene sheets was carried out as shown in Scheme 1 by first  
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55 performing the diazonium salt of the aminostyrene groups present in polymer PVIM-co-PVPy  
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3 under typical conditions with tetrafluoroboric acid and sodium nitrite in methanol. Separately, a  
4 partial reduction of GO was carried out by reaction with *l*-ascorbic acid at a low 1:1 weight ratio  
5 of GO:acid to increase the graphitic domains available for reaction with the diazonium species.  
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8 The partially reduced GO (prGO) which remained dispersed in water was rapidly chilled and  
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10 subsequently added to the diazonium containing PVIM-co-PVPy solution as shown in reaction  
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12 scheme. A mass excess of the polymer PVIM-co-PVPy versus GO was used to promote more  
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14 extensive functionalization of the graphene sheets. Using TGA, it was found that this  
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16 functionalization resulting in extensive decoration of the graphene sheets, as approximately 37%  
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18 of the mass in the composite can be attributed to polymer (Figure S5).  
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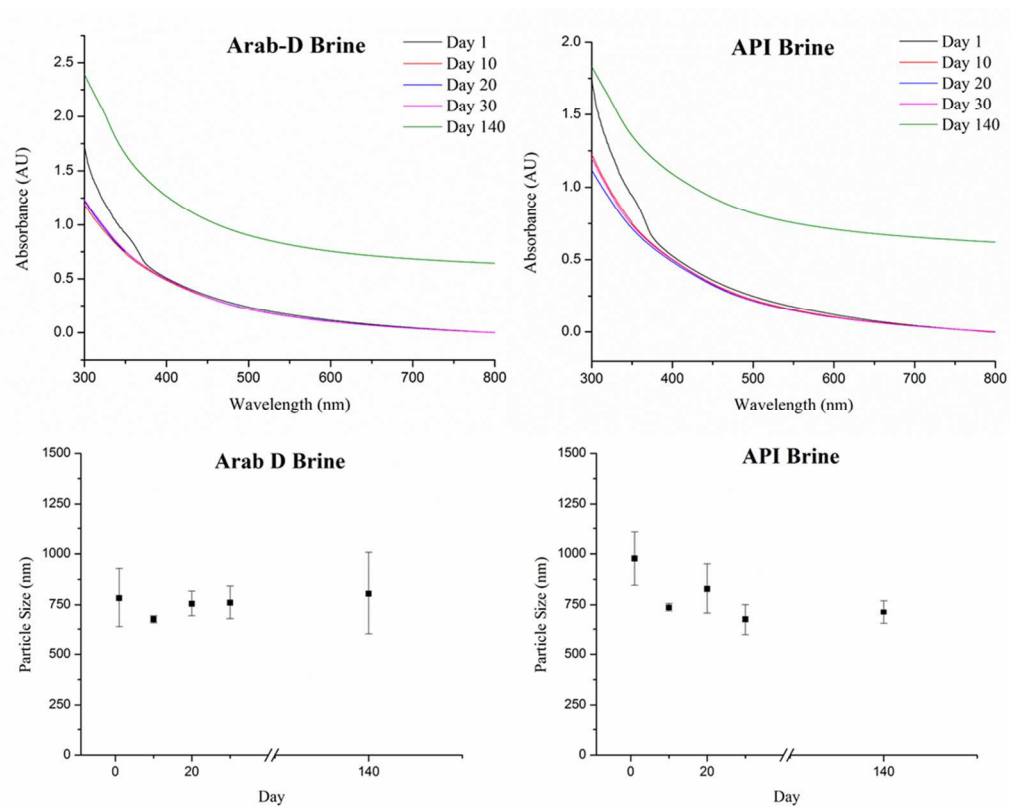


