

Measurement and Modeling of Poly(vinyl acetate)–Solvent Viscosity Mixtures

Hamid Modarress,¹ Mohsen Mohsen-Nia²

¹Department of Chemical Engineering, Amir-Kabir University of Technology, Tehran, Iran

²Department of Science, Kashan University, Kashan, Iran

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ABSTRACT: The viscosities of various poly(vinyl acetate) (PVAc)–solvent mixtures (PVAc–toluene, PVAc–benzene, and PVAc–cyclohexanone) were measured at different temperatures with a Haake viscometer. The required molecular weight of a commercial-grade PVAc sample was measured with an Ubbelohde viscometer. The measured viscosities were correlated with a previously proposed viscosity model,

and the model parameters were calculated. The results indicated the applicability of the model to the viscosity calculations of PVAc–solvent mixtures. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1244–1249, 2005

Key words: modeling; viscosity; poly(vinylacetate); polymer–solvent mixture

INTRODUCTION

The rheological behavior of polymer solutions is one of the important characteristics for the design and processing of polymer–solvent mixtures.¹ Solutions of a high-molecular-weight polymer, even at low concentrations, can flow only slowly. The addition of a small amount of the polymer to the fluid can make it viscous and, therefore, prevent unwanted turbulence in the flow.² This arises because of the large differences in the sizes of the polymer and solvent molecules and can be significant even at very low polymer concentrations, especially for polymers with high molecular weights.³

Solution viscosity is basically a measure of the size or extension in space of polymer molecules. It is related to the molecular weight for linear polymers; the simplicity of the measurement and the usefulness of the viscosity/molecular-weight correlation are so great that viscosity measurements constitute an extremely valuable tool for the molecular characterization of polymers.⁴ Therefore, viscometry provides useful information related to the size of polymer molecules in solution, including effects on the chain dimensions of the polymer structure, molecular shape, degree of polymerization, and polymer–solvent interactions.

In calculations for the design and operation of polymer processing units, the average molecular weights of polymers are important and necessary data.⁵ There are numerous types of polymer molecular weights, including the number-average molecular weight (M_n),

the weight-average molecular weight (M_w), and the viscosity-average molecular weight (M_v). If there is no molecular weight distribution, that is, if the molecular weights of all species in a sample are the same, all three types will be equal. The ratio M_w/M_n , called the polydispersity, is a useful measure of the spread of a polymer distribution. A large value of M_w/M_n indicates a very wide spread, with substantial amounts of materials at both extremes. When M_w/M_n is 1, all polymeric molecules have the same molecular weight, and there is no spreading.

There are experimental methods for determining the molecular weights of polymers. Osmotic pressure^{6,7} and intrinsic viscosity ($[\eta]$)^{8–12} methods are used for the determination of M_n .^{13,14} Sedimentation,^{15,16} diffusion,^{17–19} and light scattering^{20–24} methods are suitable for the determination of M_w . These methods of molecular weight determination are primary methods, and other methods, such as high-performance liquid chromatography²⁵ and electrophoresis,^{26,27} are considered secondary methods.¹³

We performed experimental and theoretical studies of the viscosities of poly(vinyl acetate) (PVAc)–solvent mixtures. The average molecular weights of PVAc samples were determined from viscosity measurements of PVAc–toluene mixtures at 25°C. The obtained PVAc molecular weights were used for viscosity calculations of PVAc–solvent mixtures at various temperatures.

EXPERIMENTAL

Materials

The PVAc sample was a commercial product from Aldrich Chemical Co, Inc. (PVAc, Germany). Toluene

Correspondence to: H. Modarress (hmodares@cic.aku.ac.ir).

(purity > 99.5%), benzene (purity > 99.7%), and cyclohexanone (purity > 99.0%) were supplied by Merck Co. (Germany). All chemicals were used without further purification.

