

CIVE 898 SECTION 3

DEPARTMENT OF CIVIL ENGINEERING
UNIVERSITY OF NEBRASKA - LINCOLN

Project Summary

Viscosity as a function of Shear Rate and Concentration of Solutes

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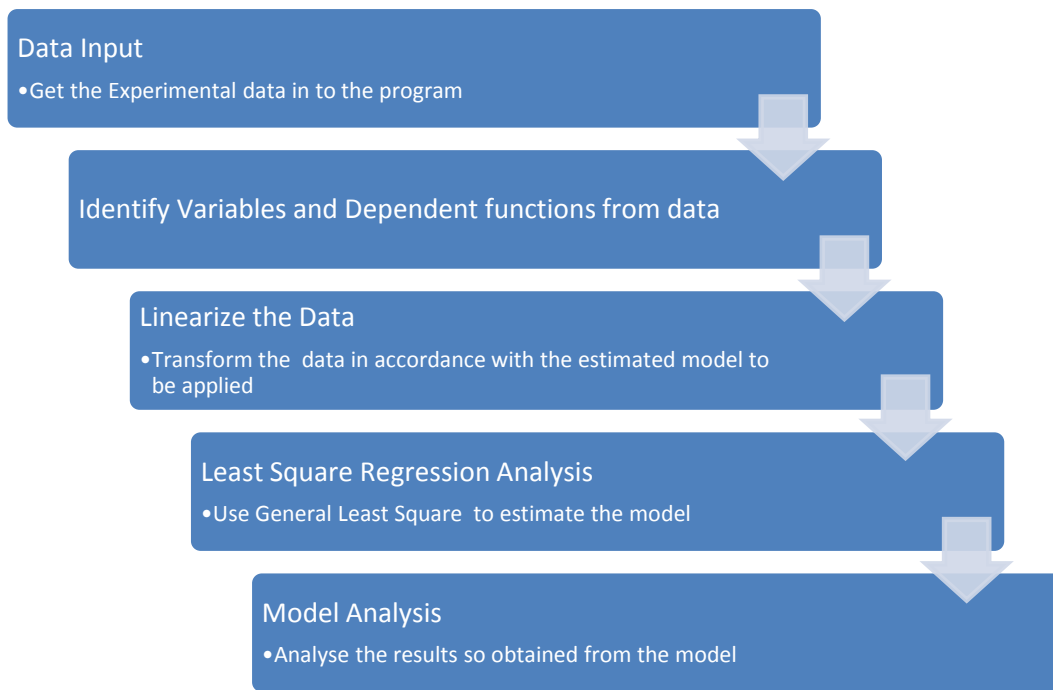
An effort was made to develop a program to do regression analysis and obtain a relationship between the Viscosity, concentration of solutes and shear rate with a good degree of accuracy, “R” values ranging from .9583 and .9824 were obtained for the model suggested by the program.

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Objective

The purpose of this project is to apply the Numerical methods and MATLAB learned in the class to solve practical real life problems. I employed Multivariate Regression Analysis to establish a relationship between the change in Viscosity of a solution with respect to changing concentrations of Xanthan Gum, MnO_4 and varying shear rate. Below is a brief framework of the steps I carried out to prepare the model



Introduction

Viscosity (Poise – P or Pa s) is the measure of a fluid's resistance to flow, flow occurs only when some shear rate (s^{-1}) is applied to the fluid. For most fluids the viscosity remains constant with varying shear rates but for some fluids viscosity changes with the varying shear rate applied to them, these are known as Non Newtonian. Fluids whose viscosity decreases with the increase in shear rate are called **pseudo plastics**. Xanthan gum has this special property that makes it loose its viscosity with increasing shear rates. Xanthan gum is widely used to increase the viscosity of a liquid under normal conditions and flow when stress is applied on them. This property has a wide

range of applications in the real world; it's used in products from salad dressings to paints and drilling fluids.

The nature of the interaction among xanthan gum molecules in aqueous solution is not certain, although both hydrogen bonding and ionic interactions are believed to be involved. In salt-free solutions, viscosity is built through the entanglement of the random polymer coils, to the extent allowed by the mutual repulsion of the negatively charged side chains. Whereas when an electrolyte is present, colloidal network forms. This network of entangled stiff molecules accounts for the characteristic rheological properties of xanthan gum solutions. We tried to formulate a definite relationship between the concentrations of Xanthan and electrolyte on the viscosity of the solution.

