Rheological behavior of Hydroxyethylcellulose (HEC) Solutions

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Abstract. The polymers have a wide applicability in several domains particularly in the food, cosmetics, pharmaceuticals industry and petroleum industry. They guarantee a high degree of mix-ability, pump-ability, and pour-ability during their treatment. For this, the flow properties of aqueous non ionic derivative cellulose solutions at different concentrations were measured over a wide range of shear rates (0-1000 s⁻¹), and the temperature was kept at 20°C. The studied concentrations of the polymer solutions show a marked non-Newtonian shear-thinning behavior. No yield stress and thixotropy were detected. In order to define the type of flow behavior, several rheological models such as Power law, Williamson, and Mendes-Dutra were used to fit the rheogramms based on the correlation coefficient (R²). These models are all applicable and have an equivalent ability to describe the shear flow behavior of concentrated solutions. Rheological parameters such as consistency index, flow index, derived from these models were then subjected to further analysis.

1. Introduction

Natural polymers have a large range of applications such as food industry, detergents, cosmetics, coating technology, pharmaceuticals, and drilling muds [1-6]. The HEC polymer has a very high affinity for water, when the dry polymer is introduced into water, HEC powders swell and hydrate, which means the polymer molecules become associated with many water molecules. The HEC powder in aqueous solution can exhibit high viscosity, which varies depending on the shear rate and temperature, showing a pseudoplastic behavior. For flow in the matrix, a fluid-rheology function was used with shear thickening at high shear rates and shear thinning at medium and low shear rates. For flow in fractures, a shear-thinning constitutive law with a zero shear-rate plateau was used [7]. A clay dispersions aging study in aqueous solutions of CMC showed the effect of time, in particular the existence of a yield stress and its evolution. From a structural point of view, HEC is very similar to CMC, grace to its non-ionicity, it is effective for reducing filtration and for thickening solutions in presence of salt. However, HEC is used in drilling and completion fluids. Magnesium oxide stabilizes the thickening action of HEC in salt waters at high temperatures [3]. The thickening medium is caused by chain entanglements between the long polymer molecules, which are solvated and extended in an aqueous medium. Rheometric measurements have shown the effect of the polymer and the KCl on the rheophysical parameters of bentonite- polymer system [8], the addition of KCl to the clay suspension causes an increase in viscosity and the yield stress is explained by aggregate of clay particles due to...
the compression of the electrical double layer, moreover, such characteristics are interest in many other industrial areas and a further development of the utilization of this polymer may be expected from these studies. Particularly Cellulose derivative polymers are intensively used in pharmaceutical applications to modify the release of drugs in tablets and capsule formulations and to improve their dissolution in the gastrointestinal fluids. This process is known as hydrophilization [9] showed that both low and high viscosity grade cellulose ether polymers can be mixed uniformly, in different proportions, in order to produce matrices with modulated drug release properties. At higher concentrations, the swelling behavior changes drastically, suggesting a gradual degradation of the matrices and the dissolution of ibuprofen from mixtures of MC/HPMC or HPC/HPMC matrices was found to be more effective when either the MC or HPC content was increased. [10] studied the flow behavior of two types of cellulose derivatives (CMC and HEC) in aqueous solution, he showed that the viscous behavior is roughly similar with two critical concentrations \( c^* \) and \( c^{**} \), delimiting three flow regions, and a third critical concentration \( c_\alpha \), intermediate between \( c^* \) and \( c^{**} \), determined from the variation of the relaxation time with concentrations. There have been several studies of interaction between cellulose derivatives and surfactants, [11] showed that some homogeneous mixtures have higher viscosity and elasticity than predicted by the log-additivity rule from partial concentration, the relative polymer proportion at which the maximum synergy is obtained and the degree of synergy vary depending on the substituent content. Rheological studies of cellulose derivative are of importance for estimating and understanding on a molecular basis, the function of these components in fracturing fluids and in drilling fluid. Several works were carried to improve the stability of emulsions by adding natural cellulose derivatives to increase the viscosity of the medium [12], [13], to perform and control the texture of foodstuffs, they are also used as thickener, binder, stabilizer suspending and water retaining agent [14], [15]. In [16] study, oscillatory test was used to study, the viscoelastic properties of aqueous and milk systems. Both the type of dispersing media and the CMC concentration clearly affected the viscoelastic behavior of samples, which ranged from liquid-like to weak gel.