Molecular weight measurements

Viscometry is a simple method used for the determination of the average molecular weights of polymers. In dilute polymer solutions, a linear relationship between the reduced viscosity [$\eta_{\text{red}} = \eta_{\text{sp}}/c$, where η_{sp} is the specific viscosity and c is the concentration] and c for a polymer in solution exists, except for polyelectrolytes in solvents. Upon extrapolation $c = 0$, $[\eta]$ can be obtained, and this makes it possible to determine the polymer molecular weight.

The Mark-Houwink empirical equation can be applied for various polymer-solvent mixtures:^{5,28}

$$[\eta] = KM_v^a \quad (1)$$

where M_v^a is the viscosity-average molecular weight and K and a are constants for a given polymer-solvent system at different temperatures. Generally, we find $0.5 \leq a \leq 0.8$ for flexible chains, $0.8 \leq a \leq 1.0$ for inherently stiff molecules, and $0.1 \leq a \leq 1.7$ for highly extended chains such as polyelectrolytes in solutions of very low ionic strength. K tends to decrease as a increases, and for flexible chains, it is typically 10^{-3} – $10^{-1} \text{ cm}^3 \text{ g}^{-1}$.²⁸ Equation (1) allows the evaluation of M_v from the $[\eta]$ value of a polymer solution as long as

TABLE I
Measured η_{sp} Values of the PVAc-Toluene Mixture at 25°C

c (g/L)	2.56	6.60	7.16	10.84
η_{sp}/c	0.3613	0.3874	0.3980	0.4216

K and a are known for the system under study. The most widely used method for the evaluation of K and a involves the measurement of $[\eta]$ for a series of polymer standards with known M_n or M_w values. Generally, a plot of $\log [\eta]$ versus $\log M$ is fitted to a straight line, from which K and a are determined.

Ubbelohde viscometry

A calibrated Ubbelohde viscometer was used to perform the viscosity measurements of dilute PVAc-toluene mixtures.

Viscosity measurements were carried out in a constant-temperature bath. The temperature of the bath was controlled by a thermostat with 0.1°C precision.

The η_{sp} values of the polymer-solvent mixtures [$\eta_{\text{sp}} = (t - t_0)t_0$] were determined from the flow times of the solvents (t_0) and polymer solutions (t) for low polymer concentrations in the mixtures. Table I presents the measured η_{red} values for PVAc-toluene mixtures at 25°C with four different polymer concentrations.

The Huggins equation reveals the correlation between η_{sp}/c and c in dilute solutions if the proper

