

Viscosity Measurements and Modelling of Aqueous Polyvinyl Alcohol Mixtures

Hamid Modarress¹, Mohsen Mohsen Nia², and Raana Mostafa³

(1) Department of Chemical Engineering, Amir-Kabir University of Technology
Tehran, I.R. Iran

(2) Department of Science, Kashan University, Kashan, I.R. Iran

(3) Department of Chemistry, Amir-Kabir University of Technology, Tehran, I.R. Iran

Recived: 4 April 2004; accepted: 11 August 2004

ABSTRACT

A Haake viscometer was used for viscosity measurements of aqueous polyvinyl alcohol mixtures at temperatures of 288, 298, and 308 K. It was observed that at low concentration of polyvinyl alcohol, variations of the measured shear stress (τ) versus shear rate ($\dot{\gamma}$) were linear and therefore, the Newtonian behaviour of the studied mixtures is considered. The modified Eyring viscosity model previously proposed by the authors were used to test the measured data for aqueous polyvinyl alcohol mixtures. It was shown that the model is well capable to fit the data and the parameters, of the model are evaluated.

Key Words:

polyvinyl alcohol;
viscosity;
Haake viscometer;
Eyring equation.

INTRODUCTION

For designing and optimizing of chemical industrial processes, viscosity is an essential parameter. The lack of experimental viscosities data led researchers to propose the modelling equations for estimating the viscosities of liquids and their mixtures.

In this respect Eyring theory [1] for viscosity, played a central role. Some authors attempted to combine the UNIFAC model with Eyring theory [2]. The others used group contribution methods [3, 4] and the equation of state approach, to make this theo-

(*)To whom correspondence should be addressed.
E-mail: hmodares @cic.aku.ac.ir

ry applicable to fluids and their mixtures [5]. Recently the authors of this paper modified and extended the Eyring theory and used it to fit the experimental data for several liquids and their mixtures [6, 7].

The propose of this paper is to apply this model to the measured viscosities data of aqueous polyvinyl alcohol mixtures and to evaluate parameters of the model for predicting the viscosities of these mixtures at various temperatures and concentrations in engineering applications.

Theory

The Eyring viscosity model which has been derived from the reaction rate theory [1] provides a valuable route for calculating the viscosities of pure liquids.

$$\eta = h/v (2\pi mkT/h^2)^{1/2} e^{E_a/kT} \quad (1)$$

As $M = N_0 m$, $R = N_0 k$, $V = N_0 v$ and $E_a = N_0 \epsilon_a$, the final Eyring viscosity model will be expressed as [2]:

$$\eta = (2\pi MRT/V^2)^{1/2} e^{E_a/RT} \quad (2)$$

where M , R , T , V and E_a are the molar mass, gas constant, absolute temperature, liquid molar volume, and molar activation energy, respectively.

For a c -component mixture of total molecules of type N_i , where, $N = \sum_{i=1}^c N_i$, the following equation is derived as [6]:

$$\eta = \prod_{i=1}^N \left(\frac{h}{v_i}\right)^{x_i} \left(\frac{2\pi m_i kT}{h^2}\right)^{x_i/2} e^{x_i \epsilon_{ai}/kT} \quad (3)$$

where, x_i is the mole fraction of component i . Also this equation can be written in terms of molar properties as:

$$\eta = (2\pi RT)^{\sum x_i/2} \prod_i^c (M_i/V_i^2)^{x_i/2} e^{x_i E_{ai}/RT} \quad (4)$$

Since $\sum x_i = 1.0$, for a binary mixture, we have [6, 7]:

$$\eta = (2\pi RT)^{1/2} [M_1^{x_1/2} M_2^{x_2/2} / V_1^{x_1/2} V_2^{x_2/2}] e^{E_{am}/RT} \quad (5)$$

In above equation, we have introduced the activation energy of the binary mixture E_{am} as [7]:

$$E_{am} = x_1 E_{a1} + x_2 E_{a2} \quad (6)$$

and the temperature functionality for E_{am} in the following form:

$$E_{am} = a_m + b_m T \quad (7)$$

By considering low concentration of polymer in polymer-solvent mixtures ($x_2 \ll x_1 \approx 1$), the following approximation is valid:

$$V_1^{x_1} V_2^{x_2} \approx V_1 \quad (8)$$

Then the final form of the modified viscosity model for a binary mixture will be obtained as:

$$\eta = (2\pi RT/V_1^2)^{1/2} M_1^{x_1/2} M_2^{x_2/2} \exp[(a_m + b_m T)/RT] \quad (9)$$

This equation can be rewritten in a condensed form as:

$$\eta = A \exp[(a_m + b_m T)/RT] \quad (10)$$

where,

$$A = (2\pi RT/V_1^2)^{1/2} M_1^{x_1/2} M_2^{x_2/2} \quad (11)$$

As it is seen from Equation (10), there are three parameters in the modified Eyring viscosity model, namely A , a_m and b_m . These parameters will be interpreted in the light of obtained results for viscosity measurements. Equation (10) was used to correlate measured viscosities of aqueous polyvinyl alcohol mixtures and, values of a_m and b_m were evaluated.

