

Experimental and Theoretical Studies of Polymer/Solvent Viscosity Mixtures

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ABSTRACT: Viscosity of the binary mixtures of polymers/solvent: (polystyrene/toluene), (polymethylmethacrylate/acetone), (polystyrene/benzene), (polystyrene/cyclohexane), and (polymethylmethacrylate/chloroform) were measured at different temperatures by a Haake viscometer. The samples of polymer/solvents mixtures used in the viscometry measurements were in low concentration of poly-

mer (maximum concentration 0.25 g/cm³). The measured viscosities were used to evaluate the parameters of the modified Eyring's viscosity equation. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1724–1729, 2004

Key words: viscosity; polymer/solvent mixtures; Eyring's equation; polystyrene; polymethylmethacrylate

INTRODUCTION

In calculations related to design and operation of plant process units, viscosity is an important transport property. Also the temperature dependency of the viscosity is a main characteristic determining the quality of the fluids and fluid mixtures. For fluid mixtures the compositions' viscosity dependency is an essential feature.

There are different routes for calculating viscosity of fluids and fluid mixtures.^{1–3} Although equations of state have widely been used for calculating thermodynamic properties, viscosity calculations are essentially based on either the corresponding state principles or Eyring's theory.^{4–6}

Some of the methods of viscosity calculations are based on a group contribution of components in the mixture. However, the models are usually limited to a certain temperature region.^{7–9}

Use of the proper mixture model is also another determining factor in calculating the viscosity of fluid mixtures. Cao et al.^{10,11} developed a viscosity–thermodynamic model, which correlated both viscosity and liquid equilibrium data by the UNIQUAC model.

Lee et al.¹² estimated the excess activation free energy of flow in Eyring theory with the aid of an equation of state. Martins et al.¹³ developed a model based on Eyring's theory and the UNIQUAC equation for calculation of the viscosity of multicomponent liquid systems. Multicomponent liquid systems appear

frequently in chemical processing and the mixture viscosity has attracted much attention,^{14–19} particularly with the aim of developing models for its estimation to be implemented in computer simulation programs.

EYRING VISCOSITY MODEL

The Eyring viscosity model, derived from reaction rate theory,⁷ provides a valuable route for calculating the viscosity of pure components. The model can be derived by considering the following basic equation, which holds for a Newtonian fluid:

$$f = -\eta \frac{\Delta v}{l_1} \quad (1)$$

where f is the shear force per unit area, Δv is the difference of two molecular layer velocities, l_1 is a distance between two molecular layers, and η is the dynamic viscosity of the fluid. The difference between two molecular layer velocities can be expressed as

$$-\Delta v = l_2(k_f - k_b) \quad (2)$$

where k_f and k_b are, respectively, the frequency (s⁻¹) or velocity constants for forward and backward movement of the molecule and l_2 is the distance between two molecular layers in a direction perpendicular to the direction of l_1 . It is worth noting that the distances between the molecular layers in these arbitrary perpendicular directions are represented as l_1 , l_2 , and l_3 . Assuming that

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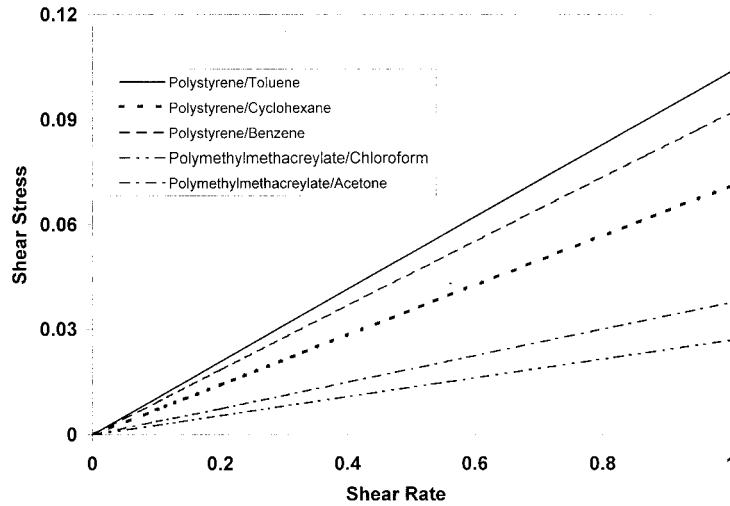


