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THE PH INFLUENCE ON THE CARBOPOL® SOLUTIONS STABILIZATION BY ADDITION OF NAOH

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Abstract. *Carbopol® solutions are widely used in experimental investigations as fluid with ideal viscoplastic characteristics. These solutions have an excellent potential for mimicking the gel materials' viscoplastic behavior in different industrial processes, such as the oil and gas drilling fluid used in the oil and gas industry, explaining its vast application in fluid dynamics and rheology research projects. Nevertheless, the use of Carbopol® has been limited due to the complexity in preparing large uniform samples, presenting difficulties in assessing its rheology and long stabilization times. The control of the pH level during the preparation of these solutions is essential to guarantee a proper stabilization of the rheological properties and increase the fluid's lifetime, allowing a reduction of time, cost, and resource waste. This paper concerns the pH value's behavior during its formulation stage, in which NaOH is added to stabilize the solution. As described by other authors and witnessed by previous works, a nonlinear relationship is depicted between the pH and the NaOH concentration until the stabilization, achieving the neutral value of 7. In such a pH zone, rheological parameters can be better controlled for more extended periods. Three Carbopol® solutions with different concentrations were prepared, and their pHs were measured and monitored until neutrality. The aim is to understand and clarify this phenomenon in order to have better control of the process. The obtained results made it possible to enlarge the analysis of some variables directly involved in the pH evolution and may influence its stability periods, such as NaOH solution concentration, rate of addition, and formulation time. By chemical studies on Carbopol® nature and rheological tests, it was possible to justify such phenomenon and support the conclusions achieved. Finally, an experimental correlation was proposed to predict and speed up the neutralization process for future formulations of Carbopol® solutions, standardizing a more efficient one, therefore, a more environmentally friendly one.*

Keywords: *Carbopol® solutions, Viscoplastic fluids, pH behavior, Oil & gas.*

1. INTRODUCTION

In the fluid dynamics area, one of the subjects that have received particular interest and attention by researchers is the usage of non-Newtonian fluids and their application in industrial processes. Such group of fluids presents a non linear steady state flow curve, meaning that the viscosity varies according to the shear stress applied (Chhabra and Richarson, 2011). One crucial aspect that has been considered of great importance and profoundly researched is the viscoplasticity of a fluid (Barnes and Walters, 1985), which can be observed in drilling fluids for oil and gas extraction or even in the cosmetic industry (Wu *et al*, 2006; Weber *et al*, 2012; Ubaid *et al*, 2016). Therefore, these fluids are frequently used for performing flow restarting, sedimentation, and particles transportation.

Unfortunately, formulating fluids with the required characteristics is not a simple task. Many of them demand a long stabilization process since they are produced after polymer dispersion and neutralization in water. Carbopol® and Laponite are examples of materials that allow flow visualization studies due to their transparency (Younes *et al*, 2021; Garg *et al*, 2021). To control the fluid formulation and achieve the required properties, it is necessary to understand the interaction between the polymer and stabilizer solutions and their effect on pH, reaction time, stability time, and rheological properties. Typically, a formulation process of Carbopol® solutions takes around 15 days. In some cases, are necessary 30 days to obtain a pH and rheological stabilized solution.

It is already known that the solution's pH plays a significant role in understanding the fluid formulation, how rheological parameters will behave, and for how long will such characteristics be stable (Di Giussepe *et al*, 2015). Therefore, the subject of this paper is to formulate an equation to control the stabilization process through the analysis of pH behavior and the evolution of rheological properties, aiming to reduce the time of preparation, costs, and resource waste.

2. CARBOPOL®

Carbopol® trademark by Lubrizol Corporation represents a group of synthetic polymers of acrylic acid with high molecular weight. These polymers are hydrophilic and present a crosslinked structure.

When in powdery, the chains are highly coiled and the particles have an average diameter of 5 to 15 microns. When in contact with water, the structure begins to uncoil and swells, increasing its volume by 1000 times, which explains its initial thickening property (Kim *et al*, 2003). To fully neutralize this polymer in solutions, it is necessary a reaction with a base, most likely NaOH, will convert the acidic into a salt and uncoil due to electrostatic repulsion. A schematic representation of the thickening process is presented in Figure 1.