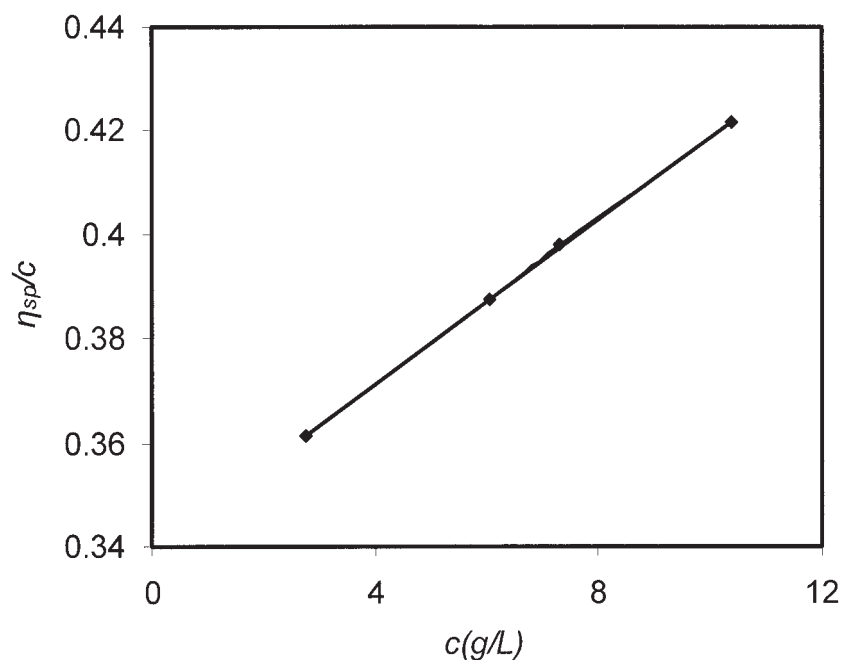


Figure 1 The variation of reduced viscosity (η_{sp}/c) versus concentration c (g/L) of poly(vinyl acetate) in solvent toluene at 25°C.

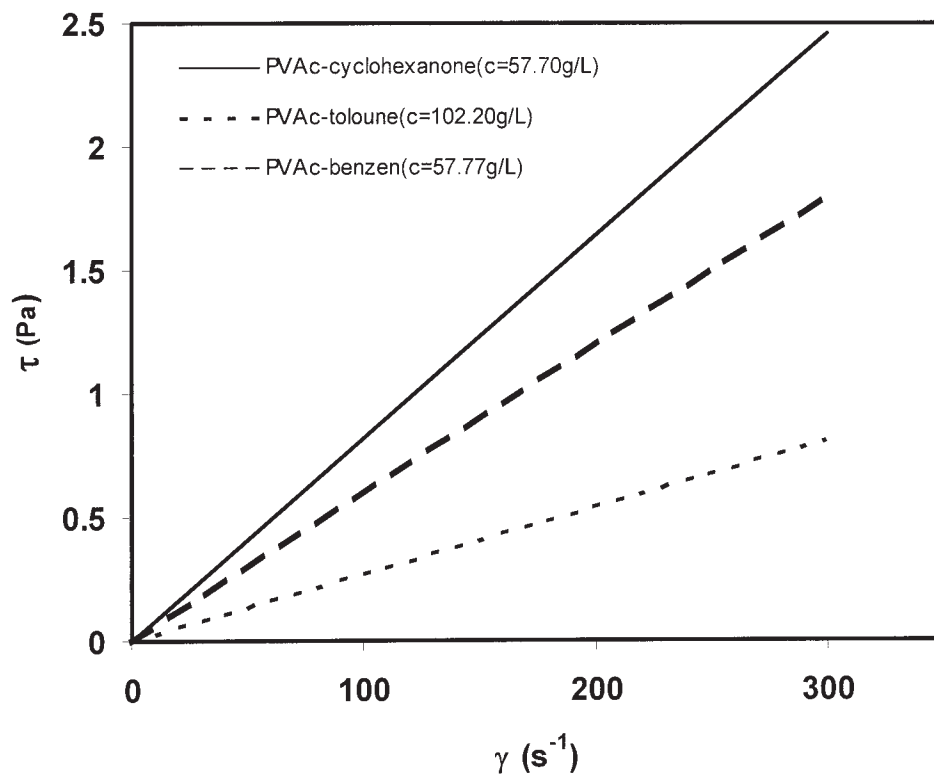


Figure 2 The variation of shear stress τ (Pa) versus shear strain for poly(vinyl acetate)-solvent mixtures at 25°C.

technique is used to determine the viscosity of polymer-solvent mixtures:⁵

$$\eta_{\text{red}} = \frac{\eta_{\text{sp}}}{c} = K'[\eta]^2 c + [\eta] \quad (2)$$

where $K[\eta]^2$ is the slope of the line and $[\eta]$ is the intercept.

Figure 1 shows plots of η_{red} (i.e., η_{sp}/c) versus c for PVAc in toluene at 25°C. $[\eta]$ was determined as $\lim_{c \rightarrow 0} \eta_{\text{sp}}/c$ for the PVAc-toluene mixtures. With eq. (1) and with $a = 0.53$ and $b = 0.0018 \text{ mL/g}$,²⁸ M_v for the PVAc sample was calculated to be $51,571 \pm 5.25 \text{ g mol}^{-1}$.