EXPERIMENTAL

Polyvinyl alcohol, degree of hydrolyses %98 and $M_n = 49000$ was supplied by Merck. The aqueous polyvinyl alcohol mixtures were made with masses weigh by an analytical balance with accuracy of 0.1 mg. Double distilled water was used for making the solutions. As polyvinyl alcohol has a remarkably slow rate of dissolution in water at room temperature or slightly above it, the solutions were slowly stirred while warming up to obtain true one phase solutions. Then after cooling, the solutions were weighed again and the evaporated water in the process of warming up, were compensated by

adding enough double distilled water. A Haake viscometer, rotovisco RV 100 with the CV 100 system, was used for the viscosity measurements at temperatures 288, 298, and 308 K.

The viscometer consisted of two rotating coaxial cylinders in which the fluid under investigation was placed in the space between them and the flow curves were recorded. The usual experimental procedure was utilized to obtain the viscosity results. First the viscometer was calibrated by the standard fluid and the instrument's constant was measured. Then the instrument's constant was used to calculate shear rates and shear stresses. The final results were presented as flow curves, $\gamma = \tau/\eta$ vs. τ , where, η is the viscosity of fluid and τ and γ are the shear stress and shear rate, respectively. The Newtonian behaviour of studied mixtures was confirmed as expected by the linear flow curves (τ vs. γ) at low polymer concentrations of aqueous polyvinyl alcohol mixtures and therefore no further corrections for Non-Newtonian behaviour was required.

RESULTS AND DISCUSSION

The dilute solution of a polymer in a solvent is defined as the concentration, which is much lower than c^* [8]. The quantitative definition of c^* is $c^* = 1/[\eta]$, where $[\eta]$ is the intrinsic viscosity of solution. The intrinsic viscosity is related to molecular weight of polymer as the following form:

$$[\eta] = kM^a \quad (12)$$

The values of k and a in Equation (12) for polyvinyl alcohol at 298 K, which is the average temperature in our viscosity measurements are 0.30 (ml/g) and 0.50, respectively [9]. For studied aqueous polyvinyl alcohol mixtures, where $M_n = 49000$, the value of relative concentrations (c/c^*) for the studied mixtures fall in the range of 0.157-0.813. Therefore, polymer-solvent mixtures are considered as dilute solutions and their Newtonian behaviours in regard to viscosities of mixtures are expected. The Newtonian behaviour is confirmed by the linearity of variations of measured shear stresses (τ) versus shear rates (γ). Figure 1, as an example, shows the linear variations of (τ) versus (γ) for three aqueous polyvinyl alcohol mixtures at 288K.

Table 1. The measured viscosities ($\eta \times 10^3$ Pa.s) of aqueous polyvinyl alcohol mixtures.

C (g/20 mL)	15°C	25°C	35°C
0.6107	3.91	3.00	2.31
0.5381	3.20	2.40	1.80
0.2467	1.41	1.11	0.90
0.1180	1.11	0.90	0.74

The measured viscosities of aqueous polyvinyl alcohol mixtures at temperatures 288, 298, and 308 K are reported in Table 1. By substituting the measured viscosities in Equation (9), values of parameters a_m and b_m were calculated and the percent average absolute deviation (AAD%) of experimental and calculated viscosities are reported in Table (2).

As it is seen from reported results in Table (2), the calculated AAD% for mixtures are less than 0.33%, which indicate the accuracy of calculations and the applicability of the modified viscosity model, based on the Eyring theory, to polymer-solvent mixtures. By considering the activation energy expressed by Equation (7) and values of activation energy parameters a_m and b_m reported in Table (2), some interesting points about the physical interpretation of these parameters become clear. Higher values of these parameters mean higher values of activation energy as a result of molecular frictions and retardations in molecular motion of polymer chains, that in turn cause higher measured viscosities of polymer-solvent mixtures. Another parameter in the modified Eyring viscosity model is A , which

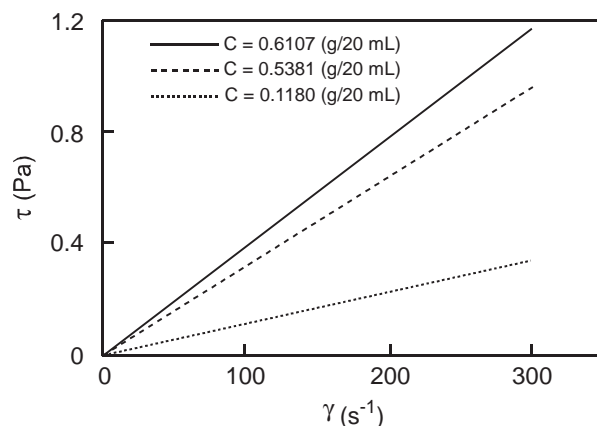


Figure 1. The linear variation of (τ) versus (γ) for three aqueous polyvinyl alcohol mixtures at 288K.

