EFFECTS OF TEMPERATURE AND CONCENTRATION ON THE PARAMETERS OF CARREAU MODEL FOR A NON-NEWTONIAN FLUID

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Abstract. *This work studies the application of factorial design to simplify the analysis of the influence of concentration and temperature factors on the partially hydrolyzed polyacrylamide. The measured steady shear viscosities are reported in this paper from 1.48 to 4.30%wt aqueous solutions of polyacrylamide. The data covers a temperature range from 10 to 50°C. By analyzing the experimental data and the interaction between the factors, it is possible to fit the Carreau parameters and to predict its range through the factorial design technique. The good results obtained show the usefulness of this type of technique in detecting interactions among the factors that would be difficult to foresee otherwise.*

Keywords. *Partially hydrolyzed polyacrylamide, Carreau model, temperature, concentration.*

1. Introduction

The material properties of fluids can be critical during a process. They can affect the process flow control, the quality of a final product, and the success of an application, to name a few. In particular, non-Newtonian fluids deserve special attention because of the strong interaction between material properties and flow conditions. Consequently, the rheological analysis of this kind of fluids is of great importance.

In case of polymeric fluids, the temperature and concentration have high influence on the fluid behavior. So, to warrant the usage of a fluid in a certain task, the environmental conditions have to be controlled and the fluid preparation requires heed. Before the application of such fluid, it is very important to perform a rheological test to analyze its behavior. However, it is possible to achieve a given fluid behavior through control of concentration and temperature only if the dependence of rheology on these variables is known *a priori*.

The study of temperature dependence of viscosity plays an important role in heat transfer analyses. In the literature, numerous articles about temperature and concentration influences on viscosity can be encountered. For example, Flew and Sellin (1993) studied polyacrylamide solutions behavior in porous media, for applications in oil reservoirs, as viscosifying agent in oilfield injection waters. Shin et al (1994) examined the effect of temperature on the viscosity of 0.1% aqueous polyacrylamide solutions, considering the Carreau fluid behavior, and verified that for this solution at low shear rates the viscosity is very sensitive to temperature while for high shear rates it is almost temperature independent. The time constant, fluid behavior index and fluid consistence index were found to vary with temperature. Lin and Ko (1995) reported an investigation about the effect of temperature and polymer concentration on two non-Newtonian aqueous polymer solutions, the Carbopol and CMC. They concluded that although both fluid behaviors can be described as power-law, their consistency and behavior indexes are functions of temperature, concentration and of the nature of polymeric solution. Cai et al (2001) also worked with polymer concentration analysis (HPAM) in gelation, and Contreras and Sánchez (2001) used the factorial design statistical method to study the viscoelastic parameters of a Carbopol gel as a function of polymer concentration.

The method presented in this paper simplifies the search for adequate concentration and temperature ranges to work with a given fluid, especially if it is used in different conditions. The factorial design (statistical method) was chosen from a polynomial that can include all the *a priori* supposed acting variables on a certain parameter indicating the interaction among these variables and the parameter. Once the polynomial is obtained, if two variables are known, the third is determined. Hence, with these data we can have a datasheet or graphical information about the ideal fluid characteristics to fulfill the expected behavior. The experimental tests were accomplished with Partially Hydrolyzed Polyacrylamide (PHPA) solutions modeled according to Carreau.

2. Methodology

Five different partially hydrolyzed polyacrylamide (PHPA) aqueous solutions were prepared with deionized water. The concentrations under study were 1.48, 2.19, 2.90, 3.61 and 4.32 %wt. The solutions were prepared using a concentrated PHPA, *ADESOL PE306*, supplied by Petrobras S.A. For each concentration, tests were performed with six samples, which were considered as replications to obtain a mean confidence interval of 94.0 % in the statistical method. Actually, the initial estimates indicated that, to assure a 94% mean confidence interval, the needed number of replications was three, but, to be conservative, we decided to perform six replications.

The rheological tests were performed with a Paar–Physica UDS 200 rotational Rheometer. Viscosity *versus* steady shear rate data were collected in a range of 0.001 – 3900 s^{-1}, using a 75mm diameter parallel plate geometry with a

0.2mm gap. For all tests, thirty points were collected in logarithmical steps of shear rate. Each point was measured in 10 seconds intervals; therefore, each sample measurement would last 5 minutes.

