

**Thermodynamic characterization of binary mixtures of poly(propylene glycol) 425 with toluene and o-, m- and p-xylenes**

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## Abstract

Density  $\rho$ , viscosity  $\eta$  and refractive index  $n_D$  have been experimentally measured for four binary mixtures of poly(propylene glycol) of average molecular weight 425 + toluene / o-xylene / m-xylene / p-xylene over the temperature range  $T = (293.15 \text{ to } 333.15) \text{ K}$  with temperature step 5 K and at atmospheric pressure. From the experimental data excess molar volumes  $V^E$ , deviations in refractive index  $\Delta n_D$ , viscosity deviations  $\Delta \eta$  and excess Gibbs free energy of activation of viscous flow  $\Delta G^{*E}$  were calculated and fitted with Redlich-Kister polynomial in order to analyze non-ideal behavior of the studied mixtures. From  $\Delta G^{*E}$  values excess entropy  $\Delta S^{*E}$  and excess enthalpy of activation of viscous flow  $\Delta H^{*E}$  were also calculated. It was shown that specific weak, but numerous, attractive interactions and entropic effect, due to difference in size of the pure component molecules, are responsible for volumetric and viscosity behaviour of the studied systems. The viscosities of the studied systems were predicted with the UNIFAC-VISCO and ASOG-VISCO models and correlated with the McAllister equation.

**Keywords:** density, viscosity, refractive index, excess Gibbs free energy of activation of viscous flow, viscosity modeling

## 1. Introduction

Poly(propylene glycol) (PPG) is approved for its use as a solvent while meeting Safer Choice VOC criteria, defined by the US EPA Safer Chemical Ingredients List. PPG, along with the poly(ethylene glycol) (PEG), has low toxicity, low volatility and reasonable biodegradability [1]. Thus, it is widely used as an antifoaming agent [2], in preparation of resins [3] or soft drinks [4]. PPG is structurally very similar to PEG, but, unlike PEG, it is liquid at ambient temperature in a wide range of average molecular mass ( $M_w$ ) (even for  $M_w = 4000$  it is a viscous liquid at  $20^\circ\text{C}$ ). Also, while liquid PEG ( $M_w=400$ ) (PEG400) is practically completely soluble in water, liquid PPG425 is not, showing immiscibility as temperature is increased to approximately  $50^\circ\text{C}$  (Lower-Critical-Solution-Temperature (LCST) liquid-liquid phase behavior) [5]. Both PEG and PPG polymers are i) highly polar - dipole moments of PEG400 and PPG400 are 3.8D and 3.6D, respectively [6] and ii) promote hydrogen bonding (hydrogen bond basicity of PEG400 and PPG1200 is 0.65 [7] and 0.67 [8], respectively). However, PPG and PEG exhibit another, quite interesting phenomenon – they adjust the structure (conformation) of their segments to the polarity of the solvent – thus, in non-polar solvents, random non-polar structure dominates [9]. This (unexpected) behavior significantly extends solvent abilities of these polymers. Thus, PEG of low average molecular mass shows either very good or even complete miscibility with non-polar arenes [10,11]. Also, the solubility tests, performed within this study, showed that low average molecular mass poly(propylene glycol) ( $M_w = 425$ ) (PPG425) exhibits complete solubility with toluene and three xylene isomers, which is certainly strongly influenced by the aforesaid phenomenon of the polar to non-polar configuration change in the polymer.

Our previous studies were related to low molecular weight PEG as alternative solvent for several aromatic compounds, widely applied in process industry [12-15]. The aim of this work is to measure and analyze thermodynamic properties - density, viscosity and refractive indices - of the PPG425 mixtures with common toxic industrial aromatic solvents – toluene and o-, m-, p-xylene. The data obtained will be useful in future consideration of PPG425 application as “green” solvent for reducing the contents of these toxics in industrial effluents.

Therefore, in this work, experimental densities  $\rho$ , refractive indices  $n_D$  and dynamic viscosities  $\eta$  are reported for four binary mixtures (PPG 425 + toluene / o-xylene / m-xylene / p-xylene) in the temperature range  $T = (288.15 - 333.15)$  K, with a temperature step 5 K and at pressure of 0.1 MPa. Excess molar volumes  $V^E$ , deviations in refractive index  $\Delta n_D$ , viscosity deviations  $\Delta \eta$ , and excess Gibbs free energy of activation of viscous flow  $\Delta G^{*E}$  were calculated and correlated by the Redlich-Kister equation [16]. From  $\Delta G^*$  values excess entropy  $\Delta S^{*E}$  and excess enthalpy of activation of viscous flow  $\Delta H^{*E}$  were also calculated.

The predictive UNIFAC-VISCO [17,18] and ASOG-VISCO [19] models were used for modelling the viscosity of the investigated binary mixtures. The viscosity data were also correlated by McAllister [20] equations.

## 2. Experimental methods

### 2.1. Chemicals

All the details regarding the chemicals used in this work: PEG425, toluene and xylenes isomers are summarized in Table 1. The chemicals were kept in dark bottles, in an inert atmosphere and ultrasonically degassed before sample preparations.

**Table 1** – Sample Description

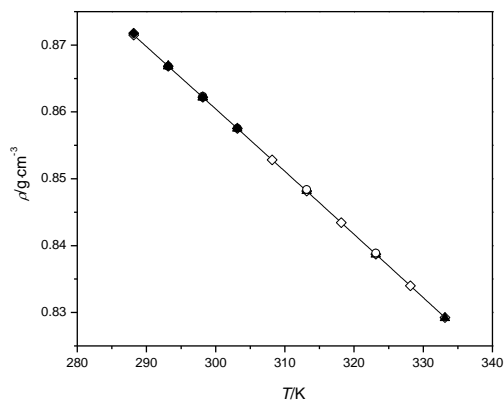
Chemical Name	Source	Initial mass fraction purity
Poly(propylene glycol) 425	Acros Organics	
Toluene	Merck	0.995
o-Xylene	Acros Organics	0.99
m-Xylene	Acros Organics	0.99
p-Xylene	Acros Organics	0.99

### 2.2. Measurements

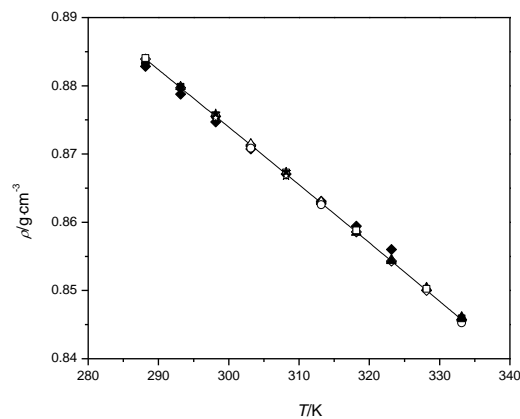
Density  $\rho$  was measured with an Anton Paar DMA 5000 digital vibrating U-tube densimeter, refractive index  $n_D$  using an automatic Anton Paar RXA 156 refractometer and viscosity  $\eta$  using a

digital Stabinger viscometer (model SVM 3000/G2). Description of the apparatus is explained in detail in our previous work [12].