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48 **Figure 2.** Photographs of aliquots of stable composite dispersions in Arab  
49 D (above) and API (below) brines at initial preparation and after 1, 10, 20,  
50 30, and 140 days at 90 °C.  
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3 The resulting polymer-prGO composite was isolated by precipitation, washed, and subsequently  
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5 reacted with propane sultone in methanol to achieve a post-reaction functionalization of the  
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7 imidazole groups to form the target imidazole-sulfobetaine groups and impart zwitterionic  
8  
9 character on the prGO attached polymer chains. The resulting black dispersion was found to be  
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11 highly stable and resisted isolation by centrifugation (even at 10,000 rpm for 10 min). Therefore,  
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13 it was decided to isolate the fraction of the composite remained as a stable black aqueous  
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15 dispersion in water after centrifugation by removal of the methanol solvent in vacuo. The solids  
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17 isolated by centrifugation may represent less functionalized materials and/or crosslinked  
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19 aggregates composed of multiple sheets. The composite may owe some its stability as a  
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21 dispersion in brine as a result of residual surface charges present. Although a purely zwitterionic  
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23 polymer would be expected to have no net charge overall, the composite likely has negatively  
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25 charged groups present from the prGO sheets helping to stabilize the material in water.  
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27 Furthermore, we believe the covalent functionalization afforded by the diazonium chemistry to  
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29 be essential to this stability, as when graphene oxide was mixed with a sulfonated polyimidazole  
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31 synthesized in a similar manner, flocculation in brine occurred after two weeks at 90 °C (see SI  
32  
33 experimental). The concentration of composite in aqueous dispersion was examined by drying a  
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35 known volume of the dispersion in vacuo. The concentration of solids was approximately 11  
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37 mg/mL. XPS analysis of the solids confirmed the presence of C, N, O and S in the composite  
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39 sample as shown in Supporting Information Figure S3. Interestingly, the large amount of sulfur  
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41 present in the XPS analysis suggests that in addition to alkylation of the polymer chain, some  
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43 functionalization of the reduced graphene oxide sheet may have also occurred.  
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54 The dispersibility and long-term stability testing at 90 °C of the aqueous composite dispersion  
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56 was carried out in Arab D and API brines. The 100 mL dispersions were prepared by adding 10  
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3 mL of the aqueous composite dispersion to 90 mL of the respective brines and sonication of the  
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5 mixtures for 5 min to achieve homogeneous dispersions that were free of aggregates by visual  
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7 inspection. After the initial preparation, a small aliquot of each dispersion was removed for  
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9 spectroscopic (%T) and dynamic light scattering (DLS) characterization. The remainder of the  
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11 dispersions in the Arab-D and API brines were allowed to stand undisturbed in an oven set at 90  
12  
13 °C. After 24h (day 1) and on days 10, 20, 30, and 140 small aliquots were removed for  
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15 characterization purposes as desired. Photographs of the aliquots taken showed no noticeable  
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17 evidence of instability, flocculation or settling of the dispersed composite in either the Arab D or  
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19 API brines after one month at 90 °C as shown in Figure 2. In order to monitor the dispersion  
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21 stability quantitatively we examined the percent transmittance of the dispersions as shown in  
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23 Figure 3. It was observed that the initial and day one data were essentially superimposable for  
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25 the initial and day one curves in Arab-D and with only subtle differences were detected in the  
26  
27 API brine. Lower transmittance was also observed in the ranges of 300 – 350 nm that was not  
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29 present in the day 10, 20, 30, and 140 curves. GO possesses absorption bands in this region and  
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31 their disappearance after 10 days is likely an indication of on-going thermal reduction process at  
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33 the elevated brine temperatures. The most notable changes in the transmittance data were in the  
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35 range of 500 – 600 nm. Examination of the %T values at the arbitrarily chosen wavelength of  
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37 550 nm revealed that the transmittance changed most between the initial and first day and then  
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39 remained essentially stable over the month long test period until day 140, where absorbance over  
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41 the entire UV-Vis spectrum increased. This is likely due an increase in the concentration of  
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43 graphene in the day 140 dispersion.  
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**Figure 3.** UV-Vis (top) spectra and DLS data of PVIM-co-PVPy solutions at 1 day, 10 days, 20 days, 30 days, and 140 days at 90 °C.