Although the smallest shear rate was set to 0.001 s^{-1}, the first valid data points could not be taken until 0.01 s^{-1}, because of the minimum torque transducer capacity. In most cases, within the range of the first five shear rates the fluid had a Newtonian constant viscosity. Beyond this range, at about 1s^{-1} , a constant and steep decrease would be observed. This rheological behavior is well described by the Carreau viscosity function with null infinite-shear-rate viscosity (η_∞=0). The Carreau viscosity function is given by the following expression:

$$\eta = \frac{\eta_0 - \eta_\infty}{\left[1 + (\lambda \cdot \dot{\gamma})^2\right]^{\frac{1-n}{2}}} + \eta_\infty \tag{1}$$

where η is the viscosity function, η_o is zero-shear-rate viscosity, n is the power-law index, λ is the time constant, and $\dot{\gamma}$ is the shear rate.

The temperature control was obtained with the aid of a Peltier plate, which is 0.01ºC accurate, gives an excellent temperature uniformity in the sample, and allows very fast temperature changes. The measurements were performed at 10, 20, 30, 40 and 50 ºC.

Figure (1) shows the behavior of PHPA solutions at two concentrations for several temperatures, whereas Fig. (2) shows the behavior of PHPA solutions at two temperatures for several concentrations. It is possible to verify that both concentration and temperature influence significantly the viscosity behavior. The importance of viscosity information at intermediate temperatures and concentrations, e.g., in numerical simulations, make it necessary to interpolate data. This interpolation can be achieved via the concept of "master curve," where the data are shifted to a reference temperature and concentration using a shift factor (e.g. Bird et al., 1987). Another possibility is to employ a statistical method with the analysis of variance to construct a high-order polynomial which interpolates the data. The latter methodology is used in the present work.

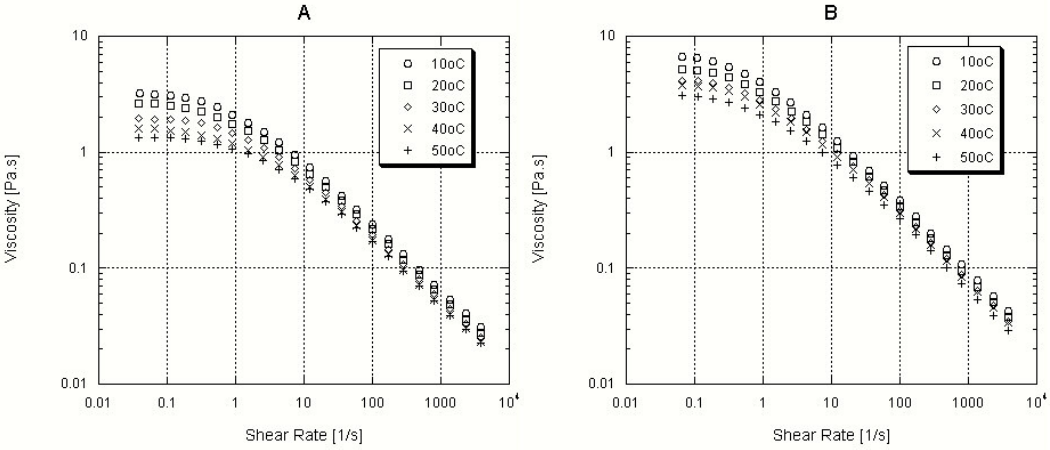

Figure 1. Viscosity versus shear rate. Constant concentration for five temperatures. (A) 2.9 %Wt; (B) 4.32 %Wt.

