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Densities and Viscosities of Binary Mixtures of Poly(vinyl chloride) and Tetrahydrofuran at Temperatures (283.15 to 303.15) K

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Viscosities and densities of poly(vinyl chloride) + tetrahydrofuran (PVC/THF) mixtures were measured at several temperatures between (283.15 and 303.15) K. The measured densities were satisfactorily correlated by a simple first-order polynomial with respect to PVC concentration. The average molecular weight of PVC is determined by measuring the specific viscosity of the PVC/THF mixtures. The obtained viscosity results are correlated by a new modified Eyring's viscosity model. The adjustment parameters are determined and presented. The comparison of correlated and experimental results indicated the applicability of the proposed model for viscosity prediction of (PVC/THF) mixtures.

Introduction

Poly(vinyl chloride) (PVC) is an important member of the plastics family with excellent physical properties and chemical resistance. It was one of the first polymers to be developed, and the products it provides are essential components of a sustainable society.

One of the most important properties of plastics and plastic solvent mixtures are their ability to flow under the action of applied stresses at different temperatures. The quantitative evaluation of flow behavior in terms of applied stress and temperature is of great practical importance and theoretical interest.[1]

Properties of PVC have been examined in various solvents. In a large variety of solvents, the high concentration of PVC can form physical gels.[2−5] PVC gels exhibit an elastic solid at low temperature and gradually become liquid with increasing temperature. The molecular weight and concentration of PVC have important roles in the dynamic viscoelastic properties of PVC gels at different temperatures.[6]

Tetrahydrofuran (THF) is utilized as a solvent in numerous PVC adhesives. THF is also used in recovery and recycling of PVC or extraction of plasticizers. Therefore, solubility and flow behavior of PVC solvent mixtures are important in application of PVC.[7−9] The interaction between PVC and THF molecules causes a linear increase of density and viscosity of PVC/THF mixtures with an increase of PVC concentration in the THF.[10] The flow behavior of PVC/THF mixtures can be studied by viscometric measurements. The viscosity of these mixtures and in general the viscosity of polymer solvent mixtures are highly dependent on the molecular weight of the polymer.[11] Fortunately, viscosity measurements of polymer solvent mixtures provide an efficient method for determination of the molecular weight of the polymer.[11,12]

The various types of PVC average molecular weight, such as number average $\bar{M}_n$, weight average $\bar{M}_w$, and intrinsic viscosity $\bar{M}_v$, are the important necessary data for evaluating the physicochemical properties of PVC/THF mixtures.[11,13] There are different experimental methods for determining the molecular weight of polymers; however, viscometry is a simple method for determination of the number average molecular weight of polymers.[11−14]

The purpose of this paper is to apply Eyring's viscosity equation derived from absolute reaction rate theory to model the viscosities measured for PVC/THF mixtures.[7] Therefore, the average molecular weight of the used PVC sample is determined by measuring the specific viscosity of PVC/THF mixtures at 298.15 K. Then the obtained PVC molecular weight is used for viscosity calculations of PVC/THF mixtures at various temperatures.

Experimental Section

Commercial grade PVC was provided by an Iranian petrochemical company, and pure grade THF was supplied from the Merck Company. The purity of THF was checked by gas chromatography, and the results confirmed the mass fraction purity was higher than 0.99.

The PVC/THF mixtures were prepared by mass, using an analytical balance with ± 0.1 mg precision (Shimadzu, model AEU 210). Then they were put in a thermostatted water bath and were allowed to attain thermal equilibrium. The temperature of the water bath was measured to a precision of ± 0.1 K by using a thermometer (Cole Parmer Instrument Company) with subdivisions of 0.1 K.

A 25 cm^3 calibrated glass pycnometer was used for density measurements at T = (283.15, 288.15, 293.15, 298.15, and 303.15) K. To calibrate the glass pycnometer, it was filled up with distilled water, and the weight of water was determined (precision ± 0.1 mg). Using reported accurate pure water densities[15] in the temperature range (298.15 to 328.15) K, the volume of the pycnometer was determined with an uncertainty of $\pm 10^{-4}$ cm^3. For each solution, four density measurements were performed, and the results were averaged. The uncertainty of the density measurements was estimated as $\pm 10^{-4}$ $\text{g}\cdot\text{cm}^{-3}$.