Data Source

In the effort to find an empirical relationship between viscosity shear rate and concentrations of xanthan and MnO_4^- in a fluid, the data obtained during the experiments conducted by Chant Chokejaroenrat and his team at University of Nebraska was used. While working to improve the sweeping efficiency of the permanganate into low permeable zones, they tried to increase the viscosity of the displacing fluids by adding Xanthan. For the purpose of the experiment aqueous solutions of Xanthan and MnO_4^- were prepared. Xanthan stock solution of 2 g/l was prepared at room temperature, by slowly adding xanthan powder to water and stirring it continuously to avoid powder formation on the glass wall. The solution was continuously mixed on a magnetic stirrer for 90 min at room temperature. The stock solution was then diluted to varying concentrations (125, 250, 500, 750, 1000 mg/l) and its Viscosity was measured with a cone/plate DV-II + Pro Brookfield Viscometer over shear rates ranging from .1 to 400 sec^{-1} . Further the viscosity effects of addition of xanthan and MnO_4^- concentrations of the solution were recorded. Xanthan solutions with concentrations of 500 1000 and 1250 mg/l were spiked with NaMnO_4 at 1250, 2500, 5000, 10000 and 12500 mg/l each, and their viscosities were measured corresponding to different stress rates. The Stress rates chosen were corresponding to what is experienced by the fluids in the aquifers.

Data Review

The following data was acquired from the experiments

Shear Rates	125	250	500	750	1000	Xanthan Concentrations (mg/l)
0.1	32.87	62.17	175.39	286.00	585.37	
0.7	37.20	52.69	106.28	148.80	373.22	
3	31.00	54.97	74.27	82.67	202.03	
6	21.70	42.74	48.60	57.27	149.77	
10	10.69	28.93	33.02	42.41	117.25	
20	4.65	13.17	17.23	22.97	63.64	
40	2.79	6.94	7.84	14.61	34.60	
60	2.36	5.32	5.72	12.21	24.95	
80	2.25	4.20	5.22	10.65	19.85	
100	2.20	3.58	4.75	9.83	16.07	
200	1.86	3.15	3.73	7.36	9.18	
400	1.70	2.11	3.07	5.70	4.85	

Table 1 - Viscosity with changing shear rate corresponding to Xanthan Concentration

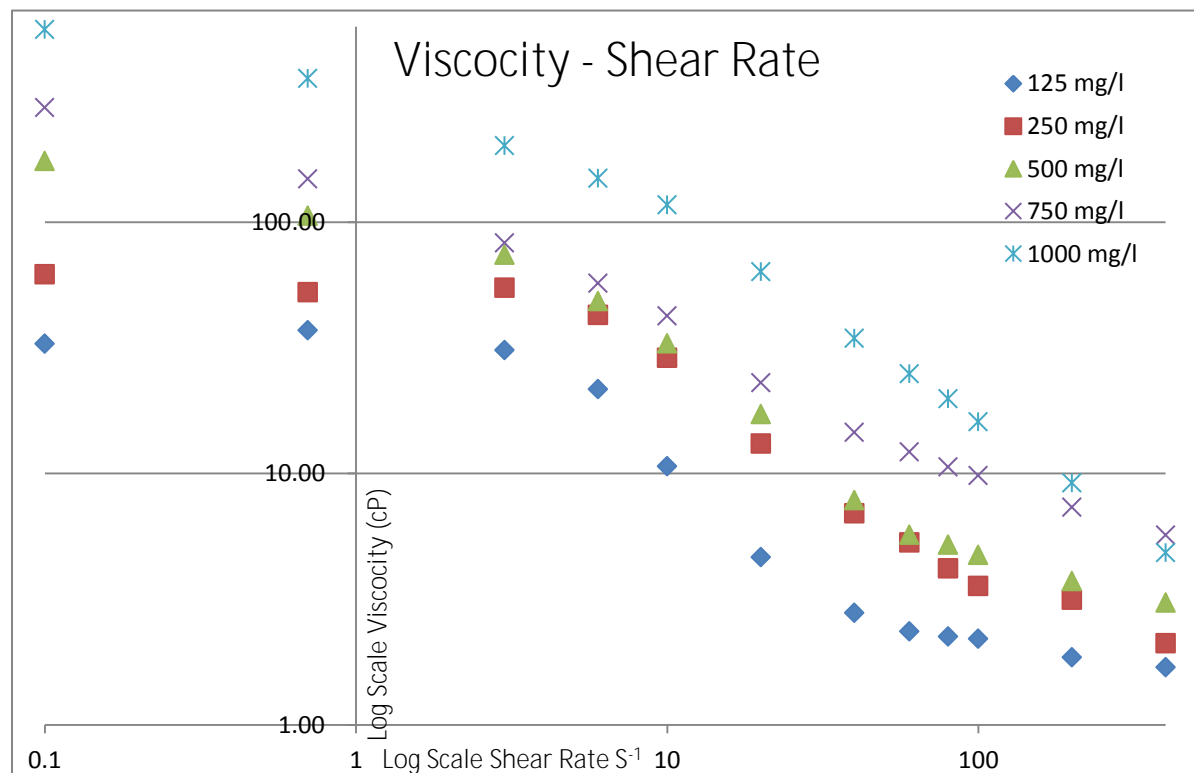


Figure 1 Viscosity with changing shear rate corresponding to Xanthan Concentration

