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Experimental study of the thermodynamic and transport properties of binary mixtures of poly(ethylene glycol) diacrylate and alcohols at different temperatures

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Abstract: Experimental density ρ , refractive index n_D and viscosity η data of three binary systems of poly(ethylene glycol) diacrylate (PEGDA) + ethanol, + 1-propanol and + 1-butanol were measured at eight temperatures from 288.15 to 323.15 K, with temperature step of 5 K, and at atmospheric pressure. The experimental data were correlated as a function of the PEGDA mole fraction and temperature. The densities and refractive indices of the investigated mixtures could be fitted well with exponential function *vs.* composition, including the temperature dependence of the parameters, while in the case of the viscosities, a polynomial function fits well the composition of the mixtures. In the case of the temperature correlation, all three properties (ρ , $\ln \eta$ and n_D) exhibited linear trends. The viscosity modeling was performed using four models: the UNIFAC–VISCO, ASOG–VISCO, McAllister and the Teja–Rice models. For application of the UNIFAC–VISCO model, interaction parameters of following groups were determined: CH₂=CH/CH₃, CH₂=CH/CH₂, CH₂=CH/OH, CH₂=CH/CH₂O and CH₂=CH/COO. In addition, in the same way, the binary interaction parameters used in the ASOG–VISCO model of the following groups were determined: CH₂=CH/CH₂, CH₂=CH/OH, CH₂=CH/CH₂O and CH₂=CH/COO.

Keywords: density; viscosity; refractive index; new UNIFAC–VISCO parameters; new ASOG–VISCO parameters.

INTRODUCTION

For a complete understanding of the thermodynamic and transport properties of pure organic compounds and multicomponent liquid mixtures, knowledge of their thermodynamic and transport properties over wide composition and tem-

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perature ranges is necessary. Studies of thermodynamic properties contribute to the understanding of the behavior of various organic compounds and their functional groups, and are of great importance for the understanding of the molecular interactions in multicomponent mixtures. This work is a continuation of ongoing research related to determination of thermophysical and transport properties of mixtures containing polymers.¹⁻⁵ In this work, a biodegradable and biocompatible polymer, *i.e.*, poly(ethylene glycol) diacrylate (PEGDA), was investigated in binary mixtures with small chain alcohols, *i.e.*, ethanol, 1-propanol, and 1-butanol.

Poly(ethylene) glycol diacrylate (PEGDA) is a low volatility and medium viscosity clear liquid with good flexibility and elongation, good water dispersibility, low skin irritancy and good reactivity. It is soluble in water and is used as a functional co-monomer for flexible plastics and as a cross linking agent between the molecular chains of polymers.⁶ Furthermore, PEGDA is a synthetic, hydrophilic starting material for the production of hydrogels in the presence of a photo-initiator and UV light. This polymer is widely known as a biocompatible and non-immunogenic material suitable for various chemical manipulations, with application in tissue engineering and regenerative medicine.⁷ One of the important usages of PEGDA in biological and biomedical applications could be for controlled release of drugs by producing well defined micro- or nano-channels inside the polymer, which would make the release of drugs through the pathways more readily predictable and controlled. A procedure for producing PEGDA particles with specific, internal channels for drug release is described in detail in the literature.⁸

The investigated short-chain alcohols are completely miscible with water and used as solvents in various fields of industry. In this particular case, their application in pharmaceutical industry is of great importance because mixtures of PEGDA and alcohols could be potentially applied in the pharmaceutical industry for the controlled release of drugs. In addition, they find application for the removal of CO₂ from the air or in biochemical applications.⁶

Alcohols are polar compounds with the following dipole moments: 5.67×10^{-30} C·m for ethanol, 5.67×10^{-30} C·m for 1-propanol and 6.00×10^{-30} C·m for 1-butanol.⁹ PEGDA, as a hydrophilic polymer, contains polar or charged functional groups (carbonyl groups adjacent to an ether linkage) which make them soluble in polar compounds, such as alcohols. From the chemical structures of PEGDA and alcohols, it is evident that alcohols contain a hydrogen responsible for hydrogen bonding between the molecules of the same alcohol or with an oxygen from the polymer, while in the PEGDA molecule, ester COO groups are present. It could be conclude that these molecules might form intermolecular hydrogen bonds, *i.e.*, hydrogen from the hydroxyl group in alcohols with the oxygen from the COO group in a polymer. There are also van der Waals dispersion

forces and dipole–dipole interactions between alcohols and polymer, and molecules of the same compound. The hydrogen bonding and dipole–dipole interactions will be much the same for all the alcohols, but the dispersion forces will increase as the alcohol becomes larger.

The intention of this work was to investigate how the thermodynamic and transport properties of PEGDA and alcohol mixtures change with respect to the alcohol chain length and with temperature, bearing in mind the possible interactions between the above-mentioned components. Thus, in this work, the densities ρ , refractive indices n_D and viscosities η of three binary systems of poly(ethylene glycol) diacrylate (PEGDA) + ethanol or + 1-propanol or + 1-butanol were measured at eight temperatures (288.15, 293.15, 298.15, 303.15, 308.15, 313.15, 318.15 and 323.15 K) and at atmospheric pressure. Additionally, the viscosity data were modeled using the UNIFAC–VISCO, ASOG–VISCO, McAllister and Teja–Rice models. Generally, if a viscosity calculation is based on already determined parameters given in the literature, the UNIFAC–VISCO and ASOG–VISCO models are actually predictive. However, since in the case of the systems investigated in the present study, some of the parameters were not known, the intention was to determine accurately their values and the UNIFAC–VISCO and ASOG–VISCO models were considered as correlative.

EXPERIMENTAL

Chemicals

Poly(ethylene glycol) diacrylate (PEGDA), with molecular formula $C_{2n+6}H_{4n+6}O_{n+3}$ and with number average molecular weight 700 g mol^{-1} , was purchased from Aldrich (CAS No.: 26570-48-9, Cat. No.: 455008, Lot No.: MKBH4151V). Alcohols of reagent grade: ethanol ($\geq 99.9 \text{ mass } \%$), 1-propanol ($\geq 99.5 \text{ mass } \%$), and 1-butanol ($\geq 99.5 \text{ mass } \%$) were purchased from Merck. The chemicals were kept in dark bottles under an inert atmosphere and ultrasonically degassed before sample preparation.

