

EFFECT OF CONCENTRATION AND TEMPERATURE ON THE RHEOLOGICAL BEHAVIOR OF HYDROXYLETHYL CELLULOSE SOLUTIONS

VPLIV KONCENTRACIJE IN TEMPERATURE NA REOLOŠKO OBNAŠANJE RAZTOPIN HIDROKSJETILNE CELULOZE

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The knowledge of the rheological properties of polymers makes their use interesting in various fields of applications, such as food industry, cosmetics, enhanced oil recovery or construction materials. Whatever the application, the effect of temperature and concentration on these properties is of great importance. This study covered a wide range of concentrations from 0.2 w/% to 1 w/%, and temperatures from 10 °C to 80 °C. The results obtained provide interesting information regarding the effects of the temperature and concentration of the aqueous solutions of the polymer since they reveal that the rheological properties remained practically unchanged in the temperature range considered. The impacts of shear rate, temperature and concentration on the flow behavior were analyzed. Small-amplitude oscillatory shear measurements were performed, and the results obtained show that the apparent viscosity is strongly influenced by the concentration of the aqueous solution of HEC, exhibiting a marked non-Newtonian shear-thinning behavior at different temperatures. The flow behavior is well described by several rheological models. The effect of temperature on the kinematic viscosity was fitted with the Arrhenius model; the behavior of this model in relation to experimental viscosity values was suitable and the linear fit showed good regression coefficients. The dynamic state was well described with the generalized Maxwell model.

Keywords: hydroxyethyl cellulose, viscoelasticity, flow properties, rheology

Poznavanje reoloških lastnosti polimerov je pomembno za njihovo uporabo na mnogih področjih, kot so na primer hrana, kozmetika, recikliranje olj, in/ali razvoj novih materialov. Kakorkoli, ne glede na njihovo uporabo je zelo pomembno poznavanje vpliva temperature in koncentracije na reološke lastnosti polimerov. V tem članku avtorji opisujejo študijo v kateri analizirajo reološke lastnosti izbranega polimera v območju koncentracij med 0,2 w/% in 1 w/% ter v temperaturnem območju med 10 °C in 80 °C. Dobljeni rezultati predstavljajo pomembne informacije o vplivu temperature in koncentracije izbranega polimera v vodni raztopini. Glavna ugotovitev je, da reološke lastnosti ostajajo v izbranem področju temperatur praktično nespremenjene. Analizirali so vpliv strižne hitrosti, temperature in koncentracije na tekočnost oziroma viskoznost raztopin. Izvedli so majhne oscilacije meritev strižnih napetosti, ki so pokazale, da je navidezna viskoznost izbranega polimera (HEC; angl.: Hydroxyethyl cellulose) močno odvisna od njegove koncentracije v vodni raztopini. Ta se izraža kot izrazito ne-Newtonsko strižno tanjšanje pri različnih temperaturah. Tekočnost so dobro opisali z več reološkimi modeli. Vpliv temperature na kinematično viskoznost so uskladili (prilagajali oz. fitali) z Arrheniusovim modelom in dobljene vrednosti so pokazale linearno odvisnost z dobrimi regresijskimi koeficienti. Dinamično stanje se da dobro opisati z posplošenim Maxwellovim modelom.

Ključne besede: hidroksietilna celuloza, viskoelastičnost, tekočnost, reologija

1 INTRODUCTION

Hydroxyethyl cellulose (HEC) is a nonionic water-soluble polymer derived from cellulose. It is utilized as a thickener, protective colloid, binder, stabilizer and suspending agent in many industrial applications. HEC has attracted the attention of many industry fields,^{1,2} especially the oil field. In order to protect the environment, cellulose derivatives are often used as drilling-fluid additives in various oil and gas drilling processes. Rheological studies have shown their effectiveness in drilling wells in less time, providing minimal permeability during drilling and completion operations.^{3,4} Hydroxyethyl cellulose is used in drilling muds to increase their stabil-

ity and avoid the swelling of clay layers. Wencong Wang⁵ studied the hydrodynamic properties and gelation of HEC as a function of molar substitution (MS), concentration and temperature; they showed that the intrinsic viscosity and gelation time of HEC solutions decrease with temperature, and their gelation kinetics is much slower than that of microcrystalline cellulose solutions in the same solvent. Other researchers^{6,7} were interested in studying the interaction between HEC and three of its drifts with SDS; they showed that these interactions lead to phase separation in an intermediate concentration range of SDS and, for higher concentrations of surfactants, when a homogeneous phase has been obtained, these interactions lead to higher apparent shear and expansion viscosity. Z. Jeirani⁸ also provides additional information on the polymers used in the flooding

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of micro-emulsions, both as a stable displacement fluid and as a mobility control agent.