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Shear Rate	1250-12500	1000-12500	500-10000	500-5000	500-2500	500-1250
0.1	5,698.46	3,548.35	1,115.99	650.99	549.54	289.33
0.7	3,162.28	2,135.98	500.42	340.11	232.50	135.51
3	3,162.28	1,621.81	72.63	57.58	34.72	18.62
6	2,698.46	1,122.02	36.76	26.95	15.50	12.40
10	2,045.98	851.14	24.92	20.13	11.69	8.56
20	1,022.99	467.74	17.20	14.37	7.90	6.42
40	511.49	288.40	12.93	10.86	7.21	4.93
60	341.00	208.93	9.98	9.31	6.66	4.37
80	255.75	177.83	8.79	7.95	5.36	4.28
100	204.60	125.89	7.87	6.67	5.06	3.89
200	102.30	74.13	5.91	5.47	3.56	3.23
400	51.15	38.02	4.28	4.71	2.81	2.67

Table 2 Viscosity with changing shear rate corresponding to Xanthan & MnO4 Concentrations

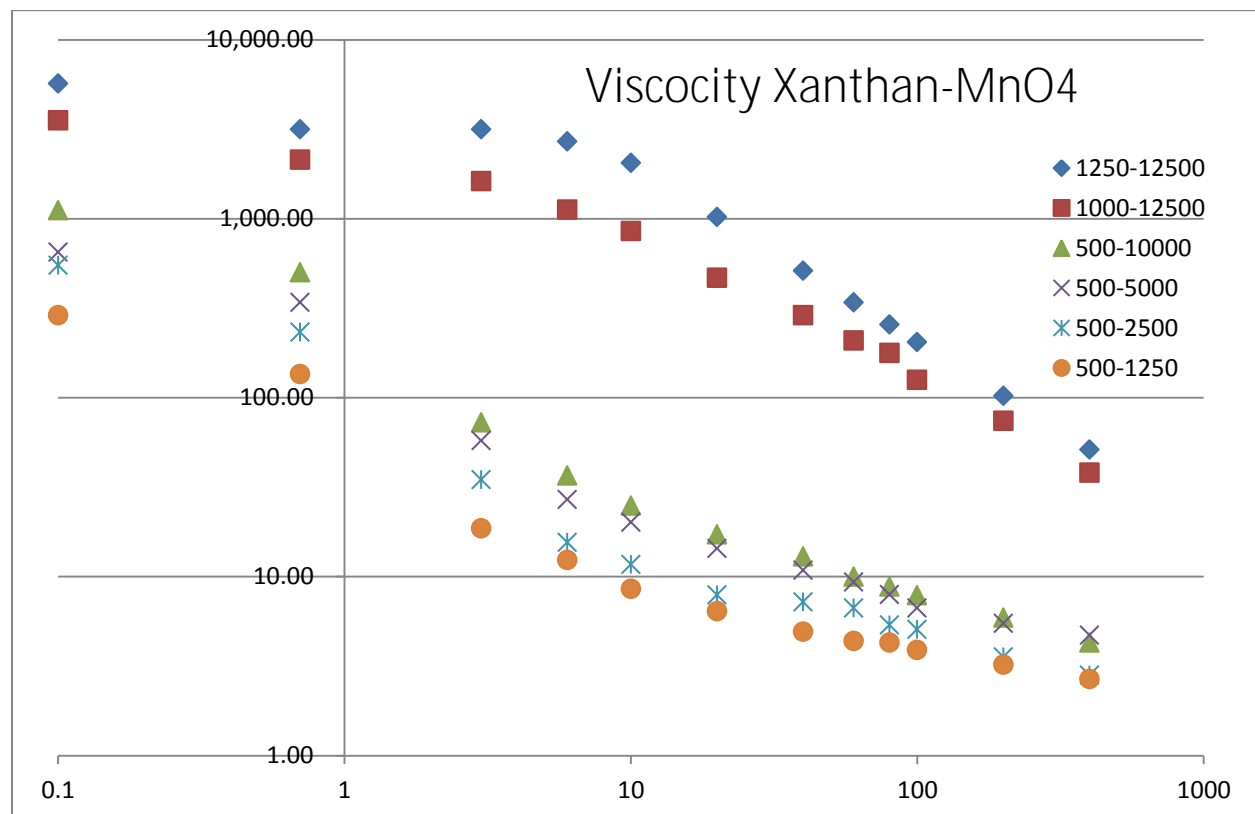


Figure 2 Viscosity at different shear rates and Xanthan MnO4 Concentrations

Looking at the data and the graphs obtained it can be inferred that a Power equation is best suited for the data as the plot is close to a straight line on the Log graph.

Representation of the Data to be analyzed

The program developed reads the data directly from the first sheet of an Excel spreadsheet. If the user of the program is using a computer that does not have Microsoft Excel installed it can read only the basic xls and xlsx spreadsheet files. For the program to function properly data needs to be in the particular format as shown below.