The PVAc-solvent mixtures were made by mass with an analytical balance with an accuracy of 0.1 mg.

Haake viscometry

A Rotovisco RV 100 Haake viscometer (Mess-Technik GmbH U. Co., Germany) with a CV 100 system was used for the viscosity measurements at various temperatures.

The viscometer consisted of two rotating coaxial cylinders; the fluid under investigation was placed in the space between them, and the flow curves were recorded. From the flow curve $\gamma = \tau/\eta$ versus τ , the

viscosity of the liquid (η) was calculated, τ and γ being the shear stress and shear strain, respectively.

The experimental procedure, including the precision of the instruments and the accuracy of the viscosity measurements, was reported in previous publications.^{29,30} In this work, the same procedure was used.

TABLE II
Measured Viscosities (cP) of PVAc-Solvent Mixtures

c (g/L)	15°C	25°C	35°C
PVAc-toluene			
53.38	2.00	1.90	0.18
66.30	2.61	2.50	0.24
74.18	3.30	3.15	0.30
102.20	7.10	6.00	0.52
PVAc-benzene			
24.45	1.20	1.14	1.10
25.10	1.28	1.20	1.15
44.99	2.20	2.00	1.80
57.77	3.00	2.70	2.50
PVAc-cyclohexanone			
17.45	3.10	2.50	2.10
31.48	4.90	4.00	3.40
39.61	6.60	5.40	4.40
57.70	10.20	8.20	6.60

TABLE III
Parameters of Viscosity Activation Energy for PVAc-Solvent Mixtures

Mixture	a_0	a_c	b_0	b_c	AAD(%)
PVA _c -toluene	5,856.70	10,714.30	-159.65	148.76	2.77
PVA _c -cyclohexanone	17,219.14	10,471.70	-188.47	202.02	4.03
PVA _c -benzene	7,394.37	9,804.50	-164.35	176.15	2.05
Total AAD(%)					2.95

Through a comparison of the viscosities of the binary mixtures measured with the Haake viscometer of the commercial-grade PVAc and solvent and the viscosities of the mixtures of pure-grade PVAc (Merck and Aldrich) and solvents in our previous works,^{29,30} we found that for polymers of the same molecular weight and for mixtures of the same composition, the measured viscosities were infinitesimally close to one another, and so the validity and accuracy of the measurements were confirmed.

In all the measurements, we found that the variation of τ versus γ was linear. Therefore, we concluded that the mixtures showed Newtonian behavior in the concentration range and temperatures used in the measurements. Figure 2 shows τ versus γ for the different measured PVAc-solvent mixtures at 298.15 K. Table II lists the measured viscosities for the studied PVAc mixtures.

MODELING

For a binary polymer-solvent mixture, the viscosity model was obtained as follows:^{29,30}

$$\eta = (2\pi RT/V_1^2)^{1/2} M_1^{x_1/2} M_2^{x_2/2} \exp[(a_m + b_m T)/RT] \quad (3)$$

where R is the universal gas constant, T is the temperature (K), m and x are molecular weight and mole fraction of solvent (1) and polymer (2) respectively and V_1 is the molar volume of the solvent. In eq. 3, a_m and b_m are the parameters of the mixture.

In this study, the model was used to correlate the measured viscosities of PVAc-solvent mixtures and to evaluate the values of a_m and b_m .

Parameters a_m and b_m can be expressed in terms of c for the polymer as follows:

$$a_m = a_0 + a_c c \quad (4)$$

$$b_m = b_0 + b_c c \quad (5)$$

a_0 and b_0 are the parameters for infinite dilution of polymer in the solvent and a_c and b_c are the parameters for concentration (c) of polymer in the solvent.

