Gelation kinetics of colloidal dispersion gels by viscoelastic-rheological methods

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Abstract. Colloidal dispersion gels are one of the methodologies implemented, such as chemical recovery processes, in mature wells, their components are mainly polyacrylamide and aluminum citrate, both aqueous unlike other types of gelling, in this there is an intramolecular process, between the polymer chains and the crosslinker, generating a ball of polyacrylamide of nanometric dimensions. The usual gelling processes increase the viscosity of a fluid because of an increase in the molecular weight of the polymer, but in this case, the viscosity of the fluid decreases to the point of being close to that of the solvent, for this reason a monitoring of its gelation kinetics, in a conventional way is not possible, in view of this problem, this research implements techniques of viscoelastic characterization of fluids, to determine the loss and storage modules $G'$ and $G''$, as well as the phase angle in the time, in order to learn more about the gelling mechanism, as well as to be able to estimate a reaction speed, from the point of view of viscoelastic variables, the results obtained revealed that despite being gelling, there is a decrease in the storage modulus, to a greater extent than the loss modulus, which implies that the material loses elastic properties, that is, from solid to become a material more viscous or liquid. With this information, an equation was proposed that can be used both in the laboratory and in oil field work. In addition to being extended to fluids with similar behaviors, where the interactions between the polymeric chains and their crosslinker generate a decrease in their elastic properties.

1. Introduction
Colloidal dispersion gels (CDG) are systems composed of polyacrylamide and aluminum citrate, the ease of being injected into water makes these systems very versatile and easy to inject, in Colombia, this type of treatment has been injected in fields such as Dina field and Tello field, in the department of Huila, Colombia.

The interactions between polyacrylamide and aluminum citrate, in this type of fluids is an intramolecular crosslinking, unlike other systems where macromolecular networks are formed, colloidal dispersion gels have structures similar to a ball, which even reach the size of nanometers, due to the formation of these structures, are gels of very low viscosity, and for this reason it is difficult to monitor the gelation kinetics and to know the state of the fluid in its injection process, currently a method known as tiorco gel unit (TGU) is used, but it is a very imprecise method, due to the dependence of the determination of a flow, which is not standardized [1-3].

This research work uses rheological methods, specifically viscoelastic, to determine the gelation kinetics of a colloidal dispersion gel, of 400 ppm of polyacrylamide and a 40:1 polymer-crosslinker ratio, this being a common composition for this type of systems. The operations in the field with the injection of CDG, have a lot of complications, because, the operators, don’t know the exact, gelling
behavior of the gel formulation, the rheology method can provide more information about that behavior and resolve the trouble in the field process.

2. Materials and methods
In order to be sure that the components of the gel are adequate, polyacrylamide and aluminum citrate were characterized by infrared spectroscopy, the gels were subsequently prepared, 400 ppm of polyacrylamide with relation polymer - crosslinker of 40:1. The phase angle and modules were determined for this fluid. at room temperature.

2.1. Polymer and crosslinker characterization
The polyacrylamide and aluminum citrate were characterized by infrared (IR) spectroscopy using Bruker Tensor 27 equipment with ATR cell.

2.2. Preparation of gels
Gels with a polyacrylamide concentration of 400 ppm, derived from an initial solution of 5000 ppm, were prepared. They were crosslinked in 40:1 ratio polyacrylamide: aluminum citrate from a 10% solution of aluminum citrate. The gels were prepared in deionized water.

2.3. Viscoelastic characterization
The viscoelastic determinations were made in the Haake Rheostress RS100 rheometer with cone-plate geometry C35 / 4º, at a frequency of 1Hz, and a shear stress of 0.2 Pa. At room temperature. The duration test was 160 hours

3. Results and discussion

3.1. Polymer and crosslinker characterization
As they are two organic molecules, their interaction with infrared radiation allows us to identify characteristic signals for each of the functional groups present in the molecules, Figure 1 shows the infrared spectrum for polyacrylamide, where the corresponding signals can be observed: to the OH group, at 3420 cm$^{-1}$, at 3200 cm$^{-1}$ for the NH bond, at 2930 cm$^{-1}$ for the CH bond, the carbonyl group It is observed in 1670 cm$^{-1}$ and 1130 cm$^{-1}$ corresponding to the C = O link. [4,5].