Table 2. The parameters of viscosity activation energy for aqueous polyvinyl alcohol mixtures.

C (g/20mL)	a_m	b_m	AAD%
0.6107	20645.52	-203.18	0.24
0.5381	22453.97	-211.13	0.33
0.2467	17792.55	-201.75	0.23
0.1180	16189.92	-198.18	0.01

is expressed by Equation (11). This parameter not only is effectively temperature dependent but also, depends on molecular weights of polymer and solvent. Thus higher molecular weight of polymer causes retardation in molecular motions of polymer chain and then led to higher viscosity for polymer-solvent mixture.

The parameters a_m and b_m are expressed in term of polymer concentration, C, as follows:

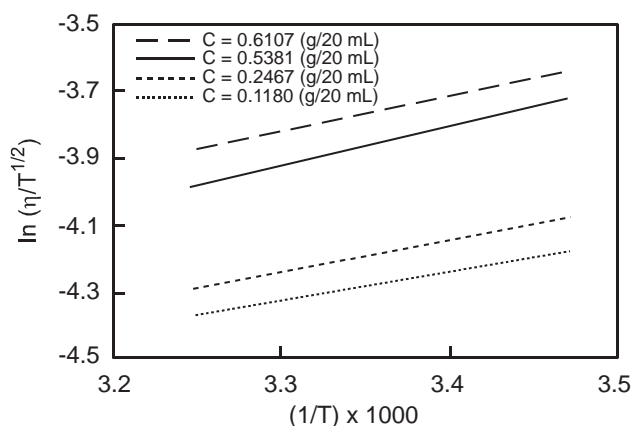
$$a_m = -9425.35C^2 + 15841.37C + 14403.37 \quad (13)$$

$$b_m = 48.87C^2 - 45.52C - 193.32 \quad (14)$$

By using the above correlations the calculated AAD% is 0.84%. By rearranging Equation (10) and writing it in the logarithmic form we have:

$$\ln(\eta/T^{1/2}) = \ln A + (a_m + b_m T)/RT \quad (15)$$

where $\ln A$ is constant for a fixed concentration of polymer-solvent mixture. According to Equation (15), the variation of $\ln(\eta/T^{1/2})$ versus $1/T$ should be linear.

**Figure 2.** The linear variation of $\ln(\eta/T^{1/2})$ versus $1/T$ for the aqueous polyvinyl alcohol mixtures.

Linearity of the plots in Figure 2 indicates consistency of measured and calculated results.

CONCLUSION

The linear relation between shear stress, τ , and shear rate $\dot{\gamma}$, indicates the Newtonian behaviour of studied aqueous polyvinyl alcohol mixtures. Viscosities of aqueous polyvinyl alcohol mixtures are calculated by using the modified Eyring viscosity model. The parameters of the model are correlated in terms of polymer concentrations. The total AAD% for viscosity calculations by the proposed model is 0.84%.

REFERENCES

- Glastone S., Laidler K. J., and Eyring, H., *The theory of rate processes*, McGraw-Hill, New York, Ch. 9, 477 (1941).
- Cao W., Knudsen K., Fredenslund A., and Rasmussen P., Group-contribution viscosity predictions of liquid mixtures using UNIFAC-VLE parameters, *Ind. Eng. Chem. Res.*, **32**, 2088-2092 (1993).
- Wu D. T., Prediction of viscosities of liquid mixtures by a group contribution method, *Fluid Phase Equilibria*, **30**, 149-156 (1986).
- Chevalier J.L.E., Petrino P.J., and Gaston-Bonhomme Y., Estimation method for kinematic viscosity of a liquid-phase mixture, *Chem. Eng. Sci.*, **43**, 1303-1309 (1988).
- Lee M.J. Chiu J.Y., Hwang S.M., and Lin T.K., Viscosity calculations with the Eyring-Patel-Teja model for liquid mixtures, *Ind. Eng. Chem. Res.*, **38**, 2867-2876 (1998).
- Mohsen-Nia M., Modarress H., and Mahdavi M.A., A new two parameters equation for viscosity calculations, *Amirkabir, J. Sci. Technol.*, **15**, 120-132 (2004).
- Modarress H., Mohsen-Nia M., and Mahdavi M. A., Experimental and theoretical studies of polymer-solvent mixtures, viscosity, *Appl. Polym. J.*, **91**, 1724-1929 (2004).
- Teraoka I., *Polymer Solutions: An introduction to physical properties; dilute solution*, John Wiley, Inc., (2002).
- Brandrup J. and Immergut E.H., Viscosity-molecular weight relationship, *Polymer Handbook*, 2nd Ed., John Wiley Inc, Ch. IV (1975).