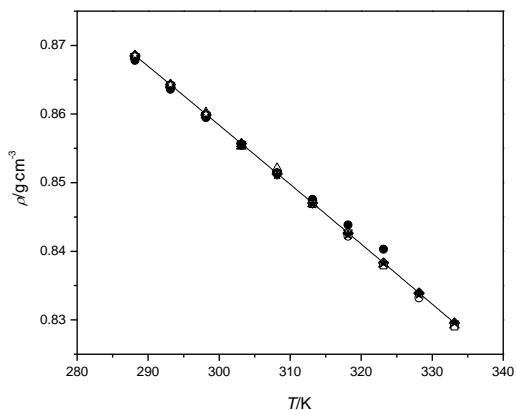
A Mettler AG 204 balance with a precision  $1 \cdot 10^{-7}$  kg was used for mass composition determination of all the mixtures herein. The uncertainty of the mole fraction calculation was less than  $\pm 1 \cdot 10^{-4}$ . Density measurements were performed with the experimental repeatability  $\pm 8 \cdot 10^{-2}$  kg·m<sup>-3</sup>, and combined expanded uncertainty, including the influence of sample purity within  $\pm 1$  kg·m<sup>-3</sup>, with a 0.95 level of confidence. The uncertainty of the refractive index data measurements is  $\pm 0.0002$  units. The relative uncertainty in dynamic viscosity measurements was estimated to be  $\pm 2\%$ . Disagreements between experimental and literature values for pure components are presented in Figures 1-3, at each temperature. Slightly higher viscosities and lower refractive indices for the aromatic compounds, compared to literature values, are probably due to their water content, ranging from 0.035% to 0.04% by mass, since water has higher viscosity but lower refractive index than the aromatics. However, to the best of our knowledge this should not affect the calculated deviations in viscosity or in refractive indices of these compounds, since the impact of water cancels in the calculations.



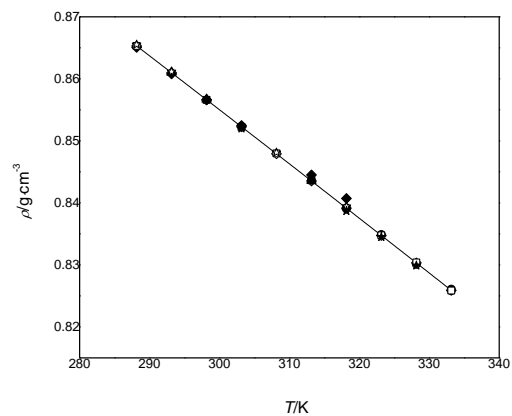
(a)



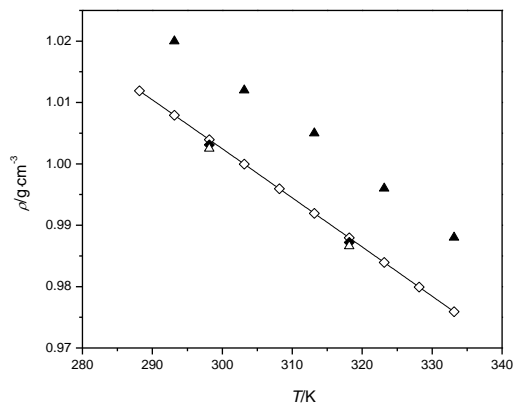
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(c)

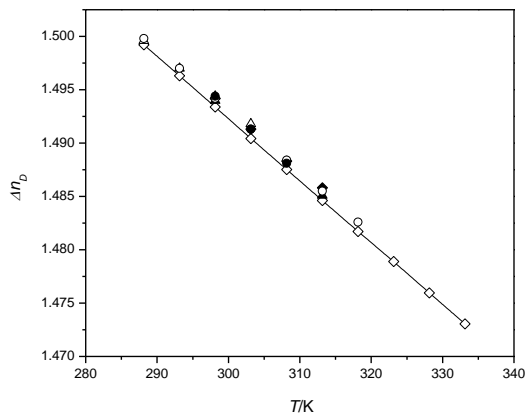


(d)

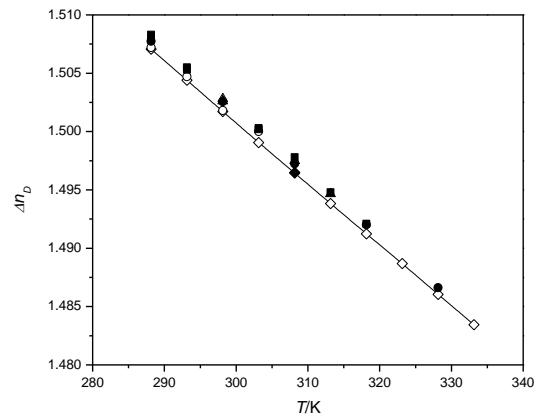


(e)

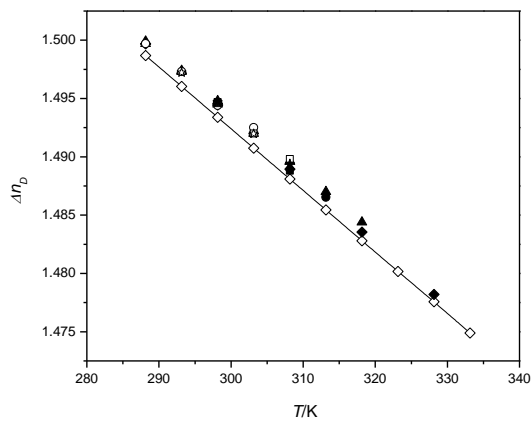
**Figure 1** - Comparison of experimental densities with available literature data for: (a) toluene: ( $\diamond$ ) exp; ( $\blacklozenge$ ) [21]; ( $\triangle$ ) [22]; ( $\blacktriangle$ ) [23]; ( $\circ$ ) [24]; ( $\bullet$ ) [25]; (b) o-xylene: ( $\diamond$ ) exp; ( $\blacklozenge$ ) [26]; ( $\triangle$ ) [27]; ( $\blacktriangle$ ) [28]; ( $\circ$ ) [29]; ( $\bullet$ ) [30]; ( $\square$ ) [31]; ( $\blacksquare$ ) [32]; ( $\star$ ) [33]; ( $\blackstar$ ) [34]; (c) m-xylene: ( $\diamond$ ) exp; ( $\blacklozenge$ ) [27]; ( $\triangle$ ) [35]; ( $\blacktriangle$ ) [33]; ( $\circ$ ) [30]; ( $\bullet$ ) [26]; ( $\square$ ) [36]; ( $\blacksquare$ ) [37]; ( $\star$ ) [38]; ( $\blackstar$ ) [39]; (d) p-xylene: ( $\diamond$ ) exp; ( $\blacklozenge$ ) [26]; ( $\blacktriangle$ ) [36]; ( $\circ$ ) [30]; ( $\bullet$ ) [31]; ( $\square$ ) [32]; ( $\blacksquare$ ) [40]; ( $\star$ ) [41]; ( $\blackstar$ ) [42]; (e) PPG425: ( $\diamond$ ) exp; ( $\blacklozenge$ ) [43]; ( $\triangle$ ) [44]; ( $\blacktriangle$ ) [45]



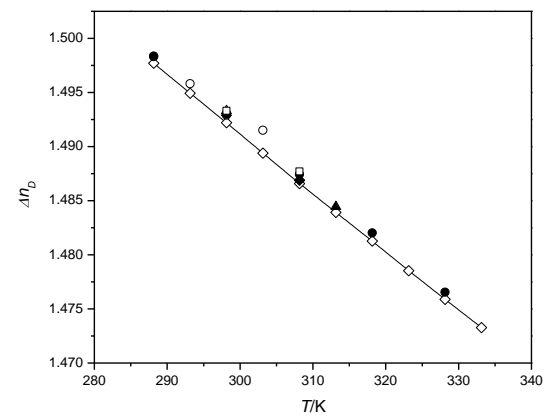
(a)



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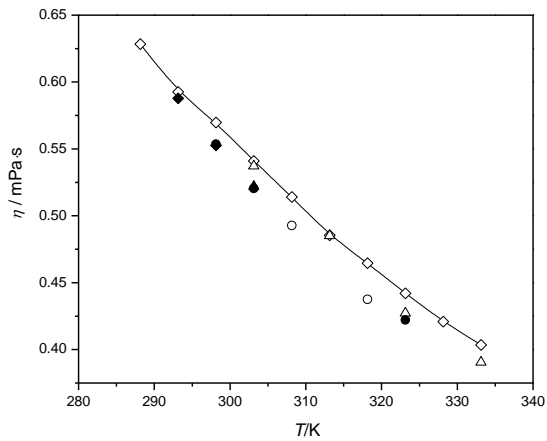


