DEVELOPMENT OF CORRELATION FOR THE DENSITY OF POLYMERS AS FUNCTION OF TEMPERATURE AND CONCENTRATION

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Abstract: - The aqueous solution of a polymer such as xanthan gum, carboxymethyl cellulose and sodium alginate are widely used in the food, drugs, pharmaceutical, cosmetic and chemical industries as a thickener, emulsifier and flow behavior modifier. Hence, it is necessary to know their thermo-physical properties with good precision, especially density which describes the degree of compactness and heaviness of the substance. The properties of any material are largely dependent on its density. Mentioned polymers were selected for study of density which shows non-Newtonian shear thinning behavior.

Density (Kg/m³) was determined using the specific gravity bottle. Experimental results concerning the direct measure of the density of the polymer solutions in a temperature range of 293.15 K–331.15 K and concentration range of 0.1-0.6% w/w are presented and detailed in this work. The correlations for density of selected polymers were derived by using Response Surface Methodology. Comparisons with already existing models were done. The general correlation which gives the best fit for all the polymers which behave as a shear-thinning fluid was studied and identified in this work.

Keywords: Power-law fluid, Thermo-physical property, Density and Response surface technology

1. INTRODUCTION

Fluids which do not unveil a direct proportionality between shear stress and shear rate are called as non-Newtonian fluid. Ostwald–De Waele model also known as the power-law model is most widely used to define their flow behavior (Rao & Anantheswaran, 1982). Among shear thinning fluid, type of non-Newtonian fluid shows elastic flow behavior to a certain extent which acts as a significant factor for many industrial applications such as food, pharmaceutical, and cosmetic manufacturing processes etc. (Song et al. 2006). Among the wide variety of non-Newtonian fluids, shear thinning fluids are used extensively as a stabilizer, binder, thickening agent (Sylwia and Zdzisław, 2012). Shear thinning fluids are treated as Newtonian fluids in food process design (Afonso et al. 2003) because of insufficient information on thermo-physical properties and flow behavior. Thermo-physical properties of shear thinning fluids are important for evaluating, designing and modeling the food processes such as refrigeration, freezing, heating, pasteurization and drying (Gut et al. 2005) especially density.

Ramos and Ibarz (1998) reported the density of juice and fruit puree as a function of soluble solids content and temperature. Peach juice density was in the range of 1010.65-1302.99 kg/m³ at concentrations between 10 and 60°Brix and for temperatures between 278.15 and 353.15 K. Tseng and King (2002) reported density of banana puree as 952-1611.61 kg/m³ in a concentration range of 10 to 80° Brix and temperature range of 278.15 -353.15 K, also presented a model for density as a function temperature and soluble solids concentration. Afonso et al. (2003) described the density dependency of the stirred yoghurt on temperature in the range of 273.15–318.15 K and found that the density of stirred yoghurt is a weak dependency on temperature. The density values of the stirred yoghurt ranged from 1042 to 1071 kg/m³. Gut et al. (2005) presented an empirical correlation to determine the density of liquid egg yolk in the temperature range of 273.55–333.95 K. Egg yolk density was in the range of 1129.7–1133.4 kg/m³, they have observed weak temperature dependence of the density of egg yolk. Cancée et al. (2008) studied the effects of temperature (303.15-323.15 K) and concentration (20-50 %w/w) on the density of cassava starch solutions, the density value of Cassava starch solution was in the range of 1044-1120 kg/m³. The density of cassava starch solutions decreases with increase in temperature and increases linearly with increase in concentration. The carbohydrate starch granule is the principal solids content of cassava starch solutions and its concentration directly affects the density. Pineapple juice density was determined by Cabral et al. (2010) for temperatures in the range of 290.55-358.95 K and soluble solids content in the range of 0-52.4°Brix. The mean absolute error observed was 0.6% of the pineapple juice density determination. Cancela et al. (2005) reported the variation of density of CMC with concentration and temperature. Biswas et al. (2008) studied density of sodium salt of carboxymethyl cellulose (CMC) at room temperature and as a function of concentration and reported density values of the sodium salt of carboxymethyl cellulose ranged from 1001.69-1003.83 kg/m³. Asmaa Hassan Dhiab (2012) studied the temperature effect on viscosity and density of xanthan gum solution (0.1-0.5 %w/v) with temperature range of 303.15-333.15 K. The density of the xanthan gum solutions decreases gradually with increases in temperature and it increases with concentration, density of xanthan gum solution was in the range of 0.8808-1.0538/cm³.