2. Materials and Methods

2.1. Materials

The HEC used in this study is a commercial product, which is used by the oil companies. Its moisture content and the pH value of aqueous 0.5 wt.% solution (25°C) were of 8.0% and 7.0 respectively. HEC can be produced by reacting ethylene oxide with cotton. The structure of the repeating unit of HEC is shown in Figure 1. Polymer solutions were prepared in different concentrations ranged from 0.2 to 0.5 wt. %. After mixing each polymer dispersion was poured in a covered vessel and left for one day at room temperature.

![Figure 1. Molecular structure of hydroxyethylcellulose](image)

2.2. Preparation of solutions

The cellulose derivative is soluble in both cold and hot water; it needs an intensive agitation upon introduction into an aqueous medium in order to avoid a formation of lumps.
In this work, water solutions of an anionic cellulose derivative with 0.2, 0.3, 0.4 and 0.5 % (w/w) concentration were prepared, the polymer was dissolved in distilled water, while a magnetic stirrer was dispersing the solution at ambient temperature for 24 hours until it was perfectly dissolved.

2.3. Rheological measurements

The rheological measurements were performed at 20°C using a controlled stress rheometer AR 2000 (Fig.2) from TA instruments using the concentric cylinder measuring system under various conditions. Furthermore, to prevent water evaporation, a cover was placed around the geometry.

The sample was pre-sheared during 2 min at shear rate of 100 s⁻¹ followed by 1 min of rest. The flow behavior was investigated over a wide range of concentrations (0.2 –0.5%). Rheological parameters (shear stress, apparent viscosity and shear rate) were obtained from the software.

![Figure 2. Rheometer AR 2000](image)

3. Rheological Models

The flow curve of fluid will not only depend on its composition, but also on the protocol used in the flow test. Therefore, in the literature, there are many rheological models, the flow curves were fitted to the following equations.

3.1. Power law model

Power law is a two-parameter model indicating a non-linear relationship between shear rate and shear stress (Ostwald, 1925), which is given as follows:

$$\tau = k \cdot \dot{\gamma}^n$$  (1)

Where k is the consistency and n is the flow behavior index. The different values of n indicate the fluid behavior. For a Newtonian fluid, n = 1. If n < 1, the fluid is called pseudoplastic; if n > 1, the fluid is dilatants.

3.2. Williamson Model

Williamson law is three-parameter model. The equation is:

$$\eta = \frac{\eta_0}{1 + k \cdot \dot{\gamma}^n}$$  (2)

3.3. Mendes-Dutra model

Mendes-Dutra rheological law is defined by four parameters, which is given by the following relation:

$$\tau = \left(1 - \exp\left(-\frac{\eta_0 \cdot \dot{\gamma}}{\tau_0}\right)\right) \cdot (\tau_0 + k \cdot \dot{\gamma}^n)$$  (3)

Where $\eta_0$, refers to the asymptotic values of viscosity at very low shear rates respectively, k is the consistency,$\tau_0$ is the yield stress, and n is the flow behavior index.
The different models were fitted to measured rheograms using rheological data analysis software, which also estimated the correlation coefficient. In a general way, an acceptable fit gives a correlation coefficient > 0.90.

4. Results and Discussion

4.1. Flow behavior

Both of the shear rate and concentration dependencies of shear flow behavior were reported from experimentally obtained data. Figures 3 and 4 show the flow curves of the polymer solutions at different concentrations. It can be clearly seen that the apparent viscosity increases with increasing concentrations, it exhibit a non Newtonian shear-thinning behavior. This rise in the apparent viscosity is due to the increase in the intermolecular interactions between the cellulose derivative polymer molecules [10], [17]; These properties could be attributed to polymer’s long chain molecules that tended to orient themselves in the direction of flow. As the shear stress was increased, the more chains rearranged themselves along the shear direction, and then the shear resistance to flow (viscosity) decreased. When a lower stress was imposed on the same solution, the viscosity was higher because random molecular orientations exhibited increased resistance to flow [18], there was no evidence of a yield stress (Figure 5).