Apparatus and procedures

The density ρ measurements were performed using an Anton Paar DMA 5000 digital vibrating U-tube densimeter (with automatic viscosity correction). The temperature in the cell was regulated to $\pm 0.001 \text{ K}$ with a built in solid-state thermostat. Calibration of the apparatus was performed daily using ambient air and Millipore quality water. A Mettler AG 204 balance, with a precision $1 \times 10^{-7} \text{ kg}$, was used for precise measurement of mass composition for all binary mixtures, using the cell and the procedure described previously.¹⁰ The uncertainty of the mole fraction calculation was less than $\pm 1 \times 10^{-4}$. The experimental uncertainty in density was about $\pm 1 \times 10^{-2} \text{ kg m}^{-3}$.

The refractive index n_D measurements were performed using an automatic Anton Paar RXA 156 refractometer, which works with the wavelength of 589 nm. Throughout this procedure, the temperature of the sample was kept constant with a built-in thermostat within an accuracy of $\pm 0.03 \text{ K}$. The estimated experimental uncertainties in the refractive index were about $\pm 1 \times 10^{-4}$.

The viscosity, η , measurements were performed using a digital Stabinger viscometer (model SVM 3000/G2). The instrument contains two measuring cells; one of which is used

for measuring the density of the sample, while the other one measures the dynamic viscosity. The kinematic viscosity was calculated from the measured density and dynamic viscosity. During this procedure, the temperature in the cells was regulated to ± 0.01 K with a built in solid-state thermostat. The relative uncertainty in the dynamic viscosity measurements was estimated to be 0.35 %.

The densities, dynamic viscosities and refractive indices of the pure substances at several temperatures and at atmospheric pressure are compared with literature values^{7,11-19} in Table I. The agreement with the literature for the density measurements in most cases was within 0.55 kg m^{-3} , while the viscosity measurements were within 0.02 mPa s . The experimental refractive indices of pure components agree with literature values within 8×10^{-4} for alcohols and within 0.002 for PEGDA.

TABLE I. Densities, ρ , viscosities, η , and refractive indices, n_D , of the pure components at temperature T and at atmospheric pressure; the standard uncertainties σ for each variables are $\sigma(T) = 0.01 \text{ K}$; $\sigma(\rho) = 5 \%$; $\sigma(x_1) = \pm 1 \times 10^{-4}$, and the combined uncertainties σ_c are $\sigma_c(\rho) = \pm 1 \times 10^{-2} \text{ kg m}^{-3}$; $\sigma_c(n_D) = \pm 1 \times 10^{-4}$; $\sigma_c(\eta) = 0.35 \%$, at the 0.95 level of confidence ($k \approx 2$)

Substance	T / K	$\rho / 10^3 \text{ kg m}^{-3}$		$\eta / \text{mPa s}$		n_D	
		This work	Lit.	This work	Lit.	This work	Lit.
PEGDA	293.15					1.47012	1.470 ⁷
	303.15					1.46618	1.465 ⁷
	313.15					1.46228	1.460 ⁷
Ethanol	293.15	0.789547	0.7900 ¹¹	1.1885	1.2097 ¹¹		
	298.15	0.785257	0.7857 ¹¹	1.0838	1.0990 ¹¹	1.35999	1.35922 ¹²
	303.15	0.780942	0.7809 ¹¹	0.98999	0.9971 ¹¹		
	313.15	0.772202	0.7733 ¹¹	0.82807	0.8280 ¹¹		
	323.15	0.763276	0.7636 ¹³	0.69427	0.7081 ¹³		
1-Propanol	288.15	0.807931	0.80749 ¹⁴				
	293.15	0.803946	0.80375 ¹⁴				
	298.15	0.799932	0.79975 ¹⁴	1.9222	1.943 ¹⁵	1.38334	1.3837 ¹⁶
	303.15			1.7158	1.725 ¹⁵		
1-Butanol	293.15	0.810205	0.8097 ¹⁴	2.9321	2.941 ¹⁶	1.39929	1.39929 ¹⁶
	298.15	0.806384	0.8060 ¹⁴	2.5656	2.571 ¹⁶	1.39725	1.39741 ¹⁶
	303.15	0.802538	0.80191 ¹⁸	2.2518	2.271 ¹⁶	1.39519	1.3959 ¹⁹
	308.15	0.798659	0.79807 ¹⁸				

RESULTS AND DISCUSSION

The experimental data of density, viscosity, and refractive index for three binary systems (PEGDA + ethanol, PEGDA + 1-propanol, and PEGDA + 1-butanol) at eight temperatures (288.15 to 323.15 K), over the entire composition range and at atmospheric pressure are reported in Table S-I of the Supplementary material to this paper.

Fitting of the experimental values of density and refractive index was performed as a function of PEGDA mole fraction with temperature dependant parameters. The quality of the fitting was estimated by the deviation between experi-

mental value and those calculated by different equations. The best results were obtained using the following equation:

$$\rho, n_D = \exp \left[(A_{00} + A_{01}T) + \frac{A_{10} + A_{11}T}{x_1 + (A_{20} + A_{21}T)} \right] \quad (1)$$

where A_{00} , A_{01} , A_{10} , A_{11} , A_{20} and A_{21} are the fitting parameters, x_1 is PEGDA mole fraction and T is temperature.

The viscosity values, unlike density and refractive index values, varied greatly with change in temperature and hence, a single equation that combined the temperature and composition dependencies did not give good results and so fitting the viscosity values as a function of PEGDA mole fraction or temperature was performed separately using the following equations:

$$\eta = B_0 + B_1x_1 + B_2x_1^2 + B_3x_1^3 \quad (2)$$

$$\ln \eta = C_0 + \frac{C_1}{T} \quad (3)$$

where B_0 , B_1 , B_2 , B_3 , C_0 and C_1 are the fitting parameters, x_1 is the PEGDA mole fraction and T is the temperature.