Given the importance and variety of the polymer use, a good understanding of its rheological characteristics is crucial when determining its performance, particularly in the field of drilling muds, in order to maintain the most effective fluid properties for a safe, efficient and economical drilling operation. This paper presents a concise study of the effect of concentration and temperature on this polymer. In order to reach this objective, stress and frequency sweep measurements and steady-state tests were performed.

2 EXPERIMENTAL PART

This cellulose derivative is soluble in both cold and hot water and requires intensive agitation to dissolve in an aqueous medium to avoid the formation of lumps. The polymer was dissolved in distilled water, while a magnetic stirrer was dispersing the solution at ambient temperature for 24 h until it was perfectly dissolved. After mixing, each polymer dispersion was poured in a covered vessel and left for one day at room temperature.

In this study, the flow properties of aqueous nonionic derivative cellulose solutions at different concentrations and temperatures were measured with a wide range of shear rates (0–1000 s⁻¹), using an AR2000 controlled stress rheometer equipped with conical concentric cylinders. In order to obtain samples, the polymer was dissolved in distilled water at ambient temperature.

3 RESULTS AND DISCUSSIONS

3.1 Flow behavior

Both the shear rate and concentration dependency of the shear-flow behavior were found from experimentally obtained results, exhibiting a marked non-Newtonian shear-thinning behavior, which is in good agreement with the results reported in the literature.^{5,9,10} The increase in the apparent viscosity is due to the increase in the intermolecular interactions between the cellulose derivative polymer molecules.^{2,9} These properties can be attributed to the long-chain molecules of the polymer that tend to orient themselves in the direction of the flow field. As the shear stress increased, the chains became further rearranged in the shear direction, while the viscosity decreased.

3.2 Applicability of theoretical flow models

The flow curves were fitted with Equations (1), (2) and (3):

- Ostwald-de-Waele equation:

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

where k is the consistency and n is the flow behavior index,

- Mendes-Dutra equation

$$\tau = \left(1 - e^{-\frac{-\eta_0 \dot{\gamma}}{\tau_0}} \right) (\tau_0 + k\dot{\gamma}^n) \quad (2)$$

- Cross equation

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + (k\dot{\gamma})^n} \quad (3)$$

τ is the shear stress (Pa), τ_0 is the yield stress (Pa), $\dot{\gamma}$ is the shear rate (s⁻¹), η is the apparent viscosity (Pa·s) at a determined shear rate, and η_0 and η_∞ are the Newtonian viscosity at zero and the infinite shear rate. To determine the goodness of fit, we used the correlation coefficient (R^2) and a method based on the best iterative value (BIV).¹¹ All the used models were applied to the experimentally measured shear rate/viscosity data for all HEC concentrations. The Ostwald-de-Waele model shows good agreement between the obtained results and the experimentally measured data including a great range of shear rates, exhibiting a good ability to predict the flow behavior of the polymer solution.

According to **Table 1**, the value of the flow behavior index n decreases with the increasing concentration; HEC solutions have a higher shear-thinning effect. The flow curves of aqueous HEC solutions are well fitted by several other models; both the Cross¹² and Mendes-Dutra models are in good agreement with the experimental data as their correlation coefficients are greater than 0.99 and the best iterative values (BIVs) are between 0.98 and 1.026. Furthermore, for a shear rate greater than 10 s⁻¹, no discrepancy is observed between these models, indicating that they have the same ability to predict the flow behavior of concentrated polymer derivative solutions.¹³

Table 1: Flow models and their characteristics at 20 °C

Flow model	Concentration (w/%)	η_0 (Pa·s)	K (Pa·s ⁿ)	N	R^2	BIV
Mendes-Dutra	0.2	0.061	0.027	0.847	0.999	0.997
	0.4	0.092	0.174	0.796	0.982	1.026
	0.6	0.684	0.318	0.770	0.996	0.982
	0.8	1.317	0.575	0.758	0.993	0.980
	1	3.950	1.563	0.701	0.995	0.972
Cross	0.2	0.065	0.057	0.605	0.998	0.998
	0.4	0.143	0.087	0.650	0.997	0.997
	0.6	0.798	0.108	0.755	0.998	0.997
	0.8	1.542	0.125	0.753	0.998	0.997
	1	4.812	0.306	0.723	0.999	0.998
Ostwald-de-Waele	0.2	–	0.017	0.872	0.999	0.993
	0.4	–	0.301	0.627	0.999	0.981
	0.6	–	2.343	0.453	0.998	0.989
	0.8	–	4.662	0.418	0.997	0.952
	1	–	9.598	0.358	0.996	0.993