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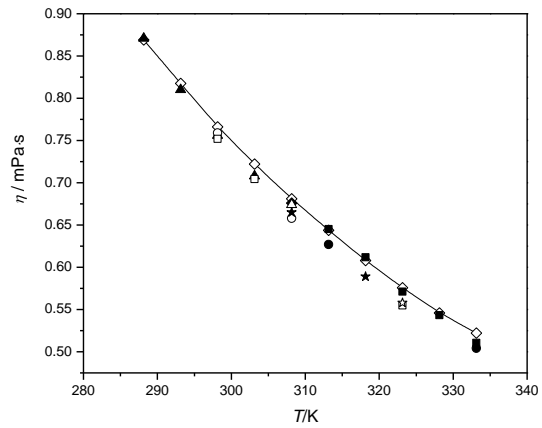


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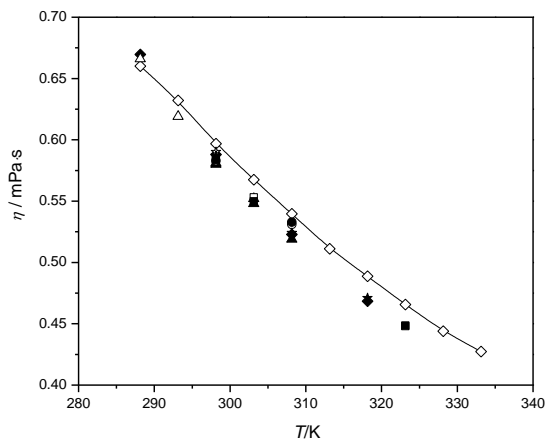
**Figure 2** - Comparison of experimental refractive indices with available literature data for: (a) toluene: ( $\diamond$ ) exp; ( $\blacklozenge$ ) [46]; ( $\triangle$ ) [32]; ( $\blacktriangle$ ) [47]; ( $\circ$ ) [48]; ( $\bullet$ ) [49]; (b) o-xylene: ( $\diamond$ ) exp; ( $\blacklozenge$ ) [50]; ( $\triangle$ ) [28]; ( $\blacktriangle$ ) [51]; ( $\circ$ ) [32]; ( $\bullet$ ) [52]; ( $\square$ ) [35]; ( $\blacksquare$ ) [38]; (c) m-xylene: ( $\diamond$ ) exp; ( $\blacklozenge$ ) [27]; ( $\triangle$ ) [35]; ( $\blacktriangle$ ) [48]; ( $\circ$ ) [32]; ( $\bullet$ ) [51]; ( $\square$ ) [53]; ( $\blacksquare$ ) [28]; ( $\star$ ) [54]; ( $\blackstar$ ) [55]; (d) p-xylene: ( $\diamond$ ) exp; ( $\blacklozenge$ ) [50]; ( $\triangle$ ) [28]; ( $\blacktriangle$ ) [51]; ( $\circ$ ) [32]; ( $\bullet$ ) [27]; ( $\square$ ) [28]; ( $\blacksquare$ ) [56]



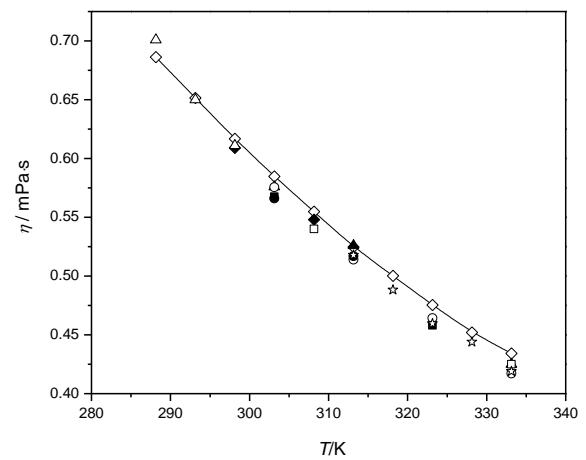
(a)



(b)



(c)



(d)

**Figure 3** - Comparison of experimental viscosities with available literature data for: (a) toluene: ( $\diamond$ ) exp; ( $\blacklozenge$ ) [57]; ( $\triangle$ ) [58]; ( $\blacktriangle$ ) [59]; ( $\circ$ ) [60]; ( $\bullet$ ) [34]; (b) o-xylene: ( $\diamond$ ) exp; ( $\blacklozenge$ ) [50]; ( $\triangle$ ) [37]; ( $\blacktriangle$ ) [61]; ( $\circ$ ) [62]; ( $\bullet$ ) [63]; ( $\square$ ) [42]; ( $\blacksquare$ ) [64]; ( $\star$ ) [65]; ( $\blackstar$ ) [28]; (c) m-xylene: ( $\diamond$ ) exp; ( $\blacklozenge$ ) [66]; ( $\triangle$ ) [37]; ( $\blacktriangle$ ) [53]; ( $\circ$ ) [28]; ( $\bullet$ ) [50]; ( $\square$ ) [31]; ( $\blacksquare$ ) [34]; ( $\star$ ) [67]; ( $\blackstar$ ) [64]; (d) p-xylene: ( $\diamond$ ) exp; ( $\blacklozenge$ ) [28]; ( $\triangle$ ) [37]; ( $\blacktriangle$ ) [62]; ( $\circ$ ) [31]; ( $\bullet$ ) [68]; ( $\square$ ) [34]; ( $\blacksquare$ ) [42]; ( $\star$ ) [40]



### 3. Results

Experimental data for densities, refractive indices and viscosities as well as the calculated values of excess molar volume, deviation in refractive index, viscosity deviation and excess Gibbs free energy of activation of viscous flow for four investigated binary mixtures were determined in the temperature range  $T = (288.15 \text{ to } 333.15) \text{ K}$  and at 0.1 MPa, with a temperature step of 5 K. Results are presented in Table S1 (Supplementary material).

**Table S1**

The excess molar volumes  $V^E$  were calculated from the density data using the following equation:

$$V^E = \sum_{i=1}^n x_i M_i \left[ \left( \frac{1}{\rho} \right) - \left( \frac{1}{\rho_i} \right) \right] \quad (1)$$

where  $x_i$  is the mole fraction of component  $i$  in the mixture;  $M_i$  its molecular weight and  $\rho$  and  $\rho_i$  are the measured densities of a mixture and a pure component  $i$ , respectively.

The deviations in refractive index  $\Delta n_D$  were calculated from the equation:

$$\Delta n_D = n_D - \sum_{i=1}^n x_i n_{Di} \quad (2)$$

where  $n_D$  and  $n_{Di}$  refer to the refractive index of a mixture and a pure component  $i$ , respectively.

In all the above given equations  $n$  denotes the number of components.

The viscosity deviations  $\Delta \eta$  were calculated from the viscosity of the mixture  $\eta$  and pure component  $i$ ,  $\eta_i$  according to the equation:

$$\Delta \eta = \eta - \sum_{i=1}^n x_i \eta_i \quad (3)$$

Excess Gibbs free energy of activation of viscous flow  $\Delta G^{*E}$  is calculated from the following equation:

$$\Delta G^{*E} = RT \left[ \frac{\ln \eta V}{\eta_2 V_2} - \frac{x_1 \ln(\eta_1 V_1)}{\eta_2 V_2} \right] \quad (4)$$

where  $\eta$ ,  $V$ ,  $\eta_1$ ,  $\eta_2$ ,  $V_1$  and  $V_2$  represent viscosity of solution, its molar volume, viscosity of component 1, viscosity of component 2, molar volume of component 1 and molar volume of component 2, respectively.

