

1 Formulation of Polymers from Locally Sourced Polysaccharides in 2 Polymer floodng 3 4

5 ABSTRACT

6 The oil industry is experiencing a paradigm shift where the use of green chemicals is been
7 encourage in order to address environmental issues associated with the use of synthetic
8 chemicals as well as the fact that most of these synthetic polymers like hydrolysed
9 polyacrylamide which is used to reduce the mobility of water in enhanced oil recovery; are
10 imported chemicals. Thus, this brings the need to locally source for polymers that are viable
11 so as to increase indigenous production for the oil industry.

12 Gum Arabic is a viscosifier mostly found in the northern part of Nigeria. Different
13 concentrations of the Gum Arabic were analysed as to study their rheology as well as the
14 effect of salinity on them which will determine their degree of resistance as this is a criteria
15 for polymer flooding. However, the stability of Gum Arabic was further enhanced by the
16 introduction of Carboxyl Methyl Cellulose (CMC) at varying concentration to determine its
17 effect on the solution viscosity. From the results, it can be concluded that increased viscosity
18 was as a result of the modification of Gum Arabic by CMC and this could be related to
19 increase bonding with CMC.

20
21 Keywords: Gum Arabic; CarboxylMethyl Cellulose (CMC); Polymer; Viscosity; Salinity.
22

23 INTRODUCTION

24 Polymer flooding has been carried out for the past 40 years in many marginal oil fields and
25 its effectiveness has proved to be successful in several fields. The general expectation from
26 polymer flooding is to obtain about 50% ultimate recovery with averagely 15 to 20%
27 incremental recovery over secondary water flooding process (Rellegadla, 2017). Both
28 naturally derived polymers like xanthan gum and synthetic polymers such as the partially
29 hydrolyzed polyacrylamide (HPAM) have been used basically for the purpose of viscosifying
30 water for polymer flooding. Typical synthetic polymers are partially hydrolyzed
31 polyacrylamide (HPAM) and its derivatives have been used for most large-scale field
32 production mostly because it is less costly (Chang, 2011). The commercial bio-polymer used
33 in oilfield application but not frequently used like the HPAM due to its higher cost is xanthan
34 gum (Sun, 2012).

35 HPAM in produced water (Back produced water) after polymer flooding in oilfield causes
36 serious environmental problems such as difficulty in oil - water separation; the treatment of
37 back produced water from polymer flooding (PWPF) is more difficult to separate than oily
38 wastewater without HPAM (Zhang, 2010; Bao, 2010; Deng, 2002) because the HPAM
39 residual component dissolved in water increases the viscosity of wastewater and also HPAM
40 is equally absorbed onto the oil/water interface, making the separation process much more
41 difficult to attain (Duan, 2014).

42 Chemical cost of a polymer flooding process is a function of the polymer selected for
43 flooding. For instance, although chemical cost as well as the treatment cost is said to be
44 higher for xanthan gum solutions compared to polyacrylamide solutions, Xanthan's cost is
45 stable when compared to the fluctuating cost of polyacrylamide polymer. The polyacrylamide
46 is actually synthesised from petroleum products and their costs in the market are very
47 sensitive to the crude oil prices. (Rellegadla, 2017). Thus, there is need to manufacture shear
48 resistant, also temperature resistant chemicals, as well as environmentally friendly

49 biopolymers that are less costly than xanthan gum as this is a sure way of generating more
50 recovery while reducing cost.

51 Gum Arabic is presently one of the oldest polysaccharides and mostly found in the northern
52 part of Nigeria also known as *Acacia Senegal*. It is produced as tear-drop-shaped globules
53 exudates from bark wounds of Acacia trees (Glicksman, 1973). Due to the presence of ionic
54 charges on the backbone of the polymer chains, the viscosity of solutions of gum Arabic is
55 based on changes in pH. Viscosity is low at low and also at high pH and reaches a maximum
56 at about a pH of 6-8. It occurs majorly as a mixture of calcium magnesium and potassium
57 salts of arabic acid and is composed of the following carbohydrates, this include: galactose,
58 arabinopyranose, arabinofuranose, rhamnose, glucuronic acid and 4-0 methyl glucuronic
59 (Anderson, 1966). The gum is a highly water soluble polysaccharide. It is principally used in
60 the food and pharmaceutical industries as stabilizer, thickener, suspending and binding agent
61 in the manufacture of confections, dairy products, beverages, cotton-seed oil emulsion and
62 tablets (Nahla, 2000). The composition of sugars within Gum Arabic is shown in the
63 Equation 1.