It was realized from our vigorous literature survey that, there exists a reasonably substantial amount of literature published on the density of fluid food but density data is available only for two polymers CMC and Xanthan gum. Density is not
available for all the shear thinning fluids at different temperature and concentration. In previous studies only a few authors reported the correlation for density which is useful for the specific fluid food they have used in their study. The unavailability of data leads to find out the correlation for density of shear thinning fluids such as xanthan gum, carboxymethyl cellulose and sodium alginate in the temperature range of 293.15-333.15 K and concentration range 0.1-0.6 %w/w. Hence the objective of the present work was to study and develop correlation for the density of shear thinning fluids which are widely used in food, drug, agricultural and cosmetics industries for a wide temperature range of 293.15 to 331.15 K and for the concentration range of 0.1-0.6 %w/w. The main purpose was to develop single correlations for predicting density under different experimental conditions, which also can be used to calculate density of any fluid food which behaves as a shear thinning fluid.

2. MATERIALS AND METHODS
2.1 Sample preparation and experimental procedure
Xanthan gum pure (food grade) was obtained from M/s. LOBA Chemie. Particle size (100-200 mesh), ash (6.5-16 %), pH of 1 % solution in water (6-8), nitrogen (1.5 %), pyruvic acid (2.40 %) and heavy metals (0.001 %) are the basic physical properties reported by M/s. LOBA Chemie. CMC pure (food grade) was furnished by M/s. Himedia. Viscosity (1 %w/v; water 20°C), assay (Na; on dried substance), pH of 1%w/v; water, chloride, Arsenic, heavy metals of 1100-1900 cps, 6.5-10.8 %, 6-8, ≤ 0.25 %, ≤ 0.000% and ≤ 0.002 % are the basic physical properties reported by M/s. Merck. Sodium alginate was purchased from M/s. Himedia. Chloride (Cl) (1 %) and Heavy metals as (Pb) (0.0003 %) are the basic physical properties reported by M/s. Himedia.

Sample solutions were prepared in 100 ml conical flask with distilled water by mixing the selected polymers to obtain different concentrations ranging from 0.1-0.6 % by weight. Magnetic stirrer was used to dissolve the polymers completely and for heating. During heating the conical flask was covered with aluminum foil to prevent moisture loss due to evaporating. The temperatures of the sample solutions were measured using a digital thermometer. The specific gravity bottle was supplied by M/s. Precision scientific Co. Trichy. First volume of the bottle was determined by using water as a sample fluid. Weight of empty specific gravity bottle was subtracted from weight of the specific gravity bottle with water, and dividing this quantity by the density of water gives the volume of the bottle. The mixture of known amount was transferred into the specific gravity bottle and the measurements of the density of the samples were done. The density values were measured at a temperature range of 293.15-333.15 K and concentration range of 0.1-0.6 % by weight and it was prudently chosen according to industrial practice.

2.2 Experimental Design
Densities of three selected shear thinning fluids were measured by using the above procedure for different concentration and different temperature. Effects of experimental parameters such as temperature and concentration on the density of shear thinning fluids were studied. The results obtained are used to model equation by Response surface methodology technique. In order to study the combined effect of these parameters on the density of these above solutions, statistical analysis of central composite design was used for the five chosen variables.

Design Expert Software (8.0.6) was used to study the effect of operating variables on the density of shear thinning fluids. Independent variables, i.e. temperature and concentration were coded at five levels between -2 and +2, where the temperature (T) range was 293.15-333.15 K and concentration(C) range was 0.1-0.6 %w/w. Independent process variable levels of shear thinning fluids of Central composite rotatable design (CCRD) are presented in Table 1.