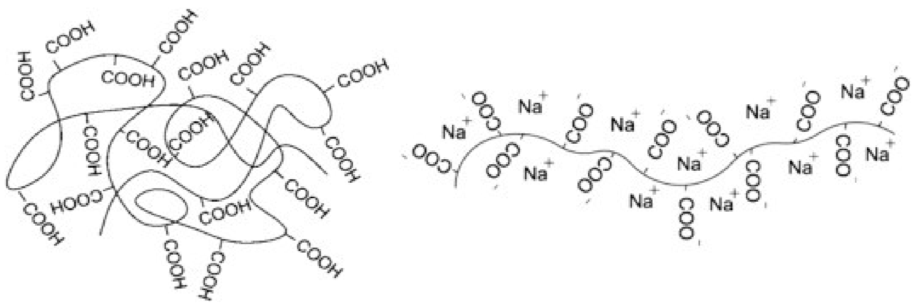

Figure 1. The thickening steps of Carbopol® gel (Shafiei, et al., 2018).

The procedure of neutralization can be performed by multiple solutions, being NaOH the most common one. According to suppliers, using NaOH 18%wt solution, it is possible to neutralize Carbopol® with a 2.3 to 1 mass ratio with the polymer.

The time for stabilization is highly dependent on the quantity of gel, varying from minutes for small portions to weeks for preparations on a large scale. Another crucial characteristic of the fluid that explains its rheological properties is the pH value. It is possible to control the desired fluid parameters and for how long they will remain stable by controlling the pH. Figure 2 shows the effect of pH on the solution viscosity.

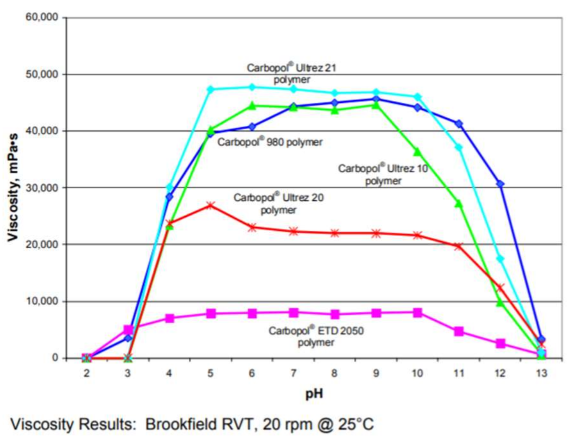

Figure 2. Carbopol® Polymers Viscosity vs. pH (0.5 wt% TS Concentration) (Lubrizol, 2009).

Another example to illustrate this influence is presented in Fig. 3, where Carbopol® samples with the same polymeric concentration 0.2% wt present a completely different behavior when analyzing rheological properties and its characterization:

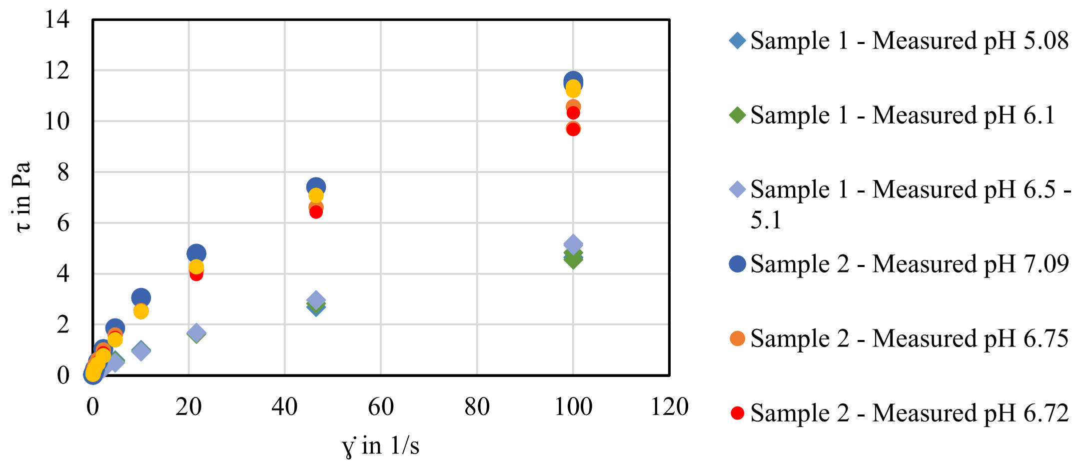

Figure 3. Flow curves behavior for 2 Carbopol® solutions. Each solution was neutralized in different pH values.

Figure 3 shows the strong influence of the pH in the behavior of the rheological properties. Sample 1 was neutralized in a 5-6 pH range, on the other hand, sample 2 was neutralized near pH 7. The difference in the pH is least than 0.5 between the solutions. Nevertheless, the influence of the pH on the final rheological properties are depicted by low shear stresses for the same deformations. The latter suggests an abrupt variation of the rheological properties when the neutral pH is reached. Since a basic solution performs the neutralization, it is expected that, by controlling this process through pH measurements, it is possible to achieve desired characteristics of the fluid.