Figure 1 Variations of shear stress τ versus shear strain D for the studies polymer/solvent mixtures at constant polymer concentration ($c = 0.15 \text{ g/cm}^3$) and temperature ($T = 303 \text{ K}$).

$$l_1 \approx l_2 \tag{3} \quad f = \eta(kT/h)(Q_a/Q)$$

and substituting from eq. (3) into eqs. (2) and (1) we have

$$f = \eta(k_f - k_b) \tag{4}$$

The energy for movement of a molecule ϵ is defined as the work done when the shear force per unit area f is applied to move a molecular layer in the direction of applied force; therefore, we have

$$\epsilon = fl_2l_3(l_1/2) = fv/2 \tag{5}$$

From eqs. (4) and (5)

$$2\epsilon/v = f = \eta(k_f - k_b) \tag{6}$$

where $v = l_1l_2l_3$ and v is the molecular volume. The concepts of absolute reaction rate⁷ can be applied to the movement of molecule forward and backward; thus, the following equations will be obtained, for k_f and k_b , respectively, as

$$k_f = \frac{kT}{h} \frac{Q_a}{Q} \exp\left(\frac{\epsilon_a - \epsilon}{kT}\right) \tag{7}$$

$$k_b = \frac{kT}{h} \frac{Q_a}{Q} \exp\left(\frac{\epsilon_a + \epsilon}{kT}\right) \tag{8}$$

where Q and Q_a are the partition functions related to, respectively, the inactivated and activated states of the molecules and ϵ_a is the activation energy for movement of a molecule. Substitution of eqs. (7) and (8) in eq. (6) results in

$$\times \left\{ \exp\left[\frac{-(\epsilon_a - \epsilon)}{kT}\right] - \exp\left[\frac{-(\epsilon_a + \epsilon)}{kT}\right] \right\} \tag{9}$$

where the other symbols in eq. (9) are as follows: k is the Boltzmann constant, h is Plank's constant, and T is the absolute temperature. On rearranging eq. (9) we have

$$\frac{2\epsilon}{v} = \eta \frac{kT}{h} \frac{Q_a}{Q} e^{-\epsilon_a/kT} [e^{\epsilon/kT} - e^{-\epsilon/kT}] \tag{10}$$

Using the following well-known expansion and noting that ϵ/kT is small:

$$\frac{e^{\epsilon/kT} - e^{-\epsilon/kT}}{2} = \epsilon/kT + \left(\frac{1}{3!}\right)(\epsilon/kT)^3 + \left(\frac{1}{5!}\right)(\epsilon/kT)^5 + \dots \cong \epsilon/kT \tag{11}$$

The following equation for viscosity η can be derived:

$$\eta = \frac{h}{v} \left(\frac{Q}{Q_a}\right) e^{\epsilon_a/kT} \tag{12}$$

For movement of an activated molecule in a path by unit length distance ($\delta = 1m$), the ratio Q/Q_a can be presented as $(2\pi mkT/h^2)^{1/2}\delta$; then

$$\eta = \frac{h}{v} (2\pi mkT/h^2)^{1/2} e^{\epsilon_a/kT} \tag{13}$$

TABLE I
Measured Viscosities (Pa s⁻¹) of Polymer-Solvent Systems Versus Polymer Concentration at Different Temperatures