Figure 2 shows the IR spectrum of aluminum citrate, signal around 3200 cm$^{-1}$ corresponding to the OH group of the alcohol in which the aluminum citrate is dissolved. Between 2000 cm$^{-1}$ y 1500 cm$^{-1}$ are characteristic signals for the COO- group, as well as between 1200 cm$^{-1}$ and 800 cm$^{-1}$ [6,7].

3.2. Colloidal gel preparation
After confirming that the gel components are adequate, an initial solution of 5000 ppm of polyacrylamide is prepared in distilled water, said solution was stirred manually, to avoid influencing the rheological properties of the fluid, later it was added aluminum citrate, keeping a 40: 1 ratio of polymer, with respect to the crosslinker, this mixture was also homogenized manually, and the viscoelastic behavior of the gel was determined, inserting it into the viscometer, without making any type of shear or mechanical stress, to avoid modifying its rheological properties.

3.3. Viscoelastic characterization
What is expected for a gelling or crosslinking process is that its storage modulus G ′ increases because the material would have a more elastic behavior, getting closer to the behavior of a solid [8-12]. And that its viscous component G ″, the loss module and more related to a liquid behavior. [8-12]. But contrary to this as seen in Figure 3, for the CDG, the storage modulus decreases, up to 140 hours, where both modules are already stabilized, which implies that the fluid changes its viscoelastic properties, becoming a material more liquid with respect to its initial properties. Although the loss modulus also decreases, this change is not marked.
The behavior of intramolecularly cross-linked polyacrylamide can be compared with the behavior of this type of polymers in solutions with a high concentration of chlorides [13]. Where the high salinity, generate an encapsulation of the polymeric chains, drastically decreasing their viscosity. It could then be said that both cases, both for intramolecular crosslinking and for high salinity conditions, the polymer chain acquires a conformation in which, being in solution, the fluids behave more like a liquid than a solid, as they present a decrease in G'.

On the other hand, the viscoelastic behavior of Figure 3 allows observing a progressive change over time, even allowing the behavior of the phase angle and G' to be graphically correlated with that of a pseudo-first order reaction kinetics and if we take into account that one of the reactants is in a very high proportion, with respect to the other (polymer: crosslinker, 40: 1) [14]. A treatment of the curves can be carried out, such as the one carried out for this type of kinetic behavior, applying the natural logarithm, shown in Figure 4.

Figure 4 shows the behavior of the ln (G') and ln (phase angle) curves with respect to time, there is still a similarity with respect to a pseudo-first order kinetic behavior [14], therefore, if the curve of ln (G') vs time is linearized, obtained Equation (1).
\[ \ln(G') = -0.0111t - 0.8136. \]  

(1)

From Equation (1), you can define the state of gelation at any time, as well as determine a rate constant, \( k = 0.0111 \text{ h}^{-1}. \) With the kinetic data obtained, from the viscoelastic behavior curves, it will be more precise to monitor the gelation of the colloidal gel, and its behavior during an injection in the field could be estimated.

**Figure 3.** \( G' \) and \( G'' \) and \( \delta \) vs time (h).

**Figure 4.** \( \ln G' \) and \( \ln (\delta) \) vs time (h).

### 4. Conclusions

The viscoelastic analysis of the gels confirms the formation of the resulting nanoparticles by intramolecular interactions, when observing the decrease in the storage modulus, now taking the viscoelastic behavior and associating it with a pseudo-first order kinetics, a velocity equation can be obtained and its respective constant, which will make it possible to identify when adequate colloidal gelling is carried out, without the formation of other types of molecular interactions, and will facilitate the applications of colloidal gels in the field.
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