Kinematic viscosities, ν (= η/ρ), of the PVC/THF mixtures were measured using a calibrated modified Ostwald viscometer (Cannon-Fenske glass capillary viscometers, CFRU, 9721-A50) with inner diameters of (0.30 ± 2) % mm. The flow time was

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Table 1. Comparison of Densities (ρ) and Viscosities (η) of Pure Components with Literature Values at 298.15 K

	ρ/(g·cm^{-3})		η/(mPa·s)	
component	this work	lit.	this work	lit.
tetrahydrofuran	0.8829	0.8833	0.456	0.457
N,*N*-dimethyl formamide (DMF)	0.9441	0.9439	0.802	0.801

Table 2. Measured Reduced Viscosity, η_{red}, of the PVC/THF Mixtures at 298.15 K for Four Different Polymer Concentrations

PVC conc.	flow time	viscosity		
c/kg·L^{-1}	s	η/mPa·s	$\eta_{sp} = (\eta - \eta_0)/\eta_0$	$\eta_{red} = \eta_{sp}/c$
1.50	38.89	1.0103	1.0797	0.7198
2.50	56.96	1.5441	2.1785	0.9077
4.00	100.89	2.8106	4.7856	1.1964
4.80	127.10	3.5736	6.3562	1.3242

measured with a stop watch capable of recording to 0.01 s. For each solution, the experimental viscosity was obtained by averaging three to five flow time measurements. The uncertainty of kinematic viscosity measurements was estimated as $\pm\, 10^{-8}$ m^2·s^{-1}.

The measurements of solution viscosity in terms of flow time would account for the kinetic energy of the moving liquid. Considering the kinetic energy, the viscometer was calibrated by the following equation[11,16]

$$\frac{\eta}{\rho} = \kappa t - \frac{L}{t} \tag{1}$$

where η is the absolute viscosity; ρ is the density; and t is the flow time of the pure calibration liquid. κ and L were the characteristic viscometer constants. The kinetic energy term in eq 1, (L/t), is an important term in viscosity calculations if the liquid is moving fast (t is small), but if the flow is slow (t is large), the kinetic energy term, which is proportional to ($1/t$), can be ignored. In this work, by using the absolute viscosity and density ρ of pure dimethyl formamide (DMF), the characteristic viscometer constants K and L were obtained as: $3.9 \cdot 10^{-9}$ m^2·s^{-2} and $5.21 \cdot 10^{-8}$ m^2. The accuracy of the used pycnometer and viscometer was tested with the density and viscosity measurements of pure THF and DMF at 298.15 K. Table 1 shows the obtained experimental results for the density and viscosity measurements. In this table, the obtained data were compared with the available data in the literature.[15] These comparisons indicated good consistency between these results and those presented in the literature.

Molecular Weight Measurement

In dilute polymer solutions, the linear relationship between the reduced viscosity (η_{sp}/c) and concentration (c) of a polymer in solution exists except for polyelectrolytes in solvents. On extrapolating to zero concentration, the intrinsic viscosity can be obtained which makes it possible to determine the polymer molecular weight.[13]

The Mark–Houwink empirical equation has been applied for various polymer solvent mixtures[11,17]

$$[\eta] = KM_V^a \tag{2}$$

where $[\eta]$ is the intrinsic viscosity; M_V is the viscosity average molecular weight; and K and a are constants for a given polymer–solvent system at different temperatures.

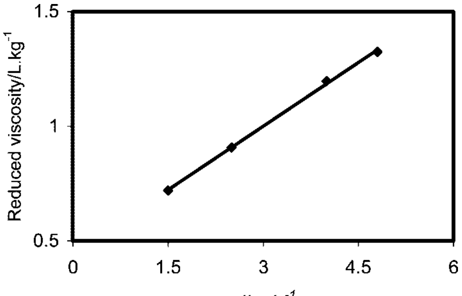

Figure 1. Plot of reduced viscosity versus concentration of PVC in PVC/THF mixtures at 298.15 K.

Table 3. Measured Density ρ/g·cm^{-3} of PVC/THF Mixtures at Different Temperatures and Concentrations

	PVC concentration c/kg·L^{-1}					
T/K	0.0148	0.0198	0.0239	0.0299	0.0398	0.0477
283.15	0.8961	0.8974	0.8985	0.9001	0.9029	0.9051
288.15	0.8927	0.8941	0.8952	0.8972	0.9001	0.9021
293.15	0.8890	0.8905	0.8917	0.8936	0.8968	0.8995
298.15	0.8861	0.8875	0.8886	0.8906	0.8937	0.8959
303.15	0.8823	0.8841	0.8851	0.8870	0.8901	0.8926

Table 4. Parameters of the Density Model, Equation 3, for the PVC/THF Mixtures

T/K	α	β	R^2
283.15	0.2741	0.8920	0.999
288.15	0.2900	0.8884	0.999
293.15	0.3188	0.8842	0.999
298.15	0.3021	0.8815	0.999
303.15	0.3098	0.8778	0.999

The specific viscosity of PVC/THF mixtures, $\eta_{sp} = (\eta - \eta_0)/(\eta_0)$, was determined by measuring the viscosity of THF (η_0) and PVC/THF mixtures (η) for low concentrations of PVC in the mixtures. Table 2 indicates the measured reduced viscosity, η_{sp}/c, of four PVC/THF mixtures at 298.15 K.