![Figure 3. Shear rate dependence of viscosity for different concentrations](image)

![Figure 4. Flow curves for different concentrations](image)
The curves exhibit a shear rate dependant viscosity above a critical shear rate $\dot{\gamma}_{\text{crit}}$ representing transition from Newtonian behavior to non Newtonian behavior; as the concentration increases the value of $\dot{\gamma}_{\text{crit}}$ is shifted to lower shear rates, below $\dot{\gamma}_{\text{crit}}$ the solution viscosity is independent of shear rate and is called the zero-shear viscosity $\eta_0$, this result is in good agreement with [10] and [13].

Thixotropy of a solution is quantified by the solution ability to regain its gel structure when the liquid is allowed to rest for a longer period time [4]. Regarding the time-depending rheological behavior of HEC polymer, the obtained results show that there is no thixotropy for all the studied solutions (Figure 6).

4.2. Applicability of rheological flow models
The Power law model shows a large agreement between the obtained results and the experimental measured data over a great range of shear rates tested, it gives a good ability for predicting the flow behavior of the polymer solution. The Williamson and Mendes-Dutra models are in good agreement
with the experimentally data, over a whole range of shear rates tested and for concentrations over 0.4% (Fig.7), they have the value of the correlation coefficient greater than 0.980. Furthermore, no discrepancy is observed between these two models, indicating that they have the same ability to predict the flow behavior of concentrated polymer derivative solutions [4].

![Diagram](image)

**Figure 7.** Applicability of some flow models

5. Conclusion
The present work analyses the effect of concentration on the rheological behavior of cellulose derivative solutions. Viscosity was strongly influenced by concentration. The results suggested that solutions behaved as non Newtonian shear thinning at the test conditions. The consistency index decreased with increasing concentration. The time-dependent viscosity has a constant value corresponding to an equilibrium state. From these results, and for the concentrations used, the solutions were found to be not thixotropic. The power law, Williamson and Mendes-Dutra models are all applicable and have an equivalent ability to describe the shear flow behavior of concentrated solutions.

References
[1] Alemdar A, Oztekin N, Gungor N, Ece O, I Erim F B 2005 Colloid. Surface. A **252** 95
[2] Bakshi M S, Kaur R, Kaur I, Kumar Mahajan R, Sehgal P and Doe H 2003 Colloid. Polym. Sci. **281** 716
[3] Darley H C and Gray G R 1988 Composition and properties of drilling and completion fluids, *Gulf Professional Publishing*, Texas
[4] Ghannam M T and Esmail M N 1997 *J. Appl. Polym. Sci.* **64** 289
[5] Gómez-Díaz D and Navaza J M 2002 *Electron. J. Environ. Agric. Food Chem* **1** 12
[6] Holme K R, Hall L D, Spears R A, and Tung M A 1988 *Food Hydrocolloid* **2** 159
[7] Ma Y and McClure M W 2017 *SPE Reserv. Eval. Eng.* **20** 394
[8] Benyounes K and Benmounah A 2012 *Int. J. Phys. Sci.* **7** 1790
[9] Kamel S, Ali N, Jahangir K, Shah S, and El-Gendy A 2008 *Express. Polym. Lett.* **2** 758
[10] Castelain C, Doublet J L and Lefebvre J 1987 *Carbohydr. Polym.* **7** 1
[11] Alvarez-Lorenzo C, Duro R, Gomez-Amoza J, Martinez-Pacheco R, Souto C, and Concheiro A 2001 *Colloid. Polym. Sci.* **279** 1045
[12] Radi M and Amiri S 2013 *J. Disper. Sci. Technol.* **34** 582
[13] Yaseen E, Herald T, Aramouni F and Alavi S 2005 *Food. Res. Int.* **38** 111
[14] Mirhosseini H, Tan C P, Aghlara A, Hamid N S, Yusof S, and Chern B H 2008 *Carbohydr. Polym.* **73** 83
[15] Menezes R Marques L Campos L Ferreira H Santana L and Neves G 2010 Appl. Clay. Sci. 49 13
[16] Bayarri S and Costell E 2011 J. Food. Process. Eng. 34 1903.
[17] Li J Xie W Cheng H Nickol R G and Wang P G 1999 Macromolecules 32 2789
[18] Yang X H and Zhu W L 2007 Cellulose 14 409