3.3 Effect of temperature

Effect of temperature is depicted in **Figure 1**. We can see a large difference in the viscosity at lower shear rates

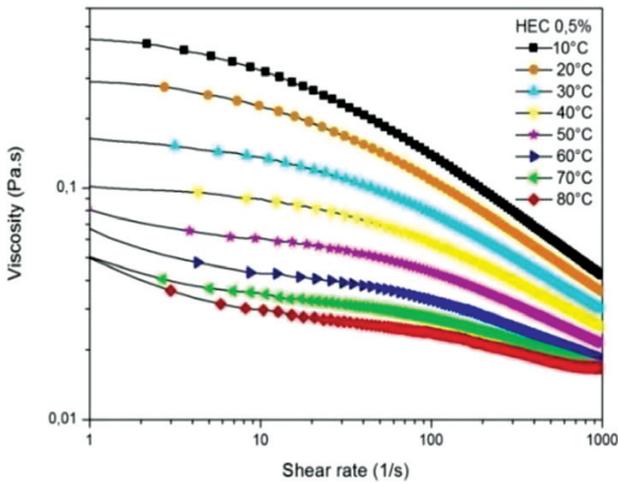


Figure 1: Viscosity as a function of shear stress for different temperatures

but at higher shear rates, the viscosity curves are close to each other; an increase in the temperature leads to a decrease in the viscosity of the fluid.

When external energy is supplied by heating, it increases the intermolecular distances due to thermal expansion, and then the viscosity is reduced. However, at a large shear rate, the flow becomes less sensitive to temperature, showing that the effect of temperature is pronounced at lower shear rates when the structure begins to distort, but at higher shear rates, the effect of shear rate in reducing the viscosity supersedes the effect of temperature (Figure 2).¹⁴

To show the effect of temperature on apparent viscosity, many empirical relations were proposed in the literature. The Arrhenius Equation (4) is commonly used to represent the viscosity as a function of temperature:

$$\eta = A \exp\left(\frac{E_a}{RT}\right) \quad (4)$$

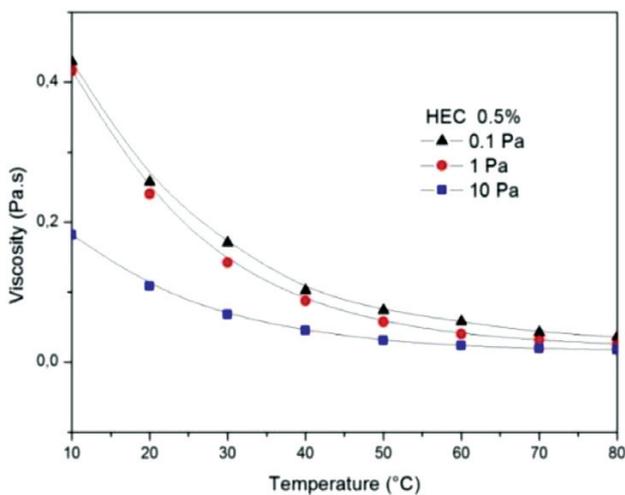


Figure 2: Viscosity of HEC solution versus temperature

where η (Pa·s) is the viscosity of HEC solutions, A is the pre-exponential constant, R (8.314 J/(mol·K)) is the universal gas constant, T (Kelvin) is the temperature and E_a (J/mol) is the activation energy for the flow. The standard error of the estimate (SEE), (Equation 5) and the correlation coefficient R^2 were used to evaluate the goodness of fit of the models.

$$SEE = \sqrt{\frac{\sum_{i=1}^n (Y_i - Y_i')^2}{n - p}} \quad (5)$$

Here, Y_i is the apparent viscosity at a given temperature, Y_i' is the predicted viscosity, n is the number of data points, and p is the number of parameters in each equation.

The high values of the correlation coefficient (0.99) and low values of the SEE indicate that the apparent viscosity of HEC can be successfully predicted with this model. The values of the activation energy, E_a , reflecting the susceptibility of the system to temperature changes, indicate an increase with the increasing concentration of the aqueous solutions (Table 2). A number of studies reported similar results for the viscosity of neutral polymer solutions, and our findings are in perfect agreement with those by Naik¹⁵, at the same time refuting the results by Bellet¹⁶ who claims that the activation energy in the Arrhenius expression is independent of the concentration.