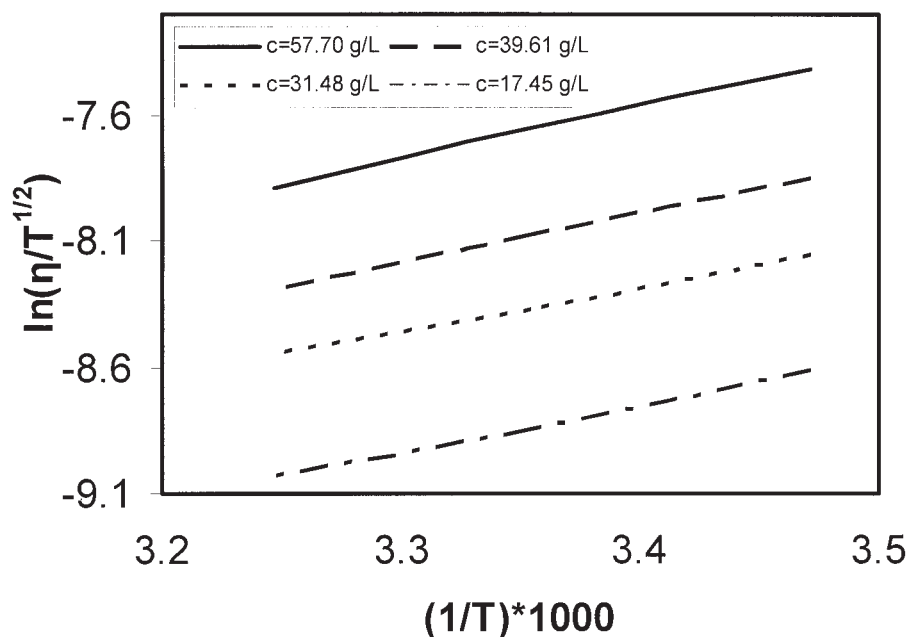


Figure 3 The linear variation of $\ln(\eta/T^{1/2})$ versus $(1/T) \times 1000$ for poly(vinyl acetate)-toluene mixture, according to eq. 6.

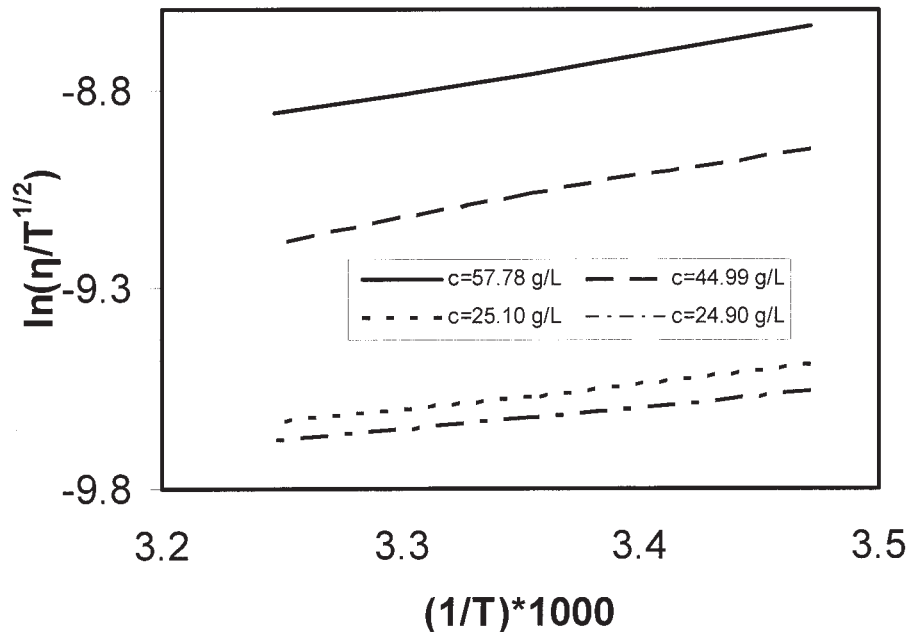


Figure 4 The linear variation of $\ln(\eta/T^{1/2})$ versus $(1/T) \times 1000$ for poly(vinyl acetate)–benzene mixture, according to eq. 6.