For the three binary mixtures at different temperatures and compositions, the parameters of Eq. (1) are presented in Table S-II and the parameters of Eqs. (2) and (3) in Table S-III (Supplementary material). The corresponding root-mean-square deviations (rmsd) σ , defined by Eq. (4) are presented in Tables S-II and S-III of the Supplementary material:

$$\sigma = \left(\frac{\sum_i^n (Y_{\text{exp}} - Y_{\text{cal}})^2}{n} \right)^{1/2} \quad (4)$$

Y_{exp} and Y_{cal} are experimental and calculated values of ρ , η or n_D , respectively, and n is the number of experimental data points.

Comparison of the densities, viscosities and refractive indices of binary systems of PEGDA and alcohols at 288.15 and 323.15 K and at atmospheric pressure are given in Fig. 1a–c, respectively. It is obvious from Fig. 1 that the experimental values of the density, viscosity, and refractive index data of pure PEGDA are significantly higher than those of the analyzed alcohols. In addition, it is evident that the densities and refractive index data of the mixtures increased exponentially with increasing PEGDA mole fraction, while the increase in the viscosities vs. PEGDA composition followed a polynomial trend. It can be observed that the density and refractive index increased considerably in the range of

lower PEGDA concentrations (from 0 to 0.3 mole fraction), while approaching higher PEGDA mole fractions, the curves trended to constant values. This means that the influence of PEGDA on the overall densities and refractive indices of the PEGDA + alcohol mixtures was far greater in comparison to the influence of the alcohols. In the case of viscosity, there was a constant increase in the values with increasing PEGDA mole fraction. In addition, it is noticeable that the densities, viscosities and refractive indices of pure compounds and their mixtures decreased as the temperature increased. This temperature influence was the most pronounced for the viscosity data. Namely, the viscosity of pure PEGDA at 288.15 K was almost six times higher than at 323.15 K.

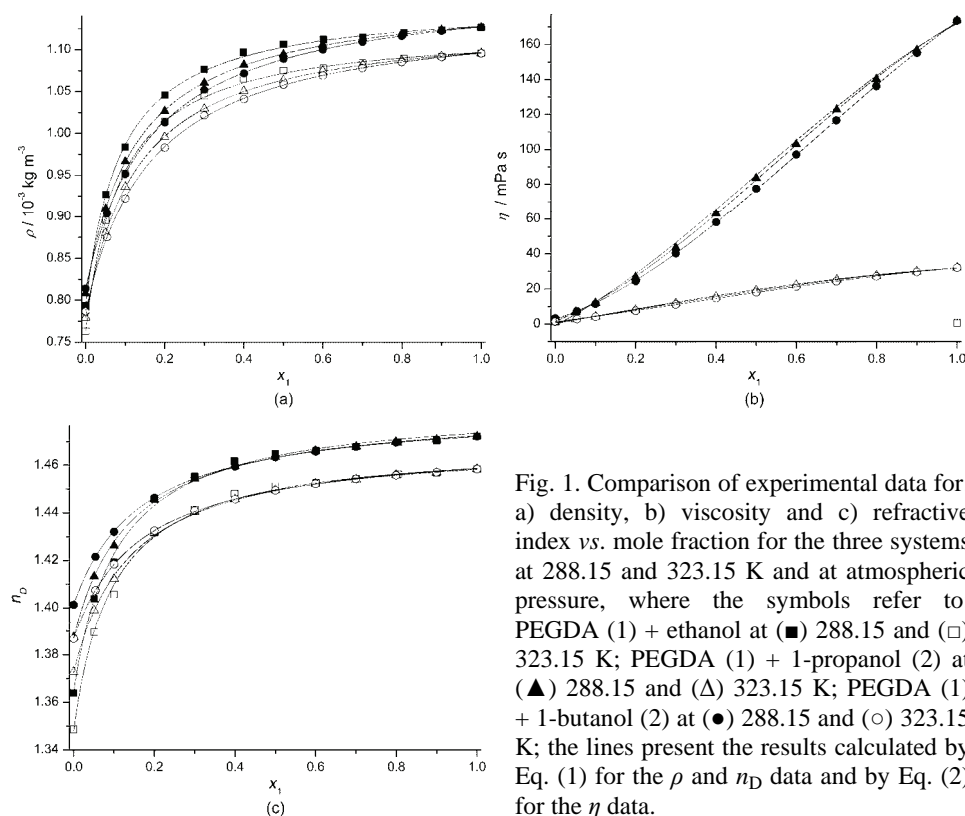


Fig. 1. Comparison of experimental data for: a) density, b) viscosity and c) refractive index vs. mole fraction for the three systems at 288.15 and 323.15 K and at atmospheric pressure, where the symbols refer to: PEGDA (1) + ethanol (1) at (■) 288.15 and (□) 323.15 K; PEGDA (1) + 1-propanol (2) at (▲) 288.15 and (△) 323.15 K; PEGDA (1) + 1-butanol (2) at (●) 288.15 and (○) 323.15 K; the lines present the results calculated by Eq. (1) for the ρ and n_D data and by Eq. (2) for the η data.

Experimental values of the density and refractive index against temperature at atmospheric pressure are presented in Figs. 2 and 3, respectively, while $\ln \eta$ vs. $1/T$ changes at atmospheric pressure are depicted in Fig. 4.

One can conclude that density and refractive index data exhibit linear dependences on temperature, with a decreasing tendency of the property with increasing temperature. Figs. 2 and 3 also prove that the changes of densities and

refractive indices are greater in the range of smaller PEGDA mole fractions (from 0 to 0.3). Function of $\ln \eta$ vs. $1/T$ exhibited a linear trend as well, confirming that with increasing temperature the PEGDA + alcohols mixtures become less viscous (Fig. 4).