Xanthan	MNo4	Shear Rate	Viscosity
1250	12500	0.1	5,698.46

The program reads the last column of the dataset as the dependent function and the ones before it as the independent variables. It can handle up to 3 variables. The dataset should be modified such that the dependent function is the last column, the variable columns can be in any order, and the output coefficients will be in the same order respectively. However it is advisable to setup the data such that the First column has the concentration of Xanthan in mg/l, second column is the concentration of MnO₄ in mg/l, third column is the shear rate and the last column is the dependent function Viscosity (*Appendix 1b & 1c*) that way the plots and the coefficients are displayed correctly. If the order is not as shown above you will have to interpret the plots differently.

Methodology

Looking at the data and the plot so obtained on the log graph I inferred that a Power equation is the best possible fit to the case of viscosities relationship with shear rate and Solute concentrations. To develop a model that fits the data and tries to get the best estimate of the relationship between viscosity shear rate and concentrations I used Least Squares Regression. Least Square Regression is a method of estimating the model such that sum of squares of the difference between the function value obtained from the model and the value observed is min.

The relationship between the dependent function and the independent variables is a nonlinear (power) one, which is represented as shown below

$$Y = a \cdot X_1^b \cdot X_2^c$$

To make it linear the data has to be modified. The simplest way to do so is to take log of the equation on both sides

$$\text{Log } Y = \text{Log } a + b \log X$$

Once the data has been transformed in to a linear format, General Linear Least Square Regression Analysis is used. Which is given by the equation

$$\{A\} = [[Z]^T [Z]]^{-1} \{ [Z]^T [Y] \}$$

Where A is the coefficients of the estimated model i.e Log a, and b. Z is the matrix of the independent variables Log X (shear rate and concentrations), and Y is the observation of the dependent function (Viscosity – Log Y) corresponding to different values of the variables.

Once the coefficients are calculated the values of Y are calculated as per the estimated model and the results are compared with the observed data. Than the Coefficient of Determination (R^2) is computed and checked how good the fit is. Ideally it should be 1, and closer the value of R is to 1 better is the fit.

Algorithm

1. The first step of the project execution is to import the data in to the program, for this `load` command is used to read data from the Excel spread sheet which contains the data in the format as described "Representation of Data" section.
2. Once the Data has been acquired program breaks it down to acquire the dependent function and the independent variables.
3. Program acquires the information about the number of variables and the number of experiment data points.
4. It checks the number of variables and transfers the program to the respective loop. Since the program is designed to handle up to 3 independent variables, it gives error message if the number of variable is more than 3 or less than 2. There is no such limit on the number of experiment sets.

5. The data is then transformed to make it linear, i.e. log of the values are taken so that the power equation is converted into a linear equation, these log values are stored as the independent variables and used for estimating the model.
6. Data is setup in the Matrices required by the General Least Square regression. i.e. Z matrix is made of x_1 x_2 x_3 , y is the viscosity values
7. Average of the data set and its spread around its mean is calculated.
8. Then program performs the General Least square regression on the transformed data to estimate the coefficients of the linear equation.
9. Using the coefficients obtained program finds the estimated values of the dependent function based on the dependent variables.
10. The estimated values are then compared with the experimental data to check for the fit of the program. Coefficients of Regression like correlation coefficient, sum of residual squares etc are computed.
11. Estimated values from the model are plotted with the experimental data to give a clear picture of the fit.

For reference code is provided in *Appendix 1(a)*

Using the Program

Program has been designed to tackle up to 3 variables and using it is very simple, all one needs to do is type in the command window `run(file_name)`, where file_name is the name of the spreadsheet containing the data as described in Representation of data section. The file should be in the "current folder". The program runs fine with R2012a version of MATLAB. If you are using older version of MATLAB you will have to include the file extension also.

Program gives output as following terms

- a) Coefficients for the power equation (a, b, c, d)
- b) Sum of Squares around Mean (S_t)
- c) Sum of Squares of residuals around regression line (S_r)

- d) Correlation Coefficient (R)
- e) And a plot of Viscosity suggested by the program along with the observed values.

Results and Estimated Model

When I ran the program on the Viscosity data corresponding changing shear rate and Xanthan Gum concentration following results were produced by the program.

A =

-0.5180
0.9257
-0.5317

Elements of the power equation $a.X_1^b.X_2^c...$ are (a,b,c,...)

Coefficients =

0.3034 0.9257 -0.5317

St =

24.8583

Sr =

2.0307

R =

0.9583

This gives us the following model

$$V_{\text{viscosity}} = 0.3034 * C_{\text{xantan}}^{.9257} * S_{\text{rate}}^{-0.5317}$$

And the following plot was obtained, the lines are the values predicted by the above model for different concentrations of the xanthan gum in mg/l and the stars are the observed values.