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7 Visual inspection and spectroscopic data supported the conclusion that the polymer wrapped  
8 sheets were stable in these brines. Furthermore, the lack of observable precipitates/flocculants  
9 and the negligible changes in the monitored transmittance (as a function of time) suggested that  
10 polymer detachment was not occurring appreciably owing to the covalent attachment between  
11 the polymer and the basal plane.  
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19 Further confirmation of the stability of graphene-polymer composites in brine was obtained from  
20 the examination of hydrodynamic diameter changes in samples kept at 90°C by DLS (Figure 3).  
21 Based on the DLS results, the average hydrodynamic diameter of the graphene oxide sheets in  
22 water was found to be  $338.2 \pm 27.9$  nm. The data for the initially prepared composite dispersed  
23 in Arab-D brine demonstrated particles with a mean diameter of  $770 \pm 92$  nm and in API brine a  
24 diameter of  $1077 \pm 218$  nm. It was assumed that the composite dispersed in brine was comprised  
25 by pseudospherical nanoparticles consisting of partially reduced GO (prGO) nanosheets wrapped  
26 by attached zwitterionic polymer chains. In the high ionic strength environment of the brines, the  
27 electrolyte ions present can effectively screen the interactions of the zwitterionic sulfobetaine  
28 ionic groups and the chains can expand providing sufficient steric repulsion effect to solubilize  
29 and prevent aggregation/flocculation of the composite particles.<sup>13,14</sup> The DLS measured  
30 diameters of the composite dispersion in Arab-D brine showed excellent stability over 30 days  
31 with stable mean diameters of ca. 750 nm. In the case of the API brine dispersed composite, the  
32 initial data points indicated particles of ca. one micron size in diameter that stabilized over time  
33 to a mean diameter of ca. 750 nm (based on the day 10, 20, 30, and 140 data points).  
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3 The excellent stability of the composite in the complex and higher ionic strength Arab-D brine  
4 (containing a higher content of divalent ion species, such as calcium (II) and magnesium (II))  
5 was particularly promising. It is further noted that the relative stability of the composite particles  
6 was for 140 days with no appreciable destabilization having occurred up to that point. Based on  
7 the data at hand, is likely that composite dispersions should have prolonged stability at elevated  
8 temperatures in brine.  
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## 22 **Conclusions**

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25 Partially reduced graphene covalently functionalized with a polyzwitterionic polymer was  
26 synthesized and shown to display highly stable dispersions in the high salinity brines known as  
27 Arab-D and API at elevated temperatures for 140 days. These findings were well supported by  
28 the noted stability of the dispersions by visual inspection, spectroscopic monitoring and the  
29 relative stability of the particle sizes as determined by DLS. Creating brine stable graphene-  
30 based systems has been a challenge and it is our view the functionalization of graphene basal  
31 plane, as reported herein, represents an attractive and useful platform. One could envision the use  
32 of these functional composites both as a carrier for delivery molecules and as a protective  
33 “wrapper” of nanomaterials. Furthermore, the polymer developed may be applicable in imparting  
34 brine stability to other types of particles or materials. The application of our polyzwitterion-  
35 graphene system is of use in the petroleum industry for reservoir mapping and/or improving oil  
36 recovery. In addition, the functionalization of the prGO nanosheets achieved through diazonium  
37 chemistry for covalent attachment of polymer chains to the basal plane of graphene will likely  
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3 find utility in the development of other graphene-polymer composites for various types of  
4 applications.  
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9 ASSOCIATED CONTENT

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12 **Supporting Information.** Additional supporting information is provided detailing brine stability  
13 of a composite formed with non-covalently associated poly(1-vinylimidazole)-sulfobetaine  
14 polymer, XPS spectra of graphene oxide flocculated in API brine and of the zwitterionic  
15 polymer I – prGO composite, the <sup>1</sup>H NMR spectrum and HSQC of PVIM-co-PVPy, and the  
16 TGA graph of zwitterionic polymer I – prGO composite. This material is available free of charge  
17 via the Internet at <http://pubs.acs.org>.  
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41 **Author Contributions**

42  
43  
44 The manuscript was written through contributions of all authors. All authors have given approval  
45 to the final version of the manuscript. ‡These authors contributed equally.  
46  
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