Through the fitting of the measured viscosities, the calculated values of parameters a_0 , a_c , b_0 , and b_c and the average absolute deviations (AADs) of the experimental and calculated viscosities were determined, and they are reported in Table III.

According to Table II, the maximum AAD was 4.03%, and so the applicability of the proposed model for PVAc–solvent mixtures is considerable.

By rearranging eq. (3) and rewriting it in a logarithmic form, we obtain

$$\ln(\eta/T^{1/2}) = A(a_m + b_m T)/RT \quad (6)$$

where A is a constant for a mixture with a fixed composition:

$$A = \ln[(2\pi R/V_1^2)^{1/2} M_1^{x_1/2} M_2^{x_2/2}] \quad (7)$$

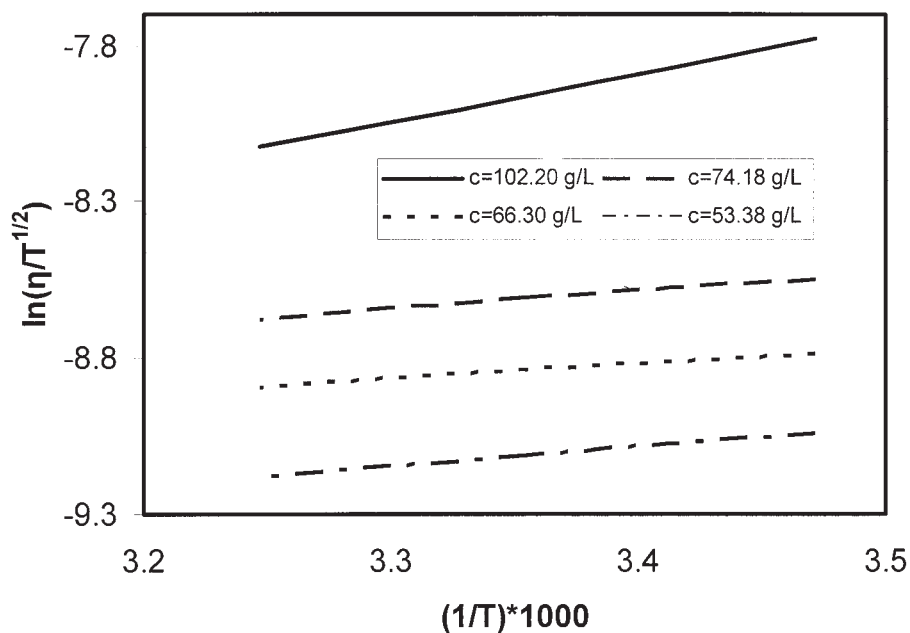


Figure 5 The linear variation of $\ln(\eta/T^{1/2})$ versus $(1/T) \times 1000$ for poly(vinyl acetate)–cyclohexanone mixture, according to eq. 6.

The validity of the proposed model can be evaluated from plots of $\ln(\eta/T^{1/2})$ versus $1/T$. According to eq. (6), the variation of $\ln(\eta/T^{1/2})$ versus $1/T$ is linear. Figures 3–5 are consistent with the linear form of eq. (6).

CONCLUSIONS

M_v of commercial-grade PVAc has been determined from Ubbelohde viscosity measurements. Because of the low PVAc concentration in the solvents and the linear relationship between τ and γ according to Haake viscosity measurements, the Newtonian behavior of the studied PVAc–solvent mixtures has been proved. A new viscosity model for polymer–solvent mixtures has been applied to the studied PVAc mixtures. The parameters of the model have been correlated in terms of the polymer concentrations. The total AAD for viscosity calculations by this model is 2.95%. Therefore, it can predict the viscosity of PVAc mixtures with good accuracy.

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