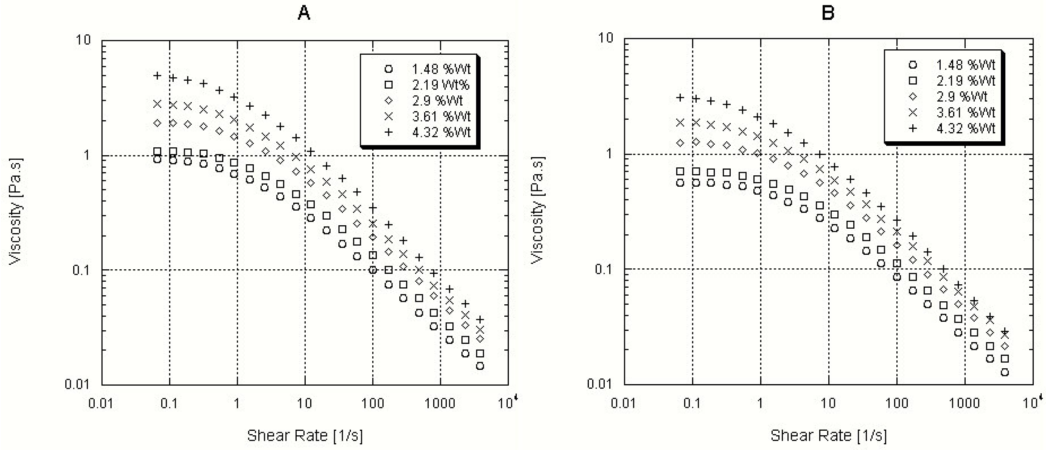

Figure 2. Viscosity versus shear rate. Constant temperature for five concentrations. (A) 30ºC; (B) 50ºC.

The mean and the standard deviation for each temperature and concentration experimental data are given in Tab. (1) for the following parameters: zero-shear-rate viscosity, η_0; characteristic time, λ; and power-law index, n.

Table 1. Mean and standard deviation for η_0, λ, and n parameters.

	η_0 [Pa.s]									
%wt	**10ºC**		**20ºC**		**30ºC**		**40ºC**		**50ºC**	
	Mean	**St. Dev.**	**Mean**	**St. Dev.**	**Mean**	**St. Dev.**	**Mean**	**St. Dev.**	**Mean**	**St. Dev.**
1.48	1.3725	0.0809	1.0617	0.0636	0.8425	0.0547	0.6530	0.0463	0.5342	0.0141
2.19	1.6570	0.1113	1.2658	0.0587	0.9888	0.0627	0.7801	0.0365	0.6342	0.0197
2.90	3.0568	0.2331	2.3353	0.0916	1.8116	0.0938	1.4416	0.0783	1.1819	0.0561
3.61	4.0672	0.1656	3.2571	0.1648	2.4857	0.2051	2.2201	0.1848	1.8134	0.0466
4.32	6.5043	0.3080	5.3330	0.4597	4.4283	0.2937	3.6289	0.2566	3.2497	0.3351
	λ [s]									
	10ºC		**20ºC**		**30ºC**		**40ºC**		**50ºC**	
	Mean	**St. Dev.**	**Mean**	**St. Dev.**	**Mean**	**St. Dev.**	**Mean**	**St. Dev.**	**Mean**	**St. Dev.**
1.48	1.2594	0.1892	0.9814	0.1281	0.7973	0.1043	0.5517	0.0799	0.4000	0.0334
2.19	0.9320	0.0801	0.7358	0.0430	0.5947	0.0554	0.4643	0.0512	0.3671	0.0240
2.90	1.4062	0.2555	1.0779	0.1075	0.8389	0.0680	0.6410	0.0850	0.5167	0.0521
3.61	1.3589	0.0720	1.2142	0.0808	0.8810	0.0729	0.8189	0.0361	0.7128	0.0462
4.32	1.6662	0.1340	1.4535	0.1713	1.1811	0.0802	1.0779	0.1410	1.0430	0.0367
	n									
	10ºC		**20ºC**		**30ºC**		**40ºC**		**50ºC**	
	Mean	**St. Dev.**	**Mean**	**St. Dev.**	**Mean**	**St. Dev.**	**Mean**	**St. Dev.**	**Mean**	**St. Dev.**
1.48	0.4879	0.0061	0.4940	0.0033	0.4993	0.0026	0.5023	0.0032	0.5062	0.0039
2.19	0.4830	0.0026	0.4893	0.0016	0.4937	0.0014	0.5030	0.0089	0.5058	0.0025
2.90	0.4717	0.0039	0.4726	0.0032	0.4766	0.0016	0.4785	0.0026	0.4835	0.0011
3.61	0.4502	0.0017	0.4596	0.0026	0.4645	0.0020	0.4754	0.0021	0.4841	0.0019
4.32	0.4362	0.0028	0.4362	0.0029	0.4421	0.0038	0.4548	0.0052	0.4589	0.0030

The influence of polyacrylamide concentration and temperature on the Carreau parameters was studied using a factorial design with replication, following Montgomery (1997). The method of orthogonal polynomials was used in the analysis of variance to estimate the coefficients of the high-order polynomial to be obtained for the Carreau parameters at various combinations of the design factors. The analysis of variance gives the significant components for a significance level of $\alpha = 0.05$. The components that are not significant were eliminated using this criterion. The significant components were obtained using the least-squares method available in the statistical software STATISTICA R. 5.0.