64
65 Carboxyl methyl cellulose (CMC) is the most popular and cheapest cellulose derivative, It is
66 an anionic and also a water-soluble natural polymer that is well known as a safe and
67 biodegradable polymer, which is widely used in the food industries as food additives, oil
68 exploration and paper, textile industries e.t.c due to its high viscosity (Ibrahim, 2014). CMC
69 is synthesize by reacting cellulose with sodium hydroxide in the presence of sodium
70 chloroacetate.

71 In line with Nigerian Oil and Gas Industry Content Development Act, 2010 which seeks to
72 increase indigenous participation in the oil and industry by prescribing minimum threshold
73 for the use of local services and materials as well as promoting the transfer of technology and
74 skills to Nigerian staff and labour in the industry, this work investigates the use of Gum
75 Arabic (locally sourced) as a suitable polymer in enhanced oil recovery while CMC was
76 added to determine the effect on its stability at increased water salinity.

77 MATERIALS AND METHOD

78 In this analysis, different concentrations of Gum Arabic (Figure 1) from 10,000ppm,
79 30,000ppm to 50,000ppm were dissolved using 500ml of water. The solution was stirred
80 gently to achieved homogeneity in order to avoid the formation of fish eye, this was then
81 allowed to hydrate for a period of 24hrs. Rheological characterisation was carried out using
82 Fann Viscometer to determine the rheology at different Speeds from (600, 300, 200, 100 6)
83 rpm to 3rpm. The stability of the solutions were further analysed using NaCl (1wt%). The
84 concentration of CMC utilized in the formulation was increased from 1wt% to 1.4wt% to
85 study the effect of CMC on the viscosity with respect to salinity after another 24hrs. The
86 rheological study equally captured the investigation of CMC alone as well as when blended
87 with Gum Arabic