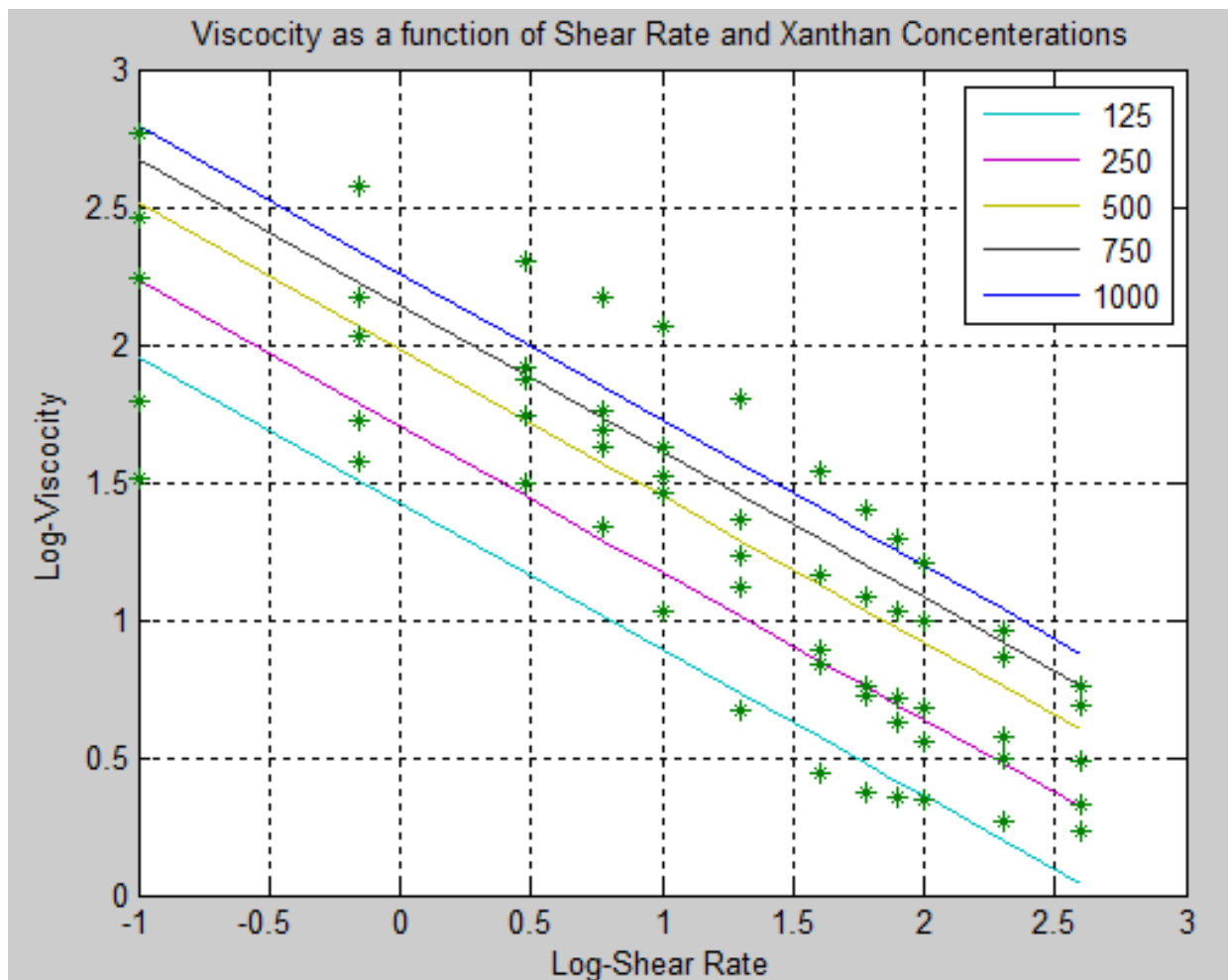


Figure 3 Plot of Model predicted and Observed Values corresponding to Varying Xanthan Concentrations

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The program produced the following results from the Viscosity data corresponding to Xanthan MnO₄ concentrations and shear rate.

A =

-9.1055
3.4698
0.4907
-0.6250

Elements of the power equation $a.X_1^b.X_2^c...$ are (a,b,c,...)

Coefficients =

0.0000 3.4698 0.4907 -0.6250

St =

68.1644

Sr =

2.3765

R =

0.9824

This gives us the following model

$$V_{\text{viscosity}} = 10^{-9.1055} * C_{\text{xantan}}^{3.4698} * C_{\text{MnO4}}^{0.4907} S_{\text{rate}}^{-0.6250}$$

And the following plot was obtained, the lines are the values predicted by the above model for different concentrations of the xanthan gum in mg/l and the stars are the observed values.