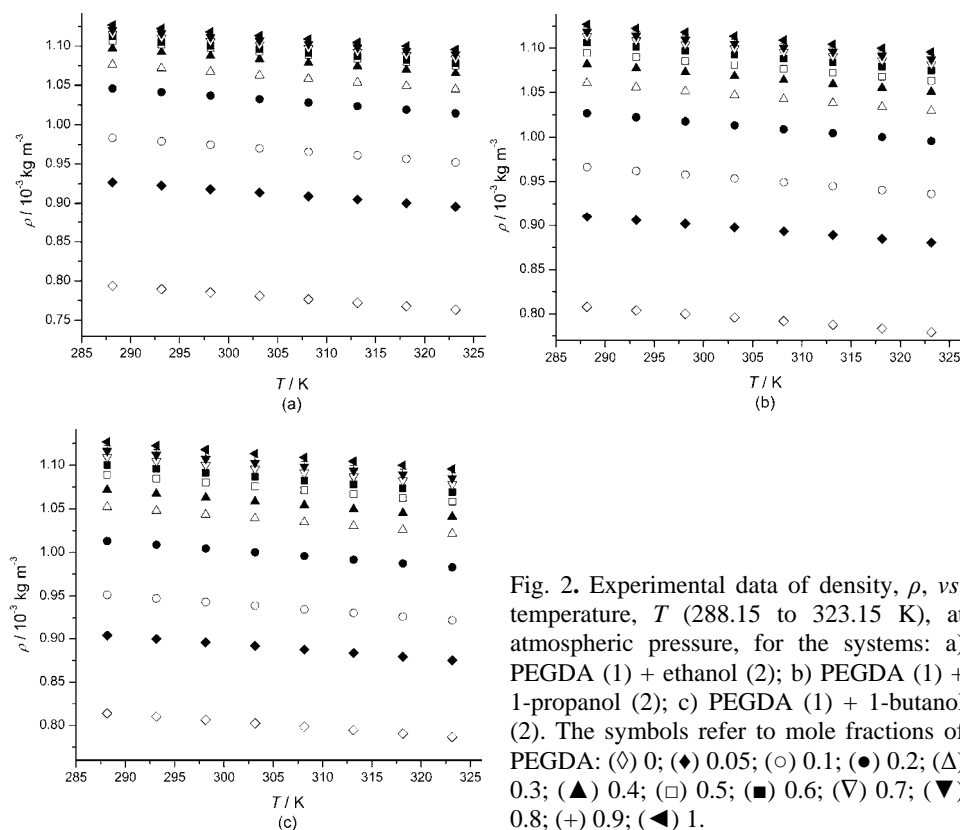


Fig. 2. Experimental data of density, ρ , vs. temperature, T (288.15 to 323.15 K), at atmospheric pressure, for the systems: a) PEGDA (1) + ethanol (2); b) PEGDA (1) + 1-propanol (2); c) PEGDA (1) + 1-butanol (2). The symbols refer to mole fractions of PEGDA: (◇) 0; (♦) 0.05; (○) 0.1; (●) 0.2; (Δ) 0.3; (▲) 0.4; (□) 0.5; (■) 0.6; (∇) 0.7; (▼) 0.8; (+) 0.9; (◀) 1.

In addition, modeling of viscosity experimental data was performed using predictive and correlative types of models. In this work UNIFAC-VISCO^{20,21} and ASOG-VISCO²² models were used for the determination of the dynamic viscosity of the three binary mixtures. UNIFAC-VISCO and ASOG-VISCO are group contribution models aimed at activity coefficient determination. In both methods, the activity coefficients in the mixtures are related to interactions between structural groups. Consequently, the parameters characterizing interactions between pairs of structural groups, called group interaction parameters, are necessary (α_{nm} for UNIFAC-VISCO and m_{kl} and n_{kl} for ASOG-VISCO). If the parameters are given in the literature, it is not necessary to determine them again. In this work, new group interaction parameters were determined from the experi-

mentally measured viscosities using the Marquardt²³ optimization technique for the minimization of the objective function:

$$OF = \frac{1}{n} \sum_{i=1}^n \left(\frac{\eta_{\text{exp}} - \eta_{\text{cal}}}{\eta_{\text{exp}}} \right)_i^2 \rightarrow \min \quad (5)$$

where η_{exp} and η_{cal} denote the experimental and calculated values of the dynamic viscosity η and n is the number of experimental data points.