The Huggins equation reveals the correlation between η_{sp}/c and c in dilute solution, if the proper technique is employed to determine the viscosity of the polymer solvent mixture[18]

$$\eta_{red} = \frac{\eta_{sp}}{c} = K'[\eta]^2 c + [\eta] \tag{3}$$

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

Figure 1 shows the plots of the reduced viscosity η_{sp}/c versus concentration of PVC in PVC/THF mixtures, c, at 298.15 K. The intrinsic viscosity, $[\eta]$, was determined as $\lim_{c\to 0}(\eta_{sp}/c)$. By using eq 2, $a = 0.92$, and $K = 0.00363$ mL·g^{-1},[13] the average viscosity molecular weight of the PVC sample is evaluated as 28495 g·mol^{-1}.

Results and Discussion

Density Model. The obtained density results in Table 3 were correlated to a first-order polynomial with respect to PVC concentration, c, in the following form

$$\rho/\text{g·cm}^{-3} = \alpha c + \beta \tag{4}$$

where ρ is the density; c is the PVC concentration; and α and β are the coefficients of the above linear equation. Coefficients of eq 4 for PVC/THF mixtures are presented in Table 4. The values of R^2 reported in this table indicate that without recourse

Table 5. Measured Viscosity η/mPa·s of PVC/THF Mixtures at Different Temperatures and Concentrations

	T/K				
c/kg·L^{-1}	283.15	288.15	293.15	298.15	303.15
0.0154	1.1445	1.0702	0.9903	0.9301	0.8677
0.0206	1.3775	1.2992	1.2324	1.1741	1.1125
0.0241	1.6397	1.5783	1.5178	1.4654	1.4116
0.0301	2.0194	1.9278	1.8263	1.7414	1.6764
0.0402	3.0746	2.9634	2.8575	2.7569	2.6829
0.0481	3.9156	3.7481	3.5738	3.4368	3.2845

Table 6. Parameters of the Viscosity Model, Equation 8, for PVC/THF Mixtures

c/kg·L^{-1}	α_m	β_m	R^2
0.0154	581.08	−3.219	0.999
0.0206	441.39	−2.647	0.999
0.0241	342.30	−2.220	0.999
0.0301	417.21	−2.394	0.999
0.0402	320.90	−1.872	0.999
0.0481	390.31	−2.011	0.999

to the tedious and time-consuming density measurements the densities of the studied PVC/THF mixtures, required in the viscosity model, can be calculated accurately, by using eq 4.

Viscosity Model. The measured kinematic viscosities of PVC/THF mixtures at different temperatures and concentrations are presented in Table 5. The viscosity data are correlated by a newly modified Eyring's viscosity model for binary PVC (2)/THF (1) mixtures using an equation in the following form[18−20]

$$\upsilon = (2\pi RT)^{1/2}[M_1^{(x_1/2)-1}M_2^{x_2/2}]\exp(E_{am}/RT) \qquad (5)$$

where υ, x, M, R, T, and E_{am} represent, respectively, kinematic viscosity, mole fraction, molar mass, gas constant, temperature, and molar activation energy of the mixtures.

Equation 5 is rearranged in the following linear form[18]

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

where

$$A = \ln[(2\pi R)^{1/2}M_1^{(x_1/2)-1}M^{x_2/2}] \qquad (7)$$

Then, eq 6 can be presented in the following simple form

$$\ln(\upsilon/T^{1/2}) = \alpha_m/T + \beta_m \quad \text{and} \quad \alpha_m = Aa_m/R,\ \beta_m = Ab_m/R \qquad (8)$$

According to eq 8, the variation of $\ln(\nu/T^{1/2})$ versus $1/T$ is linear. Equation 8 was used to correlate the measured kinematic viscosities of PVC/THF mixtures and to evaluate the parameters α_m and β_m. The results are given in Table 6.

Conclusion

In this work, the viscosity of PVC/THF mixtures was measured and fitted to a modified Eyring's viscosity model proposed by the authors. According to the kinematic viscosity model, eq 7, the density of PVC/THF mixtures and the average molecular weight of the PVC sample are needed as input data in the viscosity correlations. Therefore, the densities of PVC/THF mixtures were measured and correlated by a first-order polynomial with respect to PVC concentration, c, and the evaluated parameters were reported. The average molecular weight of the PVC sample was determined by measurements of the intrinsic viscosity of PVC/THF mixtures at 298.15 K. The parameters of the viscosity model were calculated and reported. The values R^2 reported in Table 6 indicate the high quality of fitting according to eq 8.

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