Excess molar volumes  $V^E$ , deviations in refractive index  $\Delta n_D$ , viscosity deviations  $\Delta\eta$  and excess Gibbs free energy of activation of viscous flow  $\Delta G^{*E}$  were correlated with the Redlich–Kister (RK) equation [16]:

$$Y = x_i x_j \sum_{p=0}^k A_p (2x_i - 1)^p \quad (5)$$

where  $Y$  represents  $V^E$ ,  $\Delta n_D$ ,  $\Delta\eta$  or  $\Delta G^{*E}$  of the mixture,  $A_p$  are fitting parameters, and  $k + 1$  is the number of parameters, which was optimized using the F-test.

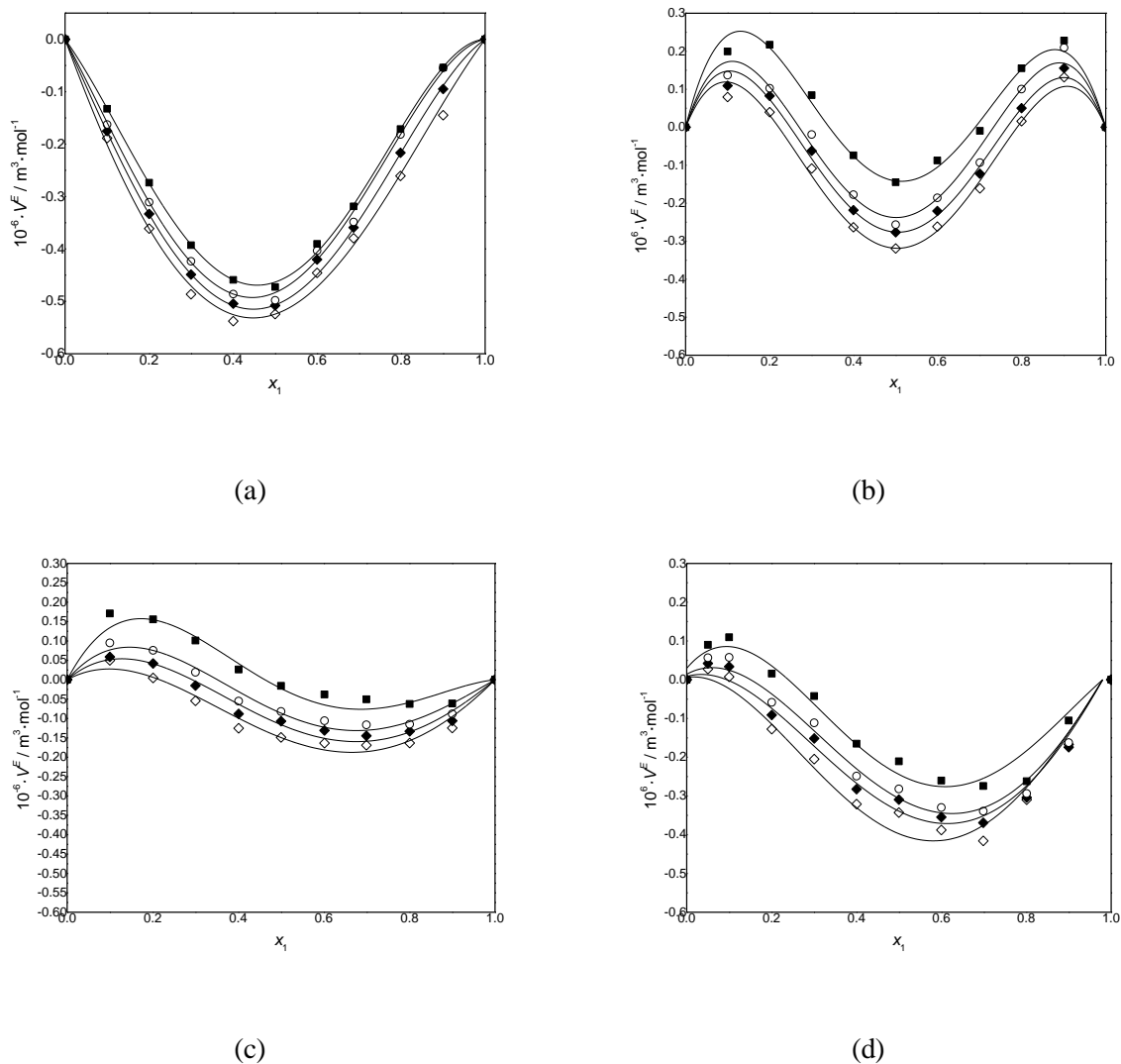
The fitting parameters and the corresponding root-mean-square deviations (rmsd)  $\sigma$ , defined by:

$$\sigma = \left( \sum_{i=1}^m (Y_{\text{exp}} - Y_{\text{cal}})^2 / m \right)^{1/2} \quad (6)$$

are given in Table S2 (Supplementary material), for  $V^E$ ,  $\Delta n_D$ ,  $\Delta\eta$  or  $\Delta G^{*E}$ , where  $m$  is the number of experimental data points.

## Table S2

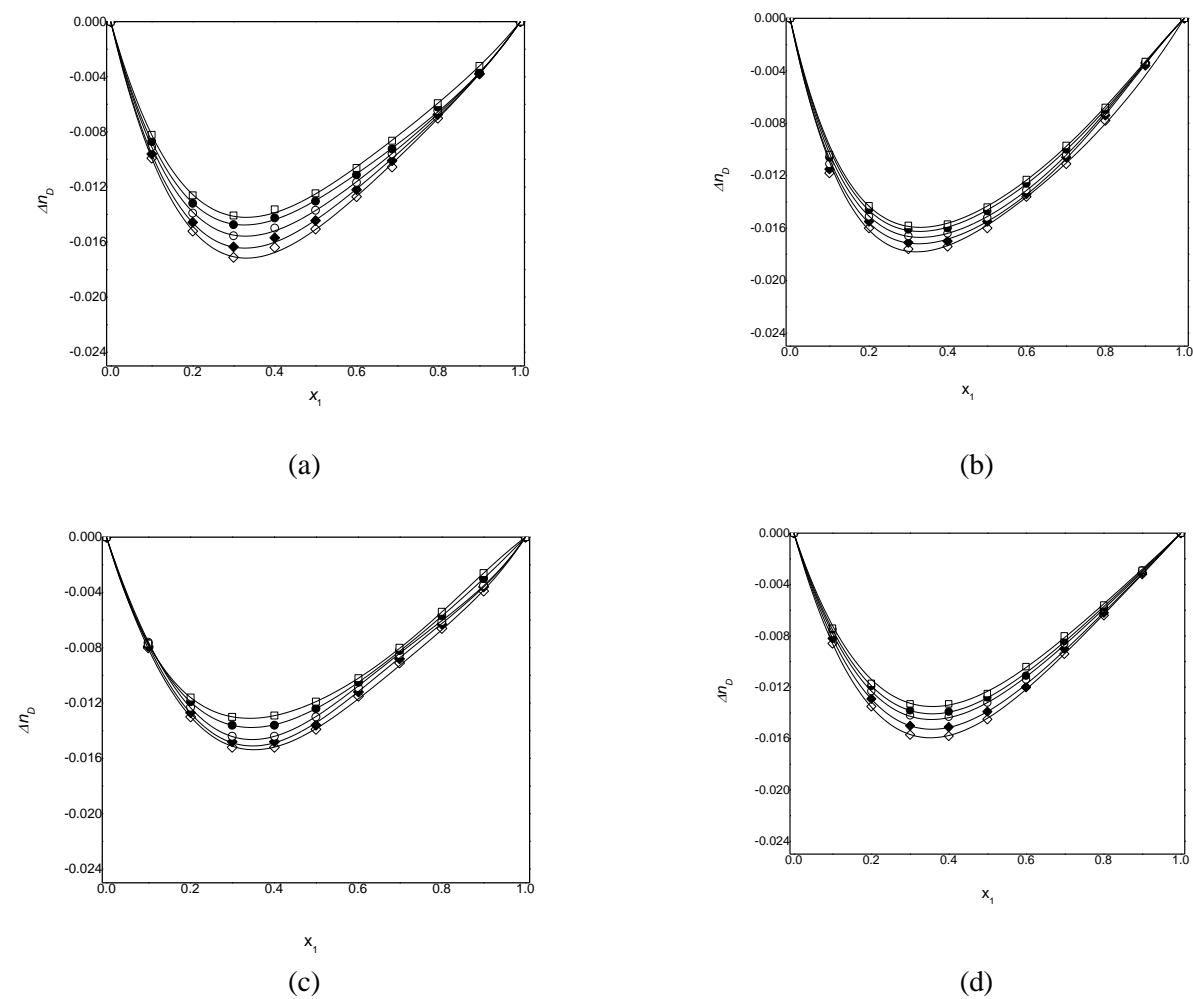
Excess molar volumes ( $V^E$ ), deviations in viscosity ( $\Delta\eta$ ) and in refractive indices ( $\Delta n_D$ ) are graphically presented in Figures 4-6, at several selected isotherms, for the purpose of good visibility. For the same reason, excess Gibbs free energies of activation of viscous flow ( $\Delta G^{*E}$ ) are given only at a single isotherm, in Figure 7.