3. Results

Tables 2, 3 and 4 show the analysis of variance (ANOVA) for each parameter, as well as the linear and non-linear terms for the same parameter. The ANOVA tables show the influence of terms using the statistical function F (the term is significant if $F_0 > F_{0.05,DF,125}$). Each factor (in our case, temperature or concentration) can be modeled with a polynomial of order up to K-1, where K is the number of levels in each factor. The interactions can be modeled with a polynomial of order up to $(K-1)^2$. The subscripts are the order of the orthogonal polynomials: L for linear, Q for quadratic, C for cubic, and 4 for forth power. In the concentration and temperature interaction, the numbers i × j indicate the order of interactions between the factors.

Table 2. Analysis of variance for η_0 data.

Source of Variation	**Sum of Square**	**Degrees of Freedom**	**Mean Square**	**F_0**	**$F_{0.05,DF,125}$**
Concentration	2.776E+02	4	6.940E+01	28.498	2.444
C_L	2.526E+02	1	2.526E+02	103.714	3.917
C_Q	2.303E+01	1	2.303E+01	9.458	3.917
C_C	3.247E-01	1	3.247E-01	0.133	3.917
C_4	1.678E+00	1	1.678E+00	0.689	3.917
Temperature	6.578E+01	4	1.644E+01	6.752	2.444
T_L	6.358E+01	1	6.358E+01	26.108	3.917

Continuation

Source of Variation	Sum of Square	Degrees of Freedom	Mean Square	F_0	$F_{0.05,DF,125}$
T_Q	2.187E+00	1	2.187E+00	0.898	3.917
T_C	4.154E-03	1	4.154E-03	0.002	3.917
T_4	4.181E-03	1	4.181E-03	0.002	3.917
CT Interaction	1.537E+01	16	9.605E-01	0.394	1.725
1×1	1.399E+01	1	1.399E+01	5.744	3.917
1×2	4.681E-01	1	4.681E-01	0.192	3.917
1×3	2.907E-03	1	2.907E-03	0.001	3.917
1×4	1.433E-03	1	1.433E-03	0.001	3.917
2×1	4.483E-01	1	4.483E-01	0.184	3.917
2×2	9.880E-04	1	9.880E-04	0.000	3.917
2×3	1.931E-02	1	1.931E-02	0.008	3.917
2×4	3.048E-02	1	3.048E-02	0.013	3.917
3×1	6.078E-04	1	6.078E-04	0.000	3.917
3×2	2.288E-03	1	2.288E-03	0.001	3.917
3×3	1.115E-02	1	1.115E-02	0.005	3.917
3×4	6.172E-02	1	6.172E-02	0.025	3.917
4×1	2.941E-01	1	2.941E-01	0.121	3.917
4×2	7.163E-03	1	7.163E-03	0.003	3.917
4×3	2.438E-03	1	2.438E-03	0.001	3.917
4×4	2.911E-02	1	2.911E-02	0.012	3.917
Error	4.105E+00	125	2.435E+00		
Total	3.628E+02	149			

In Tab. 2 it is observed that the temperature has a linear effect and the concentration has a linear and non-linear effect (second-order). Only the linear interaction is significant for the concentration-temperature interactions. Therefore, Eq. (2) models the influence of temperature and concentration in the zero-shear-rate viscosity:

$$\eta_0(C,T) = a + b \cdot C + c \cdot T + d \cdot C^2 + e \cdot (C \cdot T) + error(C,T) \tag{2}$$

where *a*, *b*, *c*, *d*, and *e* are the polynomial coefficients, while the interpolation error is expressed by *error*(C,T).