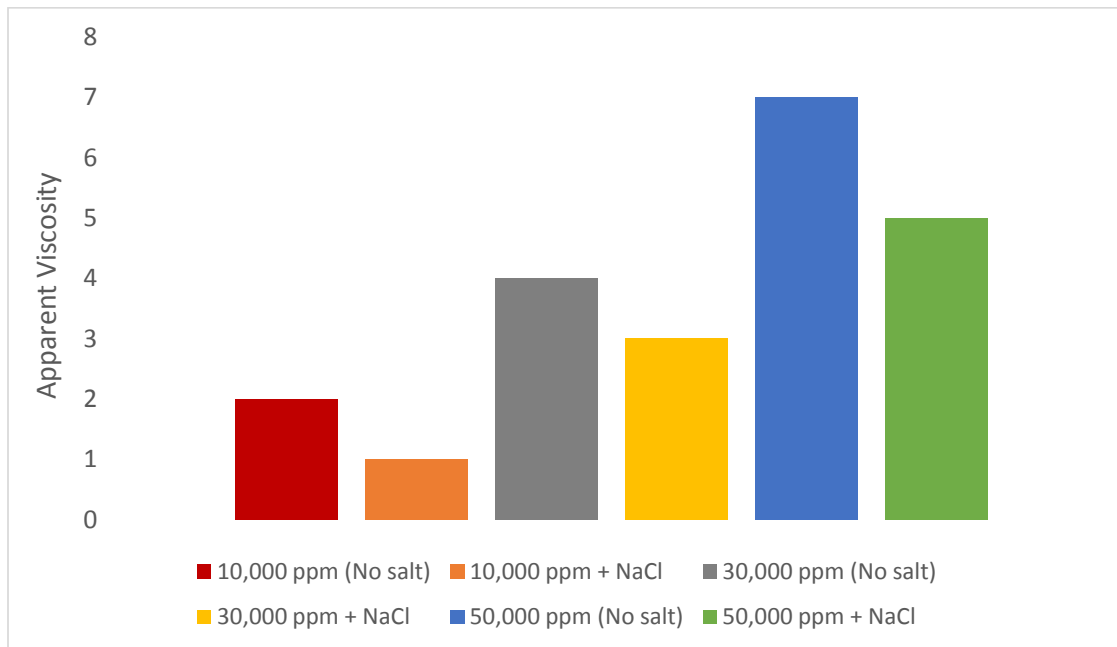
Figure 1: Gum Arabic

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90 RESULTS AND DISCUSSION

91 From Figure 2, it is obvious that increasing the Gum Arabic's concentration improved the
 92 solution's viscosity at higher concentration of 50,000ppm just like some other
 93 polysaccharides like Xanthan gum, Guar gum e.t.c that show very good rheology at
 94 increasing concentrations (Chatterji, 1981; Eiroboyi, 2018). Though, Gum Arabic's viscosity
 95 did not show much appreciable rheology at low concentration of the gum alone, this could be
 96 as a result of the nature of its molecular structure. Also, the effect of salt affected the
 97 viscosity, this is because of the fact that the gum is polyelectrolyte hence its interaction with
 98 NaCl.



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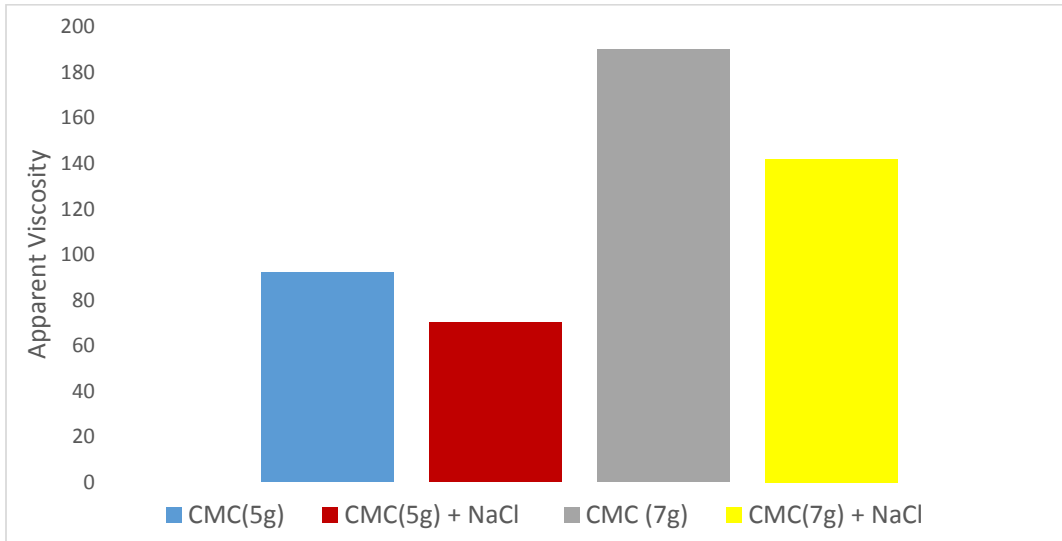
Figure 2: The Effect of salinity on Gum Arabic at increasing concentration

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101 Figure 3 displays the rheological behaviour of Carboxymethyl Cellulose at increasing
 102 concentration as well as in the presence of NaCl. However, in this case it was used an
 103 additive in the formulation. The results show that 1wt% of CMC was very viscous even more
 104 viscous at increasing concentration of 1.4wt%. This particular analysis was necessary to

105 actually ascertain if there was synergy between the polymers after blending. Both 1wt% and
106 1.4wt% reflected reduction in viscosity in the presence of 1wt% NaCl.