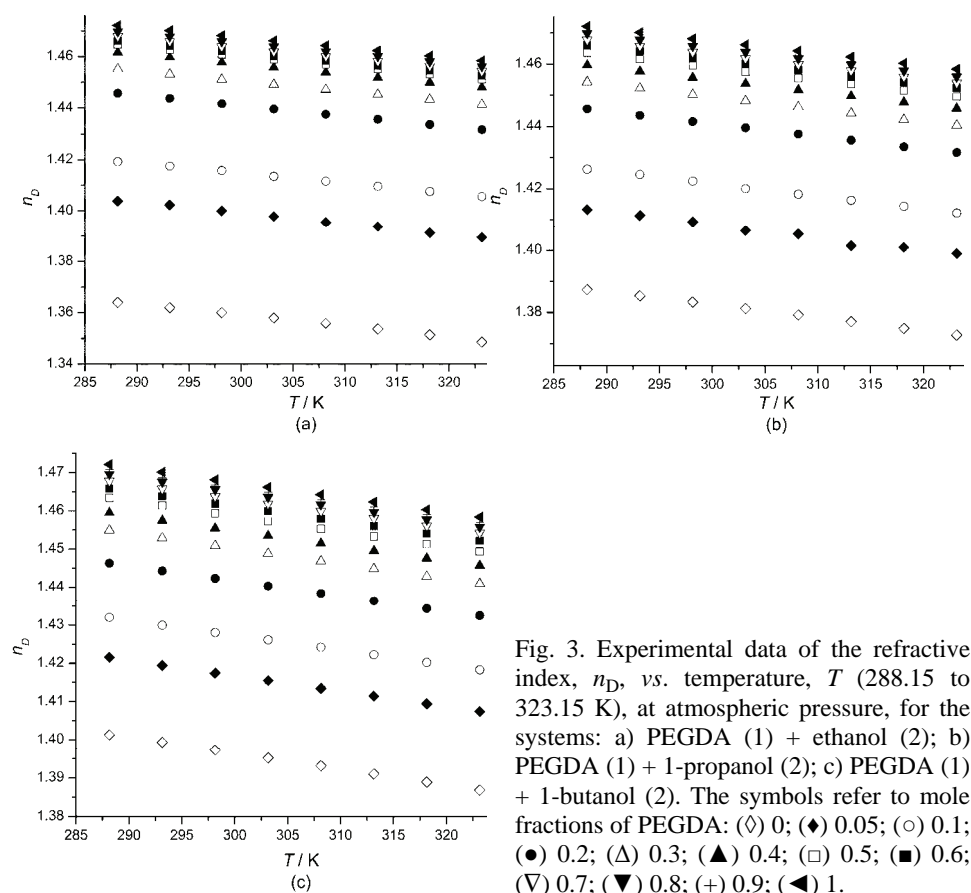


Fig. 3. Experimental data of the refractive index, n_D , vs. temperature, T (288.15 to 323.15 K), at atmospheric pressure, for the systems: a) PEGDA (1) + ethanol (2); b) PEGDA (1) + 1-propanol (2); c) PEGDA (1) + 1-butanol (2). The symbols refer to mole fractions of PEGDA: (◇) 0; (◆) 0.05; (○) 0.1; (●) 0.2; (△) 0.3; (▲) 0.4; (□) 0.5; (■) 0.6; (▽) 0.7; (▼) 0.8; (+) 0.9; (◀) 1.

The new UNIFAC–VISCO interaction parameters, α_{nm} , between the following groups: $\text{CH}_2=\text{CH}/\text{CH}_3$, $\text{CH}_2=\text{CH}/\text{CH}_2$, $\text{CH}_2=\text{CH}/\text{OH}$, $\text{CH}_2=\text{CH}/\text{CH}_2\text{O}$ and $\text{CH}_2=\text{CH}/\text{COO}$ are summarized in Table II. The remaining interaction parameters were taken from the original model^{20,21} and previous papers.^{5,24}

In the similar way, new ASOG–VISCO group interaction parameters, m_{kl} and n_{kl} , of following groups $\text{CH}_2=\text{CH}/\text{CH}_2$, $\text{CH}_2=\text{CH}/\text{OH}$, $\text{CH}_2=\text{CH}/\text{CH}_2\text{O}$,

$\text{CH}_2=\text{CH}/\text{COO}$ were determined using the original interaction parameters²² and parameters from previous papers.^{3,24} The results are summarized in Table III.

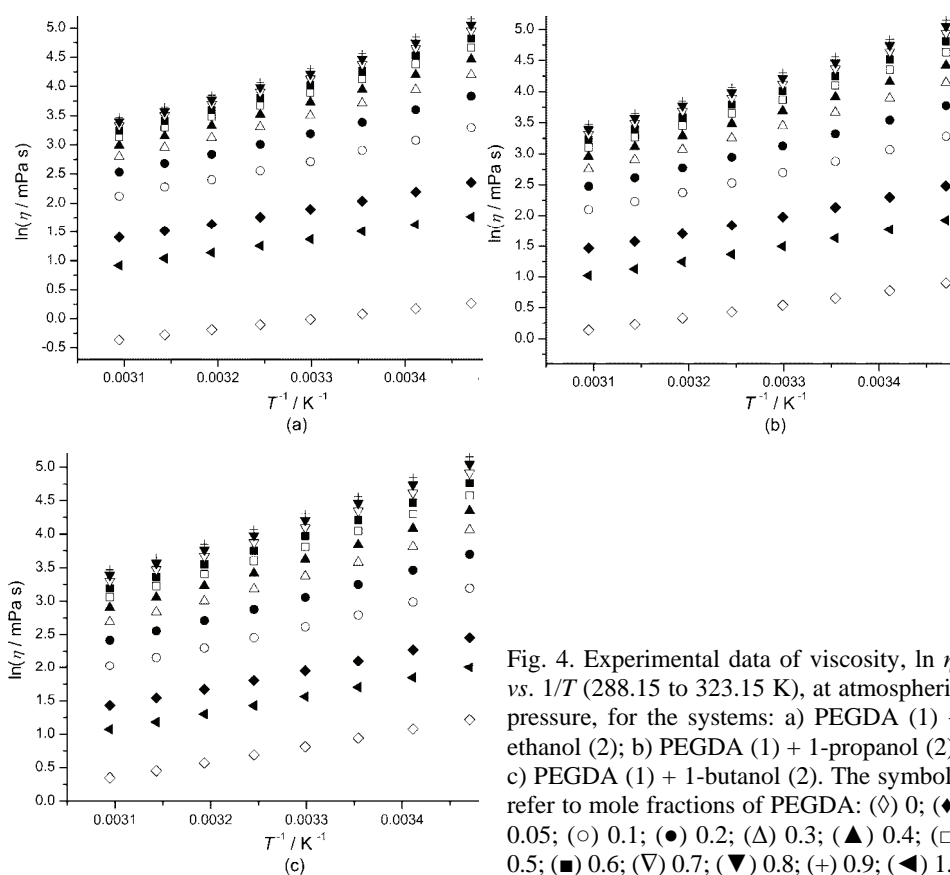


Fig. 4. Experimental data of viscosity, $\ln \eta$, vs. $1/T$ (288.15 to 323.15 K), at atmospheric pressure, for the systems: a) PEGDA (1) + ethanol (2); b) PEGDA (1) + 1-propanol (2); c) PEGDA (1) + 1-butanol (2). The symbols refer to mole fractions of PEGDA: (◇) 0; (◆) 0.05; (○) 0.1; (●) 0.2; (Δ) 0.3; (▲) 0.4; (□) 0.5; (■) 0.6; (∇) 0.7; (▼) 0.8; (+) 0.9; (◀) 1.