T (K)	Concentration of polymer (g/cm ³)			
	0.25	0.20	0.15	0.10
Polystyrene/Toluene				
298	0.4799	0.1183	0.1180	0.0275
303	0.4477	0.1080	0.1038	0.0256
308	0.4018	0.0980	0.0992	0.0230
313	0.3714	0.0923	0.0891	0.0217
318	0.3477	0.0870	0.0788	0.0198
323	0.3160	0.0769	0.0727	0.0185
328	0.2907	0.0732	0.0640	0.0177
333	0.2800	0.0690	0.0580	0.0170
338	0.2571	0.0658	0.0540	0.0156
343	0.2450	0.0620	0.0488	0.0146
353	0.1981	0.0560	0.0419	0.0128
Polystyrene/Benzene				
303	0.3900	0.1480	0.0711	0.0262
308	0.3130	0.1369	0.0648	0.0247
313	0.2760	0.1323	0.0603	0.0230
318	0.2350	0.1261	0.0565	0.0219
323	0.2020	0.1177	0.0520	0.0206
328	0.1710	0.1100	0.0488	0.0196
333	0.1345	0.0999	0.0445	0.0186
Polystyrene/Cyclohexane				
303	0.5700	0.2939	0.0920	0.0267
308	0.4199	0.2522	0.0821	0.0249
313	0.3123	0.2175	0.0732	0.0234
318	0.2575	0.1830	0.0663	0.0223
323	0.1820	0.1641	0.0601	0.0209
328	0.1360	0.1412	0.0554	0.0187
333	0.1022	0.1230	0.0515	0.0175
Polymethylmethacrylate/Acetone				
303	0.3304	0.1852	0.0269	0.0097
308	0.2970	0.1504	0.0245	0.0089
313	0.2610	0.1208	0.0231	0.0079
318	0.2200	0.1038	0.0198	0.0071
323	0.1850	0.0831	0.0183	0.0065
Polymethylmethacrylate/Chloroform				
303	0.1721	0.1050	0.0376	0.0168
308	0.1622	0.0940	0.0360	0.0153
313	0.1562	0.0830	0.0346	0.0138
318	0.1434	0.0759	0.0330	0.0132
323	0.1352	0.0700	0.0317	0.0123
328	0.1288	0.0603	0.0303	0.0115

Because $M = N_0m$, $R = N_0k$, $V = N_0v$, and $E_a = N_0\epsilon_a$, the final Eyring model for viscosity of a fluid will be expressed as

$$\eta = (2\pi MRT/V^2)^{1/2} e^{E_a/RT} \quad (14)$$

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 N molecules of type N_i , where $N = \sum_{i=1}^c N_i$, we have⁷

$$\left(\frac{Q}{Q_a}\right)_{\text{mix}}^N = \prod_i^c \left(\frac{2\pi mkT}{h^2}\right)^{N_i/2} \quad (15)$$

Then

$$\left(\frac{Q}{Q_a}\right)_{\text{mix}} = \prod_i^c \left(\frac{2\pi mkT}{h^2}\right)^{N_i/2N} = \prod_i^c \left(\frac{2\pi mkT}{h^2}\right)^{x_i/2} \quad (16)$$

where x_i is the mole fraction of component i . From eqs. (16) and (13) the following equation for viscosity of a mixture will be obtained:

$$\eta = \prod_{i=1}^N \left(\frac{h}{v_i}\right)^{x_i} \left(\frac{2\pi m_i kT}{h^2}\right)^{x_i/2} e^{x_i \epsilon_{ai}/kT} \quad (17)$$

Also this equation can be written in terms of molar properties as

$$\eta = (2\pi RT)^{\sum x_i/2} \prod_i^c [(M_i/V_i^2)^{x_i/2} e^{x_i E_{ai}/RT}] \quad (18)$$

Because $\sum x_i = 1.0$, for a binary mixture, we have

$$\eta = (2\pi RT)^{1/2} [M_1^{x_1/2} M_2^{x_2/2} / V_1^{x_1} V_2^{x_2}] e^{(x_1 E_{a1} + x_2 E_{a2})/RT} \quad (19)$$

TABLE II
Parameters of Equation (23) and the Average Absolute Deviations in Viscosities of Polymer/Solvent Mixtures

g/cm ³	a_m (J mol ⁻¹ k ⁻¹)	b_m (J mol ⁻¹ k ⁻¹)	AAD % ^a
Polystyrene/Toluene			
0.25	14,384.54	-132.57	1.50
0.20	13,258.51	-140.56	1.35
0.15	17,811.06	-155.71	1.58
0.10	13,285.00	-152.63	1.16
Polystyrene/Benzene			
0.25	28,560.28	-180.58	2.36
0.20	11,117.49	-131.06	1.52
0.15	14,028.03	-146.75	0.64
0.10	10,763.11	-144.31	0.41
Polystyrene/Cyclohexane			
0.25	48,671.85	-242.50	1.96
0.20	25,680.44	-172.08	0.77
0.15	17,840.41	-155.94	0.84
0.10	13,346.28	-151.26	1.44
Polymethylmethacrylate/Chloroform			
0.25	10,888.87	-131.70	0.60
0.20	18,622.76	-161.33	1.13
0.15	83,863.12	-136.05	0.20
0.10	13,493.20	-159.72	0.28
Polymethylmethacrylate/Acetone			
0.25	25,738.63	-172.57	2.12
0.20	33,904.19	-204.75	0.94
0.15	17,403.29	-166.24	1.33
0.10	17,665.54	-175.65	0.55

^a AAD % = $|\eta_{\text{exp}} - \eta_{\text{calcd}}|/\eta_{\text{exp}}$.