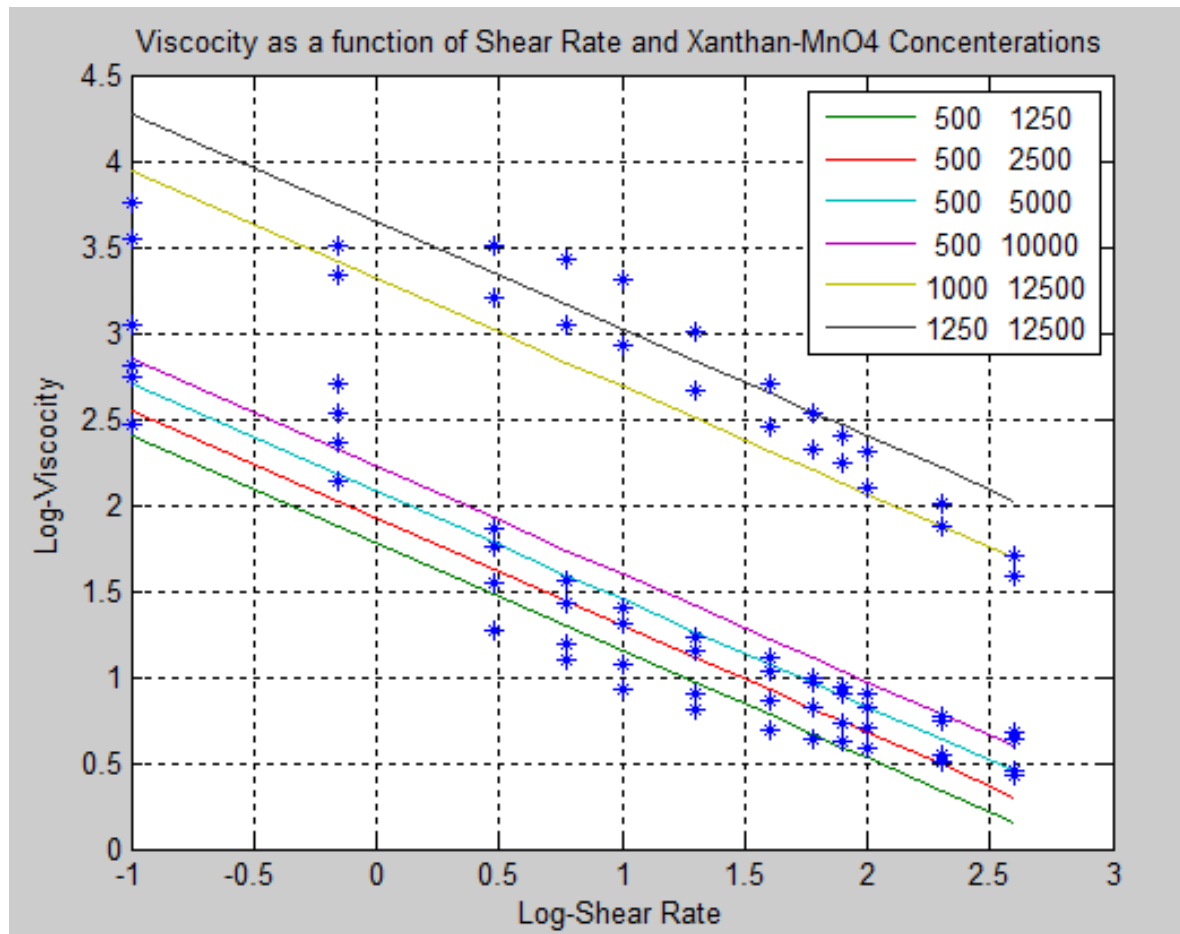


Figure 4 Plot of Model predicted and Observed Values corresponding to Varying Xanthan-MnO₄ Concentrations

Conclusions

The model so obtained from the program has an R value of close to 1 with an **R** value of **.9583**, for the Xanthan data set and **0.9824** for the Xanthan MnO₄. We can say with confidence that the model suggested by the program is of acceptable accuracy for the range of our data sets and can be used in making estimates of viscosity under various shear rates and concentrations values with good level of confidence.

References

- (1) C. Chokejaroenrat; S.Comfort; C. Sakulthaew. Improving the sweeping efficiency of permanganate into low permeable zones to treat dissolved phase TCE
- (2) J.Higiro a, T.J. Herald S. Alavi, Rheological study of xanthan and locust bean gum interaction in dilute solution.
- (3) Kelco Oil Group, Rheology Technical Bulletin.
- (4) W. M Kulicke and R.Kniewske The shear viscosity dependence on concentration, molecular weight, and shear rate of polystyrene solutions.
- (5) Steven Chapra Numerical Methods for Engineers. Chapter 17.
- (6) Matlab Help function was used extensively while writing the code.