TABLE II. The UNIFAC–VISCO interaction parameter, α_{nm}

n/m	CH_3	CH_2	$\text{CH}_2=\text{CH}$	OH	CH_2O	COO
CH_3	0	-709.5 ^a	-570.861 ^d	594.4 ^a	-50.17 ^b	-172.4 ^a
CH_2	66.53 ^a	0	1161.742 ^d	498.6 ^a	-319.930 ^b	1172 ^a
$\text{CH}_2=\text{CH}$	-872.856 ^d	1489.036 ^d	0	-869.851 ^d	-2243.897 ^d	-57.440 ^d
OH	1209 ^a	-634.5 ^a	-549.041 ^d	0	-619.360 ^b	68.35 ^a
CH_2O	456.91 ^b	-340.250 ^b	248.157 ^d	25.340 ^b	0	-56.95 ^c
COO	-44.25 ^a	541.6 ^a	-445.344 ^d	186.8 ^a	-137.945 ^c	0

^aOriginal UNIFAC–VISCO parameters;^{20,21} ^bUNIFAC–VISCO parameters from the literature;⁵ ^cUNIFAC–VISCO parameters from the literature;²⁴ ^dnew UNIFAC–VISCO parameters

Moreover, the experimental viscosity data were correlated with the one-parameter Teja and Rice,^{25,26} and McAllister²⁷ two-parameter three-body and

three-parameter four-body models. These models are described in detail in a previous papers.^{28,29}

TABLE III. The ASOG–VISCO interaction parameters

<i>k/l</i>	CH ₂	CH ₂ =CH	OH	CH ₂ O	COO
<i>m_{kl}</i>					
CH ₂	0	0.2428 ^d	−0.3570 ^a	−10.9924 ^b	0.3682 ^a
CH ₂ =CH	1.7603 ^d	0	1.6245 ^d	−6.3287 ^d	−2.5891 ^d
OH	14.1460 ^a	−0.3330 ^d	0	−2.2661 ^b	−40.2000 ^a
CH ₂ O	−33.9591 ^b	−173.2012 ^d	1.5287 ^b	0	−2.9720 ^c
COO	0.0952 ^a	197.1496 ^d	19.1310 ^a	−4.7468 ^c	0
<i>n_{kl}</i>					
CH ₂	0	356.102 ^d	469.650 ^a	−1.928 ^b	112.590 ^a
CH ₂ =CH	187.229 ^d	0	413.379 ^d	299.095 ^d	298.614 ^d
OH	−6137.000 ^a	476.584 ^d	0	−14.965 ^b	11583.000 ^a
CH ₂ O	−8.176 ^b	298.966 ^d	−127.018 ^b	0	−835.188 ^c
COO	−383.600 ^a	300.577 ^d	−5747.000 ^a	−433.643 ^c	0

^aOriginal ASOG–VISCO parameters;²² ^bASOG–VISCO parameters from the literature;³ ^cASOG–VISCO parameters from the literature;²⁴ ^dnew ASOG–VISCO parameters

The ability of these models to predict successfully the dynamic viscosities of the investigated binary mixtures and to correlate the experimental viscosity data is presented with percentage deviations, PD_{\max} , between the experimental and calculated viscosities, using the following equation:

$$PD_{\max} = \frac{100}{n} \sum_{i=1}^n \left| \frac{\eta_{\text{exp}} - \eta_{\text{cal}}}{(\eta_{\text{exp}})_{\max}} \right|_i \quad (6)$$

where $(\eta_{\text{exp}})_{\max}$ is the maximum of the experimental η values.

The results obtained by the UNIFAC–VISCO, ASOG–VISCO, Teja–Rice and McAllister models for the mixtures of PEGDA + ethanol or 1-propanol or 1-butanol over the investigated temperature range are given in Table IV. A graphical presentation of the experimental viscosity deviation from the values obtained by the selected models is given in Fig. 5.

TABLE IV. Results of the viscosity prediction and correlation for the investigated binary systems at the temperatures (288.15 to 323.15) K and at atmospheric pressure

<i>T</i> / K	Predictive approach		Correlative approach		
	UNIFAC–VISCO	ASOG–VISCO	Teja–Rice	McAllister-3	McAllister-4
	PD_{\max} / %	PD_{\max} / %	PD_{\max} / %	PD_{\max} / %	PD_{\max} / %
PEGDA (1) + ethanol (2)					
288.15	7.62	2.16	11.03	4.46	1.59
293.15	5.79	2.65	10.48	4.66	1.67
298.15	4.08	2.40	10.10	4.88	1.84
303.15	2.82	1.76	9.70	4.97	1.84

TABLE IV. Continued

T / K	Predictive approach		Correlative approach		
	UNIFAC-VISCO	ASOG-VISCO	Teja-Rice	McAllister-3	McAllister-4
	$PD_{\max} / \%$	$PD_{\max} / \%$	$PD_{\max} / \%$	$PD_{\max} / \%$	$PD_{\max} / \%$
PEGDA (1) + ethanol (2)					
308.15	2.20	1.08	9.38	5.15	1.92
313.15	2.19	0.66	9.04	5.32	2.05
318.15	2.95	1.17	8.88	5.49	2.20
323.15	3.74	1.57	8.51	5.50	2.15
PEGDA (1) + 1-propanol (2)					
288.15	4.66	1.54	5.96	3.01	1.11
293.15	3.14	0.77	5.68	3.13	1.15
298.15	1.76	0.50	5.52	3.30	1.15
303.15	0.87	0.84	5.29	3.40	1.20
308.15	1.39	1.34	5.07	3.49	1.27
313.15	2.78	1.95	4.90	3.59	1.31
318.15	4.17	2.61	4.72	3.66	1.36
323.15	5.32	3.07	4.65	3.73	1.42
PEGDA (1) + 1-butanol (2)					
288.15	4.56	1.56	3.89	2.13	0.65
293.15	3.46	0.78	3.79	2.22	0.68
298.15	2.47	0.66	3.63	2.32	0.78
303.15	1.69	0.51	3.57	2.45	0.72
308.15	1.04	0.47	3.49	2.54	0.78
313.15	0.72	0.44	3.41	2.64	0.82
318.15	1.25	0.44	3.35	2.74	0.86
323.15	1.98	0.45	3.35	2.78	0.92

UNIFAC-VISCO model gave very good results for the prediction of the viscosity of the three investigated binary systems. In almost all cases, the maximum percentage deviation PD_{\max} did not exceed 5 %. The largest deviations were obtained at the lowest temperature (systems with ethanol and 1-butanol), or at the highest investigated temperature in the case of the system containing 1-propanol. Inspection of Figs. 5a and 5b confirms this conclusion. The ASOG-VISCO model gave even better results, with maximum percentage deviations PD_{\max} of 2.65 % in almost all cases. The best results were obtained for the PEGDA + 1-butanol binary mixture, with PD_{\max} of less than 0.78 %, except at 288.15 K, when the deviation was 1.56 %. However, this model fits the experimental data satisfactorily (Fig. 5c). From the results obtained from correlative models, it could be concluded that the best results for all three systems were obtained with the McAllister-4 model. This conclusion is supported by the graphical representation given for the systems PEGDA + ethanol, or + 1-butanol (Fig. 5a and c) where the model correlates the experimental points very well. The Teja-Rice model gave the worst correlations of the experimental data, with the

highest PD_{\max} values, up to 11.03 % for the PEGDA + ethanol binary mixtures. This conclusion is obvious from Figs. 5b and 5c, especially at lower temperatures. The best results for all three types of correlative models were obtained for the PEGDA + 1-butanol binary system, for which the lowest PD_{\max} deviations were obtained for the McAllister-4 model (less than 1 %).