Table 2: Values of Arrhenius-model parameters, influenced by concentration

	Concentration (w/%)					
	0.4	0.5	0.6	0.7	0.8	1
$A \times 10^6$ (Pa·s)	2.87	1.44	1.49	1.65	2.38	2.63
E_a (J/mol)	23609	27263	29776	30891	31507	33858
SEE	0.004	0.011	0.042	0.056	0.124	0.336
R^2	0.994	0.993	0.995	0.985	0.992	0.988

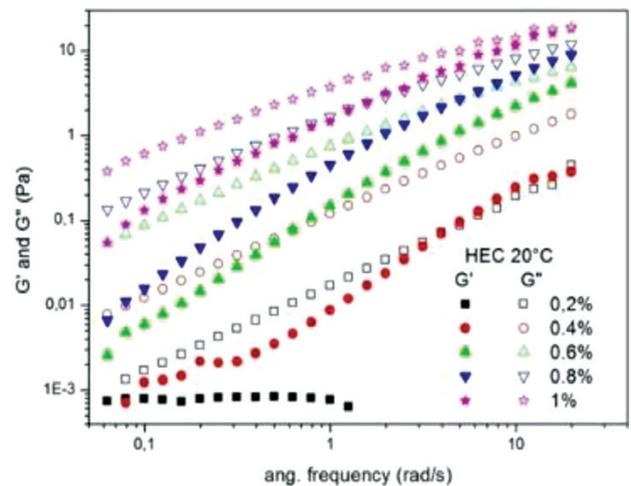


Figure 3: Loss and storage modulus as a function of frequency at various concentrations

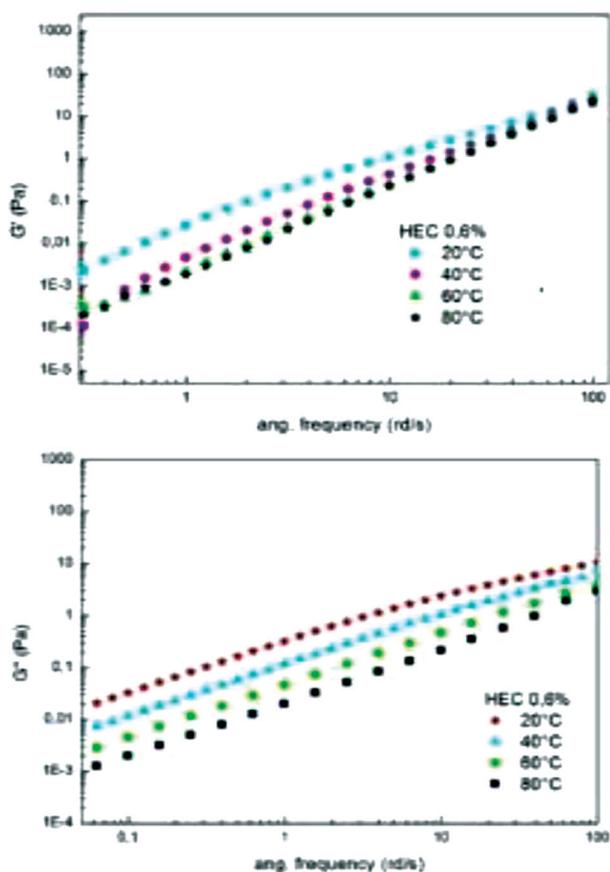


Figure 4: Function of frequency at various temperatures: a) storage modulus, b) loss modulus

3.4 Dynamic shear rheology

Oscillatory tests are a very useful tool for studying and evaluating the viscoelastic behavior of polymers. This study allows us to characterize the properties of these aqueous solutions while keeping the conditions of rest and without destroying the internal structure of a polymer.