Appendix 1

(a) Project Code

```
function [ ] = sonitp2( datafile )
% sonitp2 provides the best estimate of the curve
% for a power equation that satisfies the given data
% This model is designed to handle upto 3 variables (x1, x2, x3)
% The program is designed for understanding the effect of the
% concentrations of various solutes and shear rates on viscosity
% datafile is the file containing the data to be analysed
% datafile should be entered with single quotes 'XXXXXXX'
% File should be an excel spread sheet and data should be in the specified
% Order of columns i.e last column should be the function (Viscosity) and
% the initial columns should be the first variables and the

clc
dataread = xlsread (datafile);
[m,n] = size (dataread); % gets the number of variables and no of experiments
% Checks the number of Variables and employs the respective if loop

if n == 2
shrate = xlsread (datafile, 'a:a');
viscosity = xlsread(datafile, 'b:b');

y = log10 (viscosity); %y is the log of viscosity
x1 = log10 (shrate); %x1 is the concentration of xanthan

z = [(ones (a,1)), x1];
end

%%
if n == 3
Xconc = xlsread (datafile, 'a:a');
shrate = xlsread (datafile, 'b:b');
viscosity = xlsread(datafile, 'c:c');

y = log10 (viscosity); %y is the log of viscosity
x1 = log10 (Xconc); %x1 is the log of concentration of xanthan
x2 = log10 (shrate); %x2 is the log of shear rate applied
z = [(ones (m,1)), x1, x2];
end

if n == 4
Xconc = xlsread (datafile, 'a:a');
Mconc = xlsread (datafile, 'b:b');
```

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```
shrate = xlsread (datafile, 'c:c');  
viscosity = xlsread(datafile, 'd:d');
```

```
y = log10 (viscosity);%y is the log of viscosity  
x1 = log10 (Xconc); %x1 is the concetration of xanthan  
x2 = log10 (Mconc); %x1 is the concetration of xanthan  
x3 = log10 (shrate);%x2 is the log of shear rate applied  
z = [(ones(m,1)), x1,x2,x3];  
end
```

```
ymean = mean (y); % Average of the dependent data set  
% Finding the spread of the dataset  
for i = 1:m  
    diffyymean (i) = y(i) - ymean;  
end
```

```
A = [z'*z]^(-1)*z'*y % calculates the coefficients
```

```
% calculate the Values of Viscosity as per estimated model  
if n == 2
```

```
    for i = 1:m  
        Ycalc (i) = [ A(1)+A(2)*x1(i)];  
    end  
    disp ('Elements of the power equation a.X1^b.X2^c... are (a,b,c,...)')  
    Coefficients = [10^A(1), A(2)]  
end
```

```
% calculate the Values of Viscosity as per estimated model  
if n == 3  
    for i = 1:m  
        Ycalc (i) = [ A(1)+A(2)*x1(i)+A(3)*x2(i)];  
    end  
    disp ('Elements of the power equation a.X1^b.X2^c... are (a,b,c,...)')  
    Coefficients = [10^A(1), A(2), A(3)]  
end
```

```
% calculate the Values of Viscosity as per estimated model  
if n == 4  
    for i = 1:m  
        Ycalc (i) = [A(1)+A(2)*x1(i)+A(3)*x2(i)+A(4)*x3(i)];  
    end  
    disp ('Elements of the power equation a.X1^b.X2^c... are (a,b,c,...)')  
    Coefficients = [10^A(1), A(2), A(3), A(4)]  
end
```


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%calculate the difference between the Estimated value and Observerd Value

Yestimated = Ycalc';

for i = 1:m

 estidev(i) = y(i) - Yestimated(i);

end

% Calculate the coefficients of Regression

St = sum (diffyymean.^2)

Sr = sum ((estidev).^2)

R = (((St-Sr)/St))^.5

% Plotting the estimated values against observed data

if n == 3

 xconcentration = unique (Xconc);

 shearrates = unique (x2);

 [numbofconc,a] = size (xconcentration);

 [numbofshear,a] = size (shearrates);

 for i = 1: numbofconc

 for k = 1: numbofshear

 Viscositycalc (i,k)=[A(1)+ A(2)* log10(xconcentration(i))+ A(3)*shearrates(k)];

 end

 hlines = plot (shearrates,Viscositycalc);

 grid on

 title('Viscosity as a function of Shear Rate and Xanthan Concentrations');

 xlabel('Log-Shear Rate');

 ylabel('Log-Viscosity');

 set (hlines (i),'Displayname',num2str (xconcentration (i)));

 hold all

 end

 plot (x2,y,'*')

 legend (hlines, num2str (xconcentration))

 hold off

 end

if n == 4

 xanthanmno4conc = [x1 x2];

 shearrates = unique (x3);

 xantmno4 = unique (xanthanmno4conc, 'rows');

 Union = [Xconc Mconc];

 uniquexanmno4 = unique (Union, 'rows');

 xanthanmno4 = num2str (uniquexanmno4);

 [numbofconc,a] = size (xantmno4);

 [numbofshear,a] = size (shearrates);

 for i = 1: numbofconc

 for k = 1: numbofshear

 Viscositycalc (i,k)= [A(1)+ A(2)*xantmno4(i,1)+A(3)*xantmno4(i,2) + A(4)*shearrates(k)];

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```
end
hlines = plot (shearrates,Viscositycalc);
grid on
title('Viscosity as a function of Shear Rate and Xanthan-MnO4 Concentrations');
xlabel('Log-Shear Rate');
ylabel('Log-Viscosity');
set (hlines (i),'Displayname',(xanthanmno4 (i)));
hold all
end
plot (x3,y,'*')
legend (hlines, xanthanmno4)
hold off
end

if n > 4
error('Program can handle only 2 and 3 variables');
end
if n < 2
error('Program can handle only 2 and 3 variables');
end

end
```