3. FLUID PREPARATION

For this purpose, three different Carbopol® 940 solutions were prepared. The neutralizer used was a NaOH 18%wt solution since it is the most common, and a NaOH solution easy to access. The gels had different objectives and applications; therefore, they had different quantities and also different Carbopol® concentrations.

Since the fluids were prepared to be also used by further experimental tests, large amounts were required. For their neutralization, it was necessary about two weeks.

To prepare the fluids, a standard procedure was adopted. Initially, knowing the percentage of Carbopol® needed, the precise mass of powdery was separated. Due to storage, it was necessary to sift the powder and separate particles that stuck together, forming a larger agglomerate. In parallel, the water was placed inside a mixing tank and the rotor began to rotate, with an average speed of 17 rpm. Carbopol® powdery was then dispersed in water, adding gradually small amounts. The initial pH is in the range of 3 to 4, but high viscosity can be achieved at pH levels from 6.0 up to 9.0 when it begins to decrease. After one day of mixing, the solution achieved a pH near 3.5.

At this moment, the addition of NaOH solution began. A volume from 3 to 12 ml was added on a daily basis until the gel achieved a stable pH of 7. The evolution of pH is shown in Figures 4 to 6 for the different solutions.

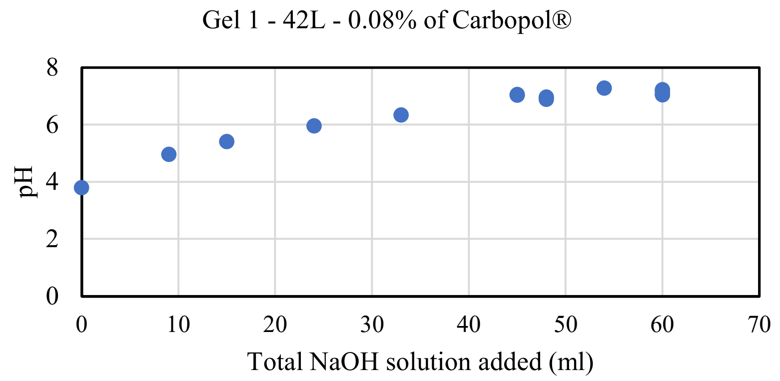

Figure 4. pH evolution after NaOH solution addition in Gel 1.

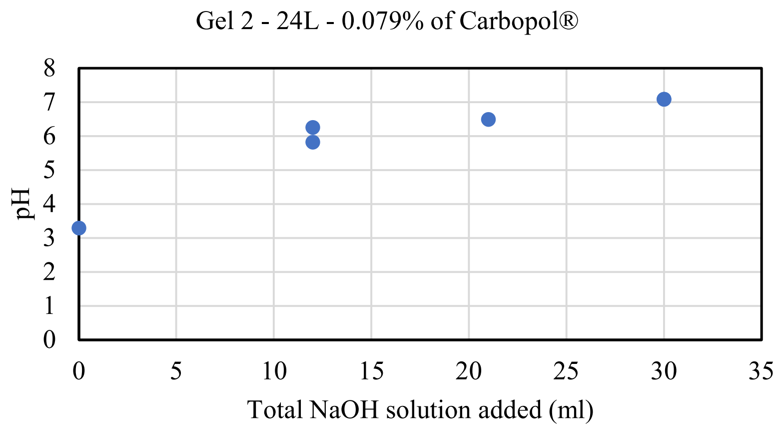

Figure 5. pH evolution after NaOH solution addition in Gel 2.

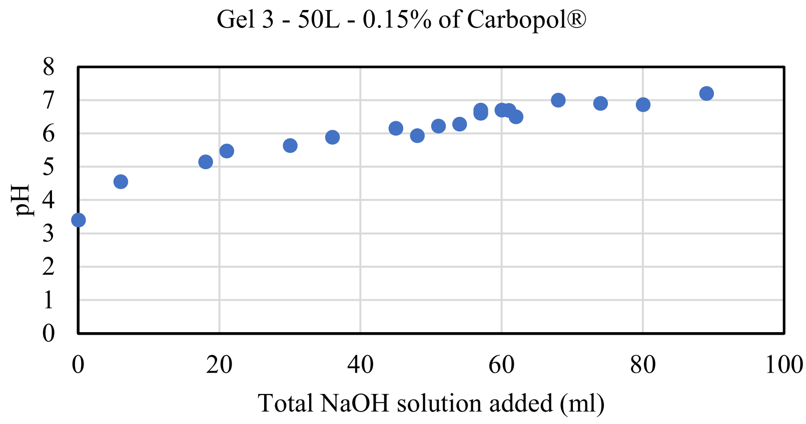

Figure 6. pH evolution after NaOH solution addition in Gel 3.