Figures 3, 4a and 4b show the variation in storage modulus G' and loss modulus G'' as a function of frequency and temperature, respectively. For concentrations below 0.8 w/%, the behavior is that of a purely viscous fluid (Figure 3), but when this concentration is exceeded, the samples become viscoelastic with a predominantly viscous character at an intermediate frequency

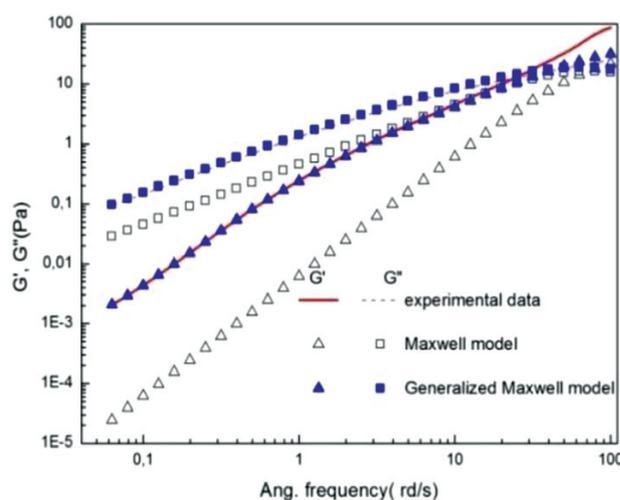


Figure 5: Predictive ability of the Maxwell model (HEC 1 w/%, 20 °C)

range, and the crossover frequencies ($G'' = G'$) decrease to lower values with the increasing concentration.

The increase in G' and G'' with the increase in polymer concentrations can be explained with macromolecular entanglement (the number of intermolecular contacts per unit volume).¹⁷ Since higher concentrations increase the entanglement density, the viscoelastic properties increase proportionally. We can also notice that the temperature has less effect on the modulus of elasticity G' and that the latter is highly dependent on the frequency (Figure 4).

3.5 The Maxwell model

The elastic or storage modulus (G') and the viscous or loss modulus (G'') were determined as a function of the frequency using the generalized Maxwell model (Equations (6) and (7)), where n is the number of the Maxwell elements considered, G_i is the plateau modulus (Pa), λ_i is the relaxation time (s) and ω the frequency (Hz).^{18,19} A study of these parameters with variables such as temperature and concentration is required to understand the thickening mechanism.

$$G'(\omega) = \sum_{i=1}^n G_i \frac{(\lambda_i \omega)^2}{1 + (\lambda_i \omega)^2} \tag{6}$$

Table 3: Generalized Maxwell parameters

Concentration (w/%)		Temperature (°C)									
		20				50				80	
0.4	λ_i (s)	0.031	0.3	–	–	0.02	0.2	0.003	0.42		
	G_i (Pa)	1.19	0.07	–	–	0.98	0.03	1.66	0.01		
0.6	λ_i (s)	0.032	0.158	0.83	–	0.004	0.04	0.02	0.2		
	G_i (Pa)	7.14	1.84	0.22	–	7.25	1.4	0.86	0.04		
1	λ_i (s)	0.016	0.12	0.68	5.58	0.02	0.2	0.01	0.1		
	G_i (Pa)	45.5	13.21	3.02	0.44	19.57	0.55	7.71	0.66		

$$G''(\omega) = \sum_{i=1}^n G_i \frac{\lambda_i \omega}{1 + (\lambda_i \omega)^2} \quad (7)$$

Figure 5 shows how a single Maxwell model (open symbols \square , Δ) is not able to fit experimental data, so to fit our experimental data, we used a model with five Maxwell elements. To adequately characterize the viscoelastic behavior of aqueous solutions, two to four elements were required.

It should be noted that G_i decreases with the increasing relaxation time (**Table 3**) for the same temperature and concentration of the HEC aqueous solutions. Increased relaxation time can be explained with the formation of intermolecular aggregates, caused by the increase in the concentration of the polymer. In fact, the molecular density becomes higher, which leads to a more limited molecular movement.

4 CONCLUSIONS

The present study analyses the effect of concentration and temperature on the rheological behavior of hydroxyethyl cellulose solutions. Viscosity was strongly influenced by concentration. The results suggest that the solutions exhibited a non-Newtonian shear-thinning behavior under the test conditions. The consistency index decreased with the increasing concentration. The study shows that solutions of HEC have high degrees of pseudo-plasticity as well as high shear stability over long periods. Several flow models were employed to make a quantitative evaluation of the shear-flow behavior, and then the applicability of these models was also examined in detail. The Ostwald-de-Waele, Cross and Mendes-Dutra models are all applicable and have an equivalent ability to describe the shear-flow behavior of concentrated solutions. The effect of temperature was investigated; experimental viscosities were fitted into the Arrhenius equation with a good fit. The storage and loss modulus (G' and G'') depend on the nature of the material, the temperature and also the frequency, at which the material is stressed during dynamic tests. As a result, a sample may be highly viscous at a given frequency and highly elastic at another frequency.

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