The number of test required for CCRD includes the standard 2ⁿ factorial with it’s origin at the centre, 2k points fixed axially at a distance, say a, from the centre to generate the quadratic terms, and replicate tests at the centre; where k is the number of variables. The axial points are chosen such that they allow rotatability, which ensures that the variance of the model prediction is constant at all points equidistance from the design centre. Replicates of the test at the centre are very important as they provide an independent estimate of the experimental error. For two variables, the recommended number of test at the centre is five. Hence the total number of test required for the two independent variables (concentration and temperature) is 2² + (2 x 2) + 5 = 13 (Obeng, 2005 & G. E. P. Box, 1957). To calculate the pure error, eight experiments were performed with five replications at the design center using RSM in randomized order.

The second order polynomial equation is expressed as follows
\[Y = b_0 + b_1X_1 + b_2X_2 + b_{12}X_1X_2 + b_{11}X_1^2 + b_{22}X_2^2 + \varepsilon_i\]  
(1)

- **Y**: Predicated response
- **X₁** and **X₂**: Operating variables
- **b₀**: - Constant
- **b₁ and b₂**: - Interacting coefficients of linear
- **b_{12}**: - Interacting coefficients between the variables
- **b_{11} and b_{22}**: - Interacting coefficients of quadratic
- **ε_i**: - Error

The correlation coefficient (R²) expresses the quality of the fit of the quadratic equation and F test was used to check the significance of the quadratic equation. The main aim of this experiment is to determine the second order polynomial equation for density of shear thinning fluids such as xanthan.
gum, carboxymethyl cellulose and sodium alginate

3. RESULT AND DISCUSSION

The density of shear thinning fluids were obtained using a specific gravity bottle with different temperature of 298.15 - 333.15 K and concentration of 0.1-0.6% w/w and presented below.

3.1 The effect of concentration and temperature on density of power-law fluid

The variation of density of three shear thinning fluids with concentration and temperature are shown in Fig. 1-3. for 0.2, 0.4 and 0.6% w/w concentration of selected shear thinning fluids. It can be seen that the density increases with increase in concentration and decreases with increases in temperature for each power-law fluid. The results for minimum and maximum density of xanthan gum, CMC and sodium alginate have given in Table 2 with corresponding values of concentration and temperature.

As the concentration increases, the quantity of mass increases for constant volume. This leads to the increase in density with concentration for each shear thinning fluid. The molecules in the fluid combined with water gain energy which is used to bend and break the hydrogen bonds when temperature increases. Due to that the size of ordered clusters molecules decreases, the number of smaller clusters increases, the number of hydrogen bond decreases and the average distance between the molecules increases. The hot fluid has a small amount of hydrogen bonds and the spaces between the molecules also increases as mentioned above. The final result is to have less mass per unit volume. This resulted in a decrease in density of the solution with increase in temperature. Increased temperatures also increase the thermal expansion of shear thinning fluids. Hence density decreases with increases in temperature. The same was observed in 0.1, 0.3 and 0.5 %w/w concentration of shear thinning fluid.

3.2 Model development and results

Using the Design Expert Software (8.0.6), a multiple regression model, the experimental data on density for each power-law fluid was fitted as a function of concentration and temperature. This yielded the following equations:

Xanthan gum
\[ \rho_x = 4463.964 - 20.54237_T + 821.8685C - 2T_Cx + 0.029688T^2 - 170C^2 \]  

(2)

CMC
\[ \rho_c = 21803.34 - 126.3177T - 348.0788C + 0.57T_C + 0.190625T^2 + 380C^2 \]  

(3)

Sodium alginate
\[ \rho_{al} = 21614.85 - 125.142T_{al} - 381.763C_{al} + 0.57T_{al}C_{al} + 0.18875T^2_{al} + 416C^2_{al} \]  

(4)

The relationship was observed to be a second-order polynomial. Response surfaces, 3D plots of density-temperature-concentration were plotted using developed model equations. Since the prediction equation was non-linear, the behaviors of response surface in Fig. 4-6 are also not flat. The performance of model equations was analyzed based on the adequacy, significance and the effect of the interacting operating parameters. Comparisons of predicted values from the models with the experimental values, shows that the model predictions match with the actual values. The fit of the model was confirmed and verified by means of the absolute average deviation (AAD) value of 0.009592, 0.0421 and 0.0405 for the density of xanthan gum, CMC and sodium alginate solution, respectively. The analysis of variance of regression model for these two quadratic equations are highly significant (p<0.0001). The goodness of the fit by quadratic equation was verified by the regression coefficient R^2. The values of R^2 for quadratic equations and adjusted R^2 were calculated to be 0.9627, 0.9362 for xanthan gum, 0.9673, 0.9440 for CMC and 0.9682, 0.9455 for sodium alginate respectively.
3.3 Analysis of Variance (ANOVA)