Figures 4 to 6 show that in a pH zone between 6 and 7, more significant amounts of NaOH are required to raise pH and finally stabilize at 7. What also happens at such zone is the instability of the gel, which means pH measures are unstable and present a large variability. To illustrate it, when the measure begins by inserting a pH meter inside a beaker containing the gel, pH values are high but keeps on decreasing. When it does not decrease anymore, it is considered to reach stability and that is the value considered.

This is a frequent phenomenon presented in such a formulation. Its explanation lies in the microstructural properties of the polymer and its interaction with water. The region of the polymer in contact with the basis has a significantly higher viscosity, which difficulties the diffusion of NaOH through the molecules (Gutowski, 2012).

4. FURTHER CORRELATIONS

Since the formulated gels present a different composition, it is possible to understand the behavior of pH during the formulation process and how it is affected by different variables.

One interesting analysis refers to the mass ratio of NaOH in the total fluid (MRf). It can be obtained by knowing the volume of NaOH solution (V_{NaOH}), the solution density (ρ_s), the NaOH concentration in the solution ($\%wt_{NaOH}$) and total mass (M) as the Eq. 1:

$$MRf = \frac{V_{NaOH}\rho_s\%wt_{NaOH}}{M} \quad (1)$$

Since the total mass can be obtained by Eq. 2 as the addition of all components:

$$M = M_w + M_c + V_{NaOH}\rho_s\%wt_{NaOH} \quad (2)$$

where M_w is the mass of water and M_c the mass of Carbopol®. Therefore, the following relationships depicted in Figure 7 were obtained.

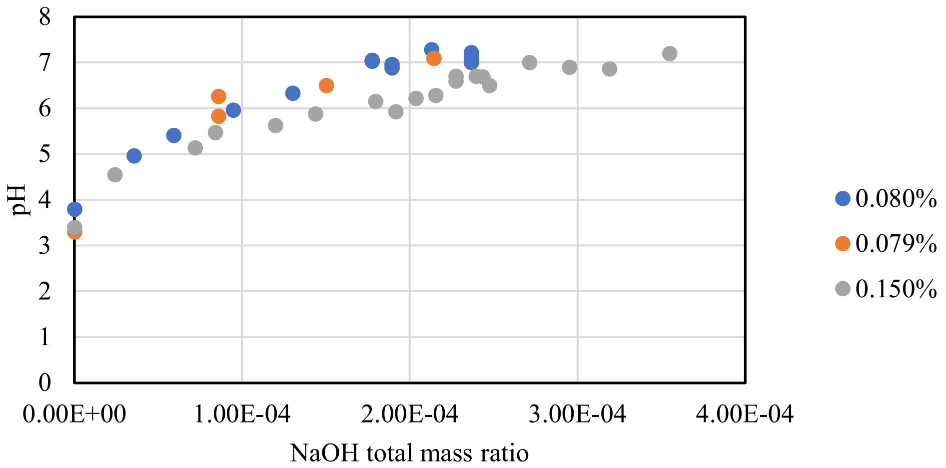

Figure 7. MRf pH relationship for different Carbopol® solutions concentrations.

Based on this data, it is possible to go further in the analysis, calculating the NaOH-Carbopol® mass ratio (MR_c) by Eq. 3 and knowing the Carbopol® concentration($C_{Carbopol}$):

$$MR_c = \frac{MRf}{C_{Carbopol}} = \frac{V_{NaOH}\rho_s\%wt_{NaOH}}{M_c} \quad (3)$$

where the results are the following in Figure 8.

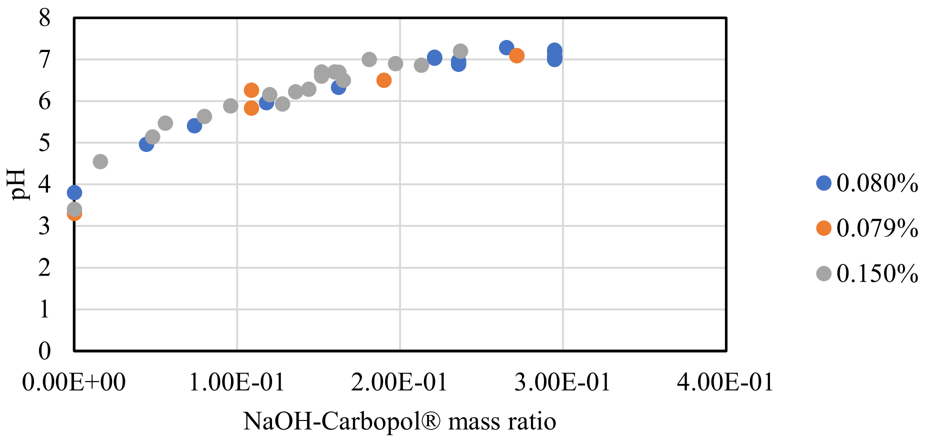

Figure 8. pH and MR_c correlation.