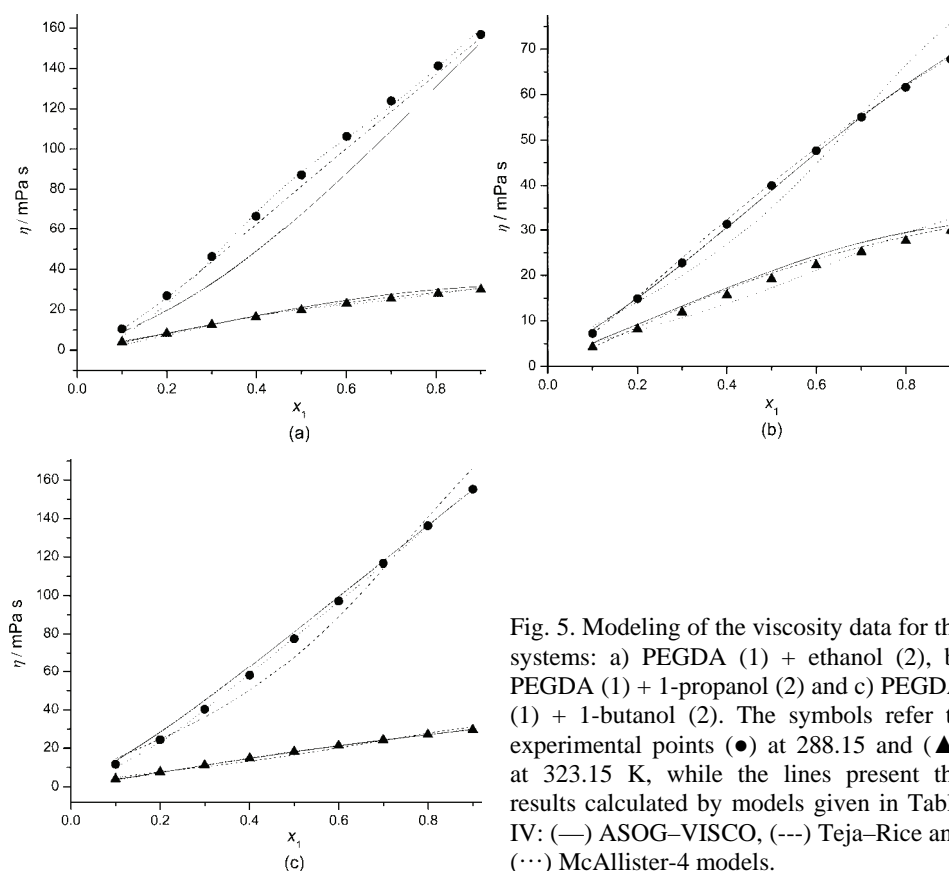


Fig. 5. Modeling of the viscosity data for the systems: a) PEGDA (1) + ethanol (2), b) PEGDA (1) + 1-propanol (2) and c) PEGDA (1) + 1-butanol (2). The symbols refer to experimental points (●) at 288.15 and (▲) at 323.15 K, while the lines present the results calculated by models given in Table IV: (—) ASOG-VISCO, (---) Teja-Rice and (···) McAllister-4 models.

CONCLUSIONS

In this work, the experimental data of the density ρ , viscosity η , and refractive index n_D are reported for PEGDA + ethanol, PEGDA + 1-propanol and PEGDA + 1-butanol binary mixtures at temperatures in the range 288.15 to 323.15 K, with a temperature step of 5 K, over the whole composition range, and at atmospheric pressure. All measured physical properties increased with increasing PEGDA mole fraction and with decreasing temperature. The measured physical properties were correlated as a function of temperature and of PEGDA mole fraction. The densities and refractive indices of the mixtures showed

exponential dependence vs. composition, including the temperature dependence of the parameters, while the viscosities exhibited polynomial dependence over the mixture composition. In the case of the temperature correlation, all three properties (ρ , $\ln \eta$ and n_D) exhibited linear trends. The influence of temperature on the viscosity of the mixtures was larger than its influence on the density and refractive index. Moreover, the influence of the PEGDA mole fraction on the overall densities and refractive indices of the PEGDA + alcohol mixtures was far greater in comparison to the influence of the alcohol type. In addition, viscosity modeling was performed using two types of models: the predictive UNIFAC–VISCO and ASOG–VISCO, and the correlative McAllister and Teja–Rice models. The predictive ASOG–VISCO gave better results between the predictive models, while of the correlative models, the best results were obtained using the McAllister-4 equation, for all three investigated binary systems. Furthermore, new UNIFAC–VISCO and ASOG–VISCO binary interaction parameters were determined from the experimental viscosity data.

SUPPLEMENTARY MATERIAL

Experimental data of densities ρ , viscosities η and refractive n_D indices and fitting parameters and root-mean-square deviations for Eqs. (1)–(3) of PEGDA + alcohol binary mixtures are available electronically from <http://www.shd.org.rs/JSCS/> or from the corresponding author on request.