**Figure 4** - Experimental deviations of excess molar volume  $V^E$  for the systems with: (a) toluene; (b) o-xylene; (c) m-xylene; (d) p-xylene; where  $x_1$  denotes mole fraction of PEGDA 425 at following temperatures: ( $\diamond$ ) 288.15 K, ( $\blacklozenge$ ) 298.15 K, ( $\circ$ ) 308.15 K, ( $\blacksquare$ ) 333.15 K, (—) RK equation

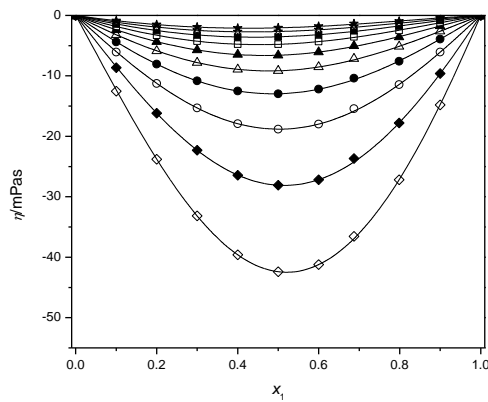
From Figure 4 it can be observed that for all the systems, except for that with toluene, excess molar volumes change sign. In particular,  $V^E$  - composition curves of the systems PPG 425 + / m-xylene / or p-xylene change sign from positive to negative, going to higher PPG 425 mole fraction. PPG 425 + o-xylene curve is changing sign twice – positive to negative to positive – going to higher PPG 425 mole fractions. The highest absolute  $V^E$  values are obtained for the system with toluene,

while the lowest are obtained for the system with m-xylene. Test measurements, using the solutions from different batches, confirmed the observed behavior.

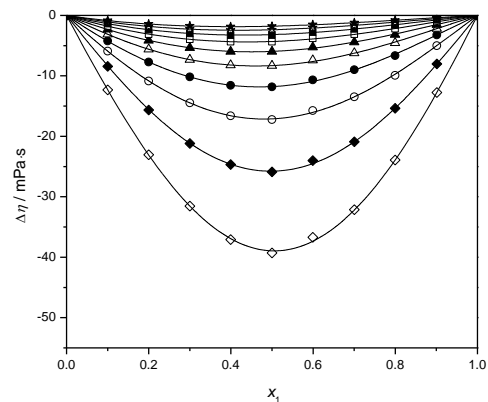


**Figure 5** - Experimental deviations in refractive indices  $\Delta n_D$  for the systems with: (a) toluene; (b) o-xylene; (c) m-xylene; (d) p-xylene; where  $x_1$  denotes mole fraction of PEGDA 425 at following temperatures: ( $\diamond$ ) 288.15 K, ( $\blacklozenge$ ) 298.15 K, ( $\circ$ ) 308.15 K, ( $\bullet$ ) 318.15 K, ( $\square$ ) 328.15 K (—) RK equation

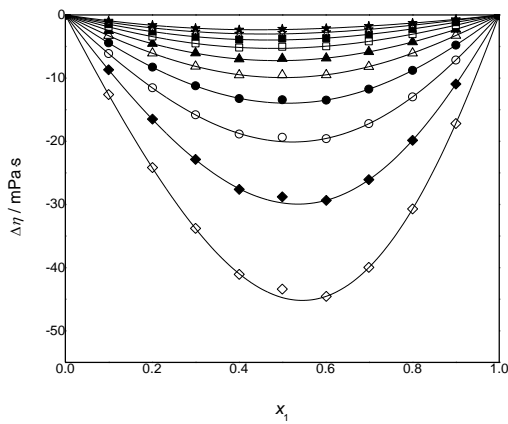
The composition curves of the deviations in refractive indices, shown in Figure 5, are slightly asymmetrical in all the cases (minimum at around  $x_1=0.3$ ). Absolute  $\Delta n_D$  values decrease as temperature is raised for all the studied systems.



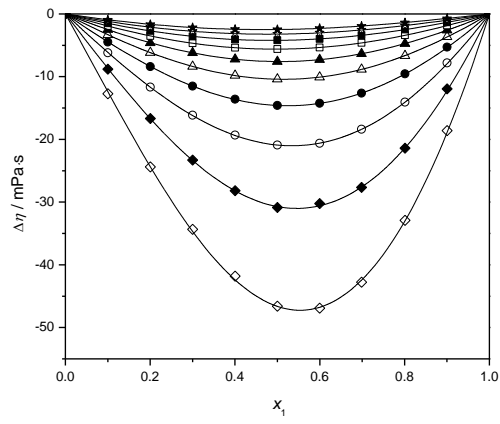
(a)



(b)



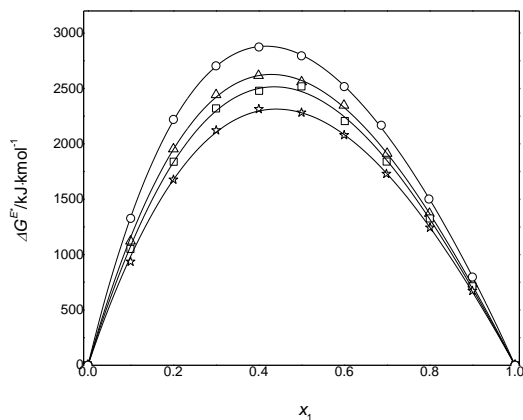
(c)



(d)

**Figure 6** - Experimental deviations in dynamic viscosities  $\Delta\eta$  for the systems with: (a) toluene; (b) o-xylene; (c) m-xylene; (d) p-xylene; where  $x_1$  denotes mole fraction of PEGDA 425 at following temperatures: ( $\diamond$ ) 288.15 K, ( $\blacklozenge$ ) 293.15 K, ( $\circ$ ) 298.15 K, ( $\bullet$ ) 303.15 K, ( $\Delta$ ) 308.15 K, ( $\blacktriangle$ ) 313.15 K, ( $\square$ ) 318.15 K, ( $\blacksquare$ ) 323.15 K, ( $\star$ ) 328.15 K, ( $\blackstar$ ) 333.15 K, (—) RK equation

Figure 6 shows negative deviations in dynamic viscosity for all the studied systems.  $\Delta\eta$  - composition curves are fairly symmetrical for all the systems. Absolute  $\Delta\eta$  values decrease as temperature increases, and this trend is more pronounced at lower temperatures. Viscosity deviations have high values in all the cases.