Table 3. Analysis of variance for λ data.

Source of Variation	Sum of Square	Degrees of Freedom	Mean Square	F_0	$F_{0.05,DF,125}$
Concentration	7.347E+00	4	1.837E+00	169.391	2.444
C_L	5.477E+00	1	5.477E+00	505.102	3.917
C_Q	1.226E+00	1	1.226E+00	113.075	3.917
C_C	2.193E-01	1	2.193E-01	20.223	3.917
C_4	4.247E-01	1	4.247E-01	39.163	3.917
Temperature	1.015E+01	4	2.538E+00	234.047	2.444
T_L	9.883E+00	1	9.883E+00	911.477	3.917
T_Q	2.542E-01	1	2.542E-01	23.440	3.917
T_C	6.621E-03	1	6.621E-03	0.611	3.917
T_4	7.148E-03	1	7.148E-03	0.659	3.917
CT Interaction	4.136E-01	16	2.585E-02	2.384	1.725
1×1	3.532E-02	1	3.532E-02	3.258	3.917
1×2	2.791E-02	1	2.791E-02	2.574	3.917
1×3	1.070E-02	1	1.070E-02	0.987	3.917
1×4	3.865E-02	1	3.865E-02	3.565	3.917
2×1	1.844E-05	1	1.844E-05	0.002	3.917
2×2	1.763E-05	1	1.763E-05	0.002	3.917
2×3	1.169E-03	1	1.169E-03	0.108	3.917
2×4	1.583E-03	1	1.583E-03	0.146	3.917

Continuation

Source of Variation	Sum of Square	Degrees of Freedom	Mean Square	F_0	$F_{0.05,DF,125}$
3×1	7.249E-02	1	7.249E-02	6.685	3.917
3×2	1.272E-04	1	1.272E-04	0.012	3.917
3×3	2.502E-03	1	2.502E-03	0.231	3.917
3×4	9.310E-03	1	9.310E-03	0.859	3.917
4×1	1.901E-01	1	1.901E-01	17.532	3.917
4×2	8.549E-03	1	8.549E-03	0.788	3.917
4×3	1.778E-03	1	1.778E-03	0.164	3.917
4×4	1.333E-02	1	1.333E-02	1.230	3.917
Error	1.355E+00	125	1.084E-02		
Total	1.927E+01	149			

Table 3 also shows that the temperature has a linear effect and the concentration has a linear and non-linear effect (second-order). For components of interactions, there is a linear interaction of temperature with two non-linear interactions of concentration. Equation (3) models the influence of temperature and concentration on λ:

$$\lambda = a + b \cdot C + c \cdot T + d \cdot C^2 + e \cdot C^3 \cdot T + f \cdot C^4 \cdot T + error(\,C,T\,) \tag{3}$$

where *a*, *b*, *c*, *d*, *e*, and *f* are the polynomial coefficients while the interpolation error is expressed by *error*(C,T).

Table 4. Analysis of variance for n data.

Source of Variation	Sum of Square	Degrees of Freedom	Mean Square	F_0	$F_{0.05,DF,125}$
Concentration	0.056908	4	0.014227	1180.36	2.444
C_L	0.054271	1	0.054271	4502.665	3.917
C_Q	0.001661	1	0.001661	137.8049	3.917
C_C	4.15E-05	1	4.15E-05	3.445597	3.917
C_4	0.000934	1	0.000934	77.52372	3.917
Temperature	0.009405	4	0.002351	195.0843	2.444
T_L	0.009316	1	0.009316	772.9088	3.917
T_Q	3.24E-05	1	3.24E-05	2.687493	3.917
T_C	3.36E-05	1	3.36E-05	2.786046	3.917
T_4	2.36E-05	1	2.36E-05	1.955002	3.917
CT Interaction	0.00119	16	7.43E-05	6.168178	1.725
1×1	0.000377	1	0.000377	31.30396	3.917
1×2	4.76E-05	1	4.76E-05	3.952356	3.917
1×3	1.8E-05	1	1.8E-05	1.491294	3.917
1×4	2.4E-05	1	2.4E-05	1.995205	3.917
2×1	1.14E-05	1	1.14E-05	0.942396	3.917
2×2	4.03E-08	1	4.03E-08	0.003339	3.917
2×3	2.37E-05	1	2.37E-05	1.966699	3.917
2×4	3.54E-07	1	3.54E-07	0.029378	3.917
3×1	3.78E-05	1	3.78E-05	3.132012	3.917
3×2	8.06E-07	1	8.06E-07	0.066871	3.917
3×3	4.51E-05	1	4.51E-05	3.741814	3.917
3×4	4.26E-06	1	4.26E-06	0.353537	3.917
4×1	0.000557	1	0.000557	46.23822	3.917
4×2	2.11E-08	1	2.11E-08	0.001751	3.917
4×3	1.24E-06	1	1.24E-06	0.103202	3.917
4×4	4.06E-05	1	4.06E-05	3.368811	3.917
Error	1.507E-03	125	1.21E-05		
Total	6.901E-02	149			