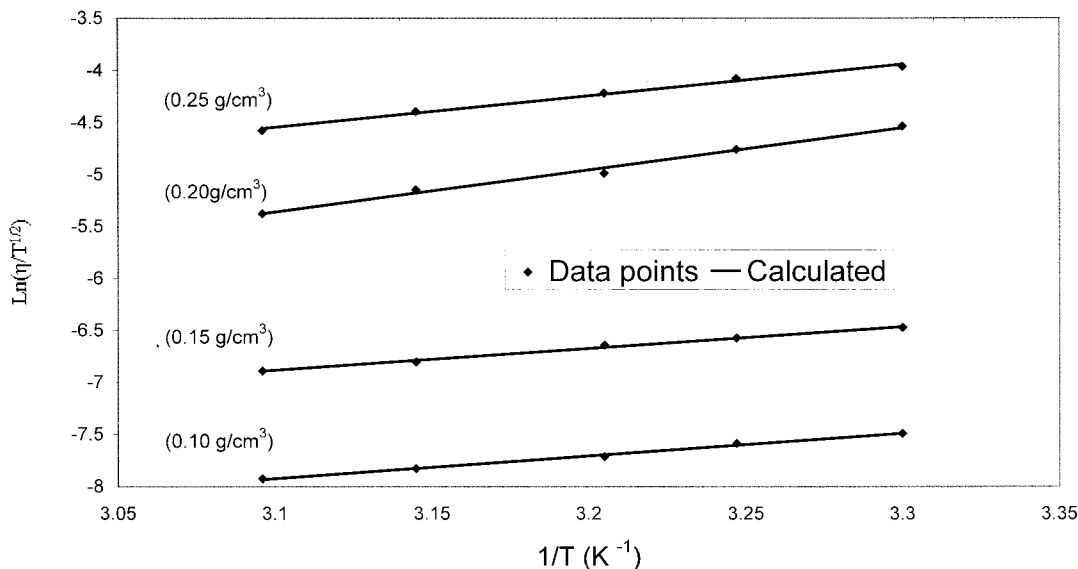


Figure 2 Variations of $\ln(\eta/T^{1/2})$ versus $1/T$ for polymethylmethacrylate/acetone mixture.

In the above equation, we introduce the activation energy of mixture E_{am} as

$$E_{am} = x_1 E_{a1} + x_2 E_{a2} \quad (20)$$

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

$$E_{am} = a_m + b_m T \quad (21)$$

By considering the small values of x_2 ($x_2 \ll x_1 \approx 1$), the following approximation is valid:

$$V_1^{x_1} V_2^{x_2} \approx V_1 \quad (22)$$

Then the final form of eq. (19) for a binary mixture will be obtained as

$$\eta = (2\pi RT/V_1^2)^{1/2} M_1^{x_1/2} M_2^{x_2/2} \exp[(a_m + b_m T)/RT] \quad (23)$$

Equation (23) is used to correlate the measured viscosity for polymer (2)/solvent (1) mixtures and the values of a_m and b_m are evaluated.

EXPERIMENTAL

Materials

Polystyrene ($M_n = 90,000$), toluene (purity > 99.5%), acetone (purity > 99.8%), benzene (purity > 99.7%),