**Figure 7** - Experimental deviations of Gibbs free energy of activation of viscous flow  $\Delta G^{E*}$  for the systems with: (○) toluene; (△) o-xylene; (□) m-xylene; (☆) p-xylene; at 308.15 K where  $x_1$  denotes mole fraction of PEGDA 425, (—) RK equation

Figure 7 depicts excess Gibbs free energy of activation of viscous flow  $\Delta G^{*E}$  at 308.15 K. Positive  $\Delta G^{*E}$  values were obtained for all the systems.

#### 4. Discussion

Non-ideal behavior of the binary mixtures of PPG 425 with toluene and three xylene isomers can be interpreted analyzing the calculated thermodynamic excess properties or deviations, taking into account some of the pure component properties, major interactions occurring between unlike and like molecules and their interplay, following the usual procedure applied in literature, as we have reviewed earlier [69].

Table 2 presents pure components' properties interesting for the present study: Kamlet-Taft parameters - hydrogen bond acidity and basicity ( $\alpha$  and  $\beta$ , respectively), dipole moments ( $\mu$ ) and dielectric constants ( $\epsilon$ ).

**Table 2** - The Kamlet-Taft parameters (hydrogen bond acidity  $\alpha$  and basicity  $\beta$ ), dipole moments ( $\mu$ ) and dielectric constants ( $\varepsilon$ ) for the studied pure components

Chemical	$\alpha$	$\beta$	$\mu/D$	$\varepsilon$
Toluene	0.00 <sup>b</sup>	0.11 <sup>b</sup>	0.36 <sup>c</sup>	2.3536 <sup>f</sup>
o-Xylene	0.00 <sup>b</sup>	0.12 <sup>b</sup>	0.62 <sup>c</sup>	2.4150 <sup>f</sup>
m-Xylene	0.00 <sup>b</sup>	0.12 <sup>b</sup>	0.30 <sup>c</sup>	2.3442 <sup>f</sup>
p-Xylene	0.00 <sup>b</sup>	0.12 <sup>b</sup>	0.00 <sup>c</sup>	2.2447 <sup>f</sup>
PPG1200 <sup>a</sup>	-0.03 <sup>d</sup>	0.67 <sup>d</sup>	-	-
PPG400	-	-	3.5 <sup>e</sup>	8.86 <sup>e</sup>

<sup>a</sup> There are no available literature data for the Kamlet-Taft parameters for PPG 425; <sup>b</sup> [70], <sup>c</sup> [71], <sup>d</sup>[8], <sup>e</sup>[6], <sup>f</sup>[72]

Table 2 shows that all of the pure compounds are hydrogen bond acceptors, with neither one of them being a donor. Dipole moments of the studied aromatics are either low or zero, having the dielectric constants lower than 5 - thus, they can all be considered as non-polar [73]. In PPG, similarly to poly(ethylene glycol), once it is dissolved in non-polar organic solvents, the non-polar random structure of low internal energy would dominate [9]. Therefore, it can be concluded that strong attractive interactions - hydrogen bonds and dipole-dipole interactions - are not the type existing in the currently studied systems. However, as in the case of PEG solutions in benzene, randomness of the non-polar structure and the number of conformations facilitate weak but numerous specific attractive interactions with non-polar solvent [74]. This is in agreement with the excess molar volumes obtained herein, that change from only slightly negative to moderately negative (at 298.15 K,  $V^E$  is in the range of  $\sim -0.10 \cdot 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$  (system with m-xylene) to  $\sim -0.5 \cdot 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$  (system with toluene)). At higher temperatures the non-polar conformation dominates and the interactions with non-polar solvents are facilitated [75], providing more negative excess molar volumes, which explains their temperature trend shown in Figure 4.

Deviations in viscosity and the related excess Gibbs free energy of activation of viscous flow ( $\Delta G^{*E}$ ) show highly negative or positive values, respectively. Fort and Moore [76] suggested that one of the reasons for the negative viscosity deviations is the presence of weak attractive interactions (they stated dispersion forces) between the unlike compounds, which is quite similar with the case of the interactions we have in the present case (vide supra). Meyer et al. [77]

proposed that it is the  $\Delta G^{*E}$  values that should be analyzed related to molecular interactions, since they take into account both volumetric and viscosity effects (see equation (4)); they also stated that (large) positive  $\Delta G^{*E}$  values imply the presence of strong attractive (associative) interactions, which, however, is not really the case we have in the studied systems. The reason for the latter discrepancy is in the fact that the molecules of the pure components of the studied mixtures quite differ by size –the ratios of molar volumes at 25°C range between 3.4 and 4. Reed and Taylor [78] as well as Heric and Brewer [79] suggested that, particularly in the case of the systems having molecules different in size, analysis of solely  $\Delta G^{*E}$  function is not sufficient. Thus, entropic but as well enthalpic contributions to the  $\Delta G^{*E}$  values ( $\Delta S^{*E}$  and  $\Delta H^{*E}$ , respectively) have to be considered in order to fully understand the system behavior. We have applied this procedure in our previous study which also covered systems having pure component molecules different by size – liquid PEG200 and ionic liquids [80].

If one calculates the  $\Delta G^{*E}$  using equation (4), at a given composition, the other two excess properties of the activation of viscous flow, excess entropy ( $\Delta S^{*E}$ ) and excess enthalpy of activation of viscous flow ( $\Delta H^{*E}$ ), can be calculated applying the equations:

$$\Delta S^{*E} = -\left(\frac{\partial(\Delta G^{*E})}{\partial T}\right)_{p,x} \quad (7)$$

and

$$\Delta H^{*E} = \Delta G^{*E} - T\Delta S^{*E} \quad (8)$$

In Table 3 we have presented the values of  $\Delta S^{*E}$  and  $\Delta H^{*E}$  for the studied systems at all studied temperatures, for the constant (equimolar) composition of the mixtures.



**Table 3.** Excess molar properties of activation of viscous flow: Gibbs free energy ( $\Delta G^{*E}$ ), entropy ( $\Delta S^{*E}$ ), enthalpy ( $\Delta H^{*E}$ ) and entropy-related energetic term  $T\Delta S^{*E}$

T/K	$\Delta G^{*E} /$ kJ kmol <sup>-1</sup>	$\Delta S^{*E} /$ kJ kmol <sup>-1</sup> K <sup>-1</sup>	$T\Delta S^{*E}/$ kJ kmol <sup>-1</sup>	$\Delta H^{*E} /$ kJ kmol <sup>-1</sup>	$V_{m1}/V_{m2}^{(a)}$
PPG425 + toluene					
288.15	2639.48	-7.09	-2043.60	595.87	3.96
293.15	2682.43	-6.93	-2030.39	652.04	
298.15	2711.05	-7.08	-2109.43	601.62	
303.15	2738.15	-7.54	-2285.45	452.70	
308.15	2761.65	-8.32	-2563.18	198.47	
313.15	2802.98	-9.41	-2947.34	-144.36	
318.15	2846.75	-10.82	-3442.65	-595.90	
323.15	2892.85	-12.54	-4053.85	-1161.00	
328.15	2942.13	-14.58	-4785.66	-1843.53	
333.15	3018.53	-16.94	-5642.80	-2624.27	
PPG425 + o-Xylene					
288.15	2372.95	-10.66	-3072.86	-699.91	3.49
293.15	2405.77	-11.35	-3329.11	-923.34	
298.15	2441.32	-12.27	-3659.37	-1218.05	
303.15	2480.92	-13.41	-4067.01	-1586.09	
308.15	2508.65	-14.78	-4555.41	-2046.76	
313.15	2572.77	-16.37	-5127.94	-2555.16	
318.15	2629.85	-18.19	-5787.97	-3158.12	
323.15	2694.50	-20.23	-6538.89	-3844.39	
328.15	2731.57	-22.50	-7384.06	-4652.49	
333.15	2856.22	-24.99	-8326.86	-5470.64	
PPG425 + m-Xylene					
288.15	2317.30	-10.07	-2901.31	-584.01	3.43
293.15	2355.63	-11.44	-3352.36	-996.73	
298.15	2376.95	-12.83	-3826.02	-1449.07	
303.15	2401.93	-14.26	-4322.75	-1920.83	
308.15	2425.70	-15.72	-4842.99	-2417.29	
313.15	2472.50	-17.20	-5387.20	-2914.70	
318.15	2506.18	-18.72	-5955.81	-3449.64	
323.15	2560.25	-20.27	-6549.30	-3989.05	
328.15	2580.35	-21.84	-7168.09	-4587.74	
333.15	2674.35	-23.45	-7812.65	-5138.30	