Again, Tab. 4 shows that the temperature has a linear effect and the concentration has a linear and non-linear effect (second-order) on the power-law index. For components of interactions, there is a linear interaction of temperature with a linear and other two non-linear interaction of concentration. Equation (4) models the influence of temperature and concentration on *n*:

$$n(C,T) = a + b \cdot C + c \cdot T + d \cdot C^2 + e \cdot C^4 + f \cdot (C \cdot T) + g \cdot (C \cdot T^2) + h \cdot (C^4 \cdot T) + error(C,T) \tag{4}$$

where *a*, *b*, *c*, *d*, *e*, *f*, *g* and *h* are the polynomial coefficients, while the interpolation error is expressed by *error*(C,T).

The polynomials coefficients for Carreau parameters were obtained using the least square technique. The Tab. 5 shows all coefficients for η, λ, and *n* equations.

Table 5. Polynomials coefficients for predictive equation for Carreau parameters.

Coefficients	η	λ	*n*
a	1.5511E+00	1.9891E+00	4.8212E-01
b	-8.3106E-01	-6.1148E-01	1.2206E-02
c	1.6347E-02	-2.1219E-02	3.7130E-04
d	4.7936E-01	1.3261E-01	-6.3313E-03
e	-2.1541E-02	3.7900E-04	3.3600E-05
f	-	-7.7100E-05	-2.4500E-05
g	-	-	1.3000E-06
h	-	-	3.0557E-07

Using the Eq. 2, 3, and 4, it is possible to plot a surface, or a contour map, that fits the observed values. Figure (3) shows the three-dimensional zero-shear-rate viscosity response surface and the observed values. It is possible verify that the concentration influence is bigger than temperature. The highest η_0 value occurs for the highest concentration and lowest temperature, and the lowest η_0 value is vice-versa.

Figure 4 shows the three-dimensional characteristic time, λ, response surface and the observed values. It is possible to verify that both parameters, concentration and temperature, have high influence in the characteristic time. The highest characteristic time occurs for the highest concentration and lowest temperature, and the lowest characteristic time value is vice-versa. There is a minimum region in λ parameter about 2.0 %wt for constant temperature.

The Figure 5 shows the three-dimensional power-law index response surface and the observed values. Similar to the zero-shear-rate viscosity, it is possible verify that the concentration influence is bigger than temperature. The power-law index value occurs for the highest temperature and lowest concentration, and the lowest power-law index value is vice-versa. This behavior is opposite to zero-shear-rate viscosity.