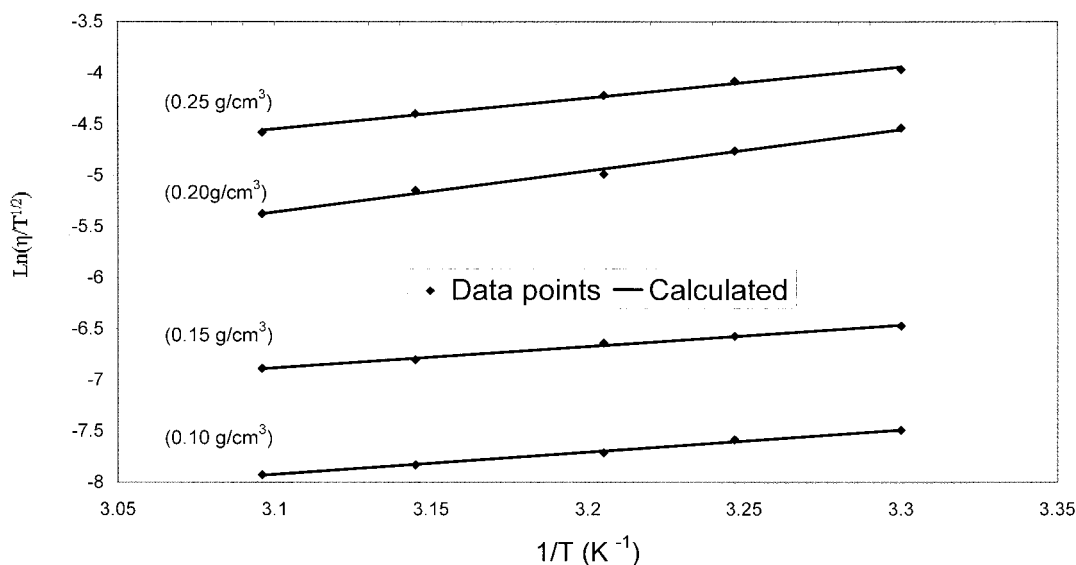


Figure 3 Variations of $\ln(\eta/T^{1/2})$ versus $1/T$ for polymethylmethacrylate/chloroform mixture.

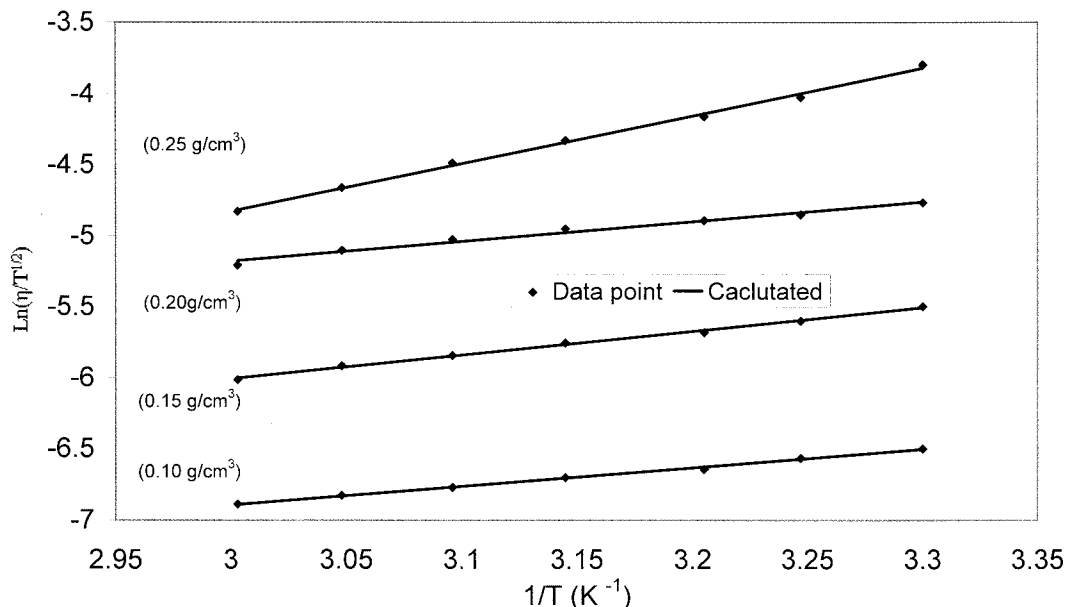


Figure 4 Variations of $\ln(\eta/T^{1/2})$ versus $1/T$ for polystyrene/benzene mixture.

cyclohexane (purity > 99.0%), and chloroform (purity 99–99.4%) were supplied by Merck (Darmstadt, Germany). Polymethylmethacrylate ($M_n = 12,000$) was supplied by Aldrich Chemical (Milwaukee, WI). All chemicals were used without further purification.