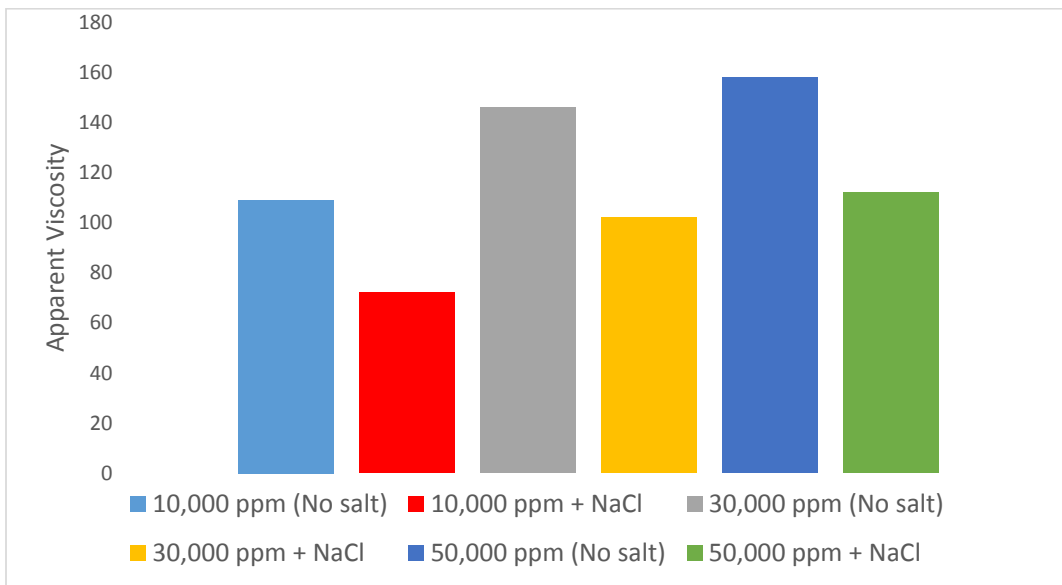
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Figure 3: The effect of salinity on CMC at increasing concentration

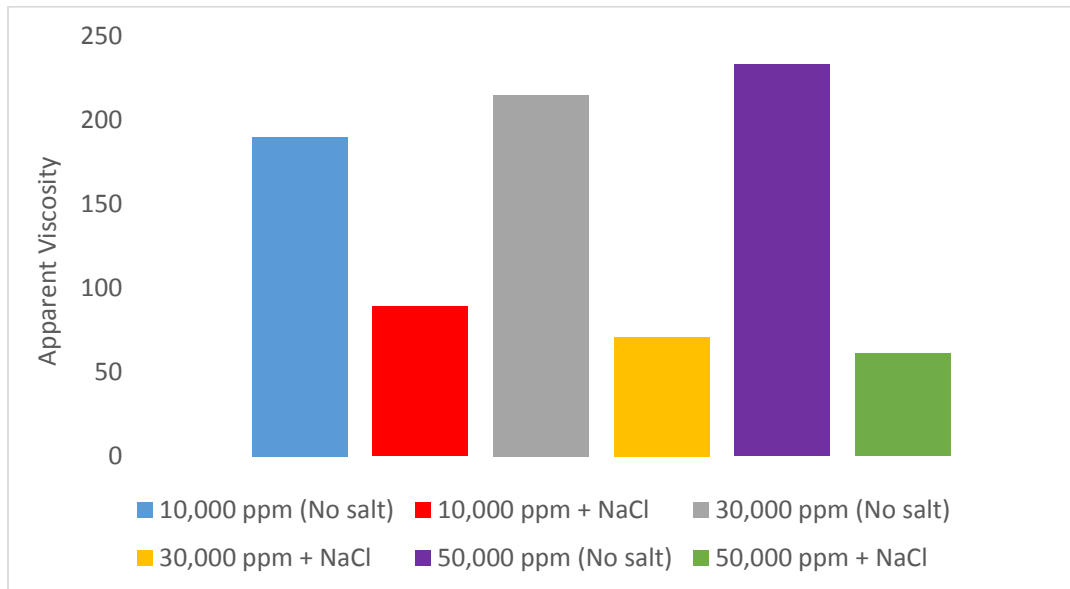


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111 Figure 4: The Effect of salinity on a blend of Gum Arabic at increasing concentration

112 and 1wt% of CMC

113 The presence of CMC in the solution strongly interacts with Gum Arabic solution increasing
114 the viscosity considerably. From Figure 4, 50,000ppm reflected the highest viscosity than
115 other lower concentrations, this could be as a result of increased intermolecular entanglement
116 from both the molecular chains of Gum Arabic and CMC. When compared with the viscosity
117 of the gum alone (Figure 2) and the viscosity of CMC alone (Figure 3), the resultant blend in
118 Figure 4 displayed synergy upon blending. Although, the reduction in viscosity based on the
119 effect of salinity was equally obvious, this is because of the nature of the ionic status of both
120 polymer chains.

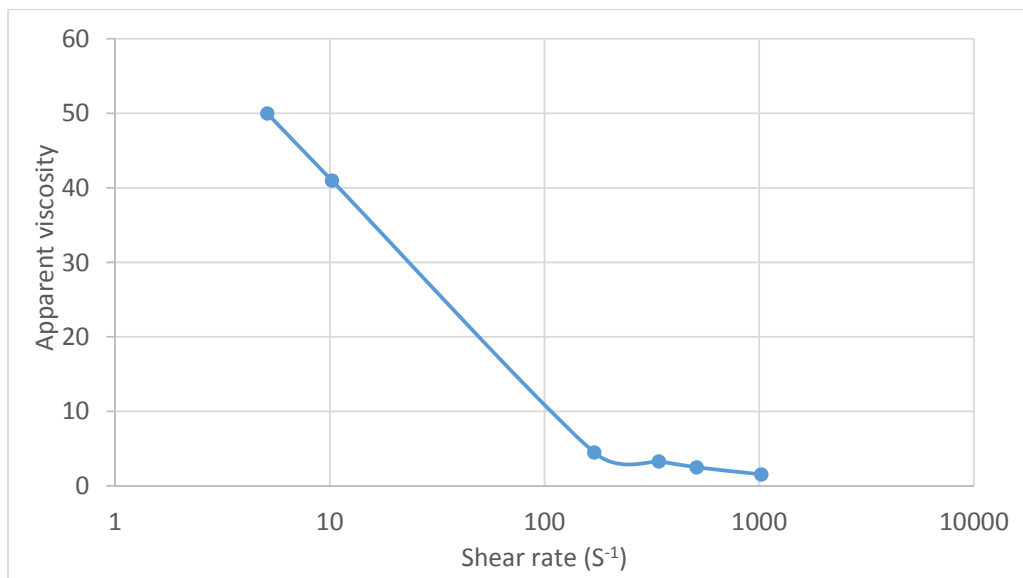


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122 Figure 5: The Effect of salinity on a blend of Gum Arabic at increasing concentration
 123 and 1.4 wt% of CMC

124 The presence of increasing concentration of 1.4wt% of CMC shown in Figure 5 without the
 125 influence of salinity increased the solution's viscosity more than that of 1wt% CMC.
 126 However, the resistance provided by Gum Arabic concentration did not improve when the
 127 concentration increased. This behaviour could be related to the fact that the presence of
 128 increased CMC concentration increased the anions present within the solution such that in the
 129 presence of NaCl, there was increased reaction with NaCl, thereby reducing the electrostatic
 130 repulsion increasingly on the polymer chains which eventually decreased the viscosity.

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133 Figure 6: Viscosity-shear rate behaviour

134 Figure 6 depicts that the viscosity reduces with increasing shear rate, this reflects Gum
135 Arabic's shear thinning behaviour.

136

137 CONCLUSION

138 During polymer flooding, one of the characteristics of a polymer is its ability to remain stable
139 in the presence of high salinity as such the injected solution must maintain its viscosity for a
140 longer duration. From the experimental analysis,

- 141 • It is obvious that Gum Arabic at increasing concentration with CMC was able to produce
142 increased viscosity which is a requirement in polymer flooding though Gum Arabic as a
143 polymer alone is a low viscous polymer.
- 144 • Gum Arabic with CMC especially at increasing concentration of CMC and Gum Arabic
145 solution did not produce adequately the stability against salinity for the solution.
- 146 • The experiment analysis proved that attraction and repulsion of molecular charges are
147 responsible for the resultant solution viscosity especially because both polymers are
148 ionic.
- 149 • This reduction could be related to the increase in anions from the polymers in solution
150 because both of them are polyelectrolytes and as such would interact strongly with the
151 cations of NaCl solutions thereby decreasing the electrostatic repulsion of the polymer
152 chains in solution.
- 153 • In the use of Gum Arabic, additives that are non-ionic would suffice better than ionic
154 polymers in the face of high salinity.

155

156 NOMENCLATURE

157 CMC – CarboxylMethyl Cellulose

158 HPAM – Hydrolysed Polyacrylamide

159 NaCl – Sodium Chloride Salt

160 PPM – Pounds per million

161 Cp – Centipoise

162 PWPF - Produced water from polymer flooding

163 REFERENCES

164 Anderson, D. M. W and Karamalla, K., (1966), Studies on uronic acid materials, Part xiii.
165 New composition on veacia gums exudates. Journal of the Chemical Society, 762764

166

167 Bao, M., Chen Q., Li Y., and Jiang G., (2010), Biodegradation of partially hydrolyzed
168 polyacrylamide by bacteria isolated from production water after polymer flooding in
169 an oil field. Journal of Hazardous Materials, 184 105–110.

170

171 Chang, H. G., (2011), Scientific research and field applications of polymer flooding in heavy
172 oil recovery. J Petrol Explor Prod Technol, 1:65–70. DOI 10.1007/s13202-011-0014-
173 6.

174

- 175 Chatterji, J., and Borchardt, J., (1981), Applications of water-soluble polymers in the oil
176 field. *J Pet Technol*, 33:2,042–042,056. doi:10.2118/9288-PA
- 177 Deng, S., Bai, R., Chen, J.P., Jiang, Z., Yu, G., Zhou, F., and Chen, Z., (2002), Produced
178 water from polymer flooding process in crude oil extraction: characterization and
179 treatment by a novel crossflow oil–water separator. *Sep. Purif. Technol.*, 29 207–216.
180
- 181 Duan, M., (2014), Treatment of wastewater produced from polymer flooding using
182 polyoxyalkylated polyethyleneimine. *Separation and Purification Technology*, 133
183 160–16
184
- 185 Eiroboyi, I., and Ikiensikimama, S. S., (2018), Improved Water Soluble Polymers for
186 Chemical Flooding. SPE 193489, Presented at Nigeria Annual International
187 Conference and Exhibition, Lagos, Nigeria 6-8 August.
188
- 189 Glicksman, M., and Sand, R. E., (1973), Gum Arabic. In: *Industrial gums* (Whistler RL ed).
190 New York Academic Press, NY, USA, pp. 197-263
- 191 Ibrahim, S. M., Mousaa, I. M., and Ibrahim, M. S., (2014), Characterization of gamma
192 irradiated plasticized carboxymethyl cellulose (CMC)/gum arabic (GA) polymer
193 blends as absorbents for dyestuffs. *Indian Academy of Sciences, Bull. Mater. Sci.*,
194 Vol. 37, No. 3, pp. 603–608.
- 195 Nahla, M. M., (2000), *Physico-Chemical Study on Guar Gum*. A Thesis Submitted for the
196 M.Sc. Degree in Chemistry Department of Chemistry Faculty of Science, University
197 of Khartoum.
- 198 Rellegadla, S., Prajapat, G., and Agrawal, A., (2017), Polymers for enhanced oil recovery:
199 fundamentals and selection criteria. *Appl Microbiol Biotechnol*, DOI
200 10.1007/s00253-017-8307-4.
- 201 Sun, Y., Laila, S., and Baojun, B., (2012), Measurement and Impact Factors of Polymer
202 Rheology in Porous Media. Petroleum Engineering Program, Missouri University of
203 Science and Technology, Rolla, Missouri, USA.
204
- 205 Zhang, Y. Q., Gao B.Y., and Lu, L., (2010), Treatment of produced water from polymer
206 flooding in oil production by the combined method of hydrolysis acidification
207 dynamic membrane bioreactor–coagulation process. *J. Pet. Sci. Technol*, 74 14–1.
208