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ИЗВОД

ЕКСПЕРИМЕНТАЛНО ИСПИТИВАЊЕ ТЕРМОДИНАМИЧКИХ И ТРАНСПОРТНИХ СВОЈСТАВА БИНАРНИХ СМЕША ПОЛИ(ЕТИЛЕНГЛИКОЛ)-ДИАКРИЛАТА И АЛКОХОЛА НА РАЗЛИЧИТИМ ТЕМПЕРАТУРАМА

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Експериментални подаци за густину, ρ , индекс рефракције, n_D , и вискозност, η , три бинарна система поли(етиленгликол)-диакрилата (PEGDA) + етанол, + 1-пропанол и + 1-бутанол су мерени на осам температура (288,15 to 323,15 K), са кораком 5 K, и на атмосферском притиску. Експериментални подаци су корелисани у функцији молског удела PEGDA и температуре. Густине и индекси рефракције испитиваних смеша су фитовани експоненцијалном функцијом у зависности од састава, док се у случају вискозности полиномска функција показала као најбоља кроз цео опсег молских удела. У случају температурне зависности, све три величине (ρ , $\ln \eta$ и n_D) показују линеаран тренд. Вискозност је моделована помоћу четири модела: UNIFAC–VISCO, ASOG–VISCO, Mc-Allister и Теја–Rice. Помоћу UNIFAC–VISCO модела одређени су интеракциони параметри следећих група: $\text{CH}_2=\text{CH}/\text{CH}_3$, $\text{CH}_2=\text{CH}/\text{CH}_2$, $\text{CH}_2=\text{CH}/\text{OH}$, $\text{CH}_2=\text{CH}/\text{CH}_2\text{O}$ и $\text{CH}_2=\text{CH}/\text{COO}$. Такође, на исти начин помоћу ASOG–VISCO модела су одређени и бинар-

ни интеракциони параметри следећих група: $\text{CH}_2=\text{CH}/\text{CH}_2$, $\text{CH}_2=\text{CH}/\text{OH}$, $\text{CH}_2=\text{CH}/\text{CH}_2\text{O}$ and $\text{CH}_2=\text{CH}/\text{COO}$.

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REFERENCES

1. J. M. Vuksanović, E. M. Živković, I. R. Radović, B. D. Đorđević, S. P. Šerbanović, M. Lj. Kijevčanin, *Fluid Phase Equilib.* **345** (2013) 28
2. M. S. Calado, G. R. Ivaniš, J. M. Vuksanović, M. Lj. Kijevčanin, S. P. Šerbanović, Z. P. Višak, *Fluid Phase Equilib.* **344** (2013) 6
3. D. M. Bajić, J. Jovanović, E. M. Živković, Z. P. Višak, S. P. Šerbanović, M. Lj. Kijevčanin, *Fluid Phase Equilib.* **338** (2013) 282
4. M. Lj. Kijevčanin, E. M. Živković, B. D. Đorđević, I. R. Radović, J. Jovanović, S. P. Šerbanović, *J. Chem. Thermodyn.* **56** (2013) 49
5. D. M. Bajić, G. R. Ivaniš, Z. P. Višak, E. M. Živković, S. P. Šerbanović, M. Lj. Kijevčanin, *J. Chem. Thermodyn.* **57** (2013) 510
6. M. Yasmin, M. Gupta, *Int. J. Thermodyn.* **15** (2012) 111
7. M. Yasmin, M. Gupta, J. P. Shukla, *J. Mol. Liquids* **164** (2011) 212
8. V. Sharma, M. Szymusiak, H. Shen, L. C. Nitsche, Y. Liu, *Langmuir* **28** (2012) 729
9. B. E. Poling, J. M. Prausnitz, J. P. O'Connell, *The Properties of Gases and Liquids*, 5th ed., McGraw-Hill, Singapore, 2007, p. A.20
10. A. Ž. Tasić, D. K. Grozdanić, B. D. Djordjević, S. P. Šerbanović, N. Radojković, *J. Chem. Eng. Data* **40** (1995) 586
11. C. Hou, Z. Jiang, B. Ren, *J. Chem. Eng. Data* **55** (2010) 4943
12. S. Urréjola, A. Sánchez, M. F. Havello, *J. Chem. Eng. Data* **55** (2010) 482
13. M. A. Mutalib, K. Kurnia, *J. Chem. Eng. Data* **56** (2011) 79
14. J. Riddick, W. B. Bunger, *Techniques of chemistry Vol. II, Organic solvents: Physical Properties and Methods of Purification*, Wiley-Interscience, New York, 1970
15. Selected Values of Properties of Chemical Compounds, Data Project, loose-leaf data sheets, extant, TRC, Texas A&M University, College Station, TX, 1980
16. J. A. Riddick, W. B. Bunger, T. K. Sakano, *Organic Solvents. Physical Properties and Methods of Purification*, 4th ed., Wiley, New York, 1986
17. A. Rodríguez, J. Canosa, A. Domínguez, J. Tojo, *Fluid Phase Equilib.* **216** (2004) 167
18. J. Vijande, M. M. Piñeiro, J. García, J. L. Valencia, J. Legido, *J. Chem. Eng. Data* **51** (2006) 1778
19. L. Sarkar, M. N. Roy, *Phys. Chem. Liq.* **49** (2011) 219
20. J. L. Chevalier, P. Petrino, Y. Gaston-Bonhomme, *Chem. Eng. Sci.* **43** (1988) 1303
21. Y. Gaston-Bonhomme, P. Petrino, J. L. Chevalier, *Chem. Eng. Sci.* **49** (1994) 1799
22. K. Tochigi, K. Yoshino, V. K. Rattan, *Int. J. Thermophys.* **26** (2005) 413
23. D. W. Marquardt, *J. Soc. Ind. Appl. Math.* **11** (1963) 431
24. E. M. Živković, D. M. Bajić, S. P. Šerbanović, I. R. Radović, M. Lj. Kijevčanin, *Fluid Phase Equilib.* **373** (2014) 1
25. A. S. Teja, P. Rice, *Ind. Eng. Chem. Fundam.* **20** (1981) 77
26. A. S. Teja, P. Rice, *Chem. Eng. Sci.* **36** (1981) 7
27. R. A. McAllister, *AIChE J.* **6** (1960) 427
28. M. Lj. Kijevčanin, V. Z. Kostić, I. R. Radović, B. D. Djordjević, S. P. Šerbanović, *Chem. Ind. Chem. Eng. Q.* **14** (2008) 223
29. E. M. Živković, M. Lj. Kijevčanin, I. R. Radović, S. P. Šerbanović, B. D. Djordjević, *Fluid Phase Equilib.* **299** (2010) 191.