Preparation

The binary polymer–solvent mixtures were made by mass using an analytical balance of accuracy 0.1 mg. The viscosity measurements were performed on the mixtures (polystyrene/toluene), (polymethylmethacrylate/acetone), (polystyrene/benzene), (polystyrene/cyclohexane), and (polymethylmethacrylate/chloroform) by using the Haake viscometer (Haake, Bersdorff, Germany), rotovisco RV 100 with the CV 100 system, at various temperatures.

The viscometer consists of two rotating coaxial cylinders in which the fluid under investigation is placed in the space between them and the flow curves may be recorded. From the flow curve $D = \tau/\eta$ versus τ , the viscosity of liquid η was calculated, where τ and D are the shear stress and shear strain, respectively.

The linearity of plots obtained by measuring shear stress versus shear strain by the Haake viscometer confirmed the Newtonian behavior of the mixtures. Figure 1 shows the shear stress versus shear strain for the measured polymer–solvent systems at a constant polymer concentration $c = 0.15 \text{ g/cm}^3$ and $T = 303 \text{ K}$. The Newtonian behavior of the studied systems was expected, given that the concentration of polymer was less than 0.25 g/cm^3 .

The measured viscosities were used to evaluate the parameters a_m and b_m in the modified Eyring viscosity equation [eq. (23)].

RESULTS AND DISCUSSION

The results of viscosity measurements were examined for Newtonian behavior of polymer–solvent mixtures. In all measurements, it was found that variation of shear stress versus shear strain is linear. Therefore, it was concluded that the mixtures had Newtonian behavior in the concentration range and temperatures used in the measurements. The measured viscosities are reported in Table I. The parameters a_m and b_m were calculated by fitting the measured viscosities in eq. (23). The values of parameters a_m and b_m and the percentage average absolute deviation (AAD%) of experimental and calculated viscosities are reported in Table II.

It is worth noting that the molar volume of solvent (v_1) is used in the calculations, by eq. (23), because as shown by eq. (22), for such a low concentration of polymers this is a good approximation.

As may be seen from the reported results in Table II the calculated AAD% for the mixtures is less than 2.36%, which indicates the accuracy of calculations and the applicability of the proposed model based on Eyring's theory to the polymer–solvent mixtures. The consistency of the viscosity measurements and the validity of the proposed model are evaluated by considering Figures 2–4, which as expected by eq. (23), show linear plots of $\ln(\eta/T^{1/2})$ versus $1/T$. This can be seen by rearranging eq. (23) and writing it in logarithmic form:

$$\ln(\eta/T^{1/2}) = A(a_m + b_m T)/RT \quad (24)$$

where A is a constant for a mixture of fixed composition, expressed as

TABLE III
Correlated Parameters a_i and b_i in Equations (26) and (27)

System	a_0	a_1	a_2	a_3	b_0	b_1
Polystyrene/Toluene	-25,423	786,370	-44,778,000	9,108,000	150.66	-171.73
Polystyrene/Cyclohexane	-8,931	101,223	10,028,870	-2,316,009	-78.99	-579.68
Polystyrene/Benzene	-3,667	128,171	-77,620	0.0	-118.14	-186.12
Polymethylmethacrylate/Chloroform	12,927	-26,351	265,660	-636,000	-167.77	117.56
Polymethylmethacrylate/Acetone	-31,827	-3,676.70	2,800,400	-5,473,300	-169.56	-58.57

$$A = \ln[(2\pi R/V_1^2)^{1/2} M_1^{X_1/2} M_2^{X_2/2}] \quad (25)$$

It may be seen that the linearity of plots in Figures 2-4 is consistent with the linear form of eq. (24).

The parameters a_m and b_m can be correlated in terms of polymer concentrations c (g/cm^3) in the following expressions:

$$a_m = \sum_{i=0}^3 a_i c^i \quad (26)$$

$$b_m = \sum_{i=0}^1 b_i c^i \quad (27)$$

Equations (26) and (27) can be used to estimate viscosity of the polymer mixtures at the desired concentrations. The calculated values of a_i and b_i by the least-squares method are reported in Table III.

CONCLUSIONS

The linear relation between the shear stress τ and shear strain D indicates the Newtonian behavior of the studied mixtures. For viscosity calculations of polymer/solvent mixtures an equation was proposed and it was shown that the measured viscosities are consistent with this equation. The parameters of the proposed equation were correlated in terms of polymer

concentrations. The total AAD% for viscosity calculations by the proposed equation was 3.5%.

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