T/K	$\Delta G^{*E} /$ kJ kmol <sup>-1</sup>	$\Delta S^{*E} /$ kJ kmol <sup>-1</sup> K <sup>-1</sup>	$T\Delta S^{*E}/$ kJ kmol <sup>-1</sup>	$\Delta H^{*E} /$ kJ kmol <sup>-1</sup>	$Vm_1/Vm_2^{(a)}$
PPG425 + toluene					
288.15	2682.43	-6.93	-2030.39	595.87	3.96
293.15	2711.05	-7.08	-2109.43	652.04	
298.15	2738.15	-7.54	-2285.45	601.62	
303.15	2761.65	-8.32	-2563.18	452.70	
308.15	2802.98	-9.41	-2947.34	198.47	
313.15	2846.75	-10.82	-3442.65	-144.36	
318.15	2892.85	-12.54	-4053.85	-595.90	
323.15	2942.13	-14.58	-4785.66	-1161.00	
328.15	3018.53	-16.94	-5642.80	-1843.53	
333.15	2639.48	-7.09	-2043.60	-2624.27	
PPG425 + o-Xylene					
288.15	2372.95	-10.66	-3072.86	-699.91	3.49
293.15	2405.77	-11.35	-3329.11	-923.34	
298.15	2441.32	-12.27	-3659.37	-1218.05	
303.15	2480.92	-13.41	-4067.01	-1586.09	
308.15	2508.65	-14.78	-4555.41	-2046.76	
313.15	2572.77	-16.37	-5127.94	-2555.16	
318.15	2629.85	-18.19	-5787.97	-3158.12	
323.15	2694.50	-20.23	-6538.89	-3844.39	
328.15	2731.57	-22.50	-7384.06	-4652.49	
333.15	2856.22	-24.99	-8326.86	-5470.64	
PPG425 + m-Xylene					
288.15	2317.30	-10.07	-2901.31	-584.01	3.43
293.15	2355.63	-11.44	-3352.36	-996.73	
298.15	2376.95	-12.83	-3826.02	-1449.07	
303.15	2401.93	-14.26	-4322.75	-1920.83	
308.15	2425.70	-15.72	-4842.99	-2417.29	
313.15	2472.50	-17.20	-5387.20	-2914.70	
318.15	2506.18	-18.72	-5955.81	-3449.64	
323.15	2560.25	-20.27	-6549.30	-3989.05	
328.15	2580.35	-21.84	-7168.09	-4587.74	
333.15	2674.35	-23.45	-7812.65	-5138.30	
PPG425 + p-Xylene					
288.15	2190.80	-8.75	-2522.70	-331.90	3.41
293.15	2196.45	-9.80	-2873.96	-677.51	
298.15	2209.83	-10.88	-3244.65	-1034.82	
303.15	2229.38	-11.99	-3635.22	-1405.85	
308.15	2249.78	-13.13	-4046.13	-1796.36	

313.15	2280.98	-14.30	-4477.83	-2196.85
318.15	2307.78	-15.50	-4930.75	-2622.98
323.15	2340.55	-16.73	-5405.36	-3064.81
328.15	2379.05	-17.99	-5902.11	-3523.06
333.15	2430.00	-19.27	-6421.43	-3991.43

<sup>(a)</sup> Ratio taken at 298.15K

Table 3 clearly shows that, for all the studied systems, entropic contributions to  $\Delta G^{*E}$  function are negative providing a substantial entropy related contribution to  $\Delta G^{*E}$  function, higher than the enthalpic one. This suggests that the viscous flow in all four systems is entropically driven and entropic effects, related to molecule difference in size, are the reason for the highly positive  $\Delta G^{*E}$  values. This entropic effect is the weakest in the system with toluene (the least negative  $\Delta S^{*E}$  values). Indeed, the related  $\Delta H^{*E}$  values, which reflect molecular interactions, are positive only at some lower temperatures in the case of the PEG425+toluene systems thus indicating limited stronger attractive interactions, as suggested by Meyer et al. [77]. This is in agreement with the fact that the lowest negative excess molar volumes are found for this system ( $\sim -0.5 \cdot 10^{-6} \text{ m}^3 \text{ mol}^{-1}$ ) and that in this case there is no change in sign. Generally, highly negative  $\Delta H^{*E}$  values for the other three systems, suggest the absence of strong associative interactions [77]; thus, they are in agreement with the excess molar volumes that are only slightly negative and do not change sign.

All studied systems have similar refractive indices and their deviations from ideality. This indicates well-packed structure and is in accordance with the entropic analysis of the viscosity flow (vide supra) and with the difference in size of the pure component molecules (see Table 3 as well).

Viscosity modelling was performed with two types of models: predictive and correlative. Viscosity was predicted using UNIFAC-VISCO [17,18] and ASOG-VISCO [19] models. Interaction parameters determined in the literature were used for the prediction and are given in Tables 4 and 5. In addition, the viscosity data were correlated with McAllister [20] two-parameter Three-body and three-parameter Four-body models.

The ability of these models to predict dynamic viscosities of selected binary mixtures and to correlate experimental viscosity data was tested by calculating the percentage deviations  $PD_{max}$  between the experimental and the calculated viscosities, from the following equation:

$$PD_{max}(\eta) = \frac{100}{m} \sum_{i=1}^m \left| \frac{\eta_{exp} - \eta_{cal}}{(\eta_{exp})_{max}} \right|_i \quad (9)$$

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

The results obtained by UNIFAC-VISCO, ASOG-VISCO and McAllister models for the mixtures PPG 425 + toluene / o-xylene / m-xylene / p-xylene over the investigated temperature range are given in Table 6. UNIFAC-VISCO showed as a better predictive model compared to ASOG-VISCO, particularly at higher temperatures and for the systems with xylene isomers. On the other hand, correlative models demonstrated a very good performance, with  $PD_{max}$  less than 1% in most cases.

**Table 4** - The UNIFAC-VISCO interaction parameters

$n/m$	$\alpha_{nm}$						
	CH <sub>3</sub>	CH <sub>2</sub>	CH	OH	CH <sub>2</sub> O	CH <sub>ar</sub>	C <sub>ar</sub>
CH <sub>3</sub>	0	-709.5 <sup>a</sup>	-911.38 <sup>b</sup>	594.4 <sup>a</sup>	-50.17 <sup>b</sup>	-119.5 <sup>a</sup>	-477.302 <sup>c</sup>
CH <sub>2</sub>	66.53 <sup>a</sup>	0	386.02 <sup>b</sup>	498.6 <sup>a</sup>	-319.93 <sup>b</sup>	406.7 <sup>a</sup>	-528.946 <sup>c</sup>
CH	-395.88 <sup>b</sup>	134.65 <sup>b</sup>	0	-684.26 <sup>b</sup>	-695.33 <sup>b</sup>	369.03 <sup>d</sup>	-70.52 <sup>d</sup>
OH	1209 <sup>a</sup>	-634.5 <sup>a</sup>	684.19 <sup>b</sup>	0	-619.36 <sup>b</sup>	197.7 <sup>a</sup>	-517.381 <sup>c</sup>
CH <sub>2</sub> O	456.91 <sup>b</sup>	-340.25 <sup>b</sup>	112.61 <sup>b</sup>	25.34 <sup>b</sup>	0	-315.736 <sup>c</sup>	-530.478 <sup>c</sup>
CH <sub>ar</sub>	237.2 <sup>a</sup>	-623.7 <sup>a</sup>	-167.52 <sup>d</sup>	419.3 <sup>a</sup>	-696.027 <sup>c</sup>	0	-446.993 <sup>c</sup>
C <sub>ar</sub>	-371.26 <sup>c</sup>	-539.68 <sup>c</sup>	396.66 <sup>d</sup>	-653.74 <sup>c</sup>	-550.277 <sup>c</sup>	-292.381 <sup>c</sup>	0