The significant effects of the operating variables were determined using ANOVA. According to ANOVA, the Fisher F-values for all regressions were large for density of shear thinning fluid studied, indicating that the variation in the response can be explained by these model equations. The associated p value is used to estimate where F is large enough to indicate whether the model is statistically significant. Any factor or interacting factors with p<0.05 is considered to be statistically significant. The ANOVA table obtained from the response surface quadratic model shows that the temperature and concentration are the highly significant linear factor compared to other factors that affect the density of xanthan gum solution. The coefficients in the model equation for individual, quadratic and interaction of temperature with concentration for density of studied shear thinning fluids were found to be more significant than the other interaction terms.

3.4 Combined Effect of Operating Parameters

The effects of concentration and temperature on density of three shear thinning fluids are shown in Fig. 4-6 for xanthan gum, CMC and sodium alginate respectively, through response surface diagram using developed model equations (Eqs. 4-6). It is observed that density values increase with concentration and decreases with temperature for all the shear thinning fluids studied. The nature of response surface shows that the effect of concentration is more significant than temperature. The result of analysis of variance (ANOVA) with high value of F for concentration also confirmed this inference. Also results are showing good agreement with experimental results (Figs. 1-3). It shows that these second order polynomial equations predict the density of each power-law solution satisfactorily.

3.5 Identification of a model equation for all shear thinning fluids at all temperatures and concentration

In order to arrive at a correlation suitable for a wide range of shear thinning fluids, the quadratic model equation was developed based on experimental studies and using quadratic equation of density of xanthan gum, carboxymethyl cellulose and sodium alginate solution. The quadratic model regression equation (7) is obtained by using quadratic equation of density of xanthan gum, carboxymethyl cellulose and sodium alginate solution and is given below

$$\rho = 15960.72 - 90.6671T + 30.6758C - 0.333337C + 0.136354T^2 + 208.6667C^2$$

(5)

The model equation was tested using the experimental values of density of shear thinning fluids. To select a best fit equation, the experimental data collected in the present study were used and comparisons with already existed correlations have been done. The correlations suggested by Tsen and King for banana puree (2002), Cansee et al. (2008) for cassava starch, Cabral et al. (2010) for pineapple juice was used for comparison who studied density variation with temperature and concentration, the correlations are given below.

Banana puree by Tsen and King (2002)

$$\rho = 1053.39 - 1.44217 + 0.2256C + 0.0864C^2$$

(6)

Cassava starch by Cansee et al. (2008)

$$\rho = 1025.8 - 0.462T + 2.116C$$

(7)

Pineapple juice by Cabral et al. (2010)

$$\rho = 998 - 0.35T + 4.75C$$

(8)

The absolute average deviations for all the equations (2…….. 8), for the present experimental data points (108), is presented in Table 3.
Table 3 Comparison between the predicted results using equation (2-8) for calculating density of shear thinning fluids.

<table>
<thead>
<tr>
<th>Eq. No.</th>
<th>No of data points</th>
<th>AAD</th>
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<tr>
<td>2</td>
<td></td>
<td>0.009595</td>
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<tr>
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<td></td>
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<td>8</td>
<td></td>
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</tr>
</tbody>
</table>

Absolute Average Deviation (AAD) value of 0.0024 which is smaller as compared to the AAD value of other correlations show that correlation (5) can be used to calculate the density of any shear thinning fluid.

4. CONCLUSION

The density of shear thinning fluids which are widely used in food, drug, agricultural and cosmetics industries were experimentally studied and used for proposing the best correlations which can be used for any shear thinning fluid. However the applicability of this correlation can be improved by incorporating additional data on more shear thinning fluids.

Abberivation

XAN  Xanthan gum  
CMC  Carboxymethyl cellulose  
CCRD  Central composite rotatable design  
RSM  Response surface methodology  
SA  Sodium alginate

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REFERENCE