(b) Modified Data from Table 1

Xanthan Conc (mg/l)	Shear Rate(/s)	Viscosity (c.p)
125	0.10	32.87
125	0.70	37.20
125	3.00	31.00
125	6.00	21.70
125	10.00	10.69
125	20.00	4.65
125	40.00	2.79
125	60.00	2.36
125	80.00	2.25
125	100.00	2.20
125	200.00	1.86
125	400.00	1.70
250	0.10	62.17
250	0.70	52.69
250	3.00	54.97
250	6.00	42.74

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250	10.00	28.93
250	20.00	13.17
250	40.00	6.94
250	60.00	5.32
250	80.00	4.20
250	100.00	3.58
250	200.00	3.15
250	400.00	2.11
500	0.10	175.39
500	0.70	106.28
500	3.00	74.27
500	6.00	48.60
500	10.00	33.02
500	20.00	17.23
500	40.00	7.84
500	60.00	5.72
500	80.00	5.22
500	100.00	4.75
500	200.00	3.73
500	400.00	3.07
750	0.10	286.00
750	0.70	148.80
750	3.00	82.67
750	6.00	57.27
750	10.00	42.41
750	20.00	22.97
750	40.00	14.61
750	60.00	12.21
750	80.00	10.65
750	100.00	9.83
750	200.00	7.36
750	400.00	5.70
1000	0.10	585.37
1000	0.70	373.22
1000	3.00	202.03
1000	6.00	149.77
1000	10.00	117.25
1000	20.00	63.64
1000	40.00	34.60
1000	60.00	24.95

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1000	80.00	19.85
1000	100.00	16.07
1000	200.00	9.18
1000	400.00	4.85

(c) Modified Data from Table 2

Xanthan Conc. (mg/l)	MnO4 Conc. (mg/l)	Shear Rate(/s)	Viscosity (c.p)
1250	12500	0.1	5,698.46
1250	12500	0.7	3,162.28
1250	12500	3	3,162.28
1250	12500	6	2,698.46
1250	12500	10	2,045.98
1250	12500	20	1,022.99
1250	12500	40	511.49
1250	12500	60	341.00
1250	12500	80	255.75
1250	12500	100	204.60
1250	12500	200	102.30
1250	12500	400	51.15
1000	12500	0.1	3,548.35
1000	12500	0.7	2,135.98
1000	12500	3	1,621.81
1000	12500	6	1,122.02
1000	12500	10	851.14
1000	12500	20	467.74
1000	12500	40	288.40
1000	12500	60	208.93
1000	12500	80	177.83
1000	12500	100	125.89
1000	12500	200	74.13
1000	12500	400	38.02
500	10000	0.1	1,115.99
500	10000	0.7	500.42
500	10000	3	72.63
500	10000	6	36.76
500	10000	10	24.92
500	10000	20	17.20
500	10000	40	12.93
500	10000	60	9.98

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500	10000	80	8.79
500	10000	100	7.87
500	10000	200	5.91
500	10000	400	4.28
500	5000	0.1	650.99
500	5000	0.7	340.11
500	5000	3	57.58
500	5000	6	26.95
500	5000	10	20.13
500	5000	20	14.37
500	5000	40	10.86
500	5000	60	9.31
500	5000	80	7.95
500	5000	100	6.67
500	5000	200	5.47
500	5000	400	4.71
500	2500	0.1	549.54
500	2500	0.7	232.50
500	2500	3	34.72
500	2500	6	15.50
500	2500	10	11.69
500	2500	20	7.90
500	2500	40	7.21
500	2500	60	6.66
500	2500	80	5.36
500	2500	100	5.06
500	2500	200	3.56
500	2500	400	2.81
500	1250	0.1	289.33
500	1250	0.7	135.51
500	1250	3	18.62
500	1250	6	12.40
500	1250	10	8.56
500	1250	20	6.42
500	1250	40	4.93
500	1250	60	4.37
500	1250	80	4.28
500	1250	100	3.89
500	1250	200	3.23
500	1250	400	2.67

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Project Summary
Bhavneet Soni