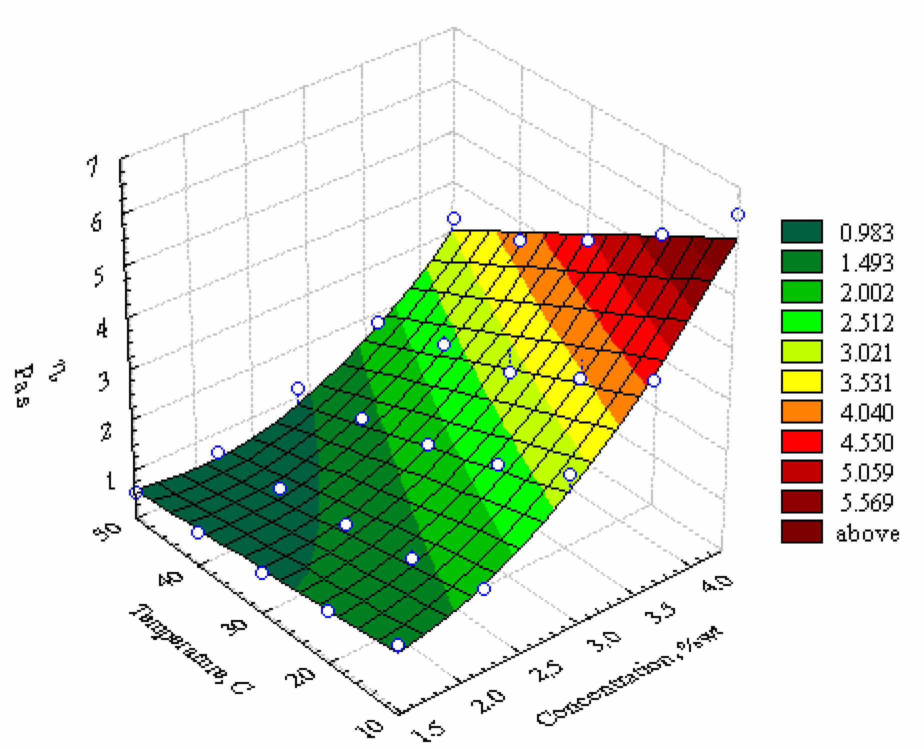

Figure 3. Measured data and the response surface for η_0(C,T). O denotes the measured data.

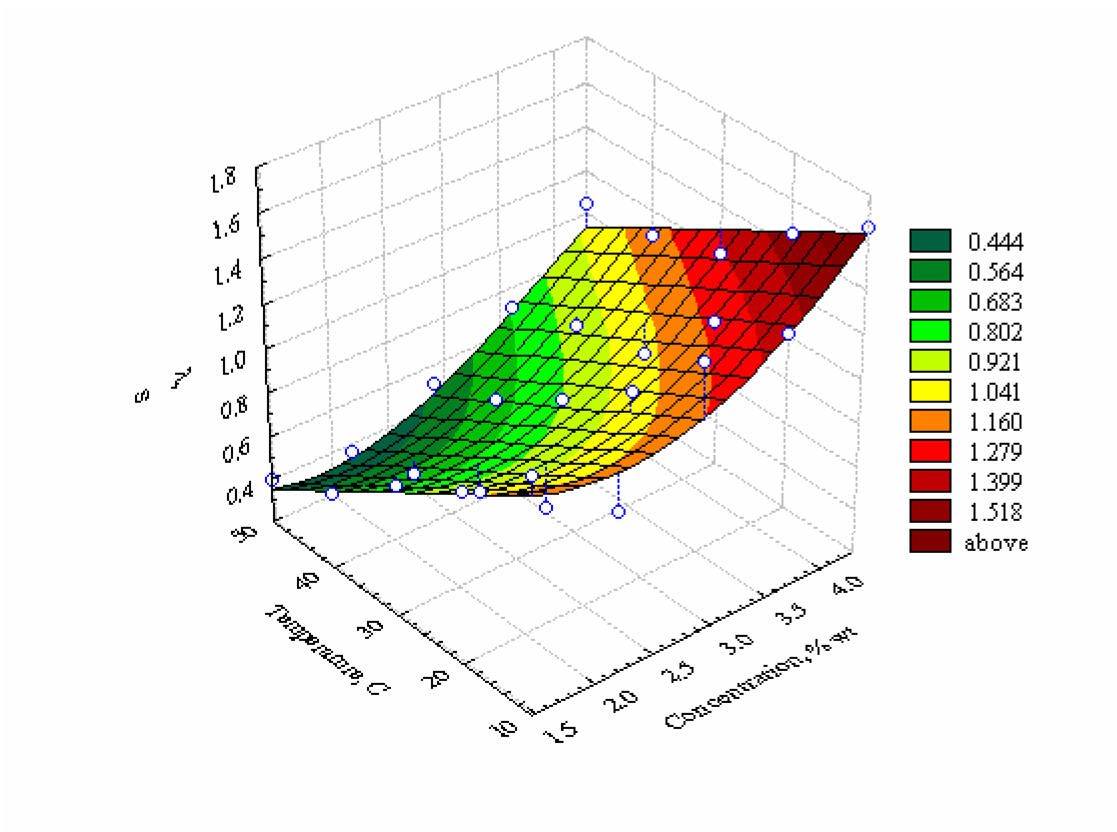

Figure 4. Measured data and the response surface for the characteristic time, λ. o denotes the measured data.