<sup>a</sup> original UNIFAC-VISCO parameters [17,18]

<sup>b</sup> UNIFAC-VISCO parameters from [15]

<sup>c</sup> UNIFAC-VISCO parameters from [12]

<sup>d</sup> UNIFAC-VISCO parameters from [81]

**Table 5** - The ASOG-VISCO interaction parameters

$k/l$	$m_{kl}$				
	CH <sub>2</sub>	OH	CH <sub>2</sub> O	CH <sub>ar</sub>	C <sub>ar</sub>
CH <sub>2</sub>	0	-0.357 <sup>a</sup>	-10.9924 <sup>a</sup>	0 <sup>a</sup>	1.8024 <sup>b</sup>
OH	14.146 <sup>a</sup>	0	-2.2661 <sup>a</sup>	5.9432 <sup>a</sup>	1.0797 <sup>b</sup>
CH <sub>2</sub> O	-33.9591 <sup>a</sup>	1.5287 <sup>a</sup>	0	0.6676 <sup>a</sup>	0.15726 <sup>b</sup>
CH <sub>ar</sub>	0 <sup>a</sup>	-11.32 <sup>a</sup>	-0.5917 <sup>a</sup>	0	-0.2366 <sup>b</sup>
C <sub>ar</sub>	-0.329712 <sup>b</sup>	0.121749 <sup>b</sup>	0.0417313 <sup>b</sup>	0 <sup>b</sup>	0

$k/l$	$n_{kl}$				
	CH <sub>2</sub>	OH	CH <sub>2</sub> O	CH <sub>ar</sub>	C <sub>ar</sub>
CH <sub>2</sub>	0	469.65 <sup>a</sup>	-1.928 <sup>a</sup>	-418.5 <sup>a</sup>	-2.0608 <sup>a</sup>
OH	-6137 <sup>b</sup>	0	-14.965 <sup>a</sup>	-1247 <sup>b</sup>	-0.0001 <sup>a</sup>
CH <sub>2</sub> O	-8.176 <sup>a</sup>	-127.018 <sup>a</sup>	0	537.3024 <sup>a</sup>	-170.5928 <sup>a</sup>
CH <sub>ar</sub>	-187.4 <sup>a</sup>	280.63 <sup>a</sup>	236.477 <sup>a</sup>	0	146.6703 <sup>a</sup>

$C_{ar}$	-70.06 <sup>a</sup>	7.877 <sup>a</sup>	23.285 <sup>a</sup>	-36.3902 <sup>a</sup>	0
<sup>a</sup> original ASOG-VISCO parameters [19]					
<sup>b</sup> ASOG-VISCO parameters from [12]					

**Table 6** - Results of the viscosity prediction and correlation for the investigated binary systems, at temperatures (288.15 - 333.15) K and at atmospheric pressure

T/K	Predictive approach		Correlative approach	
	UNIFAC-VISCO	ASOG-VISCO	McAlister - 3	McAlister - 4
	$PD_{max}/\%$	$PD_{max}/\%$	$PD_{max}/\%$	$PD_{max}/\%$
PPG 425 (1) + toluene (2)				
288.15	14.93	14.70	0.12	0.08
293.15	14.88	16.48	0.12	0.15
298.15	15.09	17.94	0.13	0.15
303.15	15.24	19.28	0.16	0.12
308.15	15.32	20.69	0.16	0.14
313.15	15.38	21.96	0.19	0.14
318.15	15.45	23.32	0.20	0.06
323.15	15.54	24.58	0.23	0.14
328.15	15.54	25.90	0.25	0.18
333.15	15.42	27.17	0.34	0.24
PPG 425 (1) + o-xylene (2)				
288.15	16.28	18.29	0.19	0.15
293.15	16.12	20.77	0.21	0.15
298.15	16.37	22.63	0.24	0.17
303.15	16.41	24.77	0.24	0.17
308.15	16.43	26.96	0.24	0.16
313.15	16.33	29.27	0.25	0.15
318.15	16.42	31.15	0.26	0.15
323.15	16.41	33.10	0.26	0.13
328.15	16.38	34.97	0.28	0.11
333.15	16.40	36.71	0.32	0.10
PPG 425 (1) + m-xylene (2)				
288.15	14.17	24.54	0.50	0.41
293.15	14.12	21.10	0.59	0.48
298.15	14.45	22.80	0.64	0.51
303.15	14.58	24.73	0.74	0.57
308.15	14.70	26.61	0.86	0.62
313.15	14.77	28.50	0.96	0.59
318.15	14.94	30.24	1.02	0.67
323.15	15.03	31.92	1.16	0.71
328.15	15.12	33.52	1.38	0.74
333.15	14.97	35.72	0.90	0.54
PPG 425 (1) + p-xylene (2)				
288.15	12.73	21.12	0.14	0.08
293.15	12.84	23.23	0.09	0.07
298.15	13.11	25.05	0.10	0.05
303.15	13.25	26.99	0.11	0.06

308.15	13.38	28.88	0.12	0.06
313.15	13.44	30.79	0.13	0.04
318.15	13.61	32.50	0.14	0.05
323.15	13.71	34.19	0.16	0.05
328.15	13.81	35.78	0.17	0.05
333.18	13.80	37.53	0.19	0.07

## 5. Conclusions

This paper reports experimental data of density, viscosity and refractive index for four binary mixtures PPG 425 + toluene / or o-xylene / or m-xylene / or p-xylene. Measurements were performed in the temperature range (288.15 - 333.15) K with a step of 5 K and at atmospheric pressure. From these data, excess molar volumes  $V^E$ , viscosity deviations  $\Delta\eta$ , deviations in refractive indices  $\Delta n_D$  and excess Gibbs free energy of activation of viscous flow  $\Delta G^{*E}$  were calculated and fitted to the Redlich-Kister polynomial equation.

The values of  $V^E$  range from slightly negative (mixture with m-xylene) to moderately negative (mixtures with toluene); also, a change of sign is observed for all the studied systems, except for the one with toluene.  $\Delta\eta$  and  $\Delta n_D$  are negative over the entire temperature and composition range for all the mixtures, while  $\Delta G^{*E}$  shows positive trend for all binary systems.

Analysis of Kamlet-Taft parameters, dielectric constant and dipole moments of the pure compounds as well as dominant random non-polar conformation of PPG in the mixtures with non-polar aromatic solvents indicate that hydrogen bonds and dipole-dipole interactions are not the type of interactions in the present systems. Weak but numerous specific attractive interactions between practically non-polar PPG425 and the aromatic solvents are the prominent interactions in the studied systems, which is in agreement with the values of the excess molar volumes and deviation properties obtained.

The analysis of the enthalpic and entropic contributions to excess Gibbs free energy of activation of viscous flow ( $\Delta G^{*E}$ ) shows that its high positive values are the consequence of the negative entropic contributions due to large difference in size between PPG and aromatic molecules and not of the strong attractive interactions in the system. Viscosity modelling was performed by UNIFAC-VISCO and ASOG-VISCO predictive group contribution models, using interaction

parameters already determined in literature and two McAllister correlative models. UNIFAC – VISCO showed as a better predictive model, particularly at higher temperatures and in systems with xylene isomers.

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