Figure 8 presentes a trend for all the fluids, then, it is possible to affirm that all the solutions present a similar pH pattern. The originally indicated 2.3 ratio (18% NaOH solution/Carbopol®), suggested by the manufacturer, showed to be more than enough to neutralize the gel since it was already achieved with a 1.1 ratio (18% NaOH solution/Carbopol®). This curve can be used to control the pH of a gel to perform tests that have the aim, for example, to research the pH effect on the viscosity of the fluid.

Therefore, the following expression is an essential tool to select the quantity of NaOH to be added to achieve the desired pH, Carbopol® concentration, and volume:

$$pH = y_0 + A_1 e^{\frac{MR_c}{t_1}} \tag{4}$$

where the initial pH is expressed by A_1, while the pH value, which indicates the fluids neutrality, is represented by y_0 and t_1 indicates the pH growing rate.

Table 1. Parameters obtained in curve fitting.

Adjusting Parameters	Value
y_0	7.33558
A_1	-3.71222
t_1	-0.10172

The plot of the values and the Eq. 4 curve is in Fig. 9, being A the MR_c and B the pH:

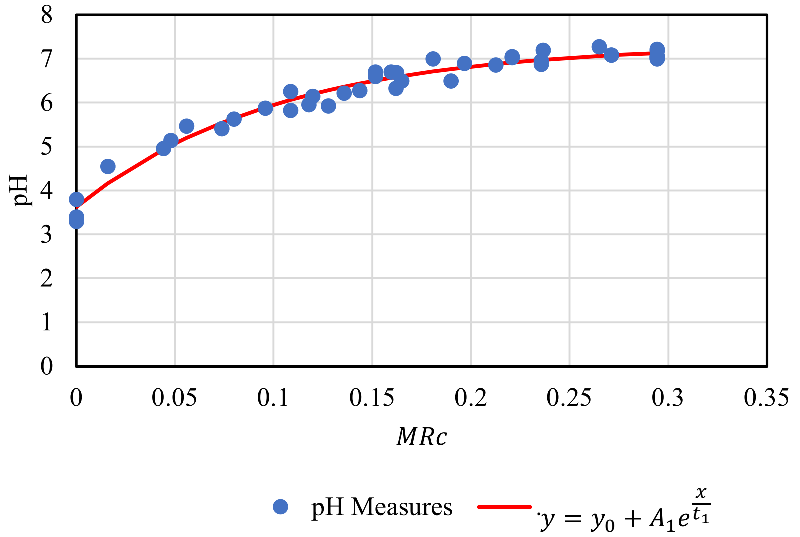

Figure 9. Adjusting curve and original points.

The curve fitting was performed considering all the pH measures for the different fluids formulated. It is possible to correlate the constant of Eq. 4 and the material parameters through a fitting process. Table 1 summarizes the fitted parameters for Eq. 4. For all the cases the y_0 value was fixed in order to guarantee neutral pH as references for the neutralization process.

5. VALIDATIONS

After a proper pH MR_c relation is achieved, the following step is to validate it by formulating new fluids with different pH goals and Carbopol® concentrations. It was also possible to analyze how these characteristics affect the rheological properties and correlate with the formulation process. Table 2 indicates the compositions of the formulated fluids.

Table 2. Characteristics of formulated Carbopol® solutions.

Sample	**Volume (ml)**	**Carbopol® concentration (%)**	**pH target**	$\boldsymbol{MR_c}$
A	600	0.098%	6	0.09
B	600	0.300%	7	0.243874
C	600	0.201%	7	0.30
D	600	0.201%	6	0.104

The adopted process of the formulation was the same for every sample. It consists of adding the necessary amount of NaOH solution and Carbopol® in a recipient containing water, mixed at a constant speed. The mixing phase lasts 30 minutes and the speed may vary according to the fluid and how it responds to the mixing, whether it presents bubbles or whether it is already gelled.

The measures of pH performed by a pH-meter, had the same behavior as the last ones, presenting an instability for values below 7. The results showed that mixing the fluid before measuring pH to homogenize it helped its stabilization, even though it did not prevent the instability from occurring.

Measures are presented in the following Table 3. The interval between measurements varied in the range of one to three days, depending on the sample. It was possible to notice that any fluid presented aging effects, since after mixing the characteristics were similar. When more than one value is presented for a single measure, it means the instability occurred in such an interval of pH.

Table 3. pH measures for formulated samples.

Sample	**Target pH**	**Measure 1**	**Measure 2**	**Measure 3**	**Measure 4**
A	6	5.4	6.2 - 5.7	6.1	6.1 - 5.1
B	7	6.1	5.74	5.8	
C	7	7.09	6.75	6.72	6.77
D	6	5.08	6.1	6.1 - 5.1	

What is possible to confirm is that, despite the instability, the reached values were close enough (averaging 5.89% of deviation with target) to the target for samples A, C, and D. Sample B, the most gelled one, always presented a value below target (averaging 16% of the difference with target), most likely explained by the difficulty in stirred all the solution.

6. RHEOLOGICAL PROPERTIES

Analyzing the samples in rheometer allowed us to achieve interesting conclusions on the effect of pH and Carbopol® concentration on the shear stress/shear rate curve. For every pH measured – presented above – a rheometric test was conducted, and the results are presented below. The tests were performed in a ThermoScientific HAAKE MARS-III Rheometer, using a double gap geometry to provide a proper analysis for fluid of low viscosity, such as sample A. They consisted in applying 13 different shear rates, decreasing it sequentially, for 100 seconds each. The shear stress values presented in curves were always the last one for every rate when the steady-state is reached for each shear stress imposed. Figures 10 to 13 present the results for each sample:

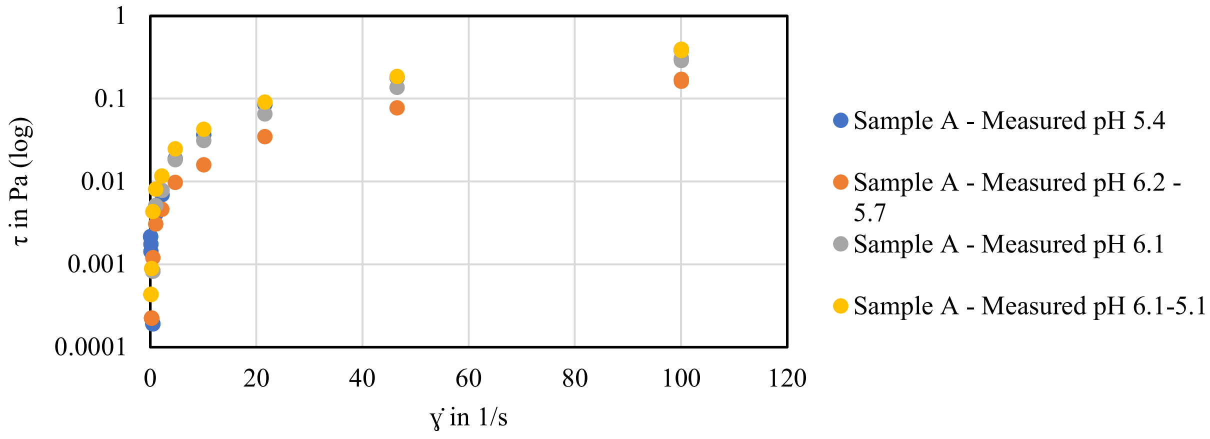

Figure 10. Sample A flow curves.

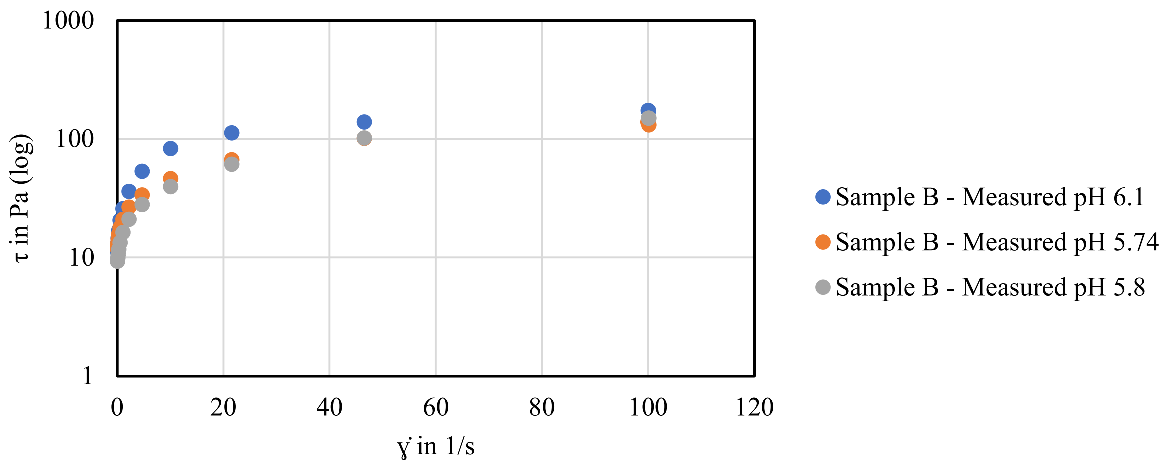

Figure 11. Sample B flow curves.

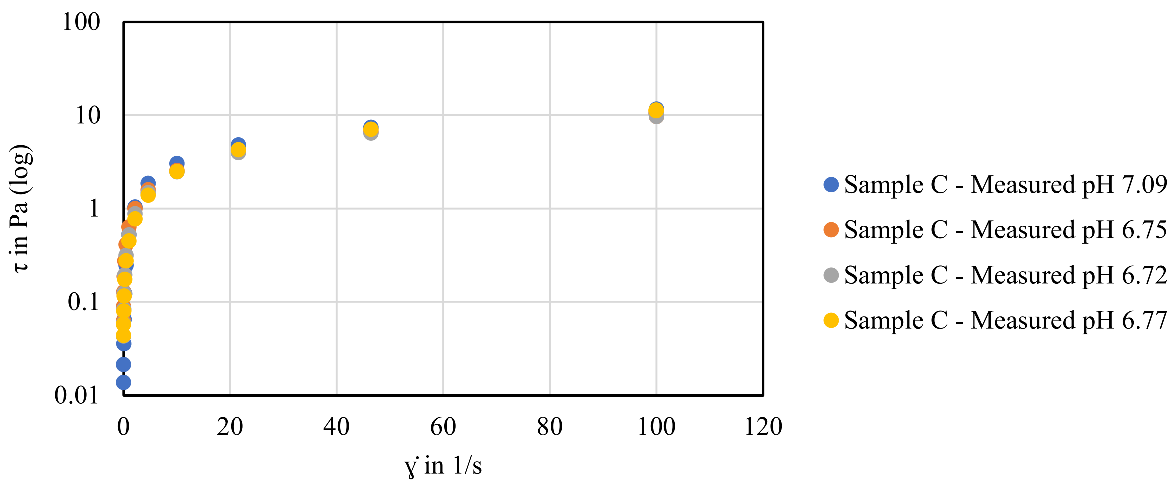

Figure 12. Sample C flow curves.

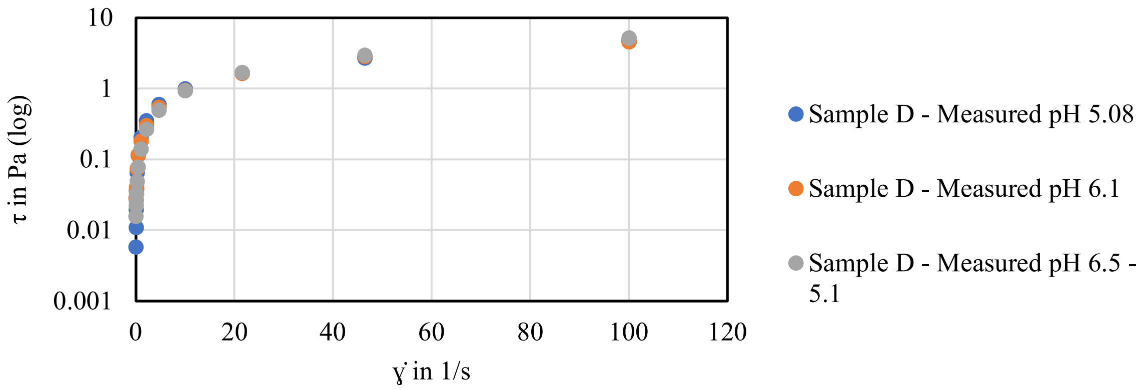

Figure 13. Sample D flow curves.

Figures 10 to13 show different steady flow curves for each solution performed on different days. The variation between the flow curves remains below 5% for each data. Then we can state that a good stabilization of the solution was achieved using the correlation given by Eq. 4. Comparing the samples, some behaviors may be clarified, as done following in Figures 14.

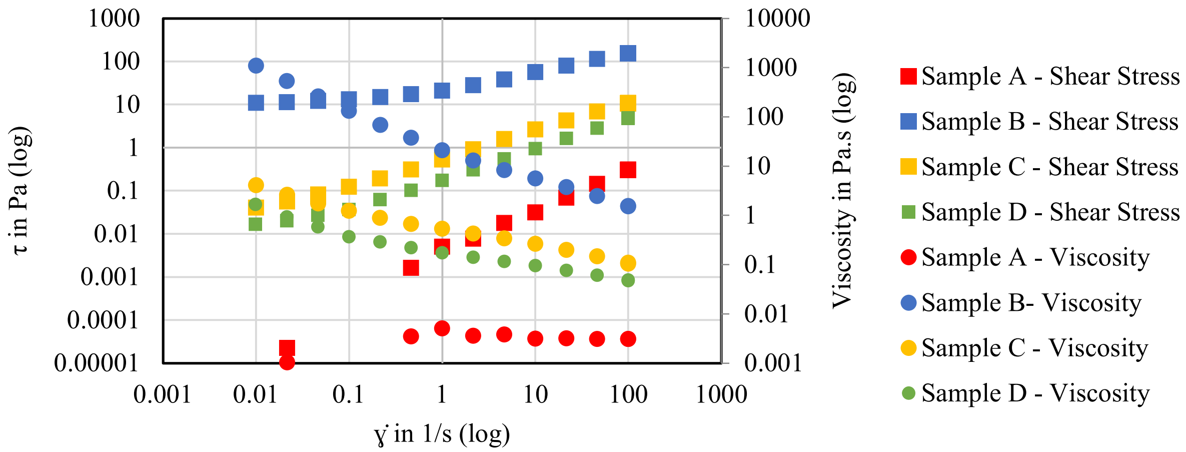

Figure 14. Flow curves and viscosity for samples A, B, C, and D.

Comparing only the effect of pH between two samples of the same Carbopol® concentrations shows how higher pH leads to higher shear stress in the sample. Even analyzing a single sample, this relation is also notable, although the difference in both pH and shear stress are much smaller. This is a clear indicator of how possible it is to use pH as a parameter to predict the characteristics and behavior of the fluid.

By comparing samples of closer pH but with different Carbopol® concentrations, it is possible to observe the vast number of possibilities with this polymer, not only on how great viscosity may be, but also how it behaves, changing from a pseudoplastic behavior to a viscoplastic one. In order to compare and quantify the fluid behavior, a fitting process with the average curves of each sample was performed by a Herschel-Bulkley model, as indicated in Eq. 5. The fitting process was performed by using the software OriginPro 2021.

$$\tau = \tau_0 + K\dot{\gamma}^n \qquad (5)$$

where τ_0 is the characteristically yield stress of viscoplastic fluids, K is the consistency coefficient, and n is the shear-thinning index of the fluid.

Table 4 presents the fitted parameters for each solution by the Herschel Bulkley model (Herschel and Bulkley, 1926). It is possible to observe that solutions A, C, and D do not exhibit yield stress, reducing the Herschel-Bulkley model to a power-law one. For the cases of the samples A and C, a trend to a low value for τ_0 is depicted, however, these values are not representative when compared with the lower resolution of the rheometric apparatus where the rheological tests were performed, then, the τ_0 value lays down in a null value which better adjusts the general trend of the steady-state flow curve data. Nevertheless, all the solutions present a general shear-thinning behavior since a shear thinning index is depicted from the fitting process.

Table 4. Herschel-Bulkley fitting constants.

Sample	τ_0	K	n
A	0	0.0043	0.92
B	7.27	16.25	0.47
C	0	0.65	0.61
D	0	0.18	0.7

7. CONCLUSIONS

To control and adjust characteristics of a non-Newtonian fluid is not as simple as for Newtonian ones. In this case, Carbopol® solutions proved to be highly sensitive to pH changes and the neutralization process. The fluids prepared during this research proved accurate in formulation since they were later used for further experimental and rheological tests. Although the preparation of this gel is complex to understand due to the size and complexity of its polymeric chains, it was possible to properly correlate pH and the added quantity of NaOH to control the properties of the formed gel. In this way, the procedure can be standardized and allows a cost and time reduction for further gels to be formulated.

Furthermore, the objective of reducing formulation time was achieved since the new samples took a maximum of 5 days to be stabilized instead of the original 30 days or more. Although the samples had different volumes, now it is possible to perform only one accurate NaOH addition to achieve the desired fluid. The stability of the samples, proved by low variations in pH measures and stable rheological behavior.

It is possible to affirm that the correlation achieved allowed a more accurate and fast formulation of Carbopol® solutions, saving resources and costs by avoiding the reformulation of samples.

8. ACKNOWLEDGEMENTS

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