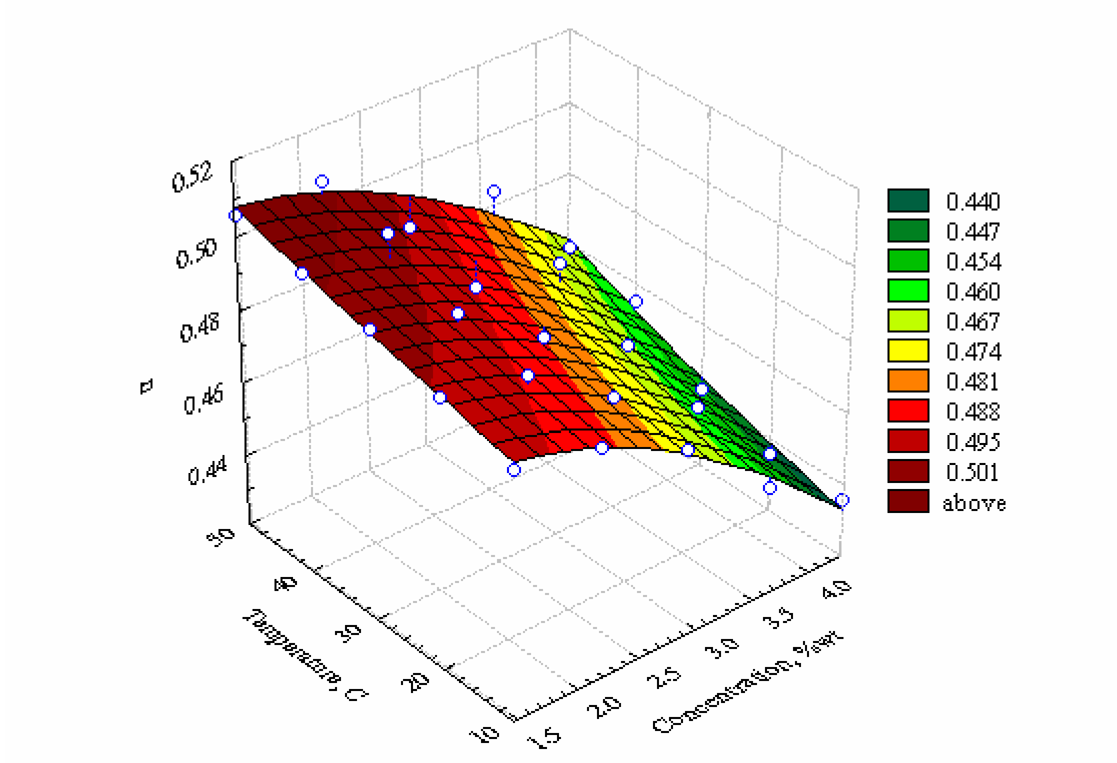

Figure 5. Measured data and the response surface for the power-law index, *n*. o denotes the measured data.

4. Conclusions

The effects of temperature and polymer concentration on the steady-state shear viscosity are opposite for the non-Newtonian aqueous polymeric solutions investigated. The analysis of variance was successfully employed to indicate the significant coefficients of the polynomials for the Carreau model parameters. The criterion of significance in the analysis of variance optimizes the data fit for the three parameters. If all terms of the general equation were used to fit the data, it could have been more difficult to get the correct coefficients with the least-squares technique. The polynomial coefficients were obtained and the three equations could be used to interpolate the parameters for $1.48 \leq C \leq 4.32$ %wt and $10 \leq T \leq 50^{o}C$. For η_o and n parameters, as observed in the analysis of variance of Tab. 2 and 4, the concentration factor is more important than the temperature one. For the λ parameter, as observed in the analysis of variance of Tab. 3, the temperature is more important than concentration. The advantage of this technique is that it gives the Carreau model parameters as polynomial functions of concentration and temperature, differently of the approach proposed by Lin and Ko (1